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PHOSGENE AND RELATED CARBONYL HALIDES

MONOGRAPH 24

TOPICS IN
INORGANIC
AND GENERAL
CHEMISTRY

A COLLECTION
OF MONOGRAPHS

EDITED BY
R. J. H. CLARK

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To: **Dr. Dave Nicholls**

- for his friendship to us all

"Give a Dog an ill Name, and he'll soon be hanged."

J. Kelly, 1721
Scottish Proverbs

"The Liberal impulse is almost always to give a dog a bad name and hang him."

George Bernard Shaw, 1928
Intelligent Woman's Guide to Socialism

"The experts feel that a still unexplained chemical reaction converted liquid methyl isocyanate into an extremely toxic breakdown gas which could be phosgene - a nerve gas reported to have been used by Nazi Germany during the second world war."

The Guardian, Front Page report
7th December, 1984

Thrown into the atmosphere, it [phosgene] did not fume. Its odour was different from that of chlorine, something like that which one might imagine would result from the smell of chlorine combined with that of ammonia, yet more intolerable and suffocating than chlorine itself, and affecting the eyes in a peculiar manner, producing a rapid flow of tears and occasioning painful sensations.

The chlorine and carbonic oxide are, it is evident from these last facts, united by strong attractions; and as the properties of the substance as a peculiar compound are well characterized, it will be necessary to designate it by some simple name. I venture to propose that of phosgene, or phosgene gas; from φως; light, and γινομαι, to produce, which signifies formed by light; and as yet no other mode of producing it has been discovered.

J. Davy, 1812

I have much pleasure now in looking back on this happy period of my life, when the whole of my time was devoted to chemical studies and pursuits, - in their most interesting and fascinating form; - and I shall never forget the lively interest which my Brother took in what I was doing. - When I ascertained the existence of phosgene gas he was out of town; - on his return I related to him all the particulars; - I am quite sure he felt more pleasure than if he had made the same discovery himself.

J. Davy, 1815

FOREWORD

Phosgene, unfortunately, retains the reputation of being a very unpleasant chemical, due to its early use as a war gas. Whilst undeniably toxic, like its precursors carbon monoxide and chlorine, it can be simply contained and easily converted into harmless added-value products, which contribute to our quality of life. Today we may consider it fully redeemed by its widespread use as an intermediate for producing the ubiquitous and useful polyurethanes, as well as contributing on a lesser scale as a reagent for synthesis of a number of valuable pharmaceuticals and crop protection agents.

This comprehensive book seeks to remind us that, although phosgene has been with us for a long time, and many of its industrial uses are well established, it is a compound with a great deal of potential in its chemical reactivity and physical properties, as well as being readily available. The discussion of its reaction with inorganic compounds is particularly interesting, as this field hints of many exciting discoveries to come.

I believe this book will rapidly assume the rôle of a definitive work that many chemists, especially synthetic ones, will find extremely useful and informative. As a reference work it is easy to follow and brings together a wealth of data. Where it covers the chemistry of phosgene, some of the more recent work suggests there are still many areas worthy of further exploration.

The undeniable enthusiasm of the authors is reflected throughout this treatise, and they are to be congratulated for achieving such a comprehensive work. I hope it may stimulate other chemists to continue the fruitful exploration of this interesting molecule.

Prof. J BEACHAM, FRSC
ICI Group Research and Technology Manager

PREFACE

Well, here it is, at last - all you ever wanted to know about phosgene, but were afraid (or rather unable) to ask. We examine phosgene and the related carbonyl halides - COF_2, $COBr_2$, COI_2, COClF, COBrF, COFI, COBrCl, COClI, and COBrI (or at least the ones that exist), materials that are extremely hazardous. It is therefore essential to have a good working knowledge of their reactive chemistry, physical and thermodynamic properties, toxicity, hazards and (perhaps most important) first aid and preventative measures before working with them. However, it became clear to us that the literature was awash with errors and fallacies regarding phosgene. All of the following statements will be found in the primary, secondary, or tertiary literature:

- Phosgene is responsible for 80% of the gas casualties in World War I
- Phosgene is a nerve gas used in World War II
- Phosgene is rapidly destroyed by water
- Phosgene is an effective chemical warfare agent
- Phosgene was responsible for:
    - (a) The disaster at Bhopal
    - (b) The Yokohama train terror (April 1995)
    - (c) Legionnaire's disease
    - (d) Uræmic coma
    - (e) "Death clouds" over major cities

None of these statements are true, but many are widely believed and propagated, and some constitute fatally dangerous misinformation (particularly the myth that phosgene is rapidly hydrolysed by water). The deeper we became involved in this topic, the more obvious it became that a book on the subject was needed, and that nobody else was likely to write it. Nor was some of the information for this book easy to come by. Many companies, clearly afraid of telling us anything, told us nothing, and hence revealed everything! The results of phosgene experimentation on humans during World War II are essentially unavailable through the normal channels, suggesting deliberate suppression of "sensitive" material. One body, whose purpose was to assess the hazards relating to phosgene, clearly had a policy decision never to report their findings, in case any mistake led to future prosecution for misleading or ill-informed advice. The Chemical and Biological Defence Establishment at Porton

Down (we are indebted to Dr. Graham Pearson, Dr. Alan Bebbington, and Mr. G.B. Carter) gave us full access to their archives, but denied permission to cite some specific sources. Thus, this work has been compiled under conditions of restricted access to public information, a situation that none of us, as practising scientists, had previously experienced. We express here our gratitude to all those individuals who gave us positive help in this endeavour (those who we are able to name are detailed later), and we would especially and particularly like to thank ICI PLC, who gave us free access to internal reports, and did not deny permission to use and cite any information that we considered relevant. We particularly wish to thank Prof. David Clark, Dr. Brian Webster and Mr. John Colchester for their invaluable aid, and particularly Prof. John Beacham, not only for his continuous encouragement and infectious enthusiasm, but also for writing the foreword. In addition, this book would not be in the form it appears without the advice and/or technical support of the following ICI personnel: Drs. Brian Bennett, Ian Campbell, Chris Dudman, Jack Loader, Graeme Milne, Archie McCulloch, Dick Powell, David Randall, Martyn Stacey, Hugo Steven and David Thorpe, as well as Dave Ashton, Andrew Bishton, Les Burgess, Liz Cullen, Judith Dobbs, Margaret Highfield, Andrew Johnstone, Alan Oldroyd, Dave Skinner, Rachel Spooncer and Brett Wolfindale.

The order and content of the book should be obvious after examining the contents pages: the pattern of treatment established for phosgene is repeated in the chapters dealing with the other carbonyl halides. The scope of this volume is extensive, but not comprehensive. We have not attempted to include every reference to the carbonyl halides, merely the key references (which total over 3000). Examination of the publication pattern shows that the extrapolated trend for the future is clear: the number of papers published annually concerning phosgene, and the number of citations of these, is on a rapidly rising curve. However, many of the papers (particularly those relating to phosgene as a synthetic reagent in organic chemistry) are highly derivative, and add little to our understanding of its reactivity. The references we have used were originally compiled from an extensive computer and manual search of *Chemical Abstracts*, and then expanded by backward reference and by the use of *Citations Index*. If we have not included a reference, it is more likely to be due to deliberate exclusion rather than oversight. We have normally referred back to, and read, all the references cited, except for those very few difficult papers (say, in Japanese or Chinese), for which we have had to rely on English abstracts. However, inclusion of a *Chemical Abstracts* number in the reference list does not imply that we only referred to the *Chemical Abstract*: these numbers have been deliberately included to enable the reader to find the more obscure sources that we have used. Nor is computer searching without its drawbacks - a search term "phosgene" picked out a paper entitled "Isolation of DNA Fragments Containing *pho*S Gene of *Escherichia coli* K-12"! For his dedicated and selfless help with compiling the original list of references, we are indebted to Paul Stanners: without his help, this work would never have got past the initial planning stages. In addition, we are indebted to Denise Carter, Lindsey Hendey, Sharon Loak and Val Miller of the ICI Runcorn Technical Centre Library, Vacky Noble and the librarians at Daresbury Laboratory, Joan Whitteker and the Staff of the Science Library of the Queen's University of Belfast, the Inter-Library

Loans librarians at the University of Sussex, the staff of the Reports Centre at ICI Runcorn Heath, and G.D. Havas of the Science Reference Library of the U.S. Library of Congress. To all of these people, we are truly grateful for their efficiency and diligence in finding many obscure, and nineteenth century, references, for which our citations were often incomplete, or (too frequently, when derived from secondary sources) inaccurate. For help with translations, particularly of pre-1900 references, we are extremely grateful to Roberto Corradi for Italian, Tanya Pang ("Tiger") and Dr. Christer Aakeröy for German, Dr. Jamila Fattah ("Jim") for French, Dr. Jitka Jenkins (for Czech), and Michelle Grange and Paul Gibson (for many languages). Finally, for help with the filing, we are indebted to Samana Hussein, Bridgette Duncombe, and Rebecca Ellis, who fought back the frontiers of boredom to keep our references under control.

One slightly unusual feature of our reference list is that for Russian papers, we have tried to include both the Russian original reference along with its English translation, instead of (as is the norm) just citing the English translation. This is because a number of our Russian colleagues have mentioned in the past that, while it is easy in the West to find an English translation if you have the full Russian reference, it is almost impossible to reverse the process from inside Russia, and trace the Russian original from the Western translation.

We also cannot acknowledge too warmly the willing aid offered by the staff of the British Museum and the Imperial War Museum, who helped with the arduous task of tracking down photographs, paintings, diaries and other pertinent records relating to World War I.

We owe a special acknowledgement to Martin Phillips of the Archives and Special Collections of the University Library at the University of Keele, for granting us access to the (largely unpublished) John Davy Archive, and for permitting us to publish parts of this material (for the first time) in Chapter 1. We are also grateful to Prof. Duncan Thorburn Burns for his advice and aid on the historical aspects of Chapter 1, to Dr. Paul Sherwood (Daresbury Laboratory) for critically reading, and for providing comments on, Chapter 17, Dr. Robert J. Fensterheim (Chemical Manufacturers Association) for help and advice on Chapters 2 and 3, Dr. Ian Wrightson (HSE) for advice on parts of Chapter 1, Ari Horvath (ICI) for aid with the prediction of unmeasured thermodynamic properties, Prof. Aubrey Jenkins (for guidance on integral and differential enthalpies of solution), and to Drs. Ken Buchanan and Roger Jones (both of AECI) for their continued interest and encouragement. Additional help was willingly supplied by Dr. Patrick Monaghan ("Paddy") of Sir Wilfred Grenfell College, Newfoundland, Dr. Alan Judd (Leeds Poisons Bureau), Prof. Norman Brown (University of Ulster), Mrs. Lynn Hesser (BIBRA), Dr. Bryn Mile (University of Wales, College of Cardiff), Dr. Paul Davies (University of Cambridge), and Dr. Margaret Gregson (Health and Safety Executive).

To avoid one of the main pitfalls of multiauthor works, we have intentionally adopted similar writing styles, and the final version of the monograph was then edited by us for consistency of grammar and style, for scientific accuracy and for similar formatting of illustrations and tables. The work has been extensively cross-referenced and indexed.

The main text of this book was produced using Vuwriter (Version 5.0c - Scientific), largely directly by the authors, with a Hewlett Packard LaserJet II printer. However, significant contributions to the typing were made by Susan Ellis ("Trouble"), Tanya Pang ("Tiger"), Jean Hudson, and Bridgette Duncombe. The illustrations were largely prepared using a combination of ChemWindow (Version 2.1) and Harvard Graphics for Windows (Version 2.0), with a Hewlett Packard LaserJet 4 printer. A number of figures were prepared using the combination of a Hewlett Packard ScanJet IIc scanner and PhotoFinish (Version 2.0) software, and we are indebted to Mel Davies and the staff of the Scientific Administration Service of the Daresbury Laboratory for providing some of the artwork used in this book, and to Ian Gibson (the Queen's University of Belfast) for his expert photographic skills. We are grateful to Tom Greenwood (Buss) for granting permission to reproduce Figures 4.5 and 4.6, and Prof. Dr. Med. Werner F. Diller (Department of Occupational Health, Bayer AG) for providing the original photographs used in Fig. 2.5. An important feature of this monograph is that many of the figures (particularly those illustrating physical and thermodynamic properties of the carbonyl halides as a function of temperature, pressure, composition, *etc.*) appear in print for the first time: we have deliberately created these of a size suitable for direct reading of the dependent variable, and hope that readers will find (as we do) these to be an invaluable aid to assessing parameters prior to their detailed calculation or measurement.

These acknowledgements would not be complete without thanking a generation of students and post-doctoral fellows at the University of Sussex, and more recent group members at Belfast, for their patient forbearance whilst we worked on this manuscript. Amongst those who suffered, and helped, the most are: Drs. Thomas Welton, Christer Aakeröy, Ala'a Abdul-Sada, Michael Parkington, Nazar Azoz, Munteser Kadim, Robert Quigley, Robin Boyett and Nicholas Blagden, and current students Anthea Lees, Peter Gibbs, Yasmin Patell, Hardip Dhaliwal, Ahmed Elaiwi and Lucy Dutta. Moreover, the help, support and friendship of four of the best (and most patient) secretaries imaginable - Rebecca Ellis, Jean Hudson, Karen ("No problem") Jones and Louise Porter - is fondly recorded.

There are, of course, many personal acknowledgements to our friends and family, whose support throughout this project has been both tangible and invaluable. We thus thank Mrs. Ada Horn, our devoted video researcher, for treading the streets of Lancashire, with an unshakeable determination to track down deleted video tapes containing references to phosgene, Lou and Tricia Ingleby for their unremitting faith in us, Marjorie Lohan ("Margaret") for her help and support at a time when it was most cherished, Dr. Paul Kummer for providing both a lifeline to the real world, and unstinting support through the latter half of this book's lengthy gestation period, Mrs Muriel Seddon and Mr. Richard Seddon for providing carpentry, repairs, food, tea and sympathy, Olga Smirnova-Holmes, Susan Ellis, Yasmin Patell and Bridgette Duncombe for exceptional support and encouragement when it was most needed, Patricia Reed ("Tish") and Dr. Sarah Caswell for countless meals and food parcels, Tracy M^{c}Guigan and Jo Ferguson (and the rest of the helots at *The Other Place*) for unlimited bottomless coffee, Dr. Ashley Pugh for his continued friendship and wise council, and our publishers (Dr. Andrew Dempster and Swan Go) for their infinite patience as one deadline after another slipped past.

The final acknowledgement goes to Dr. David Nicholls, our mentor and friend. To Dave, who imparted his superlative experimental skills, his vast knowledge of inorganic chemistry, and his sage advice to all of us, who is one of the best teachers we have ever met, who shared many a bag of fish and chips, who once rang Father Christmas, who taught us 1001 things to do with liquid air, who enlivened the Department of Inorganic, Physical and Industrial Chemistry of the University of Liverpool (particularly the Wine evenings!), who almost volunteered to stand in for an inebriate during a temperance campaign, who played snowballs on the top corridor, and who has been a true friend throughout our careers, we all say THANK YOU. This book is dedicated to you, as a small measure of our gratitude.

Christine Ryan
Kelsall

Tony Ryan
Kelsall

Elaine Seddon
Helsby

Kenneth Seddon
Finaghy

July, 1995

ABBREVIATIONS[§]

a	lattice parameter
a_t	amount sorbed at t °C
A	Antoine constant
A	Arrhenius pre-exponential factor
A.	*Asparagopsis*
A_e	equilibrium rotational constant
A_0	ground state rotational constant
A_w	van der Waals area
AC	alternating current
ACGIH	American Conference of Governmental Industrial Hygeinists
ads	adsorbed
AECI	African Explosives and Chemicals Industries
AM1	Austin Model 1
aq	aqueous
ARCO	Atlantic Richfield Company
ATP	adenosine triphosphate
ATPase	adenosine triphosphatase

b	lattice parameter
B	Antoine constant
B_e	equilibrium rotational constant
B_0	ground state rotational constant
BASF	Badische Anilin & Soda Fabrik
BCF	bromochlorodifluoromethane; $CBrClF_2$
BCNU	1,3-bis(2-chloroethyl)nitrosourea
BDF	4,4'-difluorobenzophenone
BIBRA	British Industrial Biological Research Association
BOP	benzotriazol-1-yloxy-tris(dimethylamino)phosphonium hexafluorophosphate
b.pt.	boiling point
BTDI	bitolylene diisocyanate
Bu	butyl

c	concentration
c	lattice parameter

[§] Where one abbreviation has more than one meaning (*e.g.* c), the meaning is always context sensitive.

C	Antoine constant
C_e	equilibrium rotational constant
C_o	ground state rotational constant
C_p	heat capacity at constant pressure
$C^{\circ}_{p,298}$	standard heat capacity at 298.15 K and constant pressure
C_v	heat capacity at constant volume
calc	calculated
CAS	Chemical Abstracts Service
CFC	chlorofluorocarbon
c.g.s.	centimeter-gram-second unit system
CI	configuation interaction
C.I.	colour index
CIA	Chemical Industries Association
CLV	ceiling value
CMA	Chemical Manufacturers Association
CNDO	complete neglect of differential overlap
cp	cyclopentadienyl
CT, *ct*	action product (concentration-time product); see Section 2.4
CW	continuous wave
CWE	Continental Western Europe
cych	cyclohexyl

d_m	critical density
D	bond dissociation energy
D_n	diffusion coefficient
DADI	dianasidine diisocyanate
DDT	1,1,1-trichloro-2,2-bis(chlorophenyl)ethane
dma	*N,N*-dimethylethanamide (dimethylacetamide)
dmf	*N,N*-dimethylmethanamide (dimethylformamide)
dmso	dimethyl sulfoxide
DNA	deoxyribonucleic acid
DOT	Department of Transport (USA)
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
dpu	1,3-diphenylurea
d.t.a.	differential thermal analysis

E	energy
E_a	activation energy

E_n	n^{th} energy level
EC	European Community
ECOIN	European core inventory
e.c.r.	electron cyclotron resonance
e.d.	electron diffraction
EEC	European Economic Community
EHMO	extended Hückel molecular orbital
EI	electron impact
EINECS	European inventory of existing chemical substances
$[emim]^+$	1-ethyl-3-methylimidazolium cation
EPA	Environmental Protection Agency (USA)
e.p.r.	electron paramagnetic resonance
eqQ	nuclear quadrupole coupling constant
Et	ethyl
expt	experimental
FOCI	first-order configuration interaction
g	gaseous state
g	e.p.r. g factor
G	Gibbs free energy
g.c.	gas chromatography
g.c.-m.s.	gas chromatography - mass spectrometry
h	Planck's constant
H	enthalpy
HCFC	hydrochlorofluorocarbon
He I	helium I radiation (20.21 eV)
He II	helium II radiation (40.8 eV)
HE	high explosive
HFC	hydrofluorocarbon
HLV	hygeinic limit value
HMDI	hydrogenated MDI
HMO	Hückel molecular orbital
HMSO	Her Majesty's Stationery Office
hmt	1,3,5,7-tetraazatricyclo[3.3.1.1]decane (hexamethylenetetramine)
HOMO	highest occupied molecular orbital
HREELS	high-resolution electron energy loss spectroscopy
HSE	Health and Safety Executive
htH_2	heptane-2,4,6-trione

I	intensity (of light or radiation)
I_a	moment of inertia of a molecule
I_{abs}	intensity of absorbed radiation
I_b	moment of inertia of a molecule
I_c	moment of inertia of a molecule
I_0	intensity of incident radiation
ICAO	International Civil Aviation Organization
i.c.d.r.	ion cyclotron double resonance
ICI	Imperial Chemical Industries PLC
i.c.r.	ion cyclotron resonance
IDLH	immediately dangerous to life or health
IGLO	individual guage for localized molecular orbital
imH	imidazole
INDO	intermediate neglect of differential overlap
Ins	insulin
IPDI	isophorone diisocyanate
i.r.	infrared
IUPAC	International Union for Pure and Applied Chemistry

J	nuclear spin-spin coupling constant
^nJ(AB)	nuclear spin-spin coupling constant, through n bonds between A and B
JANAF	Joint Army-Navy-Air Force

k	rate constant
K	force constant
K	equilibrium constant (expressed in pressure units)
K_c	equilibrium constant (expressed in concentration units)
K_f	equilibrium constant of formation (from elements)
K_p	equilibrium constant (expressed in pressure units)
K_{sp}	solubility product
"Kel-F"	Trademark for a series of fluorocarbon polymers, especially poly(chlorotrifluoroethane) and copolymers, available as oils, waxes and greases

l	liquid state
LC$_x$	lethal concentration for x% of a population
LC$_{50}$	lethal concentration for 50% of a population
LCT$_x$	lethal concentration-time product, responsible for x% mortality
LCT$_{50}$	lethal concentration-time product, responsible for 50% mortality
LD$_x$	lethal dose for x% of a population

LD_{100}	lethal dose for 100% of a population
LD_{LO}	lethal dose low
LDH	lactic dehydrogenase
LDIM	lysine diisocyanate methyl ester
LFP	lavage fluid protein
Ln	lanthanide
LPG	liquified petroleum gas
LUMO	lowest unoccupied molecular orbital

m	mass
M	molar mass
M	metal
M^+	molecular ion
M_{aa}	spin-rotation constants for principal inertial axes
M_{bb}	spin-rotation constants for principal inertial axes
M_{cc}	spin-rotation constants for principal inertial axes
MAC	maximum allowable concentration
MCA	Manufacturing Chemists Association
MDI	diphenylmethane-4,4'-diisocyanate
Me	methyl
MINDO	modified intermediate neglect of differential overlap
MNDO	modified neglect of differential overlap
m.o.	molecular orbital
m.p.h.	miles per hour
m.pt.	melting point
m.s.	mass spectrometry
m.w.	microwave
MXL	maximum exposure limit
m/z	mass-to-charge ratio

n	non-bonding orbital
n	number of moles
n	refractive index
n.a.	not available
NDI	1,5-naphthalene diisocyanate
NDRC	National Defence Research Committee
NDTI	2,4-diisocyanato-6-nitrotoluene
NIOSH	National Institute for Occupational Safety and Health
$[N\text{Mepy}]^+$	*N*-methylpyridinium cation
n.m.r.	nuclear magnetic resonance

np	naphthyl
n.q.r.	nuclear quadrupole resonance
$\mathrm{ntH_2}$	nonane-3,5,7-trione
OEL	Occupational Exposure Limit
OSHA	Occupational Safety and Health Authority
p	vapour pressure
p_A	partial pressure of A
p_c	critical pressure
P	total pressure
PEEK	polyether ether ketone
PEEP	positive end expiratory pressure
PEL	permissible exposure limit
Per	tetrachloroethene
PET	positron emission tomography
PFEP	poly(fluoroethenepropene)
PFIB	perfluoroisobutene
pH	$-\log_{10}([H^+])$
Ph	phenyl
pK	$-\log_{10}(K)$
PM3	Parameterized Method 3
PMDI	polymeric MDI
PMPPI	polymethylene polyphenyl isocyanate
$\mathrm{porH_2}$	porphyrin
p.p.b.	parts per billion (1 in 10^9)
PPG	Pittsburg Plate Glass
p.p.m.	parts per million
p.p.t.	parts per trillion (1 in 10^{12})
PTFE	poly(tetrafluoroethene)
py	pyridine
Q	partition function
r	correlation coefficient for linear regression
r	bond length
$\bar{r}$	mean bond length
r(AB)	bond length between A and B
r_m	reaction rate expressed in moles of product per unit weight of catalyst per unit time

R	gas constant
R-	ASHRAE refrigerant code prefix
R, R', R"	general organic group, usually alkyl
RTECS	Registry of Toxic Effects of Chemical Substances

s	solid state
S	entropy
S°_{298}	standard entropy of formation at 298.15 K
SCC	self-consistent charge
SCF	self-consistent field
SHOMO	second highest occupied molecular orbital
S.I.	Système Internationale (for units)
SNPE	Société Nationale des Poudres et Explosifs
STEL	short term exposure limit
STO-3G	Slater-type orbital with 3 Gaussians
STO-*n*G	Slater-type orbital with *n* Gaussians
STPC	Société Toulousaine de Produits Chimiques

t	time
$t_{½}$	half-life
T	temperature
T_c	critical temperature
T_m	melting temperature
TDI	toluene diisocyanate
TEA	transversely excited atmospheric (pressure)
t.g.a.	thermogravimetric analysis
thf	tetrahydrofuran
TLV	threshold linit value
tmeda	*N*,*N*,*N'*,*N'*-tetramethyl-1,2-diaminoethane (tetramethylethylenediamine)
TMI	3-isopropenyl dimethylbenzyl isocyanate
TMS	tetramethylsilane
TMXDI	tetramethyl xylene diisocyanate
TNT	2,4,6-trinitrotoluene
$TPPH_2$	5,10,15,20-tetraphenylporphyrin
Tri	trichloroethene
TVDI	trans-vinylene diisocyanate
TWA	time weighted average

U	lattice energy

udtH_2	undecane-4,6,8-trione
U.N.	United Nations
u.p.s.	ultraviolet photoelectron spectroscopy
UV, u.v.	ultraviolet
V_c	critical molar volume
V_I	volume of gas inhaled per minute
$V_{m,0}$	standard molar volume
V_w	van der Waals volume
v/v	volume for volume
x_{B}	mole fraction of B
X	halide (usually)
XDI	xylylene diisocyanate
x.p.s.	X-ray photoelectron spectroscopy
x.r.d.	X-ray diffraction
xs	excess
z	ionic charge
Z	active site on a catalyst surface
Z	number of molecules per unit cell
Z_c	critical compressibility factor
α	degree of dissociation
α	absorption coefficient
α	coefficient of thermal expansion
α_g	gas solubility
β	isothermal compressibility
γ	surface tension
δ	deformation mode
δ_{as}	asymmetric in-plane bending frequency
δ_s	symmetric in-plane bending frequency
δ(X)	n.m.r. chemical shift of X
Δ	heat
ΔBD	change in base deficit
ΔG	Gibbs free energy change
ΔG_{f}	Gibbs free energy of formation
$\Delta G^{\circ}_{\mathrm{f},298}$	standard Gibbs free energy of formation at 298.15 K
ΔH	enthalpy change

ΔH_f	enthalpy of formation
$\Delta H^{\circ}_{f,298}$	standard enthalpy of formation at 298.15 K
ΔH_{fus}	enthalpy of fusion
ΔH_{mixing}	enthalpy of mixing
ΔH_{soln}	enthalpy of solution
ΔH_{vap}	enthalpy of vaporization
Δp_z	change in p_z electron density
ΔS	entropy change
ΔS_{vap}	entropy of vaporization
ϵ	dielectric constant
ϵ	molar extinction coefficient
η	dynamic viscosity
λ	wavelength
λ	thermal conductivity
μ	electric dipole moment
ν_{as}	asymmetric stretching frequency
ν_i	i^{th} vibrational frequency
ν_s	symmetric stretching frequency
$\tilde{\nu}$	wavenumber (units of cm^{-1})
π	out-of-plane bending frequency
σ	Lennard-Jones potential parameter
σ^d	diamagnetic shielding
σ_I	Taft's inductive parameter
σ^p	paramagnetic shielding
σ_R	Taft's resonance parameter
Φ	quantum yield
$\chi(E), \chi_E$	Pauling's electronegativity of the element E
χ_m	mass magnetic susceptibility
χ_M	molar magnetic susceptibility
χ^p	paramagnetic susceptibility
$\hat{\omega}$	equilibrium out-of-plane angle

CONVERSION FACTORS

As this book is compiled from papers published over a period of nearly two centuries, it is not surprising that many systems of units and sign conventions have been encountered. We have attempted to convert all literature data to a common base, and some of the conversion factors used, and sign conventions adopted, are detailed below.

Units:

1 cal = 4.184 J

1 eV = 8066 cm^{-1} = 96.485 kJ

1 Å = 0.1 nm

1 cm^{-1} = 11.9627 J

1 Pa = 1.45033×10^{-4} p.s.i.

1 bar = 10^5 Pa

1 mm Hg = 1 Torr = 0.133322 kPa = 133.322 Pa

1 cm Hg = 1.33322 kPa = 1333.22 Pa

1 atm = 0.101325 MPa

$\log_{10}(p/\mathrm{Pa}) = \log_{10}(p/\mathrm{cm\ Hg}) + 3.124902$

1 a.u. = 2625.4 kJ mol^{-1}

1 D = 3.3356×10^{-30} C m

$\chi(\mathrm{SI}) / \mathrm{m^3\ kg^{-1}} = 4\pi\chi(\mathrm{c.g.s.}) \times 10^{-3} / \mathrm{cm^3\ g^{-1}}$

$\chi_m(\mathrm{SI}) / \mathrm{m^3\ mol^{-1}} = 4\pi\chi_m(\mathrm{c.g.s.}) \times 10^{-6} / \mathrm{cm^3\ mol^{-1}}$

1 p.p.m. of $COCl_2$ = 4 mg m^{-3}

Constants: R = 8.3144 J mol^{-1} K^{-1}

PHOSGENE
and related carbonyl halides

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SECTION B - RELATED CARBONYL HALIDES

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SECTION A

PHOSGENE

1 HISTORY OF PHOSGENE

For such a simple molecule, phosgene has an exceptional and fascinating history. It is one of the few chemicals whose name is readily recognized by the general public. It has a notoriety that exceeds scientific logic, and has a name which (certainly in our own experience) can induce fear and irrational behaviour, even in trained and experienced chemists. In this opening Chapter, the scientific debates surrounding the discovery of phosgene are summarised, and the historic, scientific, and sociological importance of phosgene is documented. We have also attempted to analyze some of the reasons for the image that phosgene holds in the popular imagination. It must be unique amongst compounds in its influence upon art, poetry, prose, theatre and cinema, which in itself serves to enhance its infamous reputation. Some of the Sections of this Chapter are certainly unusual for a chemistry text, and do not make for comfortable reading. However, we believe that these aspects have to be confronted: to avoid them is both intellectually dishonest and morally bereft. We hope that this Chapter will be accessible to both scientists and non-scientists, and will contribute to a balanced assessment of the real dangers associated with the use of phosgene.

1.1 PHOTOGENESIS

1.1.1 Events leading to the discovery of phosgene – the nature of oximuriatic acid

The history of the discovery of phosgene began almost thirty years before John Davy's notable paper presented to the Royal Society on February 6th, 1812 [467], which ended the then heated controversy concerning the nature of chlorine.

The observation that chlorine water, when exposed to bright sunlight, released molecular oxygen and produced hydrochloric acid was taken as evidence that chlorine itself was composed of oxygen and hydrogen chloride. The substance that we now know as elemental chlorine (or, more correctly, dichlorine) was thus in the late 18th century and early 19th century, referred to as oximuriatic acid [540].

The effect of oximuriatic acid (Cl_2) on a gaseous oxide of carbon (CO) was first reported in 1802 by Cruickshank [429a]. Equal volumes of the two gases were mixed in a gas jar inverted over water, and allowed to stand for a day, whence a contraction to one half of the original combined volume was noted. Furthermore, the product was completely absorbed by shaking it with lime water: it was almost certainly phosgene, although this was not recognised. Attempts to explode mixtures of the oximuriatic acid and the gaseous oxide of carbon were made without success [429a].

In 1810, Sir Humphry Davy, in his communications to the Royal Society, proposed oximuriatic acid to be an elementary substance [466a; p. 40] analogous in many of its properties to gaseous oxygen. In particular, Davy's conclusions were based on the inaction of oximuriatic acid towards hot charcoal, with which oxygen itself was known to react readily [466a; p. 21]. In addition, when dried over calcium chloride, he showed that oximuriatic acid did not show a bleaching action [1589e].

Davy's views on the nature of oximuriatic acid were met with fierce opposition by John Murray, and lengthy exchanges concerning the controversy were made in letters to *Nicholson's Journal*. Replies to Murray's open letters [1464a,1465] were made not by Sir Humphrey Davy himself, but by his younger brother Dr. John Davy [466b,466c]. These exchanges are described in some detail in Dobbin's extensive account of the history of the discovery of phosgene [540], and will be only summarised here.

Murray chose to interpret Cruickshank's experiments [429a] by suggesting that the carbonic oxide (CO) could remove oxygen from oximuriatic acid, thus forming mixtures of carbonic and muriatic acids. Indeed, Murray's main experimental efforts were centred upon proving that carbon dioxide was produced from mixtures of carbonic oxide and oximuriatic acid, and thus to establish that the oxidation was effected by the decomposition of the oximuriatic acid.

Murray's inability to observe a reaction between *dry* oximuriatic acid and carbon monoxide was reinforced, curiously, by the similar finding of a lack of action by Gay-Lussac and Thenard [727]. In a reply dated February 9th, 1811 [466b], John Davy (while still a medical student) attributed the formation of the carbonic acid produced in Murray's experiments not to the decomposition of oximuriatic acid, but to the decomposition of water. In fact, it was pointed out that in one of Murray's experiments (in which dry gases were combined over mercury), he had conceded that carbonic acid was not observed.

1.1.2 The discovery of phosgene

In a further communication of August 9th, 1811, entitled "An Account of a New Gas, with a Reply to Mr. Murray's last Observations on Oximuriatic acid", John Davy announced the existence of a new gas which he declared was present in Mr. Murray's experiments without his knowledge of it [466c]. This gas, Davy states, was the cause for the phenomena that were attributed to the formation of carbonic acid gas:

> "So satisfactory were the details of Mr. Murray's experiment, the result of which was asserted to be, 'that dry carbonic oxide gas and oximuriatic gas do not act on each other;' that at first I could hardly believe, but that water was somewhere concealed in the apparatus, and I gave myself much trouble to discover its source, but in vain.
>
> The next step I took was to examine the gas, that resulted from the now evident action of oximuriatic gas on carbonic oxide. Mr. Brande was present at the time.

> Finding that it did not fume when thrown into the atmosphere, and that it had a most intolerable suffocating odour, that it was colourless, that it did not act on the mercury, and that water absorbed it very slowly, we immediately perceived, that it was a new and peculiar compound of carbonic oxide and oximuriatic gas, and this conclusion is fully confirmed by the investigation I have made of its properties.
>
> I shall now mention only the most striking of its circumstances respecting it. It is my intention to give a full account of the experiments I have made on it, in a paper which I shall soon do myself the honour of offering to the Royal Society.
>
> I have found, that it is produced in two or three minutes when a mixture of equal volumes of carbonic oxide and oximuriatic gas is exposed in a tube over dry mercury to bright sunshine; and that the condensation, that takes place in their union, is exactly equal to one volume, ..."

John Davy's paper to the Royal Society was to follow [467] giving a complete description of his researches on the new gas. This is a landmark paper, and is reproduced in its entirety, so that both the elegance of the scientific method, and of its presentation, can be fully appreciated. Attention is drawn to the simplicity and power of the final paragraph.

VI. *On a gaseous Compound of carbonic Oxide and Chlorine. By* John Davy, *Esq. Communicated* by *Sir* Humphry Davy, *Knt. LL.D. Sec. R.S.*

Read February 6, 1812.

Since the influence of electricity and solar light, as chemical agents, are analogous in many respects, and as the former produces no change in a mixture of carbonic oxide and chlorine, it was natural to infer the same respecting the latter. M.M. GAY LUSSAC and THENARD assert that this is the case; they say that they have exposed a mixture of carbonic oxide and chlorine, under all circumstances, to light, without observing any alternation to take place:* Mr. MURRAY has made a similar statement.†

Having been led to repeat this experiment, from some objections made by the last mentioned gentleman to the theory of my brother, Sir HUMPHRY DAVY, concerning chlorine, I was surprised at witnessing a different result.

The mixture exposed, consisted of about equal volumes of chlorine and carbonic oxide; the gasses had been previously dried over mercury by the action of fused muriate of lime, and the exhausted glass globe into which they were introduced from a receiver with suitable stopcocks, was carefully dried. After exposure for about a quarter of an hour to bright sunshine, the colour of the chlorine had entirely disappeared; the stopcock belonging to the globe, being turned in mercury recently boiled, a considerable absorption took place, just equal to one-half the volume of the mixture, and the residual gas possessed properties perfectly distinct from those belonging either to carbonic oxide or chlorine.

Thrown into the atmosphere, it did not fume. Its odour was different from that of chlorine, something like that which one might imagine would result from the smell of chlorine combined with that of ammonia, yet more intolerable and suffocating than chlorine itself, and affecting the eyes in a peculiar manner, producing a rapid flow of tears and occasioning painful sensations.

Its chemical properties were not less decidedly marked, than its physical ones.

Thrown into a tube full of mercury containing a slip of dry litmus paper, it immediately rendered the paper red.

---

* Recherches Physico-Chimiques, Tom. II. p. 150.

† NICHOLSON'S Journal, Vol. XXX. p. 227.

Mixed with ammoniacal gas, a rapid condensation took place, a white salt was formed, and much heat was produced.

The compound of this gas and ammonia was a perfect neutral salt, neither changing the colour of turmeric or litmus; it had no perceptible odour, but a pungent saline taste; it was deliquescent, and of course very soluble in water; it was decomposed by the sulphuric, nitric, and phosphoric acids, and also by liquid muriatic acid; but it sublimed unaltered in the muriatic, carbonic, and sulphureous acid gasses, and dissolved without effervescing in acetic acid. The products of its decomposition collected over mercury were found to be the carbonic and muriatic acid gasses; and in the experiment with concentrated sulphuric acid when accurate results could be obtained, these two gasses were in such proportions, that the volume of the latter was double that of the former.

I have ascertained by repeated trials, both synthetical and analytical, that the gas condenses four times its volume of the volatile alkali, and I have not been able to combine it with a smaller proportion.

Tin fused in the gas in a bent glass tube over mercury, by means of a spirit lamp, rapidly decomposed it; the liquor of Libavius was formed; and when the vessel had cooled, there was not the least change of the volume of the gas perceptible; but the gas had entirely lost its offensive odour, and was merely carbonic oxide; for like carbonic oxide it burnt with a blue flame, afforded carbonic acid by its combustion, and was not absorbable by water.

The effects of zinc, antimony, and arsenic heated in the gas, were similar to those of tin; compounds of these metals and chlorine were formed, and carbonic oxide in each experiment was liberated equal in volume to the gas decomposed. In each instance the action of the metal was quick; the decomposition being completed in less than ten minutes; but though the action was rapid, it was likewise tranquil, no explosion ever took place, and none of the metals became ignited or inflamed.

The action even of potassium heated in the gas was not violent. But from the great absorption of gas, and from the precipitation of carbon indicated by the blackness produced, not only the new gas, but likewise the carbonic oxide, appeared to be decomposed.

The white oxide of zinc heated in the gas quickly decomposed it, just as readily indeed as the metal itself; there was the same formation of the butter of zinc; but instead of carbonic oxide being produced, carbonic acid was formed; and as usual, there was no change of volume.

The protoxide of antimony fused in the gas rapidly decomposed it; the butter of antimony and the infusible peroxide were formed; there was no change of the volume of the gas, and the residual gas was carbonic oxide.

Sulphur and phosphorus sublimed in the gas, produced no apparent change; the volume of the gas was unaltered, and its characteristic small was undiminished.

Mixed with hydrogene or oxygene singly, the gas was not inflamed by the electric spark, but mixed with both, in proper proportions, viz. two parts in volume of the former and one of the latter to two parts of the gas, a violent explosion was produced, and the muriatic and carbonic acid gasses were formed.

The gas transferred to water was quickly decomposed, the carbonic and muriatic acids were formed, as in the last experiment, and the effect was the same even when light was excluded.

From the mode of the formation of the gas and the condensation that takes place at the time, from the results of the decomposition of its ammoniacal salt, and from the analysis of the gas by metals and metallic oxides, it appears to be a compound of carbonic oxide and chlorine condensed into half the space which they occupied separately.

And from its combining with ammonia, and forming with this alkali a neutral salt, and from its reddening litmus, it seems to be an acid. It is similar to acids in other respects; in decomposing the dry sub-carbonate of ammonia, one part in volume of it, expelling two parts of carbonic acid gas; and in being itself not expelled from ammonia by any of the acid gasses, or by acetic acid. Independent of these circumstances, were power of saturation to be taken as the measure of affinity, the attraction of this gas for ammonia must be allowed to be greater than that of any other substance, for its saturation power is greater; no acid condenses so large a proportion of ammonia; carbonic acid only condenses half as much, and yet does not form a neutral salt. The great saturating and neutralizing powers of this gas are singular circumstances, and particularly singular when compared with those of muriatic acid gas.

In consequence of its being decomposed by water, I have not been able to ascertain whether it is capable of combining with the fixed alkalies. Added to solutions of these substances it was absorbed, and carbonic acid gas was disengaged by an acid.

I have made the experiment on the native carbonates of lime and barytes, but the gas did not decompose these bodies. This indeed might be expected, since quick-lime, I find, does not absorb the gas: a cubic inch of it, exposed to the action of lime in a tube over mercury, was only diminished in two days to nine-tenths of a cubic inch, and no further absorption was afterwards observed to take place. But even this circumstance does not demonstrate that the gas has no affinity for lime, and is not capable of combining with it; for on making a similar experiment with carbonic acid, substituting this gas for the new compound, the result was the same; in two days only about one-tenth of a cubic inch was absorbed.

Though the gas is decomposed by water, yet it appears to be absorbed unaltered by common spirits of wine, which contains so considerable a quantity of water; it imparted its peculiar odour to the spirit, and its property of affecting the eyes; five measures of the spirit condensed sixty measures of the gas.

It is also absorbed by the fuming liquor of arsenic, and by the oxymuriate of sulphur.

The former appeared to require for saturation ten times its own volume; six measures of the liquor condensed about sixty of the gas. The liquor thus impregnated was thrown into water, and a pretty appearance was produced by the sudden escape of bubbles of the gas; had not its intolerable smell convinced me that the gas was unaltered, I should have not conceived that it could pass through water undecomposed.

I cannot account for the assertion of M.M. GAY LUSSAC and THENARD and of Mr. MURRAY, that oxymuriatic gas does not, when under the influence of light, exert any action on carbonic oxide: I was inclined at first to suppose that the difference between their results and mine, might be owing to their not having exposed the gasses together to bright sunshine; but I have been obliged to relinquish this idea, since I have found that bright sun-shine is not essential, and that the combination is produced in less than twelve hours by the indirect solar rays, light alone being necessary.

The formation of the new gas may be very readily witnessed, by making a mixture of dry carbonic oxide and chlorine in a glass tube over mercury: if light be excluded, the chlorine will be absorbed by the mercury, the carbonic oxide alone remaining; but if bright sun-shine be immediately admitted when the mixture is first made, a rapid ascension of the mercury will take place, and in less than a minute the colour of the chlorine will be destroyed, and in about ten minutes the condensation will have ceased, and the combination of the two gasses will be complete.

It is requisite that the gasses should be dried for forming this compound; if this precaution is neglected, the new gas will be far from pure; it will contain a considerable admixture of the carbonic and muriatic acid gasses, which are produced in consequence of the decomposition of hygrometrical water. Indeed there is considerable difficulty in procuring the new gas tolerably pure; a good air pump is required, and perfectly tight stop-cocks, and dry gasses, and dry vessels.

I have endeavoured to procure the gas, by passing a mixture of carbonic oxide and chlorine through an earthen-ware tube heated to redness; but without success.

The specific gravity of the gas may be inferred from the specific gravities of its constituent parts jointly with the condensation that takes place at their union. According to CRUICKSHANK, 100 cubic inches of carbonic oxide weigh 29,6 grains, and according to Sir HUMPHRY DAVY, 100 of chlorine are equal to 76,37 grains: hence as equal volumes of these gasses combine, and become so condensed as to occupy only half the space they before filled, it follows that 100 cubic inches of the new compound gas are equal to 105,97 grains. Thus this gas exceeds most others as much in its density as it does in its saturating power.

To ascertain whether chlorine has a stronger affinity for hydrogene than for carbonic oxide, I exposed a mixture of the three gasses in equal volumes to light.

> Both the new compound and muriatic acid gas were formed, and the affinities were so nicely balanced, that the chlorine was nearly equally divided between them. And that the attraction of chlorine for both these gasses is nearly the same, appears to be confirmed by muriatic acid not being decomposed by carbonic oxide, or the new gas by hydrogene.
>
> The chlorine and carbonic oxide are, it is evident from these last facts, united by strong attractions; and as the properties of the substance as a peculiar compound are well characterized, it will be necessary to designate it by some simple name. I venture to propose that of phosgene, or phosgene gas; from φως; light, and γινομαι, to produce, which signifies formed by light; and as yet no other mode of producing it has been discovered.
>
> I have exposed mixtures consisting of different proportions of chlorine and carbonic acid to light, but have obtained no new compound.
>
> The proportions in which bodies combine appear to be determined by fixed laws, which are exemplified in a variety of instances, and particularly in the present compound. Oxygene combines with twice its volume of hydrogene and twice its volume of carbonic oxide to form water and carbonic acid, and with half its volume of chlorine to form euchlorine; and chlorine reciprocally requires its own volume of hydrogene and its own volume of carbonic oxide to form muriatic acid and the new gas.
>
> This relation of proportions is one of the most beautiful parts of chemical philosophy, and that which promises fairest, when prosecuted, of raising chemistry to the state and certainty of a mathematical science.

In October, 1812, Sir Humphry wrote to his brother: 'The controversy is closed' [467c]. Nevertheless, Murray never accepted the chlorine theory [467b (Vol.1, p.160),1465,1589e].

An interesting insight into the character of both John and Sir Humphry is revealed by the following *verbatim* extract from the previously unpublished pages 159–163 of John Davy's Biographical Notes, Volume 4 (Box M117/28) from the University Library, University of Keele. Judging from the preceding entry in Davy's notes, these were probably written about February 1815: the front of the Journal/Diary is inscribed Valletta, Jan 17th 1831.

> "Having thus given in connexion and in regular succession the results of his enquiries relative to chlorine, I have little more to add on this subject. – His views were readily adopted by the most eminent chemists of Europe; and with the exception of two or three instances, in less than two years from their promulgation they were universally received and taught in the schools. This was no more than might have been expected in an enlightened age and considering that his doctrine of Chlorine being a simple substance was merely an expression of facts. – The only individual who resisted with any pertinacity was Mr. Murray, an ingenious lecturer on Chemistry in Edinburgh, who I believe never gave up his early opinion that Chlorine is a compound of muriatic acid and oxygene; – or rather his modified opinion that it is a compound of oxygene and an unknown basis called dry muriatic acid, – I say unknown in as much as it was never pretended to have been seen or obtained, insulated or not in combination, which was the great fault of his argument. In support of the old doctrine he published a series of papers in Nicholson's Journal, which my brother delegated me to answer. The controversy, as most frequently happens, was conducted with unnecessary warmth and asperity; – however it was not unproductive of good. It brought the subject strongly before the philosophical public, and was probably instrumental in deciding the question sooner than if the new doctrine had encountered no active opposition; – and what was more important, it was the means of bringing to light two compounds which till then had not been known, Euchlorine the compound of chlorine and oxygene which was discovered by my Brother, and of which his account

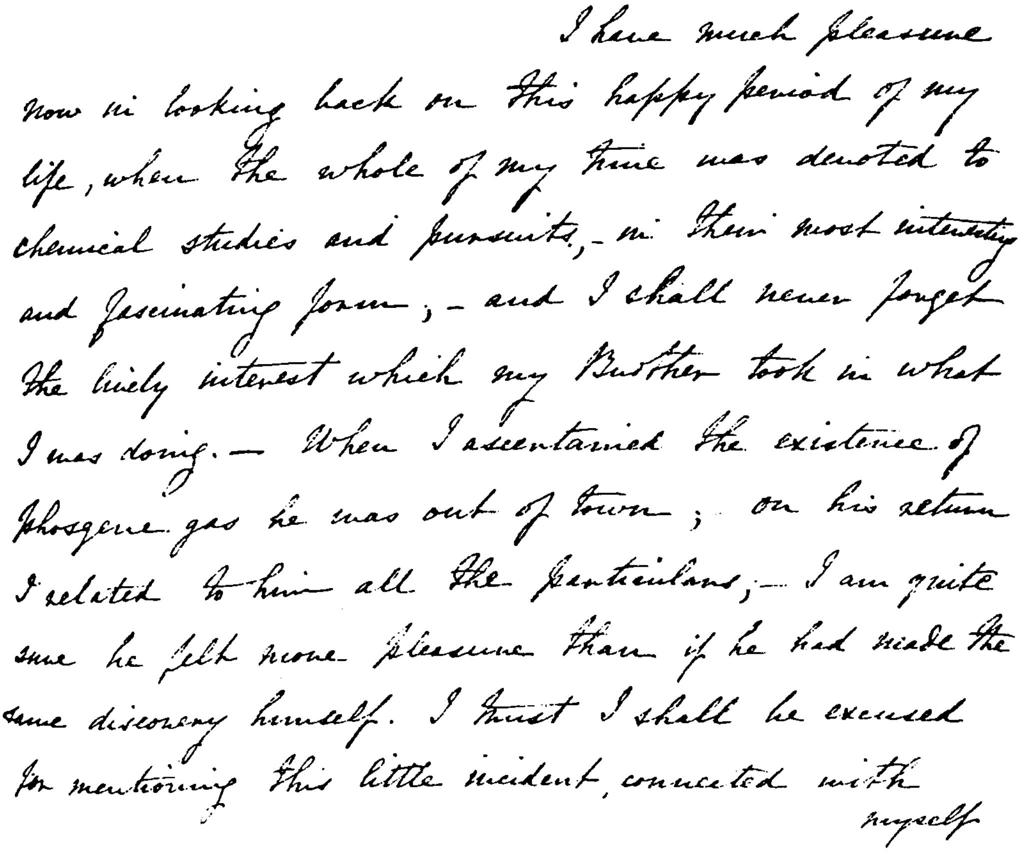
> **has been given; – and phosgene, a compound of chlorine and carbonic oxide which was discovered by myself, – both which had acted in Mr. Murray's experiments, without his being aware of it, – and which consequently had occasioned results of a deceptive character. – I have much pleasure now in looking back on this happy period of my life, when the whole of my time was devoted to chemical studies and pursuits, – in their most interesting and fascinating form; – and I shall never forget the lively interest which my Brother took in what I was doing. – When I ascertained the existence of phosgene gas he was out of town; – on his return I related to him all the particulars; – I am quite sure he felt more pleasure than if he had made the same discovery himself. I trust I shall be excused for mentioning this little incident, connected with myself as it tends to display his warm sympathy for the success of others; – his mind I believe was particularly free from the mean feeling of envy, – as much so as it was under the influence of the noble ambition of acquiring unsullied honors.**
>
> **There are parts of the preceding dissertations on chlorine which require some comment, especially that part in which he proposes a nomenclature for the combinations of chlorine, founded on a principle different from that of the system of nomenclature of the French school of Chemistry. – I shall defer what I have to offer on this subject to an after portion of the work, when I shall have to notice the opinions which he formed at a very early period relative to the language of chemistry, and of which he has left a record. I now think it preferable to make the reader acquainted with the remainder of his scientific labours for the period of his life now under consideration.**
>
> **He was one of the earliest supporters of the doctrine of bodies combining in definite proportions, or of what is commonly called the atomic theory. Previous to introducing a paper of his in which this doctrine is happily illustrated by new and curious facts, I shall give a short historical sketch equally candid and perspicuous of the origin of this doctrine, and of its progress, which forms a part of the Discourse he delivered as President of the Royal Society on the awardment of the first Royal medal to Mr. Dalton "for the developement of the chemical theory of definite proportions." – He proceeds, – "What Mr Daltons merits are, I shall briefly endeavor to state to you, though it is impossible to do justice to them in the time necessarily allotted to this address.""**

The key passage, relating to the discovery of phosgene, is illustrated in Fig. 1.1. Significant portions of this text were later published, in modified version, as parts of John Davy's "Memoirs of the Life of Sir Humphry Davy, Bart. LL.D. F.R.S." [467a; Vol. 1; pp. 417–418] and "Collected Works of Sir Humphry Davy" [467b; Vol. 1; pp. 122–124].

1.1.3 The discoverer of phosgene: John Davy (1790–1868)

John Davy was born in Penzance on May 24th, 1790, the second son of Robert and Grace. His father died only four years after his birth and his elder brother (by some 12 years), Sir Humphry Davy, was regarded by John as a father figure. Indeed, John's education was directed and funded by Sir Humphry, whom he greatly admired and respected.

John Davy graduated in medicine at Edinburgh in 1814 and became an army surgeon. He contributed a total of 152 papers to the literature, in subjects as varied as physics, geography, anatomy and sociology. In addition to his chemical researches on chlorine and its derivatives, he also published on hydrofluoric acid and phosphorus [1742a]. His portrait, painted in Malta (*ca.* 1825: by an unknown Italian artist) is reproduced in Fig. 1.2. As an intriguing aside, a photograph originally believed to be of Dr. John Davy is held in the



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phosgene gas he was out of town; on his return
I related to him all the particulars, — I am quite
sure he felt more pleasure than if he had made the
same discovery himself. I trust I shall be excused
for mentioning this little incident, connected with
myself

Fig. 1.1 An abstract reproduced (with permission) from page 161 of John Davy's Biographical Notes, Volume 4 (Box M117/28) from the University Library, University of Keele.

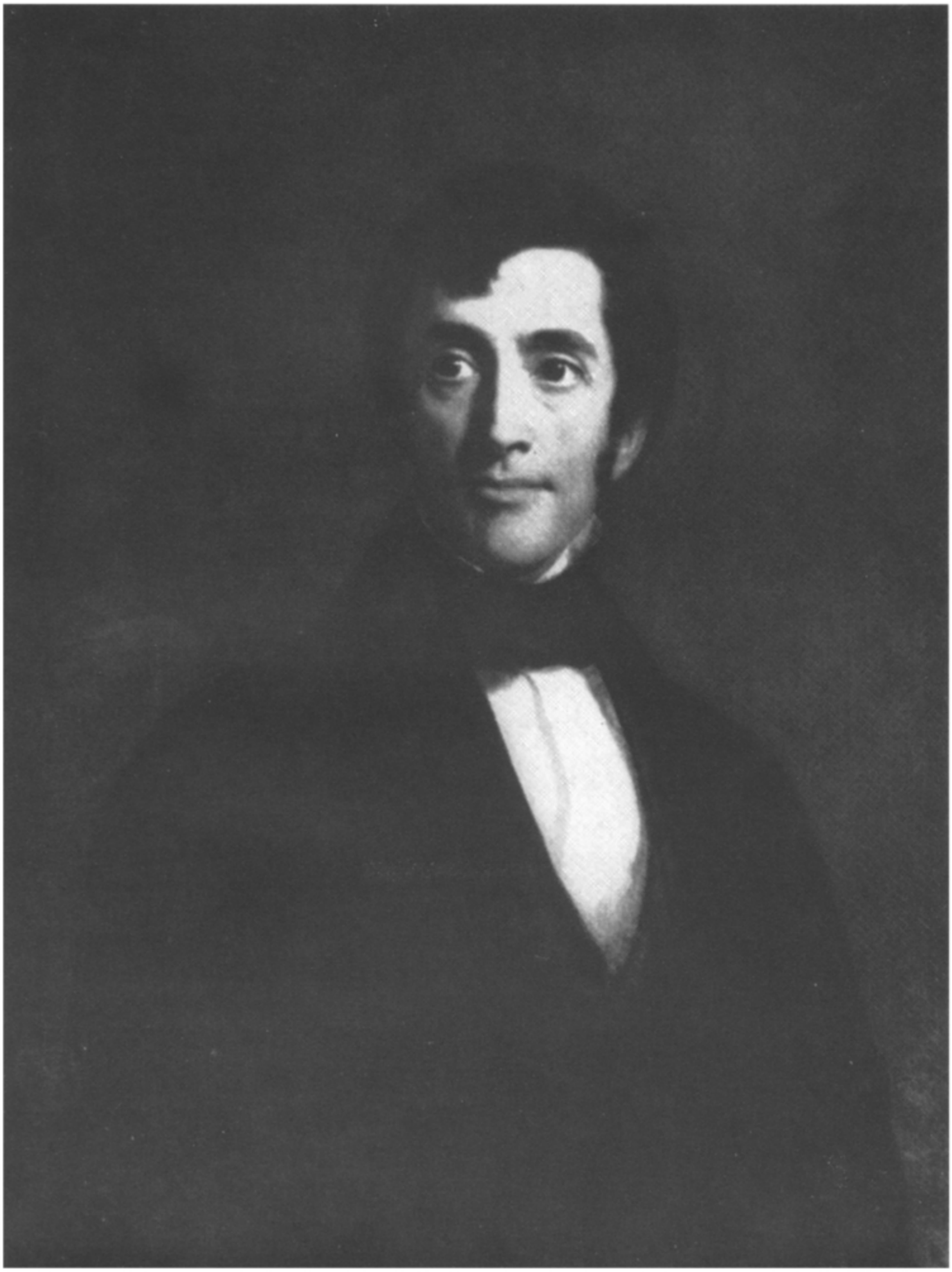

Fig. 1.2 Dr. John Davy, painted in Malta (*ca.* 1825).

Wellcome Institute for the History of Medicine (Accession No. 68,226): this has pasted on to the back of its support mount the inscription:

D^{r}. Davy
Lesketh How
Ambleside

and a short biographical sketch of John Davy. However, neither the handwriting on the address nor the biography match that of John Davy (see Fig. 1.1), and the picture bears no resemblance to that of the sitter for the portrait shown in Fig. 1.2. As a result of a series of letters and telephone calls, in late 1985, between the authors, William Schupbach (curator) and Dr. Gertrude Prescott (assistant curator), the Wellcome Institute photograph has been reassigned to an unknown sitter [1660a].

Dr. John Davy became a fellow of the Royal Society in 1834 and died in 1868, survived by a son and daughter [1742a]. A short biography has been written by Ross [1742a], although (somewhat surprisingly) his most marked contribution to science, the discovery of phosgene, is not mentioned.

Although a distinguished scientist in his own right, John Davy was in the shadow of (but not eclipsed by) his better known brother [1742a]. Indeed, John was the principal biographer of Sir Humphry [467a,467b,467c,703a,703b] and in some of the scientific battles in which Sir Humphry became involved, the conclusions were carried out in John Davy's name [703b]. The chlorine controversy is perhaps the most dramatic example of this, eventually involving John Davy accusing Murray of scientific confuscation [466c]:

> **"There is nothing further in Mr. Murray's communications, that requires notice, excepting a misuse of names. He sometimes writes properly, calling me 'Mr. J. Davy,' at other times, improperly, 'Mr. Davy,' thus creating confusion, and rendering it impossible to distinguish opinions and statements which belong to me, and for which I alone am answerable, from those of Mr. Davy, my brother."**

1.2 QUIESCENCE

It was more than fifty years after its discovery, in the year of John Davy's death, that the preparation of phosgene was achieved catalytically by Schützenberger [1824a]. Phosgene was first employed in the 1880s, for the preparation of crystal violet and the dye precursor, Michler's ketone (see Sections 3.2.3.1.1, 4.7.4 and 10.2.1.4). The insidious applications of phosgene which were to follow would change the perception of this useful industrial chemical forever – would change its character to such an extent that rational discussion of its use would become very difficult in a public forum.

1.3 THE STORM APPROACHETH

1.3.1 Production of phosgene before, and during, WW1

Prior to World War 1 (WW1), phosgene was used in Germany in moderately large quantities for various peaceful purposes, particularly for the production of synthetic dyes manufactured in the factories of Friedrich Bayer & Co. in Leverkusen and in the Badische Anilin & Soda Fabrik (BASF) works in Ludwigshafen. Phosgene was also produced before the war by Chemische Fabrik von Heyden [859a]. An early report estimated combined production at only about 70 tons per year [1153]. However, estimates [426,1522] that the smaller Bayer plant was able to produce around 360 tons of phosgene per year lends weight to Haber's estimate [859a] of a pre-war capacity in Germany's BASF plant of 1800 tons per year (probably not fully utilized), which was later raised to 7200 tons per year.

By the end of World War I, about 18000 tons of phosgene had been manufactured by the Germans for use as a war gas (10682 tons being produced between 1915 and 1918 by BASF, corresponding to 621 tons per month) [859a], more-or-less equivalent to the combined total output of the Allies. The large BASF production was attributable to ready access to cheap and abundant carbon monoxide, taken as a side-stream from an adjacent ammonia plant. Germany also produced 11600 tons of diphosgene during the last three years of the war, compared to zero production by the Allies [859a].

Production of phosgene in France during WW1 was initially based on synthesis from tetrachloromethane and sulfuric acid. About 430 tons of phosgene were produced by this method, but by 1916 the French switched to the German method using the reaction between pure carbon monoxide (obtained by burning hydrogen-free coke in dioxygen) and dichlorine (obtained from Castner-Kellner Co.) over animal charcoal [859a,1153]. By the end of the war, the French had manufactured almost 15800 tons of phosgene, mainly at the following locations:

- Societé Industrielle de l'Accumulateur Alcalin, Romainville
- Poulenc Frères, Vitry
- Chlore Liquide, Pont-de-Claix (near Grenoble)
- G. de Laire, Calais
- G. de Laire, Pont-de-Claix

of which 6200 tons were purchased by the British [1153].

In America, phosgene was made from combination of carbon monoxide and dichlorine in graphite tubes. Daily production at the Federal site, known as the Edgewood Arsenal [819,954], was 40 tons at the beginning of America's late involvement in the war. The works were eventually extended to a capacity of 80 tons per day (although the plant was closed, shortly after the signing of the Armistice, and the extended production was never fully realised [1019]) [954], with a further 10 tons per day provided by the Oldbury Electrochemical Co.

and 5 tons per day provided at Frank Hemingway Inc., of New Jersey [1153]. Despite the huge scale of production at Edgewood, and the considerable manufacturing efficiency, the total production in the United States during WW1 amounted only to about 1600 tons, of which 420 tons were transported overseas – mostly for filling artillery shells by the British [859a,1153].

Italy produced the gas at Torre de' Passeri in Pijano d'Orte, and at the Rumjanki factory in the North. Prepared from oleum and tetrachloromethane, the method was satisfactory in all but cost. The Italians went over to the German method, using a bone charcoal catalyst, thus raising their production up to 4 tons per day using this method, and up to 6 tons per day by 1918 [1153].

Phosgene was produced in the U.K. in large tonnages, for the first time, for use as a chemical weapon in World War I [881]. In England, during WW1, phosgene was prepared at several locations:

- United Alkali Co., Widnes
- United Alkali Co., Allhusen Works, Gateshead
- Ardol Works, Selby
- Electro Bleach, Middlewich.

The United Alkali Company used carbon monoxide generated from producer gas (containing only about 30% CO) and dichlorine obtained from the Weldon process, an early manufacturing process based on the reaction of hydrochloric acid with manganese(IV) oxide. These impure reactants were combined over wood charcoal and the dilute phosgene product (which could not be separated from the permanent gases present by means of refrigeration, see Chapter 4) was dissolved into tetrachloroethane and then recovered by fractionation [859a]. By the end of the war, the British had prepared a total of about 1400 tons of phosgene [859a], although additional amounts were purchased from both the French and the Americans. The British, despite their considerable efforts, had managed to produce less phosgene in four years than the Americans (having learnt from their allies' mistakes) had produced in three months, although production of dichlorine (particularly at Castner–Kellner in Runcorn) was considerable. A large quantity of dichlorine was exchanged for phosgene with the French [859a], but L.F. Haber [859a; p. 154] suggests that "Phosgene was throughout the war the great failure of the British Chemical Industry".

1.3.2 Phosgene compared with other war gases

Phosgene is said to be probably the most poisonous gas used in industry [1768]. However, there are *many* materials in common industrial practice that are *significantly* more poisonous than phosgene. The utility of phosgene (and of dichlorine) in the military chemical industry has been described in an early review [718], but recent books by Haber [859a], Richter [1711a] and Spiers [1928b] have now supplanted the earlier standard texts by Prentiss

[1660] and Sartori [1778] as sources for the experience and practice of chemical warfare. More popularist sources include "A Higher Form of Killing" [891] and "Yellow Rain" [1824b]. The former book (yes, it is THE Jeremy Paxman!) is quite outstanding, and contains "unreferenced" material which is unavailable elsewhere in an open form – in the cases relating to phosgene that we have investigated, we can verify their accounts as accurate, and understand the reasons why no supporting reference material is cited.

Fig. 1.3 shows the best estimates currently available for the war time production of the principal war gases by the chief combatants. Chlorine was demonstrably the most 'popular' gas, but, of the chemicals available at the time of World War I, phosgene was considered to be one of the most suitable, in practical terms. This was because it has the right balance between volatility and persistency. In WW1, phosgene was frequently used in combination with other materials. When combined with pumice, its rapid vaporisation is inhibited. Mixed with dichlorine, its vaporisation is enhanced, so that its deployment in cold weather could be assured. It was also compressed in shells and fired with phenylchloroarsine, diphosgene, arsenic(III) chloride, *etc.* Equal parts of phosgene and tin(IV) chloride or titanium(IV) chloride was the French "Collongite". In addition to the direct use of phosgene as a chemical warfare agent, either alone, or in combination with other materials, phosgene derivatives (*vide infra*) were frequently employed.

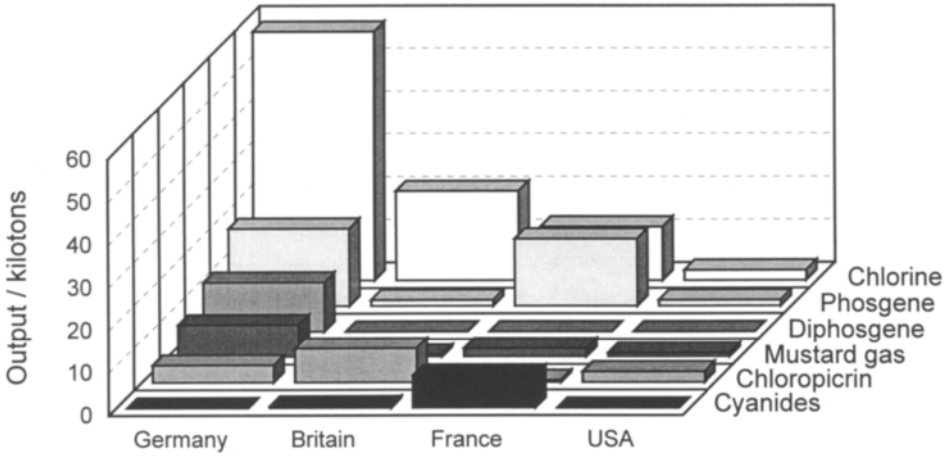

Fig. 1.3 **War time production (1915–1918) of the principal war gases by the chief protagonists [859a]**

Methyl chloroformate, $ClC(O)OCH_3$, prepared from the action of phosgene on methanol, whilst not used alone, was used as a solvent for other toxic materials. Monochloromethyl chloroformate, $ClC(O)OCH_2Cl$, is more lachramatory than phosgene, and was compressed in grenades and bombs. The dichlorinated derivative, dichloromethyl chloroformate, $ClC(O)OCHCl_2$, has a weaker lachrymatory action than the monochlorinated analogue, but is said to be closer to phosgene in its asphyxiant action [426]. Thus a mixture of monochloromethyl chloroformate and dichloromethyl chloroformate was found to posess both marked asphyxiant and lachrymatory properties. This mixture was known as "Palite" by the British and the French, and as "K-Stoff" by the Germans [426,1778].

The trichlorinated derivative, trichloromethyl chloroformate, $ClC(O)OCCl_3$, is also known as diphosgene (see Section 12.2.1) [1660,1778]. The French called it "Surpalite" and the Germans called it "Perstoff" or "Grün Kreuz" (Green Cross). It has a similar toxic action to phosgene and was used in warfare either alone or in combination with chloropicrin, phosgene or other toxic materials [426]. Diphosgene was first used in gas shells by the Germans at Verdun, France, in May 1916. It was considered to be so effective that it was adopted as the standard non-persistent lethal gas for shell filling. It was said to be the principal killing gas used in this way. Having very similar toxicity and physiological effects to phosgene, but being more suitable for shell filling since it could be put into containers in the field (phosgene shells had to be filled away from the front and had to withstand long storage and rough handling) [955aa]. However, in reality, phosgene is a simpler material to produce and has a greater killing capacity than diphosgene, especially since (owing to its higher volatility) it is able to achieve a high concentration in the surrounding air in a shorter period of time [859a]. The mystery as to why the Germans persisted in using diphosgene, instead of switching to phosgene, is elegantly summarised by L.F. Haber [859a]:

> "It is nevertheless a remarkable fact that the Germans never changed their minds about diphosgene. [...]. The episode remains inexplicable, for the Germans were relying on an inferior material which required three times as much chlorine as phosgene - a compound simpler to make and superior as a poison. They knew that their enemies, ever quick to copy them, did not, on this occasion, follow suit, a sure sign that they considered diphosgene second-best. Why did the Germans not test the one against the other and draw the consequence? Diphosgene was not the only instance of insufficient testing and administrative inflexibility. The results were to impair the effectiveness of their chemical warfare and considerably diminish the Allied gas casualties."

1.4 REFINEMENTS OF EVIL

So guns and strong explosives
are evil, evil
they let death upon unseen men
in sheer murder.

And most murderous of all devices
are poison gases and air-bombs
refinements of evil.

D.H. Lawrence, *Murderous Weapons*

We would recommend that any interested reader of this section reads the recent academic books by Haber [859a], Richter [1711a], and Spiers [1928b]. More accessible, and eminently readable, sources include the excellent "A Higher Form of Killing" [891] and "Yellow Rain" [1824b]. We have drawn heavily on these sources for the following sections, as we do not have the space, time or expertise to do justice to the wider implications of chemical warfare, and its influence on the outcome of World War I. We hope here to indicate the horror of chemical warfare, whilst at the same time retaining a logical view of the facts. Many of the exaggerations and myths associated with phosgene have arisen from its usage as a war gas in World War I; the hyperbole MUST be separated and discarded if phosgene is to be treated as a laboratory and industrial chemical, and not a symbol of death.

1.4.1 Use of phosgene, 1914–1918

The use of gases in the First World War was, perhaps surprisingly, not the earliest record of chemical warfare. The early Egyptians and Romans, who were no strangers to the use of poison as an effective means of removing rivals, both have recorded using various noxious substances against their enemies, and Leonardo da Vinci described a shell containing fine sulfur and arsenic dust which could be thrown at enemy ships and galleys. However, in terms of modern day warfare, the First World War undoubtedly saw the most extensive application of chemical weaponry that had ever been employed. Fritz Haber, the father of chemical warfare, is a pervasive figure in this account.

1.4.1.1 **Ypres, April 1914: the refinement commences**

The Germans were the first to use gas, against the Allies, at Ypres in Belgium [687,731,859a,1032,1711a,2155]. The following account owes much to the descriptions of Seagrave [1824b] and Macdonald [1289].

The use of chlorine at Ypres was long delayed, giving rise to many discounted rumours in England; Haber was a better chemist than he was a meteorologist! We are fortunate to have the following first-hand account from Herr Otto Hahn. "In the middle of January I received orders to go and see Geheimrat Haber, who was in Brussels on behalf of the Ministry of War. He explained to me that the Western Fronts, which were all bogged down, could be got moving again only by means of new weapons. One of the weapons contemplated was poison gas, in particular chlorine, which was to be blown towards the enemy from the most advanced positions. When I objected that this was a mode of warfare violating the Hague Convention,[†] he said that the French had already started it – though not to much effect – by using rifle-ammunition filled with gas[¶]. Besides, it was a way of saving countless lives, if it meant that the war could be brought to an end sooner. Haber informed me that

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[†] The Hague Declaration (1899), to which Germany was a signatory, contained the clause "The Contracting Powers agree to abstain from the use of all projectiles the sole object of which is the diffusion of asphyxiating or deleterious gases".

[¶] A reference to the limited use of tear-gas bullets by the French.

his job was to set up a special unit for gas-warfare, Pioneer Regiment No. 36. We received our first special training in Berlin, being instructed in the use of the poison gases and the relevant apparatus, including what was called the Drägersche Selbstretter, a protective device that had to be worn when discharging the gas. We also had to learn something about wind and weather, of course. From that training-course I returned to Flanders and was attached to Infantry Regiment No. 126 as their gas pioneer. My first task was to be what was called a front-line observer, *i.e.*, I had to evaluate positions from which gas might be used. Our position was in the vicinity of Gheluvelt, directly opposite the English lines, and so at times we could only talk in whispers. We were not yet very well entrenched and we were constantly under enemy fire, so the installation of the gas cylinders for the proposed attack was very difficult indeed. The gas warning was given a number of times, but the attack had to be postponed again and again because of the weather conditions. Every time the time of the attack had been fixed - which had to be twenty-four hours earlier - the wind changed and blew towards us, and the units brought up from the rear had to be taken back again. In the middle of April High Command decided to remove the gas cylinders again and take them to a sector of the front north-east of Ypres, where wind conditions were more favourable. The reason why it was not entirely successful was probably that both the troops and the Command had become nervous as a result of the many abortive attempts, and also that by then there were no longer sufficient reserves available to consolidate the gains."

At 16:00 on 22nd April, 1915, a small German plane flew along the front dropping flares, a signal to the German infantry to fall back into their trenches. The German Pioneers used 6000 metal cylinders (equivalent to 150 tons) of chlorine gas, which was released from tubes directed over the top of the trenches over a 7 km front. The Allies (African Colonials, Algerians, Belgians and Canadians) watched as a thick green cloud formed and rolled slowly (*ca.* 1 m.p.h.) towards them from the German trenches. A Belgian grenadier is reported to have said "None of us knew what was going on. The smoke cloud grew thicker, which made us believe that the German trenches were on fire!" Captain Pollard, from the British trenches, saw a "strange green cloud of death". He recorded of the African Troops, "In the gathering dark of that awful night, they fought with their terror, running blindly in the gas cloud, and dropping with breasts heaving in agony and the slow poison of suffocation mantling their dark faces. Hundreds of them fell and died; others lay helpless, froth upon their agonized lips and their racked bodies powerfully sick with tearing nausea at short intervals. They, too, would die later - a slow and lingering death of agony unspeakable." From a French army doctor, "I had the impression that I was looking through green glasses. It burned my throat, caused pains in my chest, and made breathing all but impossible. I spat blood and suffered from dizziness. We all thought we were lost." Then, from an officer of the Territorials in a field hospital on the following day, "There was no difficulty finding them. The noise of the poor devils trying to get their breath was sufficient direction. Twenty of the worst cases were on mattresses, all more or less in a sitting posture, propped against the walls. Faces, arms, hands were a shiny grey-black. With mouths open and lead-glazed eyes, they were all swaying backwards and forwards trying to get their breath, struggling, struggling for life. There was nothing that could be done except to give them salt and water emetic. The gas fills up the lungs and bronchial tubes with froth, which finally suffocates the victim. It was like slow drowning, taking sometimes two days." The lines were reinforced, but the effects of the gas were still all too apparent. From Sergeant Bill Hay, 9th Battalion (TF), The Royal Scots: "A Canadian came down and he shouted to our Captain, 'The bastards have broken through; they've gassed us and they've broken through, so give them the bloody bayonet, Jock'. [...]. You just - you were in action - your main concentration was to get there and not get killed yourself, so you lost your twitterings. Of course, the chaps were all gasping and couldn't breathe, and it was ghastly, especially for chaps that were wounded - terrible for a wounded man to lie there! The gasping, the gasping! And it caused a lot of mucus, phlegm, your eyes were stinging as well. You couldn't stop to help anybody, even if he was your brother, he'd still be lying there badly injured, and you mustn't help, so you'd got to go on with the attack or there'd be nobody to contend with the attack, so you went on and the Jerries ran back, they fell back, they didn't wait for us to get close enough." The nett effect of this, the Second Battle of Ypres, was no change in the positions on the Western Front.

The element of surprise made this a "very successful attack". However, in what will become a recognized phenomenon associated with chemical warfare, the effectiveness was more psychological than real. At that time, and for many years after the war, the public estimates of the casualties at Ypres were 15000 gas casualities, including 5000 deaths. The official British medical records show 7000 casualties, of whom between 350 [1824b] and 1000 [859a] died. Of course, at the time, it was to the Allies' advantage to exaggerate the scale of the death toll, and to accuse, with justification, the Germans of introducing a new war 'horror'. Fritz Haber claimed, in contrast, that he had examined the field of attack at Ypres an hour after the cloud had passed and "saw there a limited number of men killed by gas, not many" [859a]. In fact, the German claim was that only 200 gas victims were hospitalized, and only twelve died! The truth lies between these two, equally convenient, extremes.

1.4.1.2 Phosgene: a futher refinement

The success of the Ypres attack convinced the Germans of the effectiveness of gas warfare, and they decided to work on improving both the delivery method and on extending the types of gas used. Over the following months, gas was used extensively on the Eastern Front, on the approaches to Warsaw. These attacks included the first experimental use of chlorine-phosgene mixtures, but all the surviving records are extremely sparce [859a]. Between 22nd April and 6th August, 1915, the Germans released approximately 1200 tons of gas, over 800 tons of which were released on the Eastern Front [859a]. However, the use of gas was not demonstrably advantageous, largely due to the unpredictable nature of the wind.

Phosgene was thought to be a very effective gas: with its delayed action, many men gassed were unaware of the severity of the poisoning until several hours later [756].

Furthermore, the Germans already had a reliable system for its production (see Section 1.3.1). In fact, an inspection of the chemical plants carried out by the Americans after the war concluded that the German success was due to efficient organization, emphasis on research, and a working environment designed to be agreeable to the workers: in 1919, Bayer was still manufacturing phosgene for the dye industry, at the rate of 30 tons per month [1522].

The first documented use of phosgene on the Western Front was at Champagne at 08:15 on 19th October, 1915. It was used in admixture with chlorine: one part of phosgene to four parts of chlorine.† Again, it was the German troops attacking the Allies, and about 275 tons of gas were released from about 14000 cylinders over a 12 km front. Thus, although more gas was used than at Ypres, the concentration of the gas cloud was less dense. The Germans advanced during the day, but the French (wearing protective mouthpads) drove them back by nightfall. The following day, the Germans emptied another 4400 cylinders of the gas mixture, and in a third attack on the 27th October, a further 5000 cylinders were used. No nett advance was achieved; in the three gas attacks, the French suffered over 5700 casualties, including 500 deaths [859a].

By 19th December, 1915, the Germans were regularly using a mixture of chlorine and phosgene, this time again at Ypres [859a,1032]. The activities of the Pioneer regiment were observed by the British, who had gas helmets which offered poor protection against phosgene. The attack (at 05:15) was thus anticipated; 9300 cylinders (180 tons) of gas were used over a 4–5 km front, giving a very high concentration of gas. The helmets just about coped, and of the 25000 troops in the area, 1069 were gassed, and only 116 died [859a,891,1032, 1928b,2136,2146]. The Allies had demonstrated that with sharp observation, well trained troops, and reasonable protection, there was a counter to gas attacks. Following this attack, systematic anti–gas training was introduced throughout the British Expeditionary Force.

Although there had been an unconfirmed report (from a chemist who had been working in Germany in 1909) that German soldiers were seen experimenting with the effect of poisonous gas on a herd of sheep [953], the Allies were quite unprepared for the use of phosgene as a war gas. It created a "great panic at Allied Headquarters" [953], and early emphasis was placed upon retaliation rather than protection. In mid–1915, special Companies of the Royal Engineers were placed under the command of Major C.H. Foulkes [859a,1711a,1928b], élite troops (none of lower rank than corporal, most – but by no means all – being chemistry students or graduates) who were to specialise in chemical warfare – the British Special Brigade.¶ The first major Allied gas offensive was at Loos (15th September, 1915), using chlorine. Phosgene was first used by the French in February 1916, at Verdun, and by the British in June 1916, at the Somme.

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† The high vapour density of phosgene gas made it hug the ground, and readily flow into the trenches. However, its high boiling point (see Section 6.2.1) required the use of chlorine as a dispersal agent.

¶ Richter's recent book [1711a] focuses specifically on the British use of gas warfare, and the Special Brigade, and so this aspect of the subject will only be mentioned here *en passant*.

Delivery of the gas (for security reasons, referred to as "accessory" when shipped or discussed) was one of the biggest problems. Simply releasing the gas from cylinders (in the German manner) meant that troops had to get quite close to enemy lines, the dispersal depended on air currents, temperature, humidity, *etc.*, and there was the continuing problem of leakage from the cylinders onto one's own troops. Some of these problems were vividly illustrated in Robert Graves' "*Goodbye to All That: An Autobiography*", from which the following two quotes are taken. Graves served with the Royal Welch Fusiliers, in a company commandeered by the Special Brigade to carry the heavy and unwieldy "accessories" to the trenches. He writes: "This was worse than carrying the dead; the cylinders were cast iron, heavy and hateful. The men cursed and sulked. [...] I felt like screaming".

> **"It's damnable. Its not soldiering to use stuff like that, even though the Germans did start it. It's dirty, and it'll bring us bad luck. We're sure to bungle it. Take those new gas-companies - sorry, excuse me this once, I mean accesssory-companies - their very look makes me tremble. Chemistry-dons from London University, a few lads straight from school, one or two N.C.O.s of the old-soldier type, trained together for three weeks, then given a job as responsible as this. Of course they'll bungle it. How could they do anything else?"**
>
> **"Thomas had not over-estimated the gas-company's efficiency. The spanner for unscrewing the cocks of the cylinders proved, with two or three exceptions, to be misfits. The gas-men rushed about shouting for the loan of an adjustable spanner. They managed to discharge one or two cylinders; the gas went whistling out, formed a thick cloud a few yards off in No Man's Land, and then gradually spread back into our trenches. The Germans, who had been expecting gas, immediately put on their gas-helmets: semi-rigid ones, better than ours. Bundles of oily cotton-waste were strewn along the German parapet and set alight as a barrier to the gas. Then their batteries opened on our lines. The confusion in the front trench must have been horrible; direct hits broke several of the gas-cylinders, the trench filled with gas, the gas-company stampeded"**

These problems were greatly relieved by the invention, in 1916, of the British Livens Projector (See Fig. 1.4) [859a,891]. This consisted of a steel tube, about three or four feet long and eight inches in diameter. It was buried in the ground, at an angle of 45°, and fired by means of an electrical charge. The projectile was a drum containing 30 lbs (14 kg) of chemical (usually phosgene). Once over the enemy position, a TNT core would cause the drum to burst open and shower the enemy with a lethal concentration of gas. It had a range of *ca.* 1.5 km. The first full-scale attack using the Livens Projector was at the Battle of Arras (France), on 9th April 1917 [2146]. During this battle, the Stokes Mortar Bomb (developed in 1914) was also used. Based on a similar design to the Projector, a steel tube raised at an angle on struts, it fired four inch mortars containing two litres of liquid gas. Introduction of shells breached the Hague Declaration,[†] but all parties adopted this method of

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[†] Although the use of chlorine and phosgene released directly from cylinders, using the wind for dispersal, was clearly against the intention of the Hague Declaration, the Germans argued that, as they had not used projectiles (see Section 1.4.1.1), they were not in breach of the key clause.

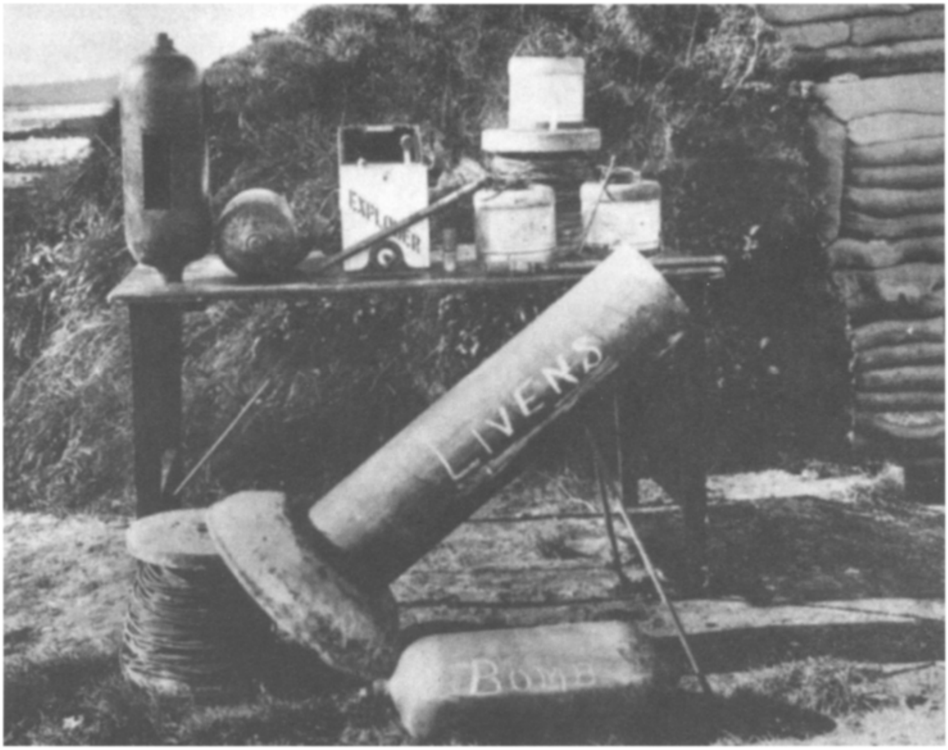

Fig. 1.4 **The Livens projector, with associated "accessories" (reproduced with permission from the Imperial War Museum).**

delivery, and the only limitation on its use seemed to be difficulties of supply (*vide infra*): by 1918, 94% of all gas was being delivered by shells [891].

The Allies had numerous supply problems, deemed by L.F. Haber [859a] as the great failure of the British chemical industry. Phosgene had been ordered from the United Alkali Co. and de Laire in August of 1915. United Alkali Co. promised to deliver one ton per day by the end of October, but it did not arrive. The Company encountered problems with the manufacture, as they had been producing phosgene by reacting concentrated sulfuric acid with tetrachloromethane – an uneconomic method. Eventually (see Section 1.3.1), phosgene plants were installed at Widnes (United Alkali Co.), Gateshead (United Alkali Co.) and Middlewich (Electro Bleach). Thus, although the British decided in Autumn 1915 to use a 50:50 mixture of chlorine and phosgene called 'White Star', supplies were not available until March 1916. The French began to make phosgene in 1916, but also had production problems. By 1918, Britain was making almost 700 tons per year by combining carbon monoxide and chlorine over a charcoal catalyst.

The Germans suffered heavy losses from Allied projector gas attacks, and developed their own projector shells, filled with phosgene, or with a mixture of phosgene and chloropicrin (trichloronitromethane, CCl_3NO_2). Furthermore, the new German design had a range of 3.5 km [756]. The Allies' favoured shell was White Star, the Germans' preferred shell was Green Cross (diphosgene, see Section 1.3.2). The mortality product (see Section 2.4) for phosgene and diphosgene is the same, at 1000 p.p.m. min. Exposure to concentrations of 10 p.p.m. causes fighting inefficiency, 40 p.p.m. for one minute is debilitating. Exposure to 10 p.p.m. for 25 min, or 5 p.p.m. for 50 min, may be fatal; the persistency of the gas in air (summer and winter) at the release site is 5–10 min [2136].

Throughout 1917, phosgene and diphosgene were the major agents of chemical warfare [1032]: by 1918, mustard gas – bis(2–chloroethyl) sulfide – was supplanting them. Although it would have been much easier to expand phosgene production than to prepare the more sophisticated mustard gas, it required much more rigorous methods to protect soldiers from the effects of mustard gas. Its terrible effects are apparent to all who have seen John Singer Sargent's unforgettable and haunting oil painting, "*Gassed*", which hangs in the Imperial War Museum in London.

1.4.1.3 Phosgene: the human dimension

The increasing use of gas by both sides in the war led to numerous accounts of the effects of phosgene poisoning on the victims [731,733,734,756,859a,953,1019]. The medical personnel had little to offer in terms of treatment, and were hampered by lack of supplies and equipment. Bleeding of poison victims and the administering of oxygen, when available, were the most recommended treatments. However, one of the most destructive aspects of gas attacks was the tremendously demoralising effect of seeing many soldiers unable to breathe because of their corroded lungs, and often taking many hours or even days to die. The Casualty Clearing Stations[†] began to classify poison cases on arrival, by the extent of their cyanosis, and only treated those that they felt had some chance of surviving. The more serious cases were often given morphine to ease and quieten them until death [859a].

Phosgene victims were described as being either blue or grey in colour. Grey victims were the most serious, as the colour represented failure of the respiratory system, rather than the heart, giving these victims the least chance of recovery. The pulse would be very rapid, breathing shallow, and blood pressure very low: death usually occurred within 24 hours. For those that managed to recover from such severe exposure, bronchitis and bronchopneumonia were common problems.

Gas victims were often sent back to duty in the symptom–free latent period of the poisoning, with disastrous results [756]. For doctors, it was very difficult to distinguish between genuine victims and malingerers, because of the time delay prior to the onset of real

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[†] The introduction of phosgene as a war gas changed the procedures for handling gas casualties. Other gases caused death to occur at the front; phosgene resulted in most deaths occurring in the Casualty Clearing Stations, due to its delayed action (see Chapter 2). This also distorted the reported casualty figures, making phosgene appear much more effective than it actually was (see Section 1.5).

symptoms (see Chapter 2) [859a]. It may seem incredible, but a recommendation that soldiers can work, providing that they are not showing any obvious symptoms, was still in operation in the Forces Technical Manual in 1974 [505].

Gerard [731] has provided detailed descriptions of the effects of phosgene attacks, when they first occurred. He quotes from a field clinician, G.W. Norris, and we cite this emotive summary *verbatim*:

> **"A field hospital full of freshly and badly gassed men is, in the estimation of all who have had an opportunity of seeing it, the most horrible and ghastly sight of the war. Even the man who has received multiple and severe wounds, when he has been splinted, put to bed, and given his morphine, is relatively comfortable; but to see a hundred or more men, hale and hearty a few hours before, slowly strangling to death from pulmonary edema with gradually increasing dyspnea, cyanosis, and pallor, making futile efforts to expectorate and to assist their breathing by voluntary effort and muscular contortions, until exhausted they pass from semidelerium into stupor, collapse, and death, is a never-to-be-forgotten sight, a sight which makes one clench one's teeth and curse the Hun who started this dastardly infamy. This is phosgene!"**

Gerard [731] concludes that the experience, gained from the war, of acute pulmonary irritants may prove useful in industrial hygiene, accidental poisoning cases, and in the treatment of civilian diseases like pneumonia: this has, indeed, proved to be the case.

1.4.1.4 Deliver us from evil

It has already been stated that the Allied command placed early emphasis upon retaliation rather than protection. This was all too apparent to the soldier in the trenches who, initially, had no protection from the gas clouds - so his terror of the unknown was compounded by his complete defencelessness. The problem was exacerbated in 1916, with the introduction of gas shells. At first, soldiers were able to distinguish between gas shells and high explosive (HE) shells, and take appropriate evasive action. However, the German tactics soon evolved, so mixtures of gas and HE shells were fired simultaneously. Various warning devices (*e.g.* gongs, klaxons, and sirens) were used with reasonable effectiveness, and various physical devices (including extractor fans, impregnated blankets, and the ludicrously ineffective Ayrton fan - essentially a large fly-swatter) were employed with rather less success [859a]. The nett effect of these various ploys was more psychological than real.

It was indeed fortunate that phosgene undergoes rapid hydrolysis, and hence complete destruction (see Section 9.10.3.1), in the presence of base, or in the presence of moist charcoal:

$$COCl_2 + 2H_2O \longrightarrow CO_2 + 2HCl$$

This is the fundamental principle behind all phosgene gas masks, from the most primitive (a moist rag) to the most advanced.

Fig. 1.5 **A simple cotton respirator (left, reproduced with permission from the Royal Engineers Museum, Gillingham, Kent) and a black veil respirator (right, reproduced with permission from Porton Down).**

The first protection was the moist flannel rag, held to the face for an extremely limited protection (see Fig. 1.5). However, without being basic, this was largely ineffectual: the rags <u>had</u> to be made basic - either with baking soda or urine. The following extracts from Canadian author Timothy Findley's powerful novel "*The Wars*" (Penguin Books Canada, 1978) illustrate the fear and helplessness perfectly, as well as reinforcing the supply problem:

> **"'Put your mask on, Corporal Bates!'**
>
> **'I can't,' said Bates.**
>
> **'What the hell do you mean?' Robert turned and shouted hoarsely to the men below him, 'Put your masks on!'**
>
> **'We *can't* sir,' said Bates. 'They sent us up so quick that none of us was issued masks.'**
>
> **'*Every* man is issued a mask!' Robert shouted out loud. (It was like being told that none of the men had been issued boots.)**
>
> **'No, sir,' said Bates. 'It ain't true.' [...]**
>
> **'Now,' he said. 'If you want to live you have about twenty seconds. Get out your handkerchiefs.'**
>
> **'We got no handkerchiefs,' said Bates.**
>
> **'THEN TEAR THE TAILS OFF YOUR GOD DAMNED SHIRTS!' [...]**
>
> **The rest of the men were waiting numbly, holding torn pieces of cloth in their hands - staring at Robert with their mouths open. 'What are we s'posed to do?' one of them asked. 'These won't save us. Not if it's chlorine.'**
>
> **'Piss on them,' said Robert.**
>
> **'Unh?'**
>
> **'PISS ON THEM!!!' [...]**

> **He prayed: *dear Jesus, let me piss.* But he couldn't. Neither could one of the other men and this other man began to weep, till Robert shouted at him: 'Damn you! *Damn you*! Give it to me!' and he ripped the shirt tail away from the man and urinated on it himself. Then, with it dripping like a dishcloth, he thrust it back at the other man and said to him: 'Put it over your face.' But the poor daft crazy was so afraid and so confused that he put the cloth on top of his head and Robert had to grab it again and slap it on the man's face so that it covered him from eyes to chin."**

The moist rag was soon supplanted by the black veil respirator (see Fig. 1.5). Originally designed for protection against chlorine, it employed a pad impregnated with an aqueous solution of sodium thiosulfate (to destroy chlorine) and sodium carbonate, with glycerine added to keep the pad moist. The respirator was worn fastened around the neck [130].

The next advance came with the introduction of the cloth helmet, impregnated as above, which had a celluloid viewing window (see Fig. 1.6). This was known as the 'H' helmet ('H' being derived from 'Hypo', the common name of sodium thiosulfate), and provided better protection than the mouthpads, but was only effective against chlorine. This was modified for protection from phosgene by using a mixture of phenol and caustic soda as impregnates, and became know as the 'P' helmet ('P' being derived from phenate), or 'Tube' helmet when fitted with a mouthpiece for exhaled air. Protection was later enhanced by the addition of hexamethylenetetramine (or hexamine; see Section 10.2.1.5) by the Russians [2155]. This was adapted by the British to develop the 'PH' helmet ('P' being derived from phenate, 'H' from hexamine; see Fig. 1.7). This shift to helmets gave better protection than the

Fig. 1.6 The 'H' helmet (reproduced with permission from Porton Down).

Fig. 1.7 The 'PH' helmet (left) and the 'PHG' helmet (right), both reproduced with permission from Porton Down.

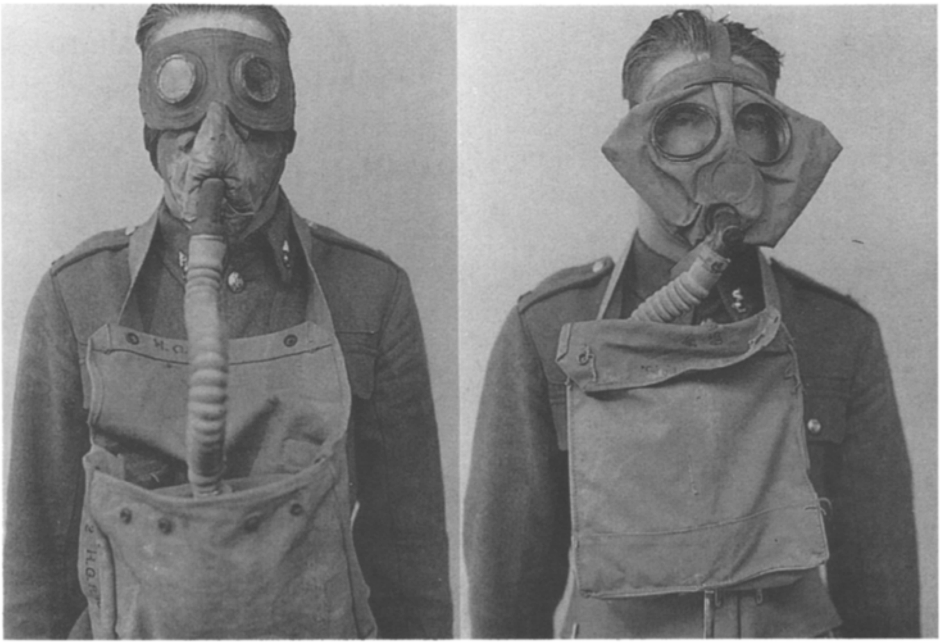


Fig. 1.8 The large box respirator (left) and the small box respirator (right), both reproduced with permission from Porton Down.

simple impregnated pads, but they were far from perfect. It was not until the autumn of 1915, after several design improvements, that they were available at the front in significant numbers, and the 'P' helmets were used at Loos. The improved 'PH' helmets were used from January 1916 onwards. However, the chief weakness of these helmets were the eyepieces, which were often leaky or broken, and gas casualty figures rose in 1916, despite the introduction of the masks. Blame for this was initially placed upon the soldiers for not fitting the masks properly, but it was a design fault. The 'PH' helmets were soon replaced with 'PHG' helmets – 'PH' helmets with improved goggles (see Fig. 1.7). In turn, they themselves were replaced (early 1917) with the box respirators (see Fig. 1.8), which were much more efficient [953]. The canisters of these respirators were filled with granules of charcoal, soda lime and potassium permanganate, and were attached to the face masks by a corrugated rubber connnecting tube [2155]. Boots manufactured the so-called "Boots granules" at the rate of 30 tons per week; the charcoal was manufactured from birch wood (by the South Metropolitan Gas Company) or carbonized coconut shells (by Sutcliffe Speakman) [2155].

Figs. 1.9–1.12 feature original photographs of troops equipped with various anti-phosgene masks. The images are evocative, and dehumanizing. Is it little wonder that all the major books on chemical warfare (Fig. 1.13) choose the gas mask as the focus for their covers, and that even scientific journals, when dealing with the subject of chemical

Fig. 1.9 **British troops manning a Vickers machine gun on the Somme, July 1916 (reproduced with permission from the Imperial War Museum).**

Fig. 1.10 Sentry in a front line trench, Salonika, wearing a 'PH' helmet (reproduced with permission from the Imperial War Museum).

Fig. 1.11 The 'PH' helmet from Fig. 1.10

Fig. 1.12 British troops wearing 'PH' helmets on gas parade (reproduced with permission from the Imperial War Museum)

warfare, also select the same motif (Fig. 1.14)? The gas mask, by an ironic twist of logic, has come to be the archetypical image of chemical warfare.

The early problems with the defective masks resulted in greater emphasis being placed on training and drill as the war progressed, while research (including work on the interaction between phosgene and rubber [1690] or charcoal [452,1509–1512]) into improvement of the mask design continued. Although effective at low concentrations of phosgene, many of the masks broke down in the high local concentrations produced by gas shells, cannisters and mines: fatal doses were often received before a mask could be properly fitted. It was empirically discovered (and later confirmed by experiment [1269]) that moist straw, grass, soil, *etc.* would offer some protection against phosgene, too.

The introduction of the small box respirator (SBR) effectively ended the major threat to the troops from phosgene exposure; the Germans introduced a very similar device, also to good effect. As noted at the end of Section 1.4.1.2, this effective protection was largely responsible for the shift in the main offensive chemical agent away from phosgene and towards mustard gas [2136]. The effectiveness of phosgene as a chemical warfare agent will be considered in Section 1.5.

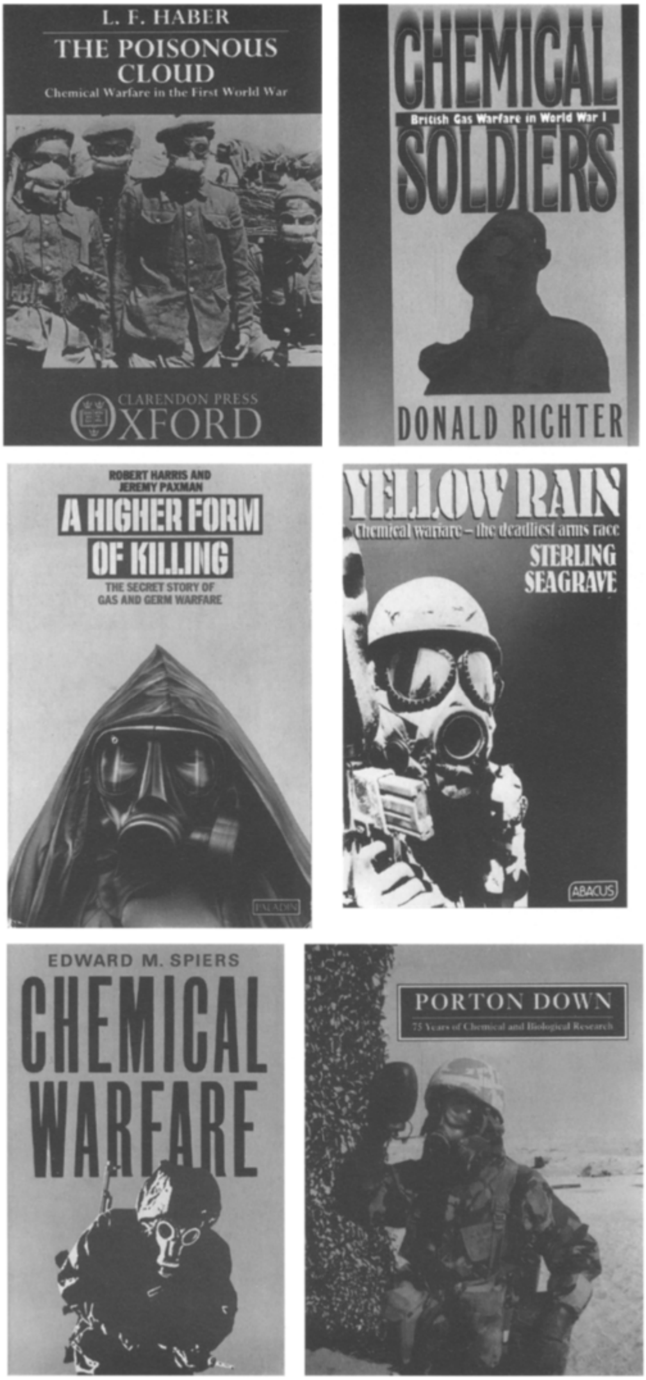


Fig. 1.13 **The gas mask motif immediately identifies the book content [338a,891,859a, 1711a,1824b,1928b].**

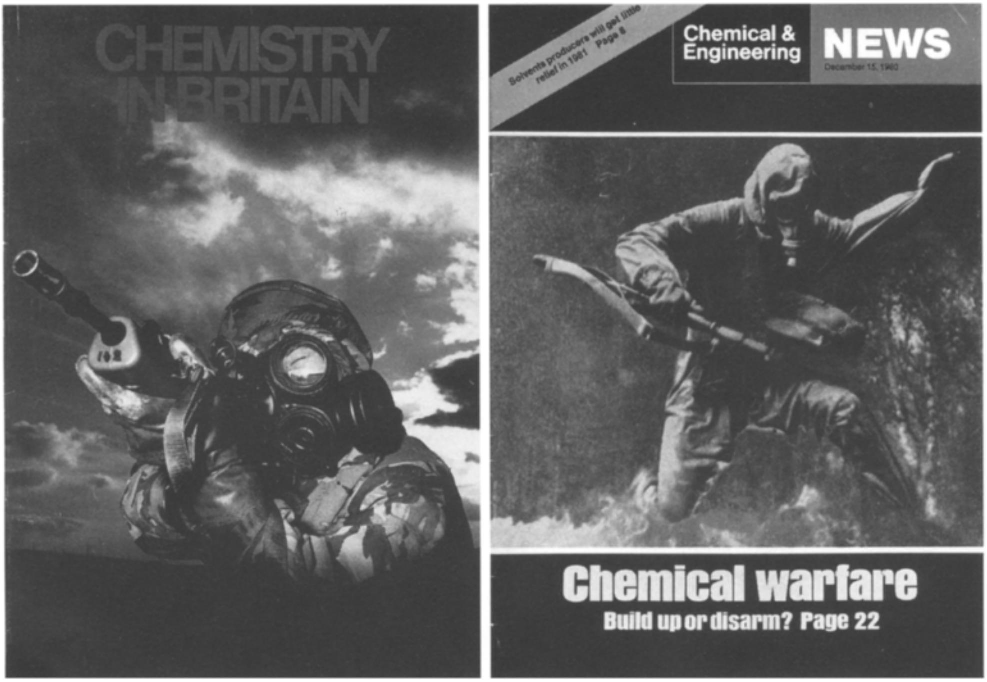


Fig. 1.14 Typical journal covers when the content features chemical warfare.

1.4.2 Fritz Haber (1868–1934): A Man of Refinement?

The figure of Fritz Haber (see Fig. 1.15) pervades this Chapter, as Kurtz dominates in Conrad's "*Heart of Darkness*". He is rarely a direct player, but his influence is profound. He was born in Breslau, Silesia, Germany (now Wroclaw, Poland) on 9th December, 1868, and died in Basle, Switzerland, of a heart attack, on 30th January, 1934. During his lifetime, he both developed a process to combine atmospheric nitrogen with hydrogen to produce ammonia (and, hence, a route to both synthetic fertilizer and explosives), and fathered chemical warfare [859]. In 1915, his first wife Clara, who was bitterly opposed to his work on chemical warfare, committed suicide, on the night that he left for the Eastern front [798a,1961a,2193b].

It is rare that one man can have spawned so much good and so much evil, and this forms the central conflict in Tony Harrison's play "*Square Rounds*" (see Section 1.6.3). He won the Nobel prize for chemistry in November 1919 (for his contribution to the Haber–Bosch process for ammonia). He was Jewish, and had to leave Germany (for Cambridge) in 1933, when Hitler came to power: he died shortly afterwards.

It is remarkable that Partington's biography [1589e] of Haber makes no mention of his contributions to chemical warfare: nor does his Nobel prize citation.

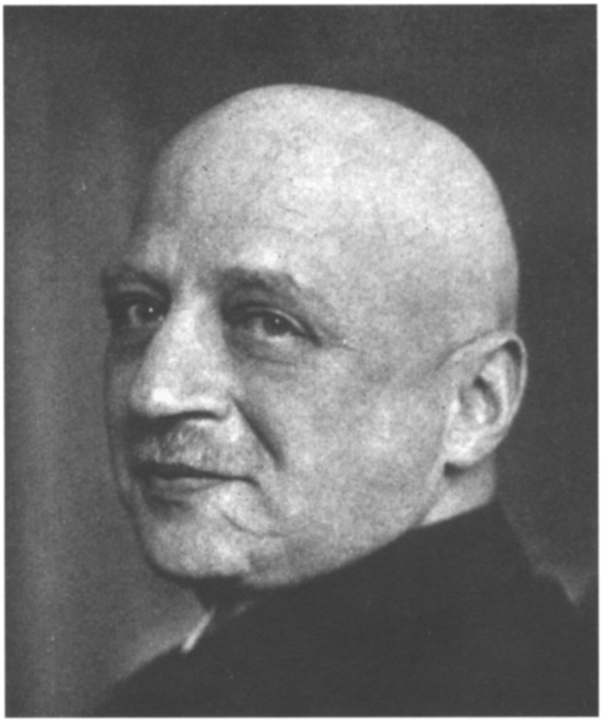


Fig. 1.15 Fritz Haber (reproduced, with permission from the Leo Baeck Institute).

1.4.3 A footnote to history

A German soldier wrote an autobiographical account of his experiences in the trenches:

> "In the night of October 13, the English gas attack on the southern front before Ypres burst loose; they used yellow-cross gas, whose effects were still unknown to us as far as personal experience was concerned. In the same night I myself was to become acquainted with it. On a hill south of Wervick, we came on the evening of October 13 into several hours of drumfire with gas shells which continued all night more or less violently. As early as midnight, a number of us passed out, a few of our comrades forever. Towards morning, I too, was seized with pain which grew worse with every quarter hour, and at seven in the morning I stumbled and tottered back with burning eyes; taking with me my last report of the war.
>
> A few hours later, my eyes had turned into glowing coals; it had grown dark around me.
>
> Thus I came to the hospital at Pasewalk in Pomerania, and there I was fated to experience – the greatest villainy of the century. [...]
>
> In the last few days I had been getting along better. The piercing pain in my eye sockets was diminishing; slowly I succeeded in distinguishing the broad outlines of the things about me. I was given grounds for hoping that I should recover my eyesight at least well enough to be able to pursue some profession later. To be sure, I could no longer hope that I would be able to draw again. [...]
>
> I, for my part, decided to go into politics"

This was written in *"Mein Kampf"* by Adolf Hitler; he was in hospital recovering from expected blindness caused by a mustard gas attack when Germany surrendered ("the greatest villainy of the century"), and there he resolved to reverse Germany's defeat. It was Hitler's rise to power that was the cause of Haber leaving Germany in 1933.

Despite huge stockpiles, and German superiority in developing new chemical warfare agents (including nerve gas), Hitler never used chemical weapons during World War II.

1.5 THE STATISTICS OF DEATH

> **Out of the air a voice without a face**
> **Proved by statistics that some cause was just**
> **In tones as dry and level as the place.**
>
> **W.H. Auden, *The Shield of Achilles***

Possibly the most cited piece of misinformation concerning phosgene is the pervasive statement that "more than 80% of the gas fatalities of World War I were caused by phosgene" [*e.g.* 609]. This statement is usually cited as originating with Prentiss [1660], whose book (published in 1937) has, until recently, been the prime source of data concerning gas casualties in World War I. The following Sections are concerned with a critical evaluation of this statement as it stands, and with a fair assessment of the situation based upon the carefully presented and considered data in Ludwig Haber's book [859a].

1.5.1 Explosion of the myth

> **A myth is, of course, not a fairy story. It is the presentation of facts belonging to one category in the idioms appropriate to another. To explode a myth is accordingly not to deny the facts but to re-allocate them. And this is what I am trying to do.**
>
> **Gilbert Ryle, *Concept of Mind*, 1949**

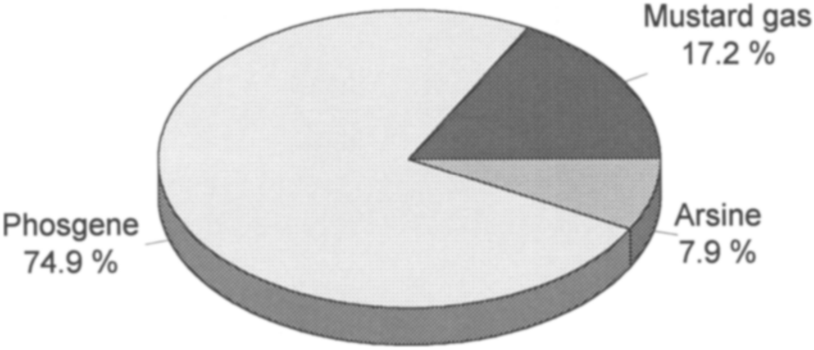
Without considering the sources or accuracy of Prentiss' data [1660], they will be examined here (initially) as received wisdom. Given this assumption, there are two possible origins for the oft-cited quote that "more than 80% of the gas fatalities of World War I were caused by phosgene". Firstly there is the following statement, taken from Prentiss [1660; p. 674]:

> **"British statistics show that over 80 per cent of men fatally gassed with phosgene died on the first day in the hospital, whereas only 1 per cent of men fatally gassed with mustard died on the first day."**

This is a perfectly reasonable statement, given that death by phosgene poisoning occurs, if it occurs at all, within forty-eight hours of the initial exposure (see Chapter 2). However, the statement that "more than 80% of the gas fatalities of World War I were caused by phosgene" is emphatically different, and quite unjustified.

The second possible source of the quote is independent analysis of Prentiss' data [1660]. Fig. 1.16 summarises the pertinent data. These data (originating with Gilchrist [755a]) represent the battle casualties, classified by gas, in the American Expeditionary Force, and were adjusted by Prentiss [1660] to take into account source errors (for example, deaths originally ascribed to chlorine were reassigned to phosgene, since no chlorine was used against U.S. troops, and unascribed battle deaths were also ascribed to phosgene, since mustard gas is slower acting). This took the number of deaths ascribed to phosgene by Gilchrist from 66 to 840. By taking the rather doubtful step of plotting a pie chart to represent the percentage case fatality figures, and rounding up the phosgene figure to the nearest 10%, a figure of 80% can be achieved. It is a meaningless statistic.

It is difficult to believe that anyone could have read Prentiss [1660] and then made the statement that "more than 80% of the gas fatalities of World War I were caused by phosgene". We fervently hope that this statement can be now laid to rest.



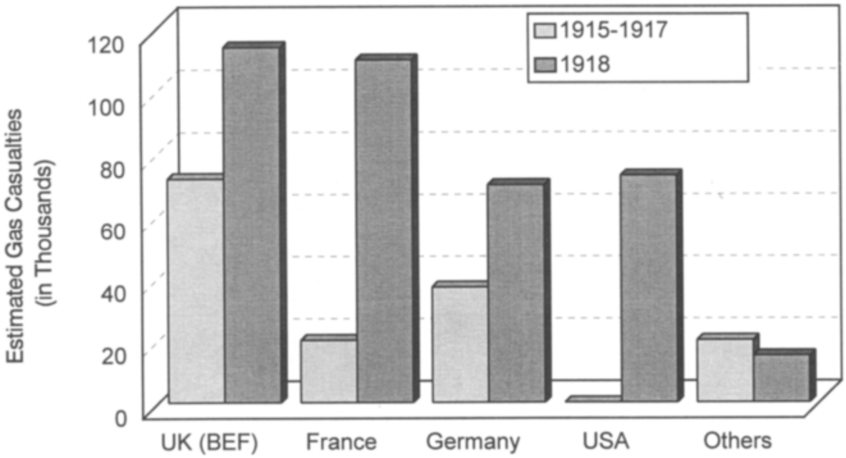
Gas	Class	Nonfatal		Deaths		Case fatality, per cent
		Number	Per cent	Number	Per cent	
Mustard gas	Vesicant	54400	75.0	616	42.1	1.13
Phosgene	Lung injurant	17010	23.4	840	57.4	4.93
Arsine	Sternutator	1156	1.6	6	0.5	0.53
TOTALS		72566	100.0	1462	100.0	2.01

Fig 1.16 Data, from Prentiss [1660; p.676], for battle casualties by gases in the American Expeditionary Forces. The pie chart is a visual representation of the final column of case fatality data.

1.5.2 An attempt at reality

> **History is a combination of reality and lies. The reality of History becomes a lie. The unreality of the fable becomes the truth.**
>
> **Jean Cocteau, *Diary of an Unknown Man*, 1953**

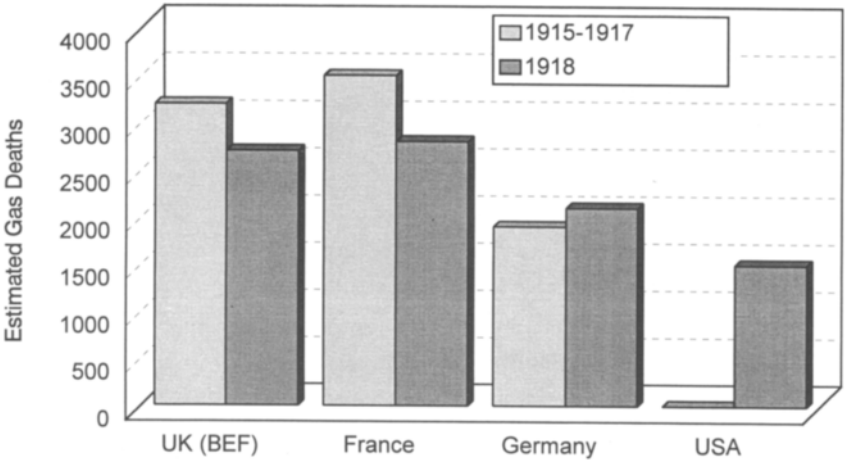
Ludwig Haber's book [859a] provides a modern, incisive and detailed analysis of the casualty statistics for World War I, and has been used here as the most reliable source available. Fig. 1.17 illustrates the estimated gas casualities, and Fig. 1.18 shows parallel data for gas deaths. The total number of casualties estimated by Haber (just over half-a-million) [859a] is less than half of Prentiss' estimate (*ca.* 1,300,000) [1660]. In a similar relationship,



Country	1915-1917	1918	TOTAL	1918 (as a % of total)
UK (BEF)	72000	114000	186000	61
France	20000	110000	130000	85
Germany	37000	70000	107000	65
USA	0	73000	73000	100
Others ‡	20000	15000	35000	43
TOTALS	149000	382000	531000	72

‡ These data are incomplete and unreliable, and include Russian, Austro-Hungarian, Italian, Canadian, Australian, New Zealand, Indian, Belgian, and Portuguese casualties

Fig. 1.17 **Estimated casualty figures (excluding civilians) caused by chemical warfare from 1915 to 1918 [859a].**

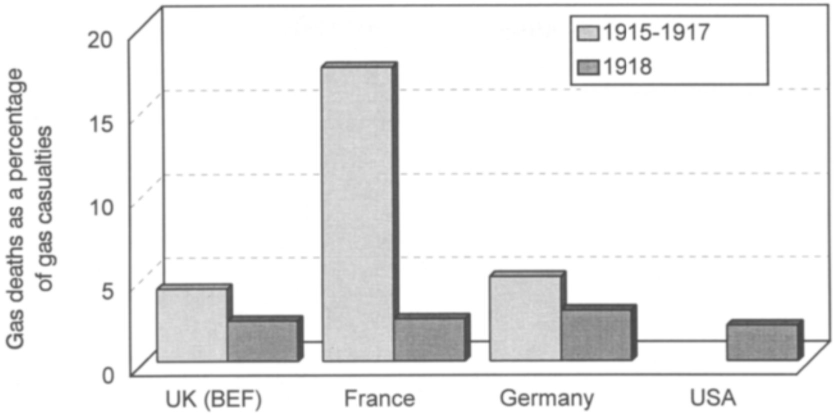


Country	1915-1917	1918	TOTAL	1918 (as a % of total)
UK (BEF)	3200	2700	5900	46
France	3500	2800	6300	44
Germany	1900	2100	4000	53
USA	0	1500	1500	100
TOTALS	8600	9100	17700	51

Fig. 1.18 **Estimated death figures (excluding civilians) caused by chemical warfare from 1915 to 1918 [859a].**

Ludwig Haber [859a] estimates a total death toll due to gas as 17,700, whereas Prentiss [1660] places it at 26,600. An examination of the graphs reveals an interesting trend. Although the number of gas casualties rose dramatically in 1918 (the final year of the war accounting for nearly three-quarters of the final total), the number of deaths dropped dramatically – a testament to the effectiveness of the new box respirators (see Section 1.4.1.4), and to the more debilitating, rather than lethal, effect of mustard gas. This effect is well illustrated in Fig. 1.19, which also shows that, on average over the war, only 3.3% of the gas casualties actually died.

Unfortunately, Haber [859a] did not attempt to analyze his data according to the gas inflicting the casualties – an impossibly difficult task to perform with any degree of precision, given the many uncertainties involved. Prentiss [1660] did attempt such an analysis, but we know that most of his casualty estimates are too high. Moreover, his analysis was based on the data of the American Expeditionary Force, which were only in action in 1918, and



Country	1915-1917	1918	TOTAL
UK (BEF)	4.3	2.4	3.2
France	17.5	2.5	4.8
Germany	5.0	3.0	3.7
USA	-	2.1	2.1
TOTALS	6.6	2.5	3.3

Fig. 1.19 **Estimated death figures (excluding civilians) caused by chemical warfare from 1915 to 1918, expressed as percentages of the total number of gas casualties for the same period [859a].**

therefore exposed to more mustard gas than phosgene. Finally, as his figures are based largely upon hospital observation, they tend to overestimate the effectiveness of phosgene. We will therefore not attempt any analysis of the effectiveness of phosgene with respect to the other chemical agents used, either. It is perhaps worth looking at one interesting statistic. The data presented in Figure 1.3 show that there was a total of 176,200 tons of war gas produced, for offensive use, during the period 1915–1918; there were 17,700 deaths. That is almost exactly 10 tons (*ca.* 10,000 kg) of gas per fatality! Chemical warfare did not prove to be an effective way of killing the enemy, nor does it appear to have had a decisive effect upon the outcome of the war, or indeed of many battles. However, it was very effective at removing men from the battlefield – a third of a ton (333 kg) of gas per casualty. Cases have been made (which relate strongly to the quotes from Auden and Cocteau, *vide supra*) that, on this basis, gas may be considered as the "the most humane weapon ever used" [687,2136]: a parallel with the sophistry of the case that the Holocaust never occurred must be noted here.

Gas, in general, and phosgene in particular, was much more effective as a psychological weapon than as a tactical weapon. Even today, when there have been no major conflicts involving war gases for nearly eighty years, the image of chemical warfare remains terrifying, despite its demonstrable ineffectiveness. The reasons for this will be examined in the following Section.

1.6 THE ART OF WAR

Although the elements (*e.g.* gold, silver, platinum, *etc.*) are frequently used as evocative images in the arts, few compounds have impinged on the popular imagination. Phosgene is an exception to this: this simple tetra-atomic molecule has come to represent death and mass destruction, an invisible and scarcely detectable killer, a symbol of the ultimate attrocity - meaningless, impersonal, unavoidable, silent, painful death. Only the neutron bomb, a device which is perhaps TOO all encompassing to be genuinely frightening (are we, as individuals, more scared by the possibility of the sun exploding and wiping out all life on Earth, or a visit to the dentist - where, of course, gas will cause us to lose consciousness!), carries this pervasive image, summed up in a song by Mick Farren, "(I know from) Self Destruction" (to be found, by persistent seekers after deleted records, on "Vampires Stole my Lunch Money"; Logo Records; LOGO 1010; 1978):

> **Because I hear you got a system**
> **That kills people and leaves buildings**
> **Is that your best idea**
> **A planet *full* of buildings?**

Phosgene has come to represent Ludwig Haber's "Poisonous Cloud", and is synonomous with chemical warfare. To take an old proverb: "Give a dog a bad name and hang him". Nothing will ever diminish the image that phosgene now holds. Chlorine may have been a contender, but then it is green, hence not invisible, and we do use it to sterilise swimming pools, so it can't be all bad, can it? Phosgene has, to the public at large, no redeeming features - in a world where religion offers us Ultimate Good, phosgene has come to represent Ultimate Evil. In Section 1.9, the tendency of the press to blame phosgene for everything from the incident at Bhopal to Legionnaire's Disease has been noted. Even chemists, who routinely handle many reagents {*e.g.* tetracarbonylnickel(0)} which are far more toxic than phosgene, find excuses to leave a laboratory when they hear that phosgene is being used (and this we know, from personal experience, to be true) - at least the creators of the images that follow can claim poetic licence!

The following Sections contain selected examples of how chemical warfare in general, and phosgene in particular, has given birth to some of the most evocative and memorable art to have been created in the twentieth century. The power of the paintings, photographs and drawings is diminished by reproduction on a small scale in black-and-white; the images induced by the poems, songs and plays are reduced without the emphasis of the professional orator. With all this removed, the power of what is left is still awesome. If "suffering is the main condition of the artistic experience", then "sweet are the uses of adversity". Wilfred Owen, who created the most powerful poem to emerge from World War I, wrote [957a]:

> **Above all I am not concerned with Poetry.**
> **My subject is War, and the pity of War.**
> **The poetry is in the pity.**
> **Yet these elegies are to this generation in no sense consolatory. They may be to the next. All a poet can do today is warn. That is why the true Poets must be truthful.**

He died in action seven days before the Armistice was signed [957b].

After examining the following Sections, no doubt will remain about the horror of chemical warfare, or the truth of its representation. This is Owen's warning. If this is all summed, and summoned, up by the word PHOSGENE, then so be it. But we hope that the remaining sixteen chapters of this book will convince the reader of the reality of the situation: that phosgene is a useful and relatively safe chemical, both in the laboratory and in industry. Many words (*e.g.* bad) have two, quite contradictory, meanings – so let phosgene be the chemical reagent of use to industry, and let PHOSGENE stand for all that is malevolent and diabolical in man's behaviour to man, let it represent creeping, invisible, tortuous death, but let us NEVER get the two meanings confused – for therein lies the slippery and degrading road to tabloid journalism.

1.6.1 Poetry

There will be no dispute that Wilfred Owen's *Dulce Et Decorum Est* is the best known, and most powerfully evocative, of the poems to be spawned in the trenches [1876a]:

Dulce Et Decorum Est

Bent double, like old beggars under sacks,
Knock-kneed, coughing like hags, we cursed through the sludge,
Till on the haunting flares we turned our backs
And towards our distant rest began to trudge.
Men marched asleep. Many had lost their boots
But limped on, blood-shod. All went lame; all blind;
Drunk with fatigue; deaf even to the hoots
of gas shells dropping softly behind.

Gas! GAS! Quick, boys! – An ecstasy of fumbling,
Fitting the clumsy helmets just in time;
But someone still was yelling out and stumbling,
And flound'ring like a man in fire or lime . . .
Dim, through the misty panes and thick green light,
As under a green sea, I saw him drowning.

In all my dreams, before my helpless sight,
He plunges at me, guttering, choking, drowning.

If in some smothering dreams you too could pace
Behind the wagon that we flung him in,
And watch the white eyes writhing in his face,
His hanging face, like a devil's sick of sin;
If you could hear, at every jolt, the blood
Come gargling from the froth-corrupted lungs,
Obscene as cancer, bitter as the cud
Of vile, incurable sores on innocent tongues, -
My friend, you would not tell with such high zest
To children ardent for some desparate glory,
The old Lie: Dulce et decorum est
Pro patria mori

An alternative version of line 8 is [1935a]:

Of tired, outstripped Five-Nines that dropped behind.

The poem exists in four complete drafts, each extensively altered and corrected. In one version, the following lines appeared (and were then scored out) between lines 8 and 9 above [1935a]:

Then somewhere near in front: Whew . . . fup, fop, fup,
Gas-shells? Or duds? We loosened masks in ease, -
And listened. Nothing. Far rumouring of Krupp,
Then sudden poisons stung us in the face.

One version [1935a] was dedicated "To Jessie Pope, etc."; in another this was scored out and replaced with "To a certain Poetess". Jessie Pope was the author of pre-WW1 children's books glorifying war, with such titles as "Jessie Pope's War Poems", "More War Poems" and "Simple Rhymes for Stirring Times".

It is literally incredible that arguments that gas may be considered as "the most humane weapon ever used" [687,2136] can be sustained; Owen's poem evokes many powerful images and thoughts - the humanity of chemical warfare is not high on the intellectual agenda!

In some poems, the effect of gas is taken as part of every day existence. Thus, from John Peale Bishop's "In the Dordogne":

And each day one died or another
died: each week we sent out thousands
that returned by hundreds
wounded or gassed. And those that died
we buried close to the old wall
within a stone's throw of Perigord
under the tower of the troubadours.

In others, the unnatural, ignominious and rapid death is the focus. In Gilbert Frankau's long poem, "How Rifleman Brown Came to Valhalla", the wounded denizens of the lower Hall of Valhalla ("the gashed heads") demand to know of the dead Joseph Brown "*Who comes, unhit, to the party?*" A spokesman appears to defend Rifleman Brown:

'My mate was on sentry this evening when the General happened along,
And asked what he'd do in a gas-attack, Joe told him: "Beat on the gong."
"What else?"
"Open fire, Sir," Joe answered.
"Good God, man," our General said,
"By the time you'd beaten that bloodstained gong the chances are you'd be dead.
Just think, lad." "Gas helmet, of course, Sir." "Yes, damn it, and *gas helmet first.*"
So Joe stood dumb to attention, and wondered why he'd been cursed'

The gashed heads turned to the Rifleman, and now it seemed that they knew
Why the face that had never a smear of blood was stained to the jawbones, blue.

'He was posted again at midnight.' The scarred heads craned to the voice,
As the man with the blood-red bayonet spoke up for the mate of his choice.
'You know what it's like in a listening-post, the Véry candles aflare,
Their bullets smacking the sand-bags, our Vickers combing your hair,
How your ears and your eyes get jumpy, till each known tuft that you scan
Moves and crawls in the shadows till you'd almost swear it was man;
You know how you peer and snuff at the night when the North-East gas-winds blow.'

'*By the One who made us and maimed us,*' quoth lower Valhalla, '*we know!*"

'Sudden, out of the blackness, sudden as Hell, there came
Roar and rattle of rifles, spurts of machine-gun flame;
And Joe stood up in the forward sap to try and fathom the game.
Sudden, their shells come screaming; sudden, his nostrils sniff
The sickening reek of the rotten pears, the sudden death that kills with a whiff.
Death! and he knows it certain, as he bangs on his cartridge case,
With the gas-cloud's claws at his windpipe and the gas cloud's wings on his face ...
We heard his gong in our dug-out, he only whacked on it twice,
We whipped our gas-bags over our heads, and manned the step in a trice -
For the cloud would have caught us as sure as Fate if he'd taken the Staff's advice.'

His head was cleft with a great red wound from the chin to the temple-bone,
But his voice was as clear as a sounding gong, 'I'll be damned if I'll drink alone,
Not even in lower Valhalla! Is he free of your free Canteen,
My mate who comes with the unfleshed point and the full-charged magazine?'

The gashed heads rose at the Rifleman o'er the rings of the Endless Smoke,
And loud as the roar of a thousand guns Valhalla's answer broke,
And loud as the crash of a thousand shells their tankards clashed on the board:
'*He is free of the mess of the Killer-men, your mate of the unfleshed sword;*
For we know the worth of his deed on earth: as we know the speed of the death
Which catches its man by the back of the throat and gives him water for breath;
As we know how the hand at the helmet-cloth may tarry seconds too long,
When the very life of the front-line trench is staked on the beat of a gong.
By the four you slew, by the case he smote, by the grey gas-cloud and the green,
We pass you mate for the Endless Smoke and the beer of the free Canteen.'

In the lower hall of Valhalla, with the heroes of no renown,
With our nameless dead of the Marne and the Aisne, of Mons, and of Wipers town,
With the men who killed ere they died for us, sits Rifleman Joseph Brown.

Valhalla, of course, was the most beautiful mansion in Asgard, where heroes slain in battle feasted each night with Odin. Each day they rode out and fought each other until they were cut to pieces: each evening they recovered from their wounds. The wounds were marks of valour.

Concern about the dehumanizing nature of death by gas is also present in Philip Bainbrigge's lines:

If I Should Die, Be Not Concerned To Know

If I should die, be not concerned to know
    The manner of my ending if I fell
Leading a forlorn charge against the foe,
    Strangled by gas, or shattered by a shell.
Nor seek to see me in this death-in-life
    Mid shirks and curses, oaths and blood and sweat,
Cold in the darkness, on the edge of strife,
    Bored and afraid, irresolute, and wet.

But if you think of me, remember one
    Who loved good dinners, curious parody,
Swimming, and lying naked in the sun,
    Latin hexameters, and heraldry,
Athenian subtleties of δηζ and ποιζ,
    Beethoven, Botticelli, beer and boys.

This poem is a vicious parody of Rupert Brooke's overly sentimental and patriotic "The Soldier", with the well-known opening lines:

If I should die, think only this of me:
    That there's some corner of a foreign field
That is for ever England. [...]

If for no other reason than symmetry, it is proper that this Section conclude with images as powerful as it began. Thus, although there is no direct reference to chemical warfare, its influence underpins the following poem by Siegfried Sassoon (March 1919); the message is one Owen would have wholeheartedly endorsed.

Aftermath

Have you forgotten yet? ...
For the world's events have rumbled on since those gagged days,
Like traffic checked while at the crossing of city-ways:
And the haunted gap in your mind has filled with thoughts that flow
Like clouds in the lit heaven of life; and you are a man reprieved to go,
Taking your peaceful share of Time, with joy to spare.
But the past is just the same - and War's a bloody game ...
Have you forgotten yet? ...
Look down, and swear by the slain of the War that you'll never forget.

Do you remember the dark months you held the sector at Mametz –
The nights you watched and wired and dug and piled sandbags on parapets?
Do you remember the rats; and the stench
Of corpses rotting in front of the front-line trench –
And dawn coming, dirty-white, and chill with a hopeless rain?
Do you ever stop and ask, 'Is it all going to happen again?'

Do you remember that hour of din before the attack –
And the anger, the blind compassion that seized and shook you then
As you peered at the doomed and haggard faces of your men?
Do you remember the stretcher-cases lurching back
With drying eyes and lolling heads – those ashen-grey
Masks of the lads who once were keen and kind and gay?

Have you forgotten yet? ...
Look up, and swear by the green of the spring that you'll never forget.

If, in Wilfred Owen's words "All a poet can do today is warn. That is why the true Poets must be truthful", then they have fulfilled their duty in a truly effective and evocative manner. WE HAVE BEEN WARNED.

1.6.2 Literature

The novel is, perhaps, the medium most capable of directly evoking the full horror of chemical warfare. Poems and paintings give us snapshots of a moment, or a short period: novels are capable of drawing on a wider canvas. It would be quite impossible, and rather pointless, to attempt to list here the large number of novels which have described life in the trenches, and the effects of chemical warfare. Robert Graves' "*Goodbye to All That: An Autobiography*", and Timothy Findley's "*The Wars*" have already been quoted here (Sections 1.4.1.2 and 1.4.1.4, respectively), and we can only recommend that any reader of this Chapter who is not familiar with these books should read them at the first opportunity! Other sources of related reading include:

"The Longman Literary Companion to Science"
W. Gratzer (editor), Longman, Harlow, 1989

"The Penguin Book of First World War Prose"
J. Glover and J. Silkin (editors), Viking, London, 1989

"Fiction of the First World War: A Study"
G. Parfitt, Faber and Faber, London, 1988

The book edited by Jon Glover and Jon Silkin is particularly accessible and broad-ranging, quoting from both well-known and obscurer writers.

1.6.3 Art

> **It is unspeakable, godless, hopeless. I am no longer an artist interested and curious. I am a messenger who will bring back word from the men who are fighting to those who want the war to go on forever. Feeble, inarticulate, will be my message, but it will have a bitter truth, and may it burn their lousy souls.**
>
> **Paul Nash, 1918**

The above quote from Paul Nash gave the title to the exhibition "A Bitter Truth: Avante-Garde Art and the Great War", which was mounted at the Barbican Art Gallery in London (28th September - 11th December 1994). This was a unique, and innovative, attempt to show the First World War through the eyes of both Allied and German artists. The exhibition was both moving and thought-provoking, and the catalogue (compiled by Richard Cork, Yale University Press, 1994) is a brillaint *tour de force*, a chronological mapping of the manner in which the views of the War changed as it progressed, from jingoistic fervour to horror and revulsion.

The following pages contain a personal selection of images depicting the effects of chemical warfare in general, and phosgene in particular (Figs. 1.20-1.28).[¶] Some are graphic, some paintings, some cartoons, but all are both harrowing and poignant. The artists span a range of very different styles (the early twentieth Century is, perhaps, the richest we have ever experienced in terms of diversity of style and innovative imagery), and include the famous and the obscure. A commentary on these pictures is redundant; they speak eloquently for themselves. However, the originals speak much louder and clearer than the reproductions in this book. It may surprise many readers to discover that the Imperial War Museum holds the second largest collection of British Twentieth Century art in the United Kingdom, and it is well worth a visit; some of the pictures illustrated here form a part of that collection.

It is, perhaps, worth noting that the three pictures by Otto Dix form part of a cycle of fifty etchings, entitled "War" ("*Der Krieg*"): this series is a testament to the horror of war, and was exhibited in its entirety at the Goethe-Institut London (1st July - 13th August, 1988). The prints form five portfolios of ten images: Fig. 1.26 is etching #3 from the first portfolio; Fig. 1.27 is etching #2 from the second portfolio; Fig. 1.28 is etching #6 from the fifth portfolio. "Skull" (etching #1; fourth portfolio) provides one of the enduring images of the futility of war, and is included here (Fig. 1.29) for its shear hypnotic graphic power. The power of Dix's imagery can be justly compared with "The Disasters of War" etchings, made by Goya between 1810 and 1814, almost a century previous, when the fate of Europe had again been under threat.

[¶] We are grateful to the Imperial War Museum for permission to publish Figs. 1.20-1.21, the Barbican for permission to publish Figs. 1.22 and 1.25, and the British Museum for permission to publish Figs. 1.26-1.29. We could not trace the owners of the copyright to Figures 1.23 and 1.24.

Fig. 1.20 Austin O. Spare: *Dressing the Wounded during a Gas Attack*

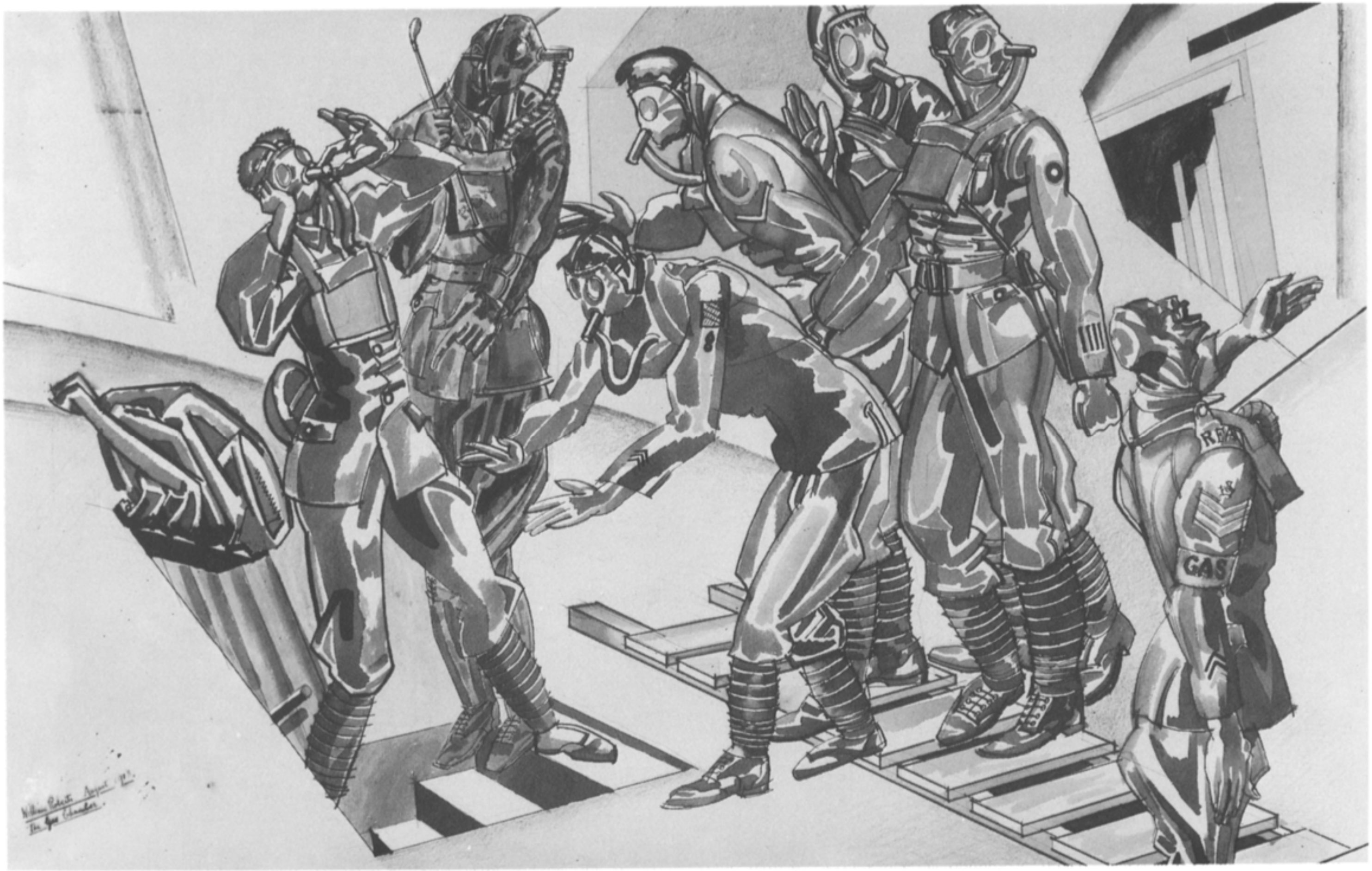


Fig. 1.21 **William P. Roberts:** ***The Gas Chamber***

Fig. 1.22 William P. Roberts: *The First German Attack at Ypres*

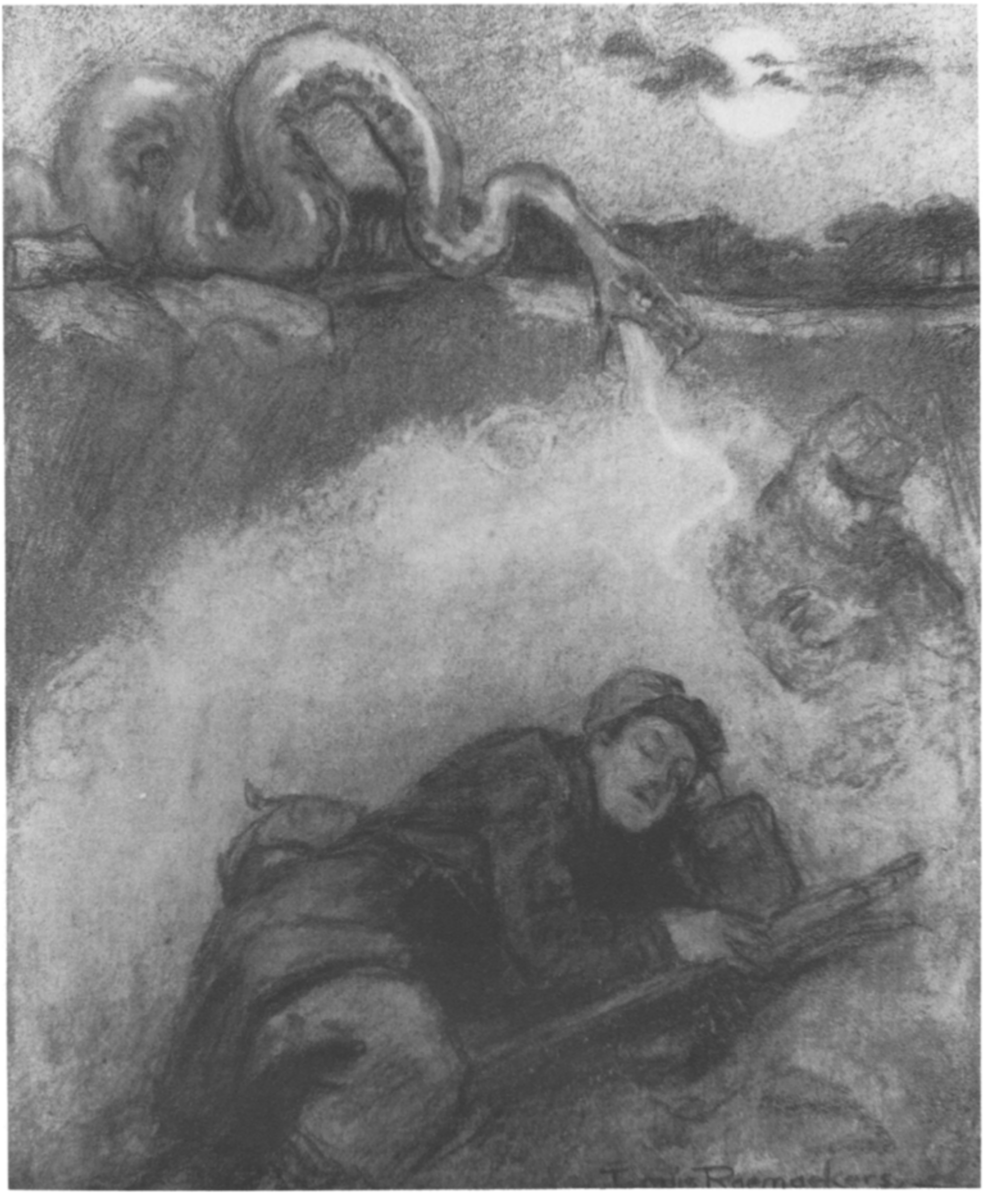


Fig. 1.23 Louis Raemaekers: ***The Gas Fiend***

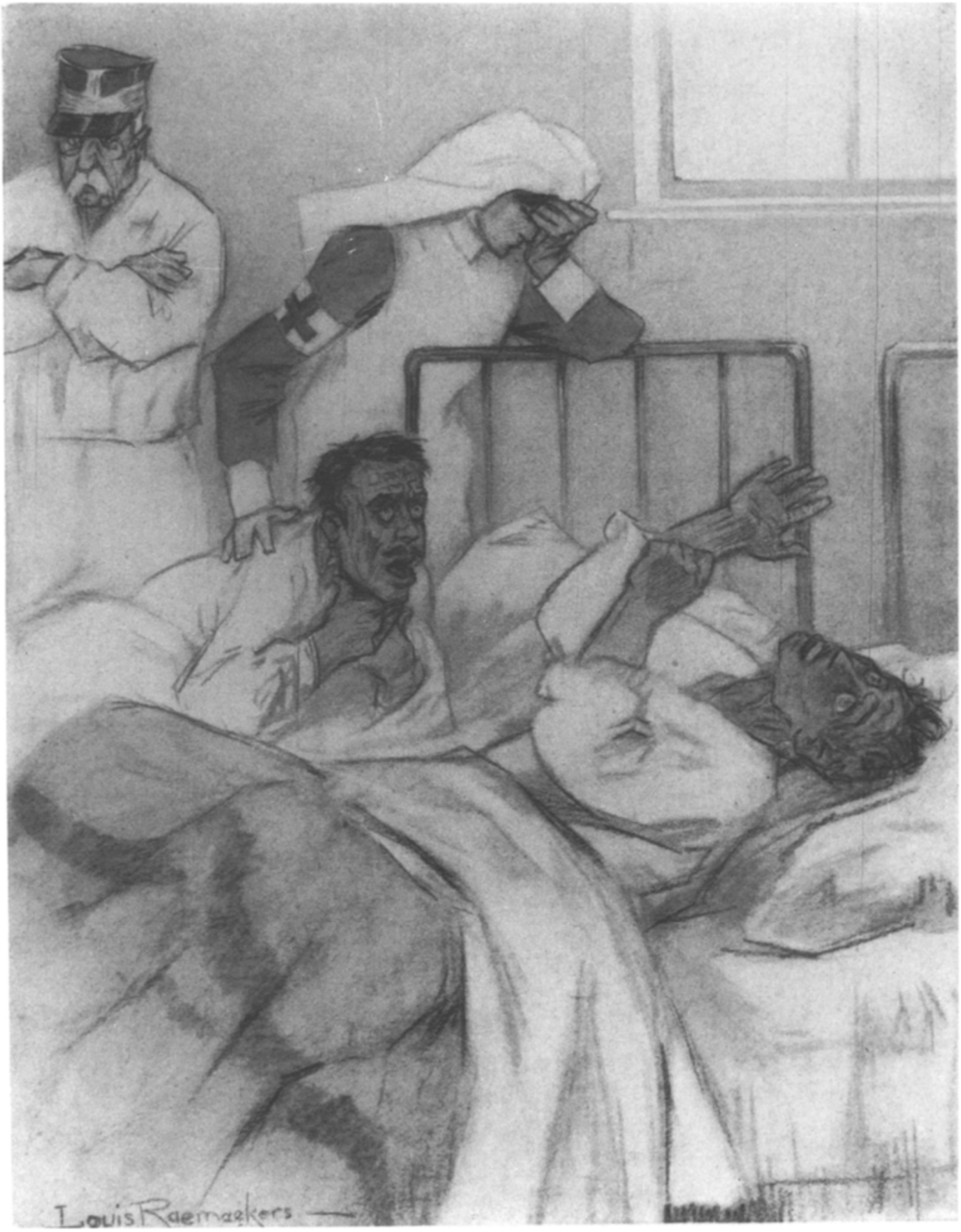


Fig. 1.24 Louis Raemaekers: *Slow Asphyxiation*

Fig. 1.25 Eric Kennington: *Gassed and Wounded*

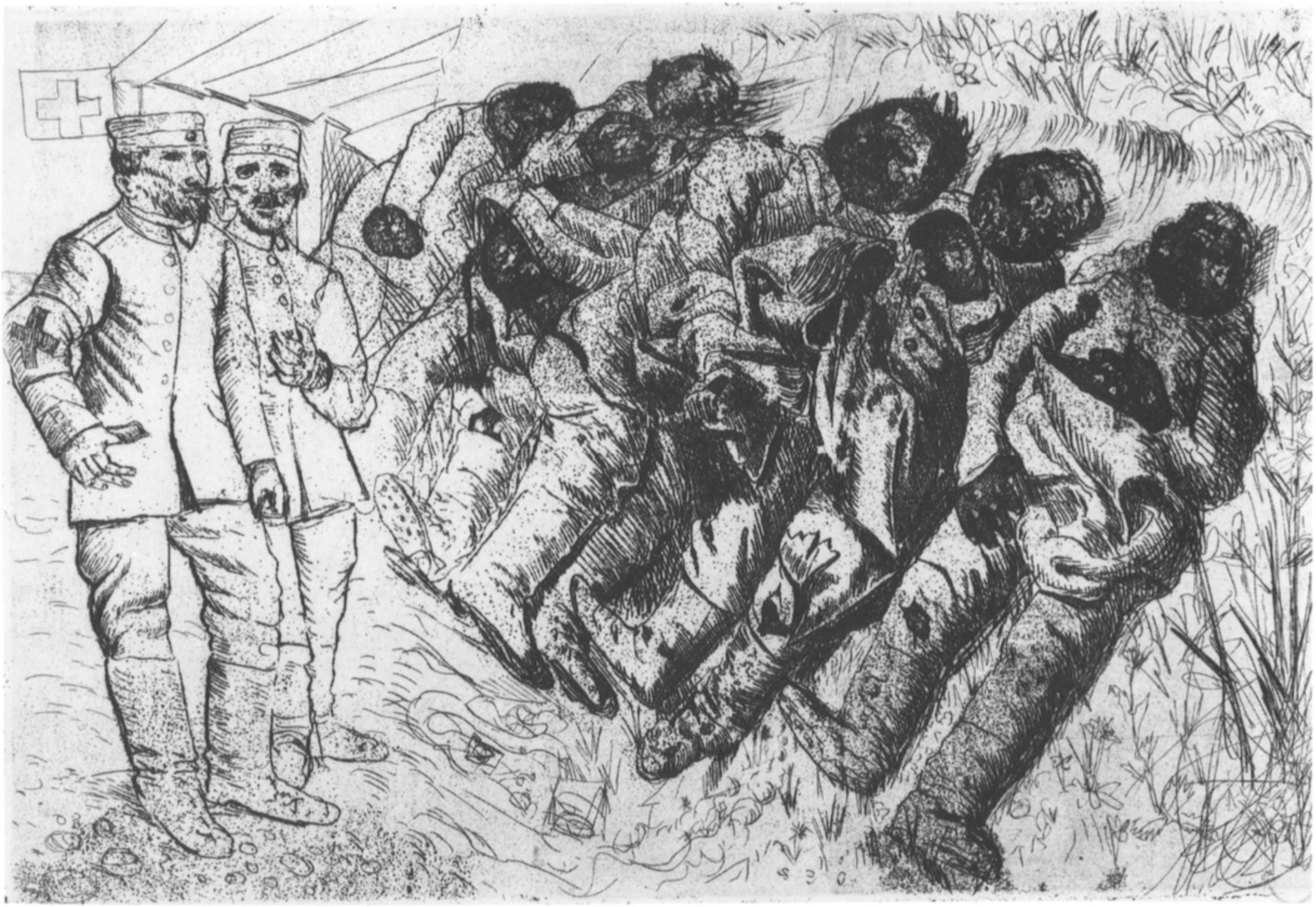


Fig. 1.26 Otto Dix: *Men Killed by Gas (Templeux-la-Fosse, August 1916)*

Fig. 1.27 Otto Dix: *Stormtroops Advancing Under Gas*

Fig. 1.28 Otto Dix: *The Sleeping Ones of Fort Vaux (Men Killed by Gas)*

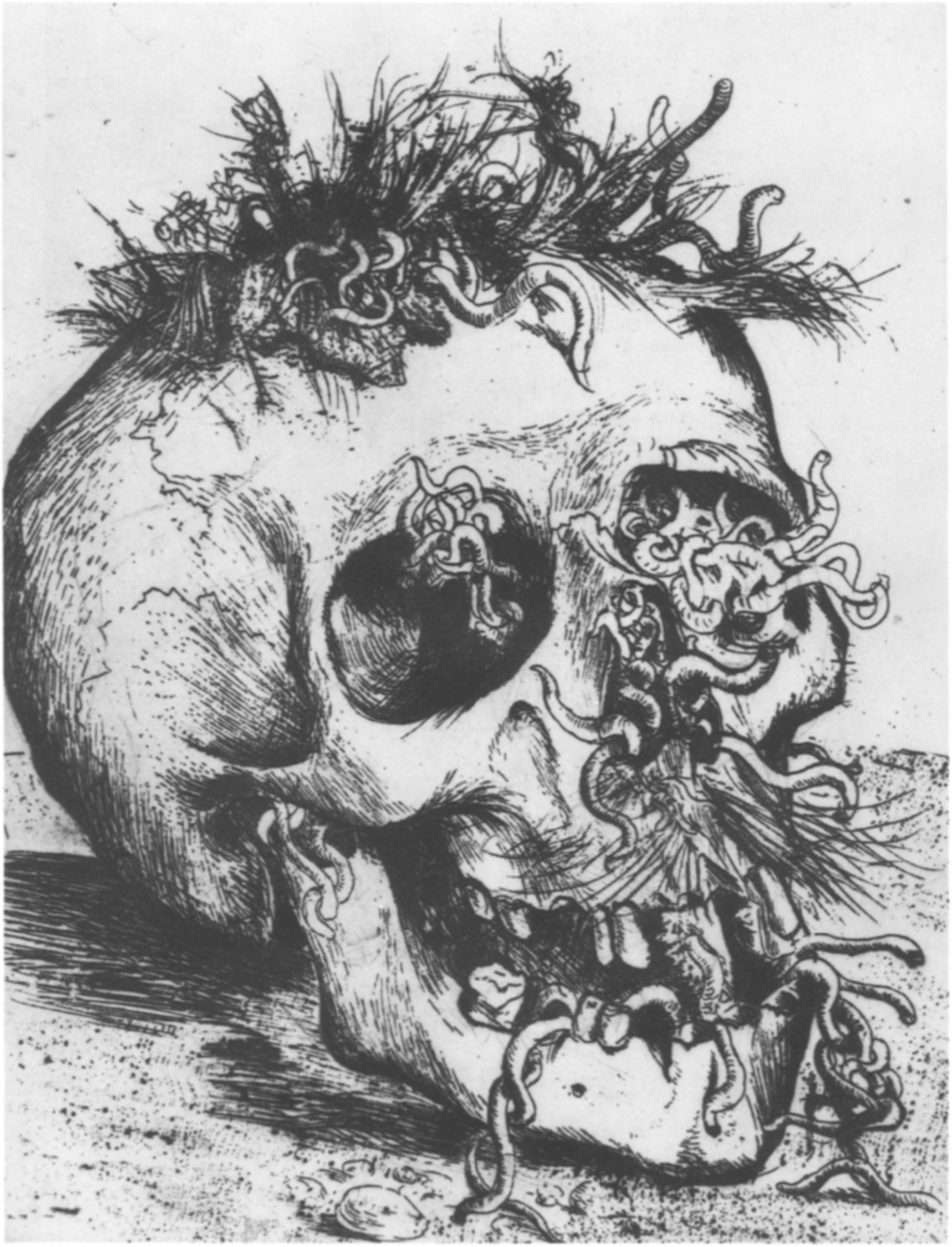


Fig. 1.29 Otto Dix: *Skull*

1.6.4 Theatre

In a recent, stunning, piece of theatre, *Square Rounds* by poet Tony Harrison [893a], Harrison has Fritz Haber (the cynosure of the play) saying:

> **The force of explosive gas that travels very very fast**
> **blows head and limbs off in its fearsome blast.**
> **It's a chemical weapon, chemicals and gas**
> **and yet the scruples of the moralist let that pass.**
> **Make delicate distinctions but, alas,**
> **the essential element of both is gas, gas, gas.**
> **One gas blows to pieces, one manages to choke**
> **its unsuspecting victims with a greenish yellow smoke.**
> **If I were a victim's mother. Imagine being her**
> **I know which of the two fates for my son I'd prefer.**
> **If one were forced to make the gruesome choice**
> **and my son were a victim then the gas would get my voice.**
> **An appalling decision but gas would get my vote**
> **because apart from internal damage to lungs and throat**
> **my boy would be intact, whole and I**
> **would have a corpse for burial I could identify.**
> **It would still be my boy, mein liebling, him**
> **not half a helmet and one mangled limb.**

and a little later:

> **With my elegant invention I put to sleep**
> **the unsuspecting enemy entrenched at Ypres.**
> **As my silky releases hissed and swirled**
> **for the first time ever in the history of the world**
> **I have to confess that I felt rather proud**
> **of the simple device of my suffocating cloud.**

The play highlights the conflicts and contradictions discussed briefly in Section 1.4.2, and deals especially with Clara's suicide. The arguments for and against chemical warfare are strongly made, and a strong connection with the chemical skills of early China is made. The text has now been published (Faber and Faber, London, 1992).

1.6.5 Cinema and Graphic Novels

Phosgene has entered the public imagination as a lethal, invisible agent of death, and this is reflected in that mirror of society's popularist views, the cinema. Thus, we have James Bond (Sean Connery - THE Bond) in "You Only Live Twice" (EON Productions, 1967; a film whose similarity to the book on which it was "based" lies only on its title, and the names of the chief protagonists) remarking, as he leaves a sea cave filled with poisonous gas: "Phosgene gas - to keep the visitors away". Perhaps only phosgene can convey the sense of an utterly lethal environment that the screen writers required - perhaps they really believed that phosgene might be used in such a situation.

In the motion picture "Earthquake" (Universal Pictures, 1975), Sam Royce (played by the late Lorne Greene), a Los Angeles construction company owner, becomes trapped in the upper floors of his own building following a catastrophic earthquake. When the initial panic has subsided, and the worst appears to be over, a woman collapses: people start to cough, and the observant Royce sees a dense, white vapour flowing from the ventilation ducts as he promptly orders his colleagues to break the windows. "IT'S PHOS-GENE GAS!", exclaims Royce as people make their way hurriedly to the emergency stairway. While the film's principal hero, Stewart Graff (Charlton Heston), fights his way upwards through the debris of the badly damaged stairway, he is told by Royce that he had "better get out of here" because "THE WHOLE BUILDING IS FULL OF PHOS-GENE"! Whilst Royce, with the aid of a makeshift harness, helps to lower people down the ruined staircase to comparative safety on the floor below, the frequent camera shots of the vapour clouds billowing forth from the building's air ducts leads one to expect the worst. Exposure to the gas, coupled with the exertion of saving all those deserving people, results in Royce suffering a seizure from which he eventually dies. Phos-gene gas has claimed yet another victim!

A similar phenomenon can be observed in the graphic novel - a medium where the text is, of necessity condensed, and so minimal words must convey maximum meaning. Thus, in Fig. 1.30, we have a policeman commenting on a scene of mass murder (fifty or sixty people dead) "Looks to us like it might've been **phosgene**! Krauts used the stuff during the first **World War**!", to which the central character Lt. Corrigan (a.k.a. The Spectre) responds "Oh, great! Now the loonies are into chemical **warfare**!". Phosgene is here to stay as an agent of death and mass destruction, despite the fact it is one of the most ineffective of modern chemical warfare agents.

1.6.6 Music

This is, rather surprisingly, one of the few areas of artistic endeavour that does not seem to have been influenced by the existence of chemical warfare. Although a number of artists (including Warren Zevon and the Dead Kennedys) have produced the odd track concerned with chemical warfare, it has scarcely become a dominant theme. There are, to our knowledge, no jazz or classical pieces in which the themes of chemical warfare have appeared, either in referential or non-referential work.

1.6.7 Conclusions

The preceding Sections have documented and illustrated the significant influence that gas warfare, and particularly phosgene, has exerted upon the world of the arts. As a mirror for the psychological effectiveness of chemical warfare, no better and no more convincing evidence could be gathered. The words and the images play upon our deep-rooted fear of the unknown; even the positive image of protection (the gas mask) is dehumanizing and frightening. Phosgene may well have been ineffective as an agent of death and war, but it is overwhelmingly successful as an instrument of irrational fear.

Fig. 1.30 A frame from the graphic novel, "*The Wrath of the Spectre*" (reproduced with permission from DC Comics).

1.7 PHOSGENE AND WORLD WAR II

The Geneva Protocol (17th June, 1925) prohibited "the use in war of asphyxiating, poisonous or other gases, and of all analogous liquids, materials or devices", and also bacteriological methods. It was signed by thirty-eight powers, including the United States, the British Empire, Germany, France, Italy, Japan and Canada, but not by the USSR (who did not attend the conference). However, the American Senate refused to ratify the treaty (with the support of the American Chemical Society, whose executive stated that "the prohibition of chemical warfare meant the abandonment of humane methods for the old horrors of battle" [891]). Japan also failed to ratify the protocol. France ratified in 1926, Italy in 1928, Germany in 1929, and Britain in 1930.¶ The Soviet Union declared herself bound by the Protocol in 1928. The USA finally ratified in 1975, fifty years after originally signing the Protocol; Japan finally signed in 1970.

The Protocol proved of little value in the years immediately preceding World War II. The Japanese openly conducted research into chemical and biological warfare agents [2191a], and made extensive use of mustard gas against the Chinese in 1937. The Italians, who <u>had</u> ratified the Protocol, shipped 700 tons of mustard gas to Abyssinia, from 1935–1936, for use by the Italian air force, who employed the new technique of aerial spraying. About one-third of the casualties in the Abyssinian war were directly attributable to chemical agents.

The Italian attack on Abyssinia resulted in the Allies reactivating their own chemical warfare agent production. In 1936, France built a new phosgene factory at Clamency [891], the British built a mustard gas plant at Sutton Oak, and a year later the World War I phosgene and mustard gas plants at Edgewood Arsenal in the United States were recommissioned. There was a real expectation, with the War approaching, that chemical warfare was inevitable. Up to 1941, nearly 200 tons of phosgene per month were being shipped from the U.S.A. to Britain, to supplement rapidly growing stockpiles manufactured (and stored!) at the Rocksavage plant, near Runcorn (where local inhabitants were issued with gas masks, in case the storage tanks were ruptured during bombing raids). The French developed 200 kg phosgene bombs, the Germans had 750 kg phosgene bombs. At one point, the Luftwaffe had available nearly 500,000 gas bombs. Preparations for use of, and defence against, the "conventional" war gases, such as phosgene and mustard gas, were manifest; the fact that the Germans, in 1937, had developed a new type of chemical agent, with properties far more "advanced", was unknown.

In Germany, the first nerve gases (tabun, sarin and soman) were invented and stockpiled (especially tabun), but never used. Germany had, with these agents, a clear

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¶ France, Britain and the USSR only signed the Protocol with the following reservations: (a) that the agreement was only binding if the country they were fighting had also ratified the Protocol, and (b) if they were attacked by chemical or biological weapons, they reserved the right to reply in kind. Thus, the Protocol only effectively banned the FIRST USE of chemical or bioogical waeapons, and allowed research into chemical and biological DEFENCE to flourish.

advantage over the Allies. If Hitler had chosen to use these gases to repel the D-Day invasion, and he had received strong advice to do so, there would have been no effective protection for the Allied troops, and no comparable means of retaliation. The Germans believed, incorrectly, that the Allies also had these materials, and there would thus be no advantage in using them.

It remains quite remarkable that Britain, France and Germany never once used chemical weapons during World War II, despite extensive stockpiles having been accumulated. An interesting and dramatic account of the history of this period, along with an analysis of the reasons why both sides refused to be the first to use chemical warfare, may be found elsewhere [891]. The existence of the Geneva Protocol was clearly not a factor in the decisions that were made. A concise, and very public, account of the activities at Porton Down during World War II is given by Carter [338a].

Although many atrocities were committed in the German Death camps, the gas of choice was hydrogen cyanide [1252a]. However, phosgene was used in "medical" experiments, in which "habitual criminals" were exposed to varying concentrations of the gas [891]. The near impossibility of obtaining direct access to Bickenbach [190a], and other papers relating to the Nazi wartime "experiments", suggests that there are more data of this type than are openly acknowledged. There are many files, relating to both British and German chemical warfare experiments from this period, which are still "closed" to public examination. Recently, the United States Environmental Protection Agency (EPA) banned the use of data from Nazi experiments in which fifty-two prisoners had been exposed to various doses of phosgene [190a], despite the fact that using those data would undoubtedly be beneficial to public health [29a,64f]. The British Institution of Chemical Engineers, in their report on phosgene toxicity, took a more pragmatic view, and used the data because "some good for society may result from the sufferings of the unfortunate victims" [1297a]. Deliberate suppression of information which, no matter how repellent and inhuman the manner in which it was obtained, could now be of some use to mankind, raises many ethical questions. Does using this information in any way condone the manner in which it was obtained? Would meaning be brought to brutal and sadistic killings, if the data obtained saved other lives? Should people now be endangered because extant information cannot be accessed? This is a profound and disturbing area of ethics - the issue will be debated for a long time to come - but the reality of the current situation is that the information sources are effectively sealed against public access, but that the data can be obtained from secondary sources if one is persistent.

In Japan, the notorious Unit 731 (the unit where Japanese soldier-scientists performed freezing, ballistics and live vivesection experiments on Russian, Chinese, American, British and Australian prisoners-of-war; the biological warfare unit) did employ phosgene - for crowd control. The prisoners were referred to as *marutas*, for reasons revealed in an interview [2191a] with Naokati Ishibashi, a medical orderly with the Unit:

> **"Prisoners were all referred to as "maruta" which is the Japanese word for a log of wood. Although, when they arrived, they had cards each with their name, birthplace, reason for arrest and age, we simply gave them a number. A maruta was just a number, a piece of experimental material. They were not even regarded as human beings."**

The following is an eye-witness account [2191a] from Naoji Uezono, a printer working for Unit 731, of a maruta riot in Block 8 of Pingfan Station, Manchuria, about two months before the end of the war:

> **"There was an emergency call to the headquarters building where I was working. We were ordered to help at the scene. And I was very curious about that building, so I rushed to the scene. I was one of the first people. I had to wear a poison gas-proof mask, and I was supplied with a gun. I saw the riot. [...]. All of us were very excited and we tried to persuade them to go back to their own cells. And then our senior came and ordered the use of gas. So we brought the gas bombs, and a tank and a rubber hose. A ladder was put up from the inner courtytard to put the hose into the cell block. We used the gas bombs and the rubber hose to poison them. I think it took about one hour to kill them all."**

Sixty marutas died of phosgene poisoning [2191a].

1.8 PHOSGENE AND MODERN WARFARE

At the end of World War II, the Allies dumped vast quantities of chemical weapons into the depths of the earth's oceans. Britain, in particular, dumped chlorine, phosgene and mustard gas shells into deep water off Ireland (and these sites are now a recognized threat to fishermen working deep sea trawlers [64c]; see also Section 1.10) and Norway. In addition, some of the serviceable phosgene weapons were exported to India. The USA dumped Japanese chemical weapons into the Pacific, and the USSR dumped them into the Baltic [1129a]. This is not to say, however, that the USA and Britain had adopted a stance against chemical weapons. Britain had come very close to using chemical weapons during the second World War, and considered that they may still be of use in the Far East. Large stockpiles of the chemicals required for gas weapons were maintained, and the widespread popular revulsion at the concept of chemical warfare was matched only by official resistance to scrap a perceived chemical defence capability. Research and development effort after World War II centred upon the nerve gases, tabun and sarin, and upon the 'new' biological agents such as anthrax, brucellosis, tularemia and the botulinal toxins – weapons whose lethal power far outstripped that of phosgene. It was not until 1956 that the economic pressures upon the British government were such that Britain declared its intention to abandon chemical weapons research and use. The remaining stockpiles of phosgene were dumped in the sea off the Inner Hebrides (see Section 1.10).

Although there was widespread adoption of nerve gases as sophisticated chemical weapons in the years following World War II, phosgene has remained (together with mustard gas) in the background as a cheap and relatively available chemical weapon that is just as capable of inflicting grievous injuries against the unwary as it was during World War I. It has been implicated in offensive action taken, *inter alia*, in the 1960s by the Egyptians during the Yemeni civil war and, more recently, in the Thai–Vietnamese–Cambodian border conflicts. Whilst gas attacks have featured in the Iran–Iraq conflict, and the UN have confirmed the use of mustard gas and nerve gases, the use of phosgene – though claimed by both sides, and suspected by UN observers – was not unequivocally proven. And, of course, the spectre of phosgene loomed large in the Gulf War in 1991, when almost all newspapers and television broadcasts found it essential to consider phosgene as a vital part of Saddam Hussein's lethal arsenal – if phosgene had been his major weapon, the war would have been even shorter! With a certain inevitability, phosgene now regularly occurs in descriptions of, and speculations concerning, the situation in the former Yugoslavia, especially as a plant run by Prva Iskra exists in Baric, with a phosgene production capacity of 27,000 tons per year.

Current stockpiles of phosgene are kept by both the US (at the Rocky Mountain Arsenal, in Colorado) and Russia, although the reason for maintaining phosgene weapons, when far superior agents are now readily available, is hard to comprehend. Although Britain no longer stockpiles phosgene, known sites of previous manufacture and storage are monitored by the Ministry of Defence (including: West Cottingworth, near York; Risely, Bedfordshire; Barnham, Norfolk; Lords Bridge, near Cambridge; Swinderby, Lincolnshire; and Bowes Moor, Durham) [1603a], and old dumps are periodically rediscovered. The latest find [885a] was that at Bramley, in Hampshire, where experts from Porton Down were summoned in October 1987 to remove old mustard gas and phosgene gas canisters (see Fig. 1.31), and shells that were apparently surplus to requirements at the end of the First World War, and buried after the Second World War.

1.9 PHOSGENE AND THE MODERN WORLD

> **We blame or praise most things merely because it is the fashion**
> ***On loue et on blâme la plupart des choses parce que c'est la mode de les louer ou de les blâmer***
>
> **Duc de la Rochefoucauld (1613–1680), *Maximes Posthumes No. 533,***

Phosgene continues to be manufactured on the multi–million ton scale, world–wide [1804a]. In the US alone, in 1994, the phosgene production capacity was well over one million tons, and in Europe it was approaching 750,000 tons. Its manufacture is detailed in Section 4.1, and its current uses are discussed extensively in Section 4.7. It is an intermediate for the production of a wide–range of organic materials, with an even more diverse range of end uses, including polyurethane foams (for automotive, furniture, thermal insulation and footwear applications) and isocyanates, chloroformates, carbonates, ureas and carbamates (for medical, agricultural, dyestuff, perfumery, solvent, explosive stabilizers or speciality polymer applications). It is also a key reagent in the total synthesis of the anti–cancer drug, taxol [1506a].

Fig. 1.31 From left to right: a Livens container (phosgene), a 4" Stokes (Mortar Bomb (chloropicrin) and a 6" shell (mustard gas), found buried at Bramley in 1987 (reproduced with permission of the Chemical Defence Establishment, Porton Down). They all exhibit an advanced state of corrosion.

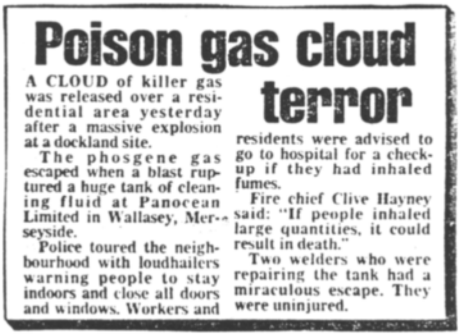
In an ironic aside, it is noted that the most recently suggested new use for phosgene is to "make safe" thousands of tons of TNT (2,4,6-trinitrotoluene) from redundant weapons, no longer required now that the Cold War has ended. Treatment of the TNT with ammonium sulfide would reduce it to 2,4-diamino-6-nitrotoluene, which could then be treated with phosgene to give 2,4-diisocyanato-6-nitrotoluene (NDTI), a potentially valuable precursor for polyurethane manufacture [64d]. Thus, instead of potentially hazardous, and certainly wasteful, destruction of the TNT, the use of phosgene could convert it into a valuable industrial commodity.

Given the huge scale of modern manufacture and usage, it is perhaps surprising that there have been relatively few major industrial accidents involving the emission of phosgene. In fact, death or serious injury due to phosgene exposure is extremely rare. A fatality at the Union Carbide plant at Bhopal in 1981 was the direct result of phosgene poisoning. In this incident, three workers, all of whom were wearing protective clothing – including respirators, were contaminated with liquid phosgene whilst trying to clean a faulty valve. The men all ran to a shower unit some thirty yards away, one of them ripping off his gas mask *en route*. The phosgene gas inhaled as a result of this action resulted in his death the following day; the other two members of the team suffered no long-term lung damage. Most of the industrial incidents involving phosgene escapes have resulted in injury, but not in the loss of life. For example, a leakage of phosgene occurred in 1984 at the Conoco oil refinery (Lake Charles, USA): it resulted in 42 people being treated for respiratory distress of varying degrees. Two leaks were reported in 1986, one at a chemical works at Sajobabony (Hungary) where 17 workers were temporarily hospitalised and a second, where the phosgene quickly dispersed, at the Slegfied plant at Aarau near Basle in Switzerland. Most recently, in April 1994, two workers at a BASF plant at Ludwigshafen (*cf*. Section 1.3.1) were exposed to phosgene from a leak in a dyestuffs unit; they were hospitilized, but later released [64e].

The most widely publicised accident in which phosgene has been implicated occurred at the Union Carbide plant at Bhopal, in India, where between 2000 and 2500 people died, and around 200,000 were injured on 3rd December, 1984 [362a]. Although the exact cause of this accident was, and still is to some extent, shrouded in uncertainty and contradiction, a theory put forward by the head of India's central chemical research body (Dr. Srinivasan Varadarajan) has some support. His enquiries have suggested that a reaction ocurred as a direct result of water leaking from a pipe with a faulty seal into the methyl isocyanate storage tank. A more rapid reaction than might have been expected ensued as the contents of the tank were at ambient temperature rather than the regulation cooler temperature - a direct consequence of deactivating the storage tank's refrigeration unit several months previously. The problems were further compounded by the inadequacy of the sodium hydroxide scrubber unit on the tank to cope with the massive throughput of escaping methyl isocyanate. However Dr. Varadarajan's rationalization of the chemical events that occurred on 3rd December, 1984, are rather counter-intuitive. He has suggested that the invading water reacted with phosgene to produce highly corrosive chloride ions, which then attacked the steel walls of the storage tank in a highly exothermic reaction. Whilst it seems highly likely that some phosgene ($COCl_2$), methylamine (CH_3NH_2) and chloroform ($CHCl_3$) were released with the methyl isocyanate (CH_3NCO) at Bhopal, it is clear from the symptoms shown by the victims (see Section 2.1 for the symptoms of phosgene poisoning in humans) that the large-scale loss of life in this incident was NOT due to phosgene poisoning.

As a result of the Bhopal disaster, attention was focussed upon the Union Carbide plant at Institute (West Virginia, USA), and it was revealed that there had been twenty-one cases of 'in-plant losses' of methyl isocyanate/phosgene mixtures and 107 cases of phosgene alone. The company was found guilty of 221 separate violations of 55 US federal safety standards, and fined $1,377,700 in April 1986. The most serious, and least expected, charge against Union Carbide was that they regularly used workers as 'human-canaries' to sniff out the sources of phosgene leaks - a practice that also appears to have been in operation at Bhopal. This charge Union Carbide strenuously denied. In July 1987, Union Carbide agreed to pay $408500 in settlement of the charges, though part of the agreement included the standard non–admission clause in which responsibility was accepted without admission of guilt.

Another incident in which phosgene was initially implicated occurred in August 1986 at the Mannesmann Demag plant in Duisberg (West Germany), where welding work on a trichloroethene storage tank led to two small explosions and a fire. The resulting uncontrolled gas emissions neccessitated the overnight hospitalisation of thirty–eight people. A very similar (though smaller scale) incident ocurred in July 1987 during welding of a trichloroethane storage tank at a chemical works in Wallasey, U.K. That phosgene *could* have been formed in these incidents is amply illustrated in Section 5.2.4.1. However, in both of these incidents, evidence gathered at the time indicated that it was NOT formed in significant quantities; the symptoms of those injured in the Duisberg incident were inconsistent with phosgene poisoning, and indeed phosgene testing at Wallasey in the vicinity of the explosions and fire proved negative [2213aa]. However, the facts were not to prevent the ***Daily Mirror***, in one of its more restrained headlines, giving a balanced, considered and responsible headline to their article of 30th July, 1987:



Poison gas cloud terror

A CLOUD of killer gas was released over a residential area yesterday after a massive explosion at a dockland site.

The phosgene gas escaped when a blast ruptured a huge tank of cleaning fluid at Panocean Limited in Wallasey, Merseyside.

Police toured the neighbourhood with loudhailers warning people to stay indoors and close all doors and windows. Workers and residents were advised to go to hospital for a checkup if they had inhaled fumes.

Fire chief Clive Hayney said: "If people inhaled large quantities, it could result in death."

Two welders who were repairing the tank had a miraculous escape. They were uninjured.

To quote directly from a very recent, and authoritative, report on phosgene toxicity [1297a]:

> **"It is important not to propagate the myth that phosgene is a major toxic hazard from chlorinated solvent fires on an industrial scale."**

We seriously hope that newspaper editors will take this advice to heart; printing misinformation which spreads unnecessary panic amongst the general public is verging on criminal irresponsibility. The temperatures in fires of this sort are too high to sustain significant concentrations of phosgene – the major hazard is hydrogen chloride.

Several near misses have also taken place; one occurred recently at the Sandoz plant in Basle, Switzerland, where a fire destroyed a warehouse next to a phosgene store. And in what must rate as ***anguis in herba*** – at the very least – reports have emerged that phosgene is being pumped from one chemical plant to another *across* central Toulouse, France.

Phosgene attracts more than its fair share of inaccurate and/or sensationalist reporting – the slightest hint of its involvement apparently justifying the summoning of the gas horrors of the First World War. A few days after the accident at Bhopal the following extract was contained in a *Guardian* front page report:

> **"... The experts feel that a still unexplained chemical reaction converted liquid methyl isocyanate into an extremely toxic breakdown gas which could be phosgene - a nerve gas reported to have been used by Nazi Germany during the second world war... "**

Three aspects of this extract merit comment. Firstly phosgene is NOT a nerve-gas (an error that *The Guardian* is not alone in making), nor has it been established that it was ever used by the Nazis during the Second World War (though it was, as described above, extensively used by the Germans *and* the Allied forces during the First World War). Finally, phosgene is NOT a breakdown product of methyl isocyanate. The level of scientific ignorance exposed by those few lines is staggering; it is of a standard expected from tabloids, not broadsheets.

Other statements include:

> **"... Phosgene, known as mustard gas during World War I, is used to make methyl isocyanate, an intermediate compound in the pesticide Sevin... "**
>
> **TWP, 1st February, 1985.**

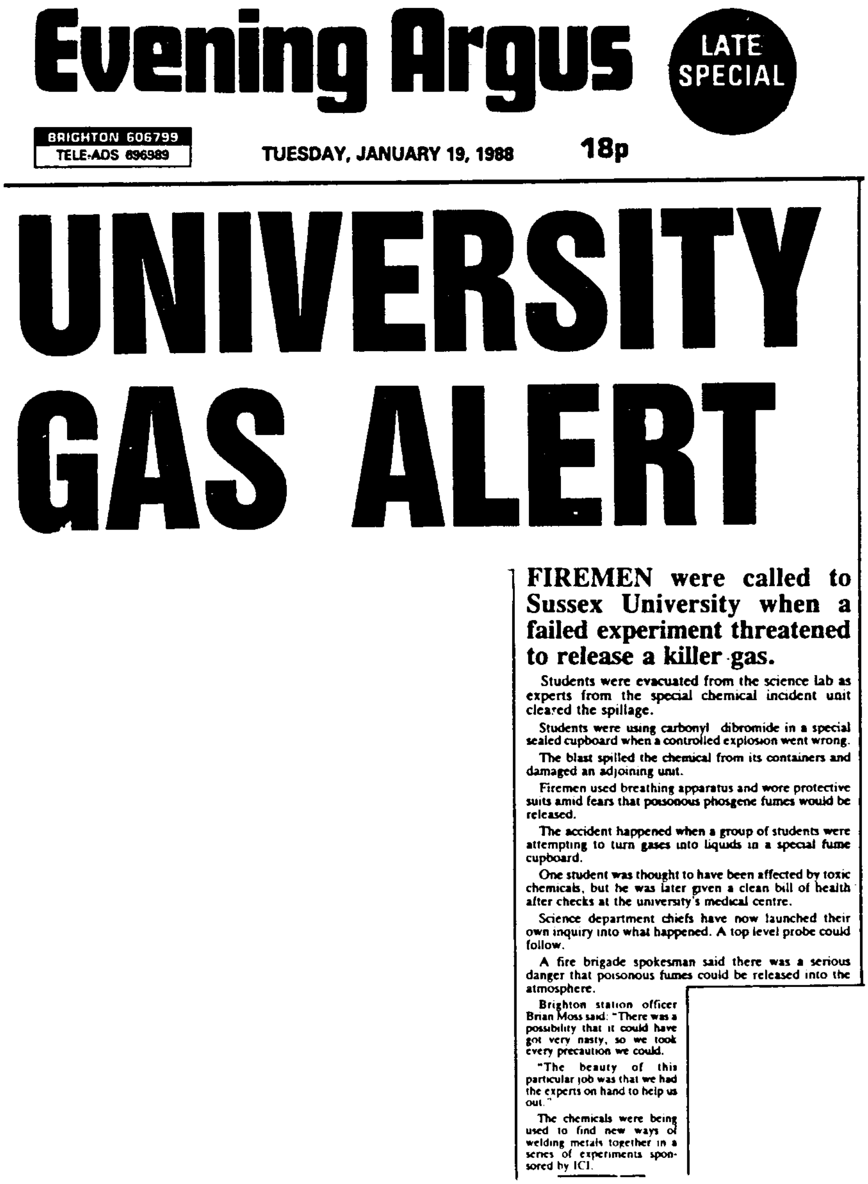
> **"... Phosgene was a major ingredient of mustard gas blamed for a million deaths in World War I... "**
>
> **The Associated Press, 24th July, 1987.**

Though still widely assumed to the contrary, phosgene is NOT mustard gas.

In an incident in our own laboratories, where less than 2 cm^3 of carbonyl dibromide were accidently released into a fume cupboard of volume sufficient to render the release safe, the local paper had the story as the main front page lead (see Fig. 1.32) - the number of errors are legion, both concerning the actual events and the science, in this short article - we suspect ICI would have been astounded to discover that it had been sponsoring experiments with carbonyl dibromide "to find new ways of welding metals together".

Another sensationalist headline is illustrated in Fig. 1.33, where phosgene is blamed for Legionnaires' Disease (which is, of course, of bacteriological origin, see Section 3.3.4). "Nobody will listen, ..." at least gives hope that the reading public of Philadelphia shows rather more discrimination than the editor of the *Philadelphia Magazine* [1863]. There can be little doubt that, if a newspaper or magazine wants to grab the attention of its readers, blaming phosgene for incidents, or claiming that death clouds are about to descend on a city, is one guaranteed way to achieve that. However, we are convinced that Tacitus and Swope have the correct attitude (see Section 1.11).

However, if it is disgraceful that newspapers and magazines propagate misinformation, it is quite unforgivable when college textbooks do the same thing: at least newspaper reporters have the excuse of meeting daily deadlines. Three general chemistry textbooks



Evening Argus

LATE SPECIAL

BRIGHTON 606799
TELE-ADS 696989

TUESDAY, JANUARY 19, 1988

18p

UNIVERSITY GAS ALERT

FIREMEN were called to Sussex University when a failed experiment threatened to release a killer gas.

Students were evacuated from the science lab as experts from the special chemical incident unit cleared the spillage.

Students were using carbonyl dibromide in a special sealed cupboard when a controlled explosion went wrong.

The blast spilled the chemical from its containers and damaged an adjoining unit.

Firemen used breathing apparatus and wore protective suits amid fears that poisonous phosgene fumes would be released.

The accident happened when a group of students were attempting to turn gases into liquids in a special fume cupboard.

One student was thought to have been affected by toxic chemicals, but he was later given a clean bill of health after checks at the university's medical centre.

Science department chiefs have now launched their own inquiry into what happened. A top level probe could follow.

A fire brigade spokesman said there was a serious danger that poisonous fumes could be released into the atmosphere.

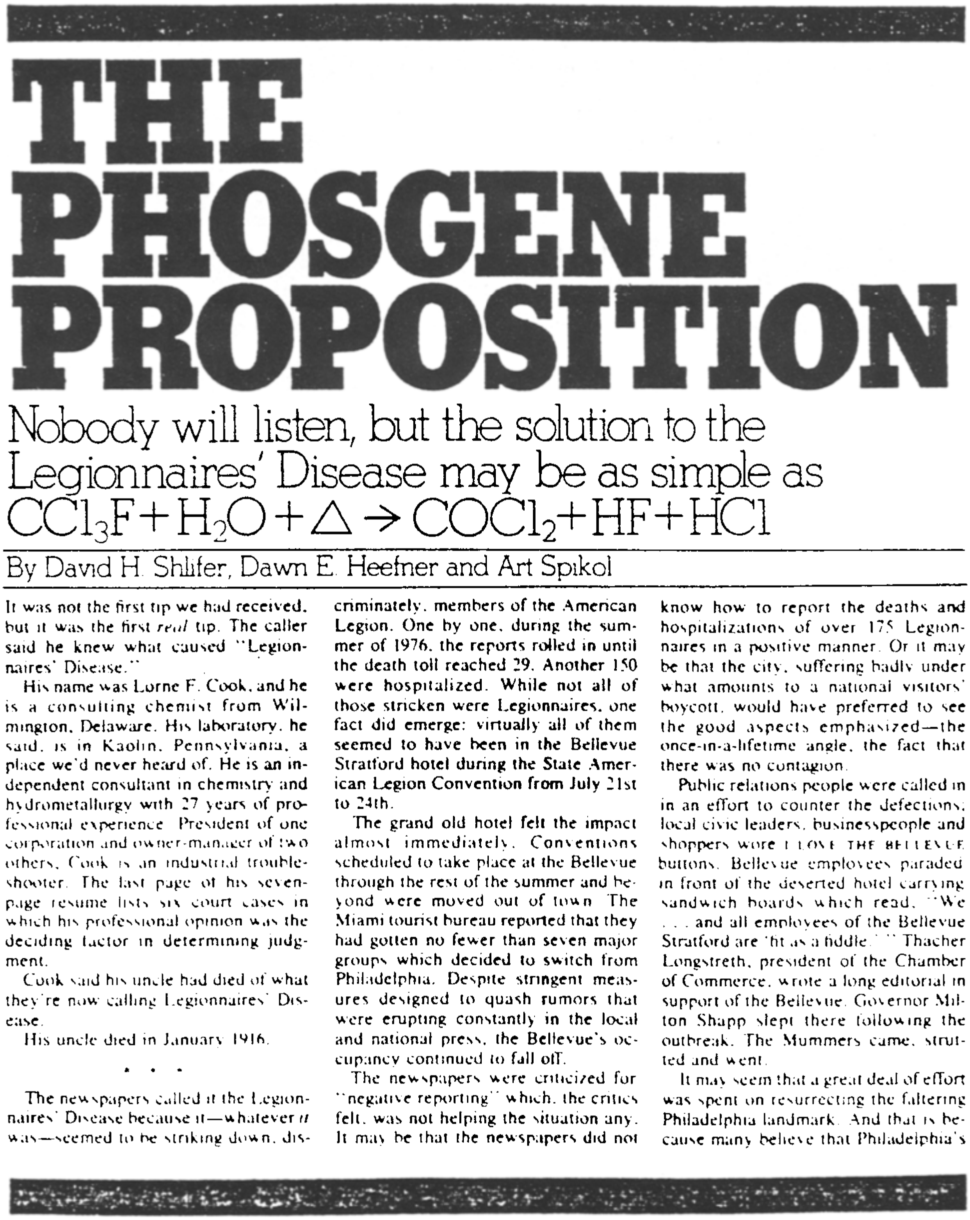
Brighton station officer Brian Moss said: "There was a possibility that it could have got very nasty, so we took every precaution we could.

"The beauty of this particular job was that we had the experts on hand to help us out."

The chemicals were being used to find new ways of welding metals together in a series of experiments sponsored by ICI.

Fig. 1.32 The lead story in the *Evening Argus*, 19th January, 1988.

[960a,1041a,1052a] all categorically state that the mechanism for phosgene poisoning is the hydrolysis of phosgene in the lungs to give hydrochloric acid, which then causes pulmonary œdema. Examination of Section 2.5.1 will show that this is totally incorrect information, and it should not be propagated in text books. We sincerely hope that these errors will be removed from subsequent editions, and not be repeated *ad infinitum*.



THE PHOSGENE PROPOSITION

Nobody will listen, but the solution to the Legionnaires' Disease may be as simple as $CCl_3F + H_2O + \Delta \rightarrow COCl_2 + HF + HCl$

By David H. Shlifer, Dawn E. Heefner and Art Spikol

It was not the first tip we had received, but it was the first *real* tip. The caller said he knew what caused "Legionnaires' Disease."

His name was Lorne F. Cook, and he is a consulting chemist from Wilmington, Delaware. His laboratory, he said, is in Kaolin, Pennsylvania, a place we'd never heard of. He is an independent consultant in chemistry and hydrometallurgy with 27 years of professional experience. President of one corporation and owner-manager of two others, Cook is an industrial troubleshooter. The last page of his seven-page resume lists six court cases in which his professional opinion was the deciding factor in determining judgment.

Cook said his uncle had died of what they're now calling Legionnaires' Disease.

His uncle died in January 1916.

* * *

The newspapers called it the Legionnaires' Disease because it—whatever *it* was—seemed to be striking down, discriminately, members of the American Legion. One by one, during the summer of 1976, the reports rolled in until the death toll reached 29. Another 150 were hospitalized. While not all of those stricken were Legionnaires, one fact did emerge: virtually all of them seemed to have been in the Bellevue Stratford hotel during the State American Legion Convention from July 21st to 24th.

The grand old hotel felt the impact almost immediately. Conventions scheduled to take place at the Bellevue through the rest of the summer and beyond were moved out of town. The Miami tourist bureau reported that they had gotten no fewer than seven major groups which decided to switch from Philadelphia. Despite stringent measures designed to quash rumors that were erupting constantly in the local and national press, the Bellevue's occupancy continued to fall off.

The newspapers were criticized for "negative reporting" which, the critics felt, was not helping the situation any. It may be that the newspapers did not know how to report the deaths and hospitalizations of over 175 Legionnaires in a positive manner. Or it may be that the city, suffering badly under what amounts to a national visitors' boycott, would have preferred to see the good aspects emphasized—the once-in-a-lifetime angle, the fact that there was no contagion.

Public relations people were called in in an effort to counter the defections; local civic leaders, businesspeople and shoppers wore I LOVE THE BELLEVUE buttons. Bellevue employees paraded in front of the deserted hotel carrying sandwich boards which read, "We . . . and all employees of the Bellevue Stratford are 'fit as a fiddle.' " Thacher Longstreth, president of the Chamber of Commerce, wrote a long editorial in support of the Bellevue. Governor Milton Shapp slept there following the outbreak. The Mummers came, strutted and went.

It may seem that a great deal of effort was spent on resurrecting the faltering Philadelphia landmark. And that is because many believe that Philadelphia's

Fig. 1.33 **An extract from the *Philadelphia Magazine* [1863].**

1.10 THE KRAKEN WAKES

> **Below the thunders of the upper deep,**
> **Far, far beneath in the abysmal sea,**
> **His ancient, dreamless, uninvaded sleep**
> **The Kraken sleepeth:**
>
> **Alfred, Lord Tennyson, *The Kraken***

Autumn 1995, and suddenly chemical agents are headline news again (although the story originally broke in the *Sunday Life* on 16th October, 1994). Of more long-term concern than the unprecedented release of sarin in the Tokyo underground, apparently by a group of "religious" extremists, is the re-appearance of our past to haunt us. As already noted in Section 1.8, many war gases were disposed of by dumping them at sea. By the last weeks of November, 1995, more than 4000 phosphorus incendiaries had been washed up on the North Antrim coast, the Isle of Man, and the West Scottish coast. Between 1955 and 1956, about 25,000 tons of chemical weapons, including 330 tons of powdered arsenic, phosgene, mustard gas, and cyanide, as well as 71,000 nerve gas bombs containing sarin and tabun, were dumped (under a previously top-secret dumping programme - Operation Sandcastle - by scuttling three ships, the *Empire Claire*, the *Kotka* and the *Vogtland*) in the Atlantic Ocean, some 80 miles north-west of Northern Ireland. In addition, Beaufort's Dyke (a marine trench on the bed of the Irish Sea between Northern Ireland and Scotland - only about eight miles from the Ulster Coast) was the primary sea disposal dump site for the Ministry of Defence between 1920 and 1976, and contains over one million tons of conventional munitions, as well as considerable quantities of phosgene (at least 14,000 tons), mustard gas and nerve gases. British Gas was forced to divert its recently laid natural gas pipeline across the Irish Sea, to avoid disturbing this "chemical time bomb".

In 1953, canisters of mustard gas and phosgene from a former RAF depot at Buxton were dumped in the North Sea. Other dumping grounds include areas between 50 and 100 miles west of the Hebrides, one 80 miles north-west of Ireland, and another 250 miles south-west of Lands End in the Western Approaches. The sites have not been monitored because, according to the Ministry of Defence, the weapons were "made safe, or put in safe containers". This is clearly some new meaning of the word "safe", not included in the Oxford English Dictionary! On 27th January, 1995, Mr Nicholas Soames (British Armed Forces Minister) stated in the Commons: "Sea dumping was considered to be the safest and most practical method of diposal at the time. Current scientific evidence indicates that such CW dump sites present no significant risk to human health or to the marine environment." Again note the unique usage of phrases like "scientific evidence" and "no significant risk"!! This story is still unfolding as this book goes to press, but its consequences could be extremely serious, especially for the people of Northern Ireland, Scotland and the Isle of Man. Let us truly hope that the kraken[¶] remains sleeping, and is not woken by, say, deep sea trawlers.

[¶] A mythical Scandanavian sea-creature [234a].

1.11 ACCURACY AND THE PRESS

Herbert Bayard Swope (the journalist who coined the phrase "the cold war"), stated in a letter to the *New York Herald Tribune* (March 16th, 1958):

> **The First Duty of a newspaper is to be Accurate. If it is Accurate, it follows that it is Fair.**

Let us now examine the accuracy and fairness of the British Press. The following recent example reveals the contrast between the broadsheets and the tabloids. From *Today* (July 24th, 1993):

Navy Officer in Phone Pest Quiz found Gassed

> **A retired Naval commander was found dead at home yesterday after inhaling lethal gas used in trench warfare.**
>
> **Former Fleet Air Arm officer Ian Cobbold, 60, was discovered just days after police questioned him about a series of threatening phone calls.**
>
> **Thirty-nine people including policemen, paramedics and milkman Colin White – who found the body – had to be treated in hospital after they also inhaled the gas, PHOSGENE.**
>
> **Mr Cobbold was quizzed after journalist Keith Chalkey, 52, received menacing calls when he objected to a plan to build holiday homes near his house. A trace revealed the calls came from Mr Cobbold's house at Over Stratton near Yeovil, Somerset.**

From *The Daily Telegraph* (8th October, 1993):

Gas Alert after Officer made Suicide Pump

by David Millward

> **A retired Navy officer caused a full-scale chemical alert when he killed himself by using a vacuum cleaner to pump a toxic gas into his home, an inquest heard yesterday.**
>
> **Lt. Cmdr. Ian Cobbold, 60, placed PHOSTOXIN tablets, normally used as a rat killer, on his vacuum cleaner's motor. Its heat generated the gas PHOSPHINE. The former Fleet Air Arm officer was found dead in his home at Over Stratton, near Yeovil, Somerset, in July.**
>
> **Chard Coroner's Court was told how police broke into the house after a suicide note was seen on the door. Police and paramedics were overcome by the fumes and had to be taken to hospital. Neighbours and a nearby school were evacuated.**
>
> **Lt. Cmdr. Cobbold, who had been depressed since his 1981 divorce, had also taken an overdose of sleeping tablets. Verdict: suicide.**

Verdict:

> **Truth is strengthened by observation and delay, falsehood by haste and uncertainty (*Veritas visu et mora, falsa festinatione et incertis valescunt*).**
>
> Tacitus (*Annals*, **Book ii, Section 39**)

Phostoxin contains aluminium phosphide, which hydrolyses in moist air to produce phosphine. It must be terribly difficult for a tabloid journalist to distinguish between words beginning with the same four letters – especially when they possess more than one syllable.

1.12 WHY THIS BOOK?

Why write a book about phosgene (and, indeed, the related carbonyl halides)? There are many reasons, not least the fact that it has not been done before. There have been a number of reviews over the years, featuring various aspects of the chemistry of phosgene [42,179,578,975,996,1019,1378,1379], and regular accounts have appeared in the Gmelin Handbuch der Anorganischen Chemie [780–783] and Beilsteins Handbuch der Organischen Chemie [155–164b]. However, for a chemical of major significance to the modern chemical industry, and one of the few chemicals whose name is known to the general public, it is quite astonishing how little substantial reviewing of the vast literature has actually occurred. When this was coupled with the, frankly, arrant nonsense that is frequently written about phosgene (*vide supra*), it was clearly timely to put the record straight, and to provide a source book which, we believe, will be of value to both industry and academia. In addition, we also had access to much previously unpublished work from ICI internal reports (we reference 118 of these). If we have made, here, a strong case that phosgene is, in fact, a relatively safe chemical to work with – a war gas, but a ***tamed*** war gas – then this book will have served its purpose well. A quote from a recent report from the British Institution of Chemical Engineers [1297a] is an apt place to finish this Chapter:

> **"Phosgene should certainly be treated with respect, as should HCl, but in accordance with the facts. Otherwise a scare campaign might be orchestrated."**

2 BIOLOGICAL ACTIVITY OF PHOSGENE

This chapter, describing the biological activity of phosgene, is undoubtedly the most vital in this book. A thorough working knowledge of its contents is an essential prerequisite for handling phosgene. As well as describing the symptoms of phosgene poisoning, and its effects on the respiratory system, the latest recommendations for first aid and treatment are discussed. In addition, the effects of phosgene exposure upon animals, and other life-forms, are described.

2.1 SYMPTOMS OF PHOSGENE POISONING

Human response to phosgene exposure is determined by both the atmospheric concentration and by the amount inhaled. Exposures may be classed as being: high (>200 p.p.m. min) [523], low to moderate (3 p.p.m. to *ca.* 150 p.p.m. min) [523], or low (*e.g.* <1 p.p.m. for 8 $\mathrm{h\ d^{-1}}$ for a five-day working week) dose over a prolonged period [1644]. However, these classifications are not rigorous, and each exposure must be considered along with its own conditions. The subject of exposure dose is considered further in Section 2.4.

2.1.1 Low-moderate dose responses

Typically the initial reactions for exposure to concentrations greater than 3 p.p.m. are watering of the eyes, general irritation of the nose and throat, coughing, dizziness, tightness and pain in the chest with the onset of rapid shallow breathing [238,253,492,526,712,936,953, 1009a,1404,1643a,1644,1691,2154,2166]. Inhalation of a single dose below 22 p.p.m. min (see Section 2.4) can be regarded as generally harmless, producing no long term effects beyond the initial reaction [531]. However, not all individuals will exhibit the full range of symptoms. Indeed, there have been incidents reported where the victim showed little immediate discomfort but later developed serious illness [2020,2147]. The following case is illustrative of this [1695]:

> A major phosgene leak occurred in a chemical plant at 14.00 on December 9th, 1977. Fifteen employees were exposed to the gas, but only four were detained in hospital. All those released by the hospital were symptom free and thought to have had minimal exposure to phosgene. One of these workers, a forty-seven year old male, felt well initially and went home. He was later admitted to hospital at 01.00 on

> December 10th in a distressed condition and exhibiting breathing problems. After treatment in the intensive care unit his condition stabilized for the first eight hours, but then rapidly deteriorated. He remained in a critical condition for three days. By December 13th, the patient began to show improvement in his condition. This improvement continued until, by December 21st, he was completely without symptoms and so was discharged from hospital. He returned to his regular work on December 22nd.

It is evident, from the above case history, that the severity of the initial symptoms is not a reliable indicator of the seriousness of the exposure. For example, an inhaled dose of 2 p.p.m. for 80 min will not stimulate the previously described irritation but will cause serious illness some twelve to sixteen hours later [524]. The victim's emotional state may also exacerbate the symptoms, as being exposed to a toxic gas is a traumatic experience which often creates panic in the victim.

The symptoms initially experienced rapidly diminish with time after removal from the poisoned atmosphere, and the patient enters a latent period that is characteristically symptom free. This period may last for up to twenty-four hours.

As the latent period comes to an end, the patient will exhibit increasing difficulty in breathing. Many produce large quantities of sputum which becomes progressively frothy and blood-stained. Moist vesicular rales[¶] may be heard and the heart rate may increase. The ears, lips and progressively the entire face may assume a bluish tinge, although this full colouring may be omitted in some individuals. A feeling of extreme anxiety and restlessness often accompanies the development of this condition [2147,2154].

Subsequently the patients state may deteriorate, ultimately resulting in death from respiratory or cardiac failure. Alternatively, the condition may gradually improve over a period of hours or days and the more serious symptoms disappear. Complete recovery may take several years and most patients complain of reduced physical fitness and breathing problems, on exertion, for months after the poisoning [756,2154]. Moreover, recovery may be adversely affected by previous lung damage (*e.g.* bronchitis) and smoking habits [526,756,1643a], although it has been recorded that sufferers have an aversion to cigarette smoke afterwards [678]. There has also been a suggestion that fair-haired people are more sensitive to phosgene poisoning than dark-haired people [1234].

2.1.2 *High dose responses*

If the exposure dose is very high (>200 p.p.m. min.) death will usually occur within a few minutes, from heart failure [523].

[¶] Abnormal crackling sound in the chest caused by the presence of fluid in the air passages.

2.1.3 Responses to long-term low dose

Individuals exposed to low doses of phosgene (<1 p.p.m.) over a prolonged period have shown no significant increase in mortality over unexposed individuals [1643a,1644]. A recent follow-up study, by Polednak, of 699 workers exposed to low (but undetermined) levels of phosgene revealed four deaths from pulmonary tuberculosis (*cf.* 2.79 expected from a normal population of 699) [1643a]. This reemergence of pulmonary tuberculosis had been reported previously (in 1933) by Gilchrist and Matz [756] in their follow-up study of 159 war gas victims. It is believed that phosgene exposure damages the host's resistance, and so allows reinfection to occur. In both reports, the sample sizes were relatively small, but the phenomenon warrants further study. Indeed, later animal experiments have indicated possible immunotoxicity of phosgene (see Section 2.5.2) [583b]. In addition, some reports have described slightly greater incidence of long-term lung disorder in some individuals [713]. No quantitative data about the effects of long-term low-dose exposure on previously diseased/damaged lungs are available.

2.2 LUNG STRUCTURE AND FUNCTION

Most of the symptoms produced by phosgene poisoning occur as a consequence of damage to the lung and its associated structures. Man's respiratory system is highly specialized for gas exchange in air. The internal surfaces of the system are brought into contact with the air *via* the respiratory tract and the operation of a tidal ventilation mechanism (see Fig. 2.1).

Adult lungs are spongy in texture, have a pinkish colour, and weigh about one kilogram in total. They are composed of lobes covered with a thin transparent coat, enclosing elastic air-filled (areolar) tissue. The bronchus, upon entry into each lung, divides and subdivides throughout the entire organ. The smaller subdivisions (1 mm or less internal diameter) are called bronchioles and their terminal sections become enlarged to form the alveolar passages. Arising from these passages, in all directions, are minute air-sacs (or alveoli). The pulmonary alveoli are the main sites of respiratory gas exchange (see Fig. 2.2). The efficiency of the lung depends upon there being an intimate relationship between the alveoli and the blood system *via* an extensive capillary network (the blood-air barrier being only *ca.* 300 nm thick). The two lungs contain approximately seven hundred million alveoli giving a total surface area of over 70 m^2 for gas exchange, and so act as the major reaction sites for gaseous poisons like phosgene.

During inspiration, air is drawn into the lungs *via* the nose and/or mouth, travels along the trachea and into the bronchi. It is then dispersed throughout the bronchioles to the alveolar regions, where gas exchange occurs by diffusion. During expiration, air leaves the body by the reverse route.

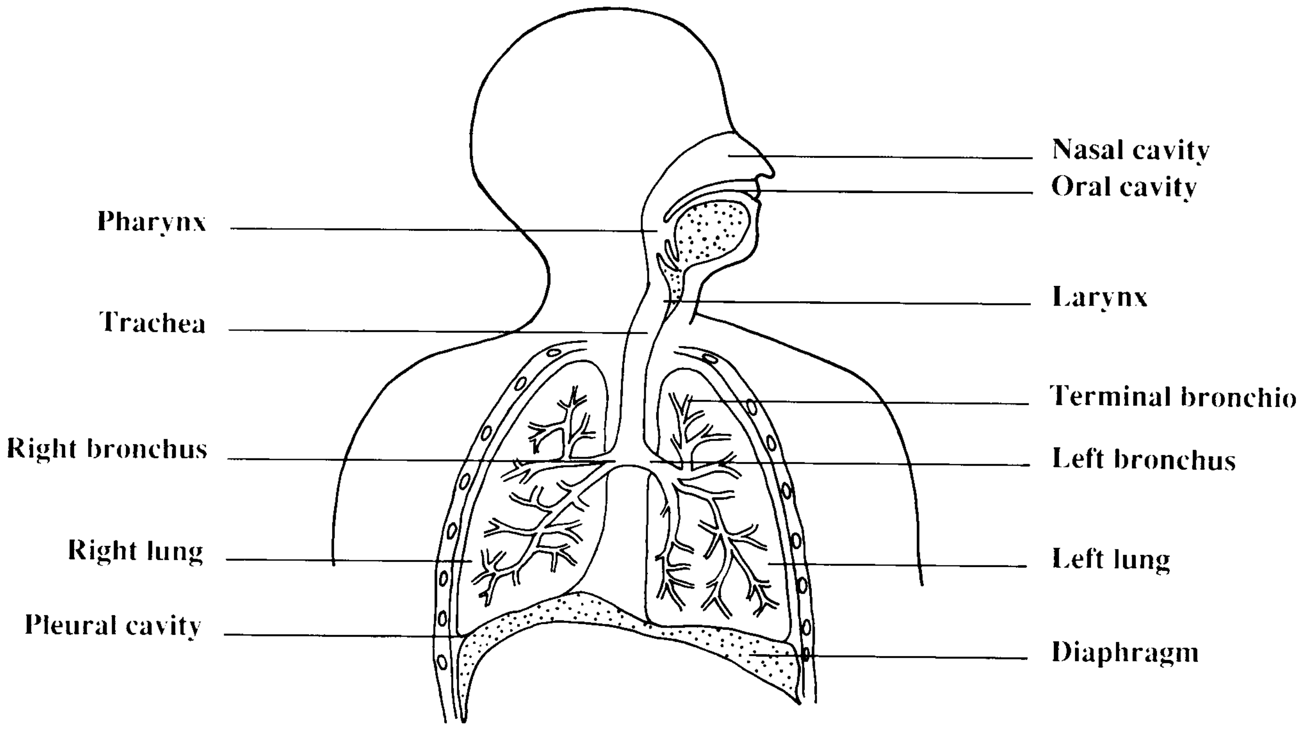


Fig. 2.1 A diagram of the human respiratory apparatus and associated structures.

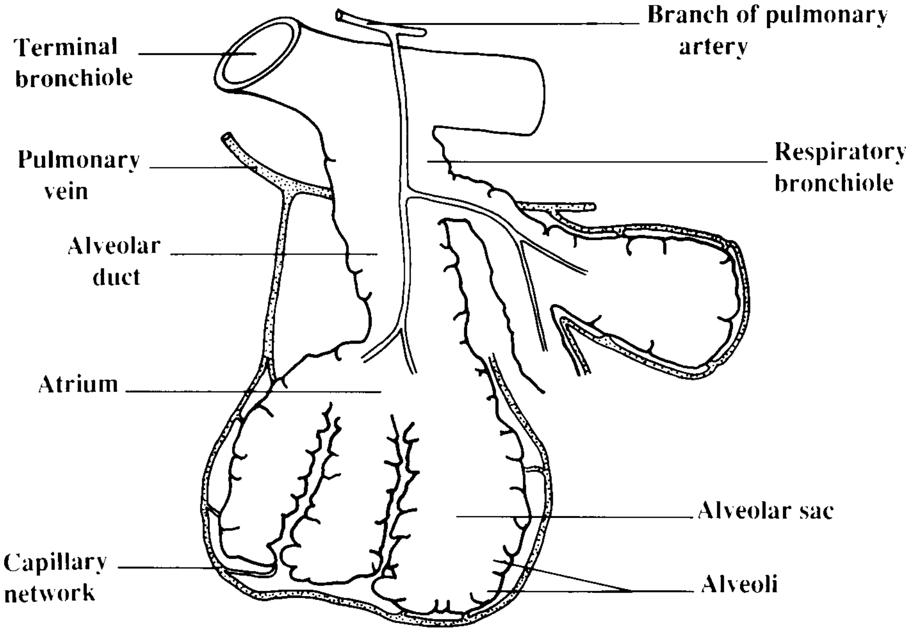


Fig. 2.2 A diagram of the principal sites of gas exchange.

2.3 EFFECTS OF PHOSGENE ON THE RESPIRATORY SYSTEM

Phosgene's toxicity is predominantly the result of its disruption of gas exchange at the bronchiolar and alveolar level [238,253,400,492,523]. Numerous case histories have been documented of individuals suffering from moderate to high level exposure to phosgene [221,250,253,492,526,712,747,756,764,794,920,1124,1644,1691,1940,2020,2166,2258], and the initial symptoms (Section 2.1) may be largely attributed to the initiation of a bioprotective reflex that is usually triggered by the presence of an irritative substance in the upper respiratory tract [253,1777a]. In the case of phosgene, some of the gas dissolves in the moisture present in the nose, throat and trachea to produce hydrochloric acid, and it is probably this substance that gives rise to the first symptoms [327,523]. However, it is not the production of hydrochloric acid that is the most dangerous aspect of phosgene's toxicity, but a more damaging series of chemical reactions that occur deep within the lungs.

Phosgene has a relatively low solubility in water and consequently is able to penetrate to the terminal bronchioles and alveoli where it reacts chemically with cellular and extracellular constituents, causing damage to the blood–air barrier [523,1893]. Desquamation¶ of the bronchioles and bronchoconstriction has also been observed [492]. The blood–air barrier disruption results in a leakage of fluid from the blood into the alveolar air space and this gradual accumulation of œdema§ is occurring throughout the "symptom free" latent period.

Eventually, sufficient fluid collects to seriously inhibit gas exchange. Consequently, anoxemia occurs and blue cyanosis is evident. The patient's breathing becomes increasingly dyspnœic,† and the now frothy, protein–rich œdema fluid emerges in the upper respiratory tract. The viscosity of the blood increases because of lost plasma, and it becomes brown due to the formation of methæmoglobin. These circulatory disorders may further compromise oxygen uptake, and the blue cyanosis may become grey.

Increasing anoxemia can then result in lethal failure of the respiratory centre [288,523, 1032]. However, cardiac failure may be the cause of death with very high phosgene doses (>500 p.p.m. min) because phosgene may then react directly with the blood in the pulmonary capillaries, causing hæmolysis and blockage of the pulmonary circulation. This, in turn, may cause the right side of the heart to become acutely enlarged [523].

If treatment prevents fatal oxygen deficiency from developing, the patient may survive the poisoning and the œdema will regress. The lung tissue damage may take several months to repair and during this time the patient is susceptible to superinfective pneumonia. There have also been reports of residual conditions, mainly chronic bronchitis, several years after exposure [756].

2.4 MEASUREMENT OF EXPOSURE DOSE

The severity of the damage experienced by an animal exposed to phosgene is dependent upon the concentration (in p.p.m.) of gas that contacts its respiratory surfaces and the exposure time (in minutes). A convenient measurement of dosage for toxic inhalatory irritants was devised by Fritz Haber [859] in the early 1920s. He proposed that a reliable estimate of dosage could be obtained by calculating the "action product" using the formula:

$$ct = \text{constant}$$

where c = concentration/p.p.m.
t = exposure time/min
ct = action product/p.p.m. min

The action product, now customarily referred to as CT, is regarded as an indication of an animal's probable biological response. Although the Haber formula is commonly used, it has been shown to be unreliable as a predictor of biological effect both at very high and very low

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¶ Shedding of surface epithelial cells.
§ Excessive fluid in the tissues and air spaces.
† Difficult or laboured.

concentrations of phosgene, and for exposure times of less than one minute [531,2171]. It must also be remembered that the CT product represents the dose offered to the organism: *it is not necessarily the same as that taken into the animal's body.* These criticisms have led to a recent proposal by Mautone *et al.* [1359] that phosgene dose, given to experimental animals, should be presented in terms of the "exposure index" (EI), *i.e.* the amount of gas, containing a known phosgene concentration, that was actually inhaled, standardized to body weight, and measured in units of p.p.m. V_I min kg^{-1} (where V_I is the volume of gas, in cm^3, to be inhaled per minute). The choice of units suggests that the proposers are medics and not physical scientists. This index may provide a method for standardizing toxicity experiments on phosgene and is discussed further in Section 2.5.6.

Nevertheless, despite the recognized drawbacks, CT appears to be a convenient way of expressing the magnitude of the phosgene dose in many instances [1009a,1717]. Dose-response relationships are generally presented as the percentage mortality of animals in relation to the magnitude of the dose. This is measured by LCT_x (LCT represents the lethal concentration time product; $x \in [0,100]$) values, and the most frequently used indicator is the lethal concentration time product responsible for 50% mortality (LCT_{50}) in test animals.

TABLE 2.1

PHOSGENE DOSE-RESPONSE RELATIONSHIPS IN ANIMALS [243,531,1078aa,1297a]

Species	LCT_{50}/p.p.m. min
Cat	200
Monkey	300
Rat	400
Guinea pig	500
Mouse	500
Man	**570**
Dog	1000
Rabbit	1500
Goat	2000
Sheep	3000

The dose-response relationships which are known for the range of animals studied are summarized in Table 2.1 [243,531]. As can be seen, man has an intermediate sensitivity to phosgene, with cats the most sensitive, and goats and sheep the least sensitive of the animals tested. This difference in sensitivity according to species may be related to the efficiency of the animals' respiratory ventilating mechanism (cats being very efficient), and is one reason for caution when attempting to extrapolate results from animal experiments to man.

2.5 ANIMAL EXPERIMENTS

Quantitative information on the effects of phosgene on human subjects are understandably difficult to obtain. Most of the data on phosgene's action have been obtained from war gas victims and later animal experiments (much of the earlier work is reviewed in [2095]). However, there is at least one recorded case [492] of a researcher deliberately exposing himself to phosgene in order to document the results. Unfortunately, he was subsequently too ill to record his observations for most of the critical time. This experimental technique is therefore not recommended!

2.5.1 Mechanism of action

Phosgene's toxic effects have, since the early 1900s, frequently been attributed to the reactions of phosgene-liberated hydrogen chloride with body tissues [145,605,608,609,756,862, 993,994,1234,2146]. As recently as 1982 [655], this was described as being the major cause of its toxicity, the hydrogen chloride being formed from phosgene as described in equation (2.1):

$$COCl_2 + H_2O \longrightarrow CO_2 + 2HCl \qquad (2.1)$$

However, this proposal may be refuted by the following observations:

(a) A lethal dose of phosgene liberates relatively little hydrogen chloride (a concentration of *ca*. 2.5×10^{-11} *M* at the air-barrier interface), a quantity easily dealt with by the lung tissue, and far below that considered lethal for hydrogen chloride [584,1483].

(b) The biological action of ketene (CH_2=C=O) is similar to that of phosgene; it is twenty times more toxic than phosgene, yet it is less acidic and contains no chlorine atoms [1651].

(c) Hexamethylenetetramine (see Section 10.2.1.5) administered before exposure to phosgene gives some protection against lung damage, but it does not protect from hydrogen chloride [523].

It is much more probable that phosgene owes most of its toxic action to its behaviour as an acylating agent (see Chapter 10). An early study established that phosgene alters lung protein [853,854], and this mechanism was investigated by the American Medical Research Committee; the results of this work were summarised in a secret Technical Report of the National Defence Research Committee (NDRC) in 1946 [1432a]. In 1949, Potts *et al.* [1651] were the first to publish that the acylating action of phosgene explained much of its toxicity, and this has been confirmed more recently [523]. Upon entering a mammal's respiratory tract, phosgene will undergo some hydrolysis in the moisture present. However, it is unlikely (owing to its low solubility) to penetrate more than a few microns (μm) below the mucous layer and therefore produces little effect in the upper respiratory regions. Much of the gas will thus be carried deep into the alveolar regions of the lungs (see Fig. 2.2), where the protective surfactant layer (comprised of a mixture of lipoproteins, chiefly lecithin and sphingomyelin) is very thin, and it is here that the gas (shown to be capable of penetrating all three layers of the blood–air barrier [1483]) will react with cell constituents. The biologically important functionalities that are capable of reacting rapidly with phosgene are the amino group ($-NH_2$), the hydroxo group (–OH), and the thiol group (–SH).

$$-NH_2 \xrightarrow[-HCl]{COCl_2} -NHC(O)Cl \xrightarrow{-HCl} -N{=}C{=}O$$

$$-OH \xrightarrow[-HCl]{COCl_2} -OC(O)Cl$$

$$-SH \xrightarrow[-HCl]{COCl_2} -SC(O)Cl$$

2.5.2 *Pathophysiology of phosgene poisoning*

Numerous experiments have been performed on a wide variety of vertebrate animals (see Table 2.2). A review of the literature enables identification of certain characteristic pathological changes associated with phosgene poisoning, which appear to show a generally similar sequence in all mammalian species. It should be noted that animal experiments on mammals have not identified a phosgene concentration that does not show some pathological effects [439], and there appears to be slight changes in lung tissue even at very low (0.2 p.p.m. for 5 h for each of 5 d) levels [422,439]. A summary of typical responses is given in Table 2.3.

Experimental evidence is inconclusive as to the first site of phosgene attack: some suggest that the initial histological changes are vesiculation of epithelial cells in the terminal bronchioles [1597] whilst others [527,678] saw the first changes occurring at the blood–air barrier. This difference in the site of action was investigated by Gross *et al.* [837], who suggested that the discrepancy arises from variations of the dose of phosgene received. Thus, with small CT values, changes are primarily at the transition from terminal bronchioles to alveolar ducts; the alveolar surface epithelium is attacked, leaving the subjacent capillary largely unaffected (resulting in chronic pneumonitis). With high CT values, most of the

TABLE 2.2

EXPERIMENTAL STUDIES UPON VERTEBRATE ANIMALS

Vertebrate	References
Cat	111,405,417,531,753,932,1211,2176,2202
Chinchilla	2124
Dog	4,111,194,249,288,352,353,405,419,474,492,527,531,574,1373, 1593,1659,2088,2173,2201
Frog	246
Goat	1068,2008
Guinea pig	249,405,418,531,852,1314,1433,1563c,1566,1774
Horse	1899
Man	190a,531
Monkey	531,2172
Mouse	243,244,248,249,531,824,852,1077,1566,1651
Rabbit	4,111,245,405,690,767,768,849aa,932,1138,1141,1211,1564,1565, 2124,2173
Rat	244,249,405,527a,531,583b,692,693,749aa,749ab,837,944,945, 1271,1459,1595,1597,1651,1659,1717,1745,1746,1837,1879

surface epithelium is destroyed, thus resulting in severe injury to the capillary, which in turn gives rise to severe pulmonary œdema (and/or acute chemical pneumonia): this work was later confirmed by Diller *et al.* [527a]. The initial changes are followed by a series of dose related responses. Fluid derived from blood plasma progressively enters the interstices and alveoli, the capillaries having lost their semi-permeability [245,531,932,1597,1740]. A proposal that œdema caused by phosgene poisoning was of purely hydrostatic origin was refuted by Gibbon *et al.* [753]. The severity of the resulting œdema is dependent upon the level of phosgene intoxication; experiments have shown an increase in respiratory tract fluid of up to sixty times normal level in some instances [245].

The œdema fluid causes some mechanical blockage of gas exchange and the blood supply of the lungs is reduced, with accompanying hæmoconcentration [245]. Cordier and Cordier [419] investigated the effect of washing the erythrocytes of phosgene poisoned dogs with artificial serum, to remove any accumulated acids. They found that washing the poisoned erythrocytes did not restore normal dioxygen affinity and that the dioxygen dissociation curve, after poisoning, was shifted to the right in comparison with normal hæmoglobin (*i.e.* the hæmoglobin had reduced affinity for dioxygen) [419]. The importance of the hæmoglobin's

TABLE 2.3

SUMMARY OF THE PATHOLOGICAL CHANGES IN MAMMALS INDUCED BY PHOSGENE

Species	CT/p.p.m. min	Response	Ref.
Cat	250	Interstitial œdema in 50% of animals	2202
Chinchilla	220	Toxic pulmonary œdema	2124
Dog	950-1080	Œdematous alveolar wall; cell-free exudate	194
	2190-5850	Bronchiole constriction; emphysema;[a] alveolar œdema proportional to dose	405
Guinea pig	747	Swelling of bronchiole mucosa; emphysema; alveolar œdema	405
Rabbit	1980	Hæmatocrit[b] and blood hæmoglobin raised	245
	5285	Emphysema; lung congestion and alveolar œdema	245
Rat	15	Typical pulmonary lesions; incipient pneumonitis	837
	50	Alveolar œdema	527a
	876-2920	Bronchiolar constriction; sloughing of bronchiolar mucosa; peribronchial then alveolar œdema approximately proportional to dose	405

[a] A pathological accumulation of air caused by destruction of the alveolar walls. [b] Volume % of erythrocytes in whole blood.

reduced dioxygen affinity in contributing to the developing anoxia is not yet known.

The collecting œdema fluid becomes frothy as the animal's breathing becomes increasingly laboured, and fluid may be seen in the upper respiratory tract. Signs of anoxia may become evident. However, at sub-lethal phosgene doses, provided dioxygen uptake is not too restricted, recovery occurs with reabsorption of œdema fluid and normal lung function is eventually restored [405,526]. Otherwise, death occurs primarily because of interference with dioxygen uptake through œdematous lungs [932,1210].

There have been some reports [756,1210,1488a,1774] of non-pulmonary damage after phosgene poisoning (*e.g.* heart and brain), but it is not likely that these result from phosgene acting directly on these organs. It is more probable that any changes seen are due to anoxia resulting from pulmonary œdema [523]. There is, however, an increase in influenza viral infectivity in rats exposed to sub-lethal concentrations of phosgene [583b]: no evidence exists for similar immunotoxicological effects in man.

TABLE 2.4

EFFECTS OF PHOSGENE ON ENZYMES

Species	CT/p.p.m. min	Enzyme Affected	Result	Ref.
Rat	240	Na-K-ATPase	Activity significantly reduced (after notable fall in [ATP])	443
	500-4300	4-nitrophenyl phosphatase; cytochrome *c* oxidase; ATPase; lactic dehydrogenase	Significant decrease in activity due to direct inhibition on enzyme and/or loss of enzymes from damaged cells	693, 1597
Mouse	2100-5300	Glycolytic and respiratory enzymes	No great changes in activity; unlikely that œdema is due to poisoning of enzymes	248

2.5.3 Experiments on metabolic activity of phosgene

Several groups have investigated the metabolic activity of phosgene [248,442,443,693, 849aa,1597,1882], particularly in relation to enzyme-controlled energy metabolism and the relationship between these metabolic pathways and the development of observable pulmonary œdema [442]. The results of some of these investigations are summarized in Table 2.4.

All workers, with one exception [248], found that enzymes and related substances were affected by phosgene, and *in vitro* studies have shown it to react with a number of tissue-specific amino acids and with some hormones (*e.g.* insulin), as well as with enzymes [731]. It has been speculated [443] that it is the decrease in available energy (*via* ATP) for maintaining pulmonary ionic and fluid homeostasis which contributes to the formation of œdema fluid [731]. Further work on this topic is needed for clarification.

Work relating to immune suppression in rats exposed to phosgene has been reviewed [1348a]: suppression of natural killer cells by phosgene may compromise the body's ability to protect itself from subsequent disease. The significance of this type of immune damage to the health of an individual has yet to be determined.

2.5.4 Rôle of phosgene in the toxicity of $CHCl_3$ and CCl_4

It has long been speculated, since the pioneering work of Müller in 1911 [1459], that phosgene may be an important intermediate in the toxicity of trichloromethane and tetrachloromethane. Experiments on rat liver microsomes have demonstrated that phosgene is generated when $CHCl_3$ is metabolized both *in vitro* [1316,1631,1635,1636,1846] and *in vivo*

[1633]. It has also been shown that phosgene is produced by the metabolism of CCl_4 *in vitro* [1177,1632,1637,1846].

The proposed mechanism for phosgene formation from $CHCl_3$ is illustrated in Fig. 2.3 [1316,1631,1635] and this has been confirmed by isotope labelling techniques [1631]. Similarly, mechanisms for the formation of phosgene from CCl_4 have also been described [1317,1637,1846], and these are summarized in Fig. 2.4.

There is some support for the mechanisms illustrated in Fig. 2.4 to be found in the established chemistry of the iron(II) porphyrins. Thus, $[Fe^{II}(TPP)]$ ($TPPH_2$ = 5,10,15,20-tetraphenylporphyrin) reacts with CCl_4 in the presence of a reducing agent (*e.g.* $[S_2O_4]^{2-}$, H_2/Pd, or Fe) to generate a dichlorocarbene complex, $[Fe^{II}(TPP)(CCl_2)(OH_2)]$ [1317b], which has subsequently been crystallographically characterized (as $[Fe^{II}(TPP)(CCl_2)(OH_2)].2dmf$) [1317a]. The complex has the expected *trans* configuration, revealing a short iron–carbon bond at 0.183 nm [1317a], and is very reactive [913a]. However, although chlorocarbene complexes are now widely accepted as being involved in the toxicity of chloroalkanes, not all sources [*e.g.* 264a,264b] recognize the importance of the intermediacy of phosgene.

Later work by Waller and Recknagel [2143] supports the view that phosgene may be important in the hepatotoxicity of trichloromethane, but does not support the idea that phosgene is important in the hepatotoxicity of tetrachloromethane. They found that only 1.5% of the original CCl_4 added could be isolated as the 2-oxothiazolidene-4-carboxylic acid derivative of phosgene. Based on these data, they proposed that toxic action from phosgene formed in this way was very unlikely, unless the phosgene was in a hydrophobic environment (because they claimed that the phosgene would be rapidly hydrolysed to carbon dioxide and hydrogen chloride). Unfortunately, this assumption is based upon the frequently quoted but fallacious idea that phosgene undergoes rapid hydrolysis in water. In reality, phosgene hydrolyses very slowly (see Section 9.10.3.1) and therefore would still be available for toxicological action, even in an aqueous environment. Thus, despite their careful experimental work, their conclusions have been invalidated by a poor knowledge of the basic chemistry of phosgene.

Clearly, further work is required to clarify these inconsistencies in the literature; there is still no consensus as to how important the *rôle* of phosgene is in the hepatotoxicity of chloroalkanes.

Phosgene formation in the kidney has also been suggested as being responsible for the nephrotoxicity of trichloromethane [257,1634], the severity of the toxicity varying according to species, variety and sex. Pohl *et al.* [1634] found that sensitivity to trichloromethane correlated with the capacity of the kidney to metabolize $CHCl_3$ to phosgene. This metabolic reaction was catalysed by cytochrome P-450, found in the microsomal and mitochondrial fraction of the kidney, probably by mechanisms similar to those already described for the liver. However, there is still no clear indication as to how phosgene formation contributes to the nephrotoxicity of $CHCl_3$.

Recent studies [258,892,893] have suggested that propan-2-ol [892,893] potentiates the

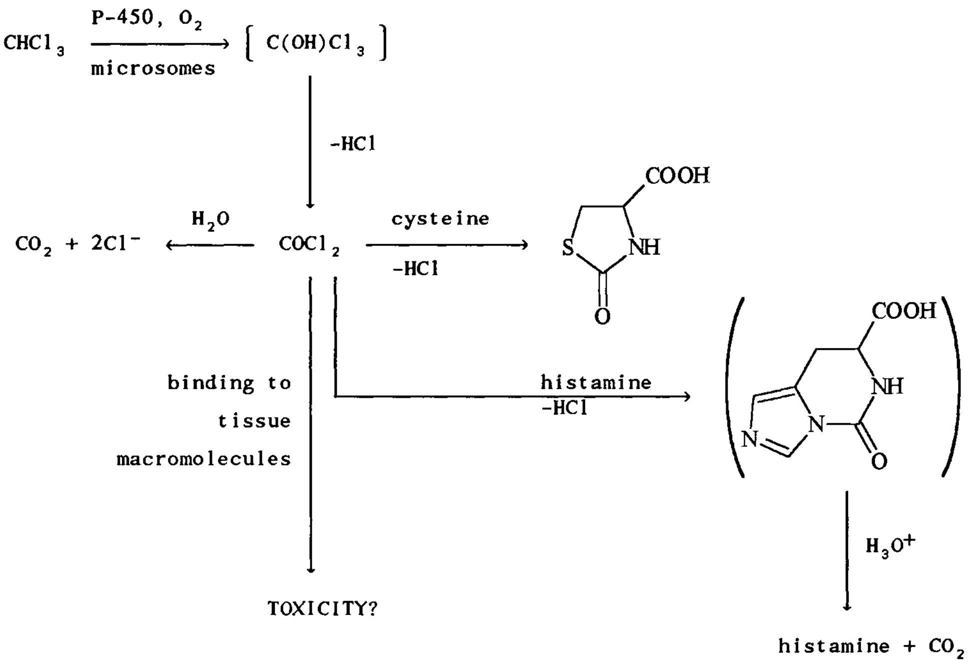


Fig. 2.3 The proposed mechanism for phosgene formation from trichloromethane in the liver [425b,1316,1631,1635].

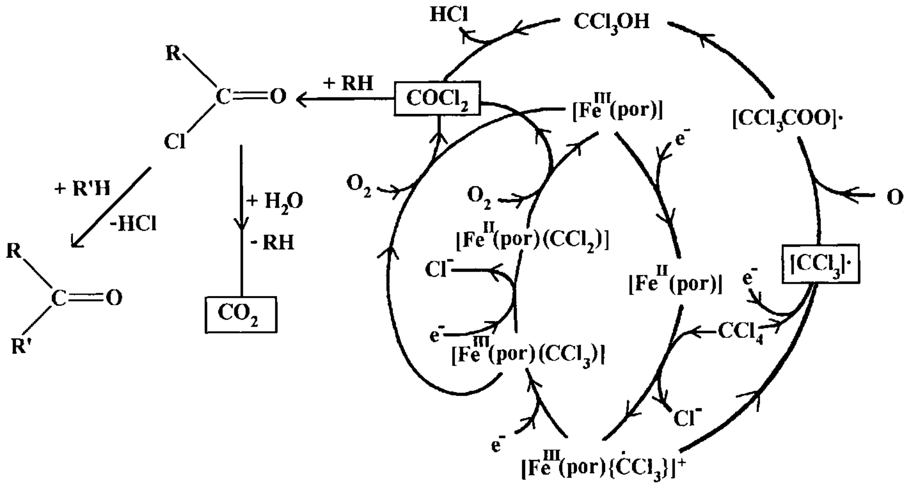


Fig. 2.4 The proposed mechanism [1317,1637,1846] for CCl_4 biotransformation by the hæm system and cytochrome P-450 ($porH_2$ = $TPPH_2$ or cytochrome P-450; RH, R'H = 1,2-dihydroxybenzene or nucleophilic groups of microsomal proteins.

hepatotoxicity of CCl_4. This is thought to occur because of either increased production of a cytochrome P–450 species that is specific to the CCl_4 to $COCl_2$ conversion or, alternatively, propan–2–ol may alter the catalytic activity of extant cytochrome P–450.

A similar mechanism is proposed [258] for the potentiation of $CHCl_3$ toxicity by hexan–2–one [258] or phenobarbital [1631]. Pretreatment with these compounds is claimed to induce formation of a specific cytochrome P–450 responsible for catalysing the metabolism of $CHCl_3$ to $COCl_2$. However, the toxicological importance of these findings remains to be elucidated.

It has also been suggested [1777a,1846] that as phosgene has two highly reactive chlorine atoms which may act on nucleic acids (or other macromolecules), and as it is an intermediate in both $CHCl_3$ and CCl_4 metabolism, it may be involved in the suspected carcinogenicity of these materials. However, it must be stressed that there is no direct evidence to show that phosgene has any carcinogenic, mutagenic or teratogenic properties, in either humans or animals.

2.5.5 *Phosgene and uræmic coma*

Uræmic coma is a condition produced when excessive by–products of protein metabolism (*e.g.* urea) are accumulated in the blood. It occurs when the kidney nephron function is inadequate at coping with excretion of urea and related compounds. It has been proposed by Sen [1839–1841] that the underlying cause for uræmic coma is the generation of phosgene by the liver. He has suggested, in effect, the following mechanism for phosgene formation (which is, of course, chemical nonsense):

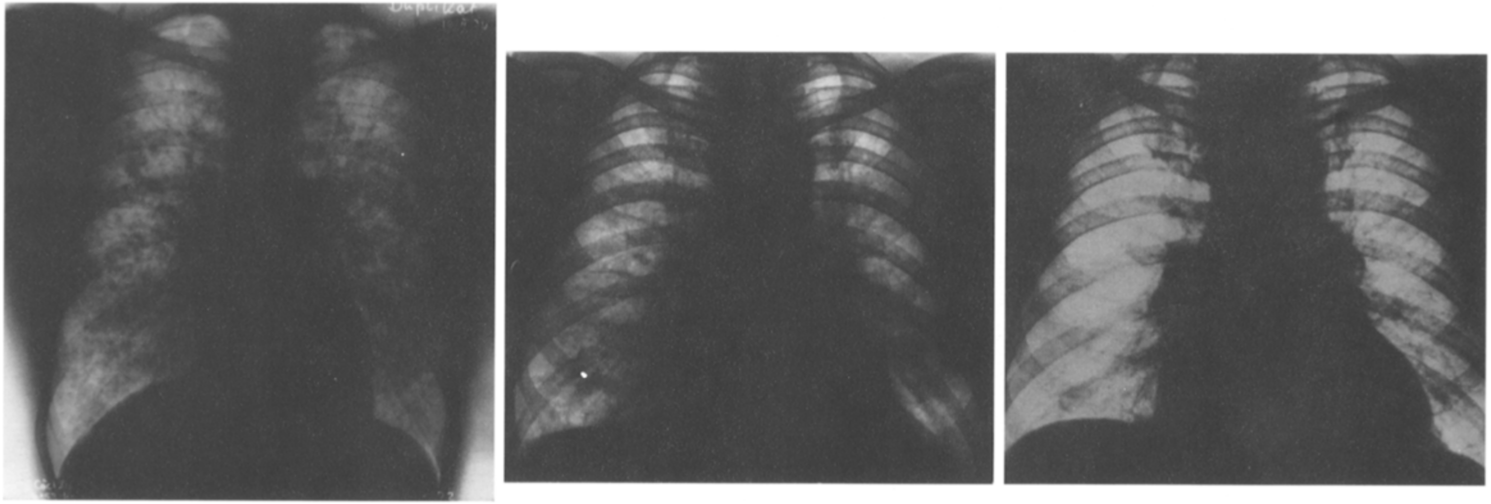
$$\underset{\text{(urea)}}{CO(NH_2)_2} + 2Cl^- \longrightarrow COCl_2 + 2[NH_2]^-$$

$$[NH_2]^- + H_2O \longrightarrow NH_3 + [OH]^-$$

Sen [1839–1841] further suggested that the ammonia formed enters the ornithine cycle and that the phosgene creates uræmic coma (although he offers no rationalization for this suggestion). On both chemical and medical grounds, these papers merit no serious consideration.

2.5.6 *Early assessment of damage due to phosgene exposure*

Assessing the extent of damage likely to occur after exposure to phosgene is often exacerbated owing to the lack of reliable information on the seriousness of exposure. Ideally, the use of phosgene indicator badges (Section 3.2.3.2.2) would permit a reliable and immediate estimation of exposure dose. Unfortunately, many individuals suffering accidental phosgene exposure do not wear such badges. The clinician is thus dependent upon recognising dose–related symptoms as the only means of assessing exposure dose and thereby instituting the required therapy. However, as demonstrated in Section 2.1.1, the severity of the initial symptoms is not a reliable indicator of the seriousness of the exposure.



(A) (B) (C)

Fig. 2.5 X-rays recorded for (A) a toxic lung œdema 15 h after exposure to phosgene (31 yr old male), (B) a heavily toxic lung œdema 8 h after exposure to phosgene (58 yr old male), and (C) the lung shown in (B), two days after intensive therapy, showing complete normalization [520a].

At present, apart from initial irritative symptoms, the most reliable early indicator of phosgene intoxication can be obtained by using soft X-ray (50-80 kV) techniques [520,521], which allow detection of developing toxic pulmonary œdema early in the poisoned condition. X-ray photographs taken at the start of the observation period may then be used for comparison with those taken during the clinical latent phase. Fig. 2.5 illustrates the changes in lung X-ray photographs recorded after exposure. Differences in the extent-of-change density and the distribution of the changes will indicate the severity of œdema, which is itself dose-related. Thus, X-ray monitoring will provide evidence for the extent of the exposure, enabling the clinician to select the appropriate treatment (see Section 2.6.2).

Other techniques which appear to be useful, but at present only in experimental situations, are (a) monitoring the subject's carbon monoxide uptake [1271,1717], (b) monitoring the change in the rate of ventilation (standardized to the subject's body weight) [1359], (c) monitoring the pH of the blood to give a measure of the change in base deficit (ΔBD) [1359], (d) measuring the change in serum lactic dehydrogenase (LDH) [690,837], and (e) measuring the changes in lavage fluid protein (LFP) concentrations and cellular differentials [442a]. Further methods that are potentially useful are described elsewhere [524,919], one of which states that hæmoconcentration rates above 2% h^{-1} give a poor prognosis [1629].

Batigelli *et al.* [139] explored the possibility of using the synthesis rate of tritiated thymidine-labelled DNA as a measure of cellular reaction to injury. However, the technique would appear to offer little advantage over other methods as results indicate that the response is coincident with histological abnormalities.

2.6 TREATMENT OF PHOSGENE POISONING

2.6.1 Animal experiments

There has been much research concerned with developing a therapy for phosgene poisoning. In addition to the trials summarized in Table 2.5, other factors have been investigated. Effects of external temperature on phosgene's toxicity were tested by Cucinell [439], on the mouse and the dog. In the mouse he found that at high dose levels toxicity increased with temperatures above or below ambient (*e.g.* ten times more toxic at 8 °C than at 27 °C). However, no such effect was seen in the dog. Venesection was recommended by early clinicians [426,2147] but more recent work does not support its use in the treatment of phosgene poisoning [532].

Administration of oxygen has long been recognized as beneficial in cases of phosgene poisoning [247,426,953,1404,2147], although animal experiments have given ambiguous results (see Table 2.6). However, the increased mortality seen in some of these experiments appears to be due to oxygen poisoning rather than, or in addition to, phosgene poisoning [287]. There have been encouraging clinical reports on the use of "positive end expiratory pressure" (PEEP) oxygen ventilation, and animal studies have also shown favourable results [532].

The use of hexamethylenetetramine (hmt; see Section 10.2.1.5) after phosgene exposure

TABLE 2.5

EFFECTS OF VARIOUS TREATMENTS UPON THE COURSE OF PHOSGENE POISONING

Substance administered[a]	Species	Effects on toxicity	Ref.
Adrenergic substances			
Adrenaline, amphetamine and ephedrine	-[b]	Inconclusive	731,1488a
Vasopressin	Mouse	Inconclusive	1745
Adrenolytic substances			
Ergotamine	Rat	Pre-exposure: reduced mortality Post-exposure: no effect	1744-1746
Aescinate	-[b]	Increased mortality	532
Amines			
Hexamethylenetetramine[c]	Dog	Pre-exposure: prevented mortality Post-exposure: largely ineffective	522,1067
	Rabbit	Pre-exposure: prevented mortality Post-exposure: ineffective	690
Ammonia inhalation	-[b]	Useless	1210
Anticoagulant	-[b]	No effect on mortality	532,1488a
Antihistaminics			
Thymoxyethyldiethylamine	Guinea pig	Reduced mortality	2051,2052
	Dog	Increased mortality	2051
	Mouse	No reduction in mortality	2051
	-[b]	Mostly beneficial	532,1488a
Phenergan	Rabbit	Prevents acute œdema	872
	Rabbit	Limited protective action	871
Antiphlogistics	-[b]	Ineffective	945aa
Antiserum	Cuinea pig	Pre-exposure: gave immunity Post-exposure: reduced mortality. Anaphylactic shock produced.	1567
	Guinea pig and mouse	Gave immunity	1563,1566
Aprotinin	-[b]	Useless	532
Asparaginate	-[b]	Suppressed œdema	532
Buffer solutions	Dog	May be beneficial in helping to control blood pH	532,1488a 1359,2088
Calcium	Rat	Protects against œdema and later effects	1743,1744
		Recent reports do not agree on beneficial effects	532,1488a
Cholinergic substances	-[b]	No effect on mortality	532,1488a

TABLE 2.5 (cont.)

Substance administered[a]	Species	Effects on toxicity	Ref.
Colchicine	Rat	Reduced lung injury and mortality	749aa, 749ab
Diuretics	-[b]	No effect on mortality	532,1488a
Glucocorticoids[d]	-[b]	Generally favourable results	509,605, 2129a
Histaminase	Guinea pig	No effect	416
Histamine	Guinea pig	No effect	415
Hypertonic solutions			
Glucose or plasma	-[b]	Mostly ineffective	532,1488a
Sodium chloride	Frog	Reduced mortality 100% by replacing Cl^- lost by higher permeability of the skin	246
	Cat	Very harmful	1211
Narcotics and sedatives	-[b]	Inconclusive	943b, 1488a, 1743
Oxygen[e]	Man	Mainly beneficial	247
	Rat	Increased mortality at high concentrations	566
	Cat and mouse	No effect on mortality	1443
	Dog and rat	No reduction in mortality	287
Phosgene inhalation (low dose)	Cat	No additive toxicity effects	417
	Guinea pig	Negative results	418
	Rat	Some protection against higher doses	944,945
Procoagulants	-[b]	Reduced œdema, no effect on mortality	1488a
Prostoglandin El	Rabbit	Reduced œdema	693a
Silicone inhalation	-[b]	Useless	943b
Spasmolytics	Dog	Increased survival time	693a
	Rabbit	Reduced mortality	1488a
	Rat	Increased mortality	532
Surfactant			
Dipalmitoyl phosphatidylcholine	Dog	Beneficial	1359
	Dog	Reduces œdema and increases lung compliance	532
Urease	-[b]	Beneficial results	1981-1983
Vitamins A,C,D,E,K	-[b]	Ineffective	532,1488a

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[a] All administered post-exposure unless otherwise stated. [b] Species stated where given, otherwise not known. [c] See Table 2.7. [d] See Table 2.8. [e] See Table 2.6.

TABLE 2.6

EFFECT OF OXYGEN ADMINISTRATION ON PHOSGENE POISONING[a]

Species	% O_2 dose[b]	Effects	Ref.
Rat	10-18	No change in course of poisoning	287
	60-80	No effect	532,1488a
	50-90	Mortality reduced 25% after forty eight hours. Mortality increased 25% in ten days	566
	90	Increased mortality	566
Dog	40	No improvement in ultimate survival	287
	40	Increased mortality	532,1488a
	50	Mortality reduced by 20%	2088
	60	Mortality reduced	532,1488a
	50-70	Mortality unchanged after forty eight hours	532,1488a
	70-80	Mortality reduced 12% after four days	532,1488a
	80	Mortality reduced 15%	532,1488a
	80-95	Survival time increased, ultimate mortality unaffected. Signs of oxygen poisoning on death	287
	95	Increased mortality	532,1488a
	40-95	No effect on mortality	532,1488a
	100	Mortality increased 35%	532,1488a
Man	40	Reduced cyanosis	532
	60-100	Relief of dyspnœa. Improved Pa O_2	412a,532, 1488a
Goat	sc.,[c] i.v.[d]	No effect on mortality	532,1488a
Dog	sc.,[c] i.v.[d]	No effect on mortality	532,1488a
Rabbit	sc.,[c] i.v.[d]	No effect on mortality	532,1488a
Goat	Intrathoracically	No effect on mortality	532,1488a
Dog	Intrathoracically	No effect on mortality	532,1488a
Rabbit	Intrathoracically	No effect on mortality	532,1488a
Dog	O_2/He (70:30)	Mortality reduced 20%	532,1488a
Goat	H_2O_2 i.v.[d]	Pulmonary embolism	532,1488a
Dog		Pulmonary embolism	532,1488a
Rabbit		Pulmonary embolism	532,1488a

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[a] Phosgene dose varies. [b] Dose of oxygen administered after exposure to phosgene. Oxygen administered pernasally unless otherwise stated. [c] Subcutaneously. [d] Intravenously.

has been recommended as a suitable treatment [1629], but there is very little convincing evidence to indicate its usefulness as a therapeutic agent. There is a report from Stavrakis [1938a] that sixty patients who were treated with hmt after phosgene exposure did not develop symptoms. However, Diller [532] quite correctly casts doubt on these results. Relevant animal studies are summarized in Table 2.7 [1067]. Again, no evidence is found to support the use of hmt after exposure to phosgene. However, when administered before phosgene exposure, results from animal experiments have shown some beneficial effects [522,532,1067].

The prophylactic use of hmt (also known as utroprine or metheneimine) is unlikely to be commonly applied in an industrial situation, even where phosgene exposure might be anticipated, as modern gas masks, *etc.*, afford good protection. The use of hmt may be considered where large numbers of people may be affected by a major gas leak, or in a war situation where gas bombardment is a real possibility [1432a].

Experiments with glucocorticoids have given variable results (Table 2.8), but clinical application has had some success [532].

Recent studies on rats have shown some therapeutic potential of the alkaloid colchicine [749aa,749ab]. Administration by injection both before or after exposure to phosgene (0.5 p.p.m. for 1 h) significantly reduced both lung injury and mortality. It is believed that colchicine inhibits the influx of neutrophils, and the associated increase in permeability of the alveolar–capillary membrane. By reducing permeability of the membranes, the life–threatening œdema which normally ensues from phosgene exposure does not develop to the same extent as in the unprotected lung. If further work confirms these results, then colchicine administration might offer a strategy for the treatment of phosgene poisoning in humans.

There have been several animal experiments suggesting that a protective effect against lethal doses of phosgene can be obtained by pre–treatment with sub–lethal levels of the gas [417,944,945,1563c]. Various reasons have been suggested to explain these observations, including selection (*i.e.* animals surviving first gassing may be better able to withstand phosgene poisoning) [244], or possible antigen/antibody reactions [1566], although the evidence is conflicting [945]. However, the "protective" reaction seen in some species is more probably due to the fact that pre–gassing damages the lungs to such an extent that the available surface area for gas exchange is much reduced [38]. Moreover, slight interstitial œdema extends the distance between the alveolar lumen and the capillaries, thus lengthening the time for hydrolysis to occur [584]. In addition, breathing tends to become more rapid and shallow after the first gassing, so that the subsequent gassings are in fact more superficial than they might appear [244].

Although many authors do not give reliable information concerning experimental method (*e.g.* exposure dose, type of experimental animal used, appropriate controls, *etc.*), thereby making interpretation of reported results difficult, a review of the extensive literature on animal experiments and clinical observations allows a recommended course for treatment of phosgene poisoning to be proposed.

TABLE 2.7

EFFECT OF ADMINISTERING HEXAMETHYLENETETRAMINE ON PHOSGENE POISONING

Species	hmt dose /g kg^{-1}	Time /min	$COCl_2$ dose /p.p.m. min	% Red^{n} in mortality	Other effects	Ref.
Before Exposure to Phosgene						
Mouse	0.125[a]	30	(LCT_{100})	30		532
	2.0	30	(LCT_{75})	70		532
Rat	0.06	30	1000	30		532,1488a
	0.5	30	1000	100		532,1488a
	0.125[b]	50	350	25		532,1488a
	0.125	50	1100	50		532,1488a
	0.2[c]	2	1200	0		532,1488a
	0.125	30	1750	50		532
	1.0	60	1600	90		532
Rabbit	0.15[d]	3-17	3000	90		532
	0.3	5-10	1040		No visible lung damage	690
	0.3	5-10	2760		Increased survival time. Reduced œdema	690
	0.3	5-10	3120		Increased survival time. Reduced œdema	690
Cat	10%[e]	120-148	750	100		532
Dog	2.0[d]	60	12000	90		1067
Man	0.06	180	1400	100		190a
	0.06[c]	3600	1400	0		190a
After Exposure to Phosgene						
Rat	4.0[d]	5-10	600	0		532
Rabbit	0.3	15	125		Increase in pulmonary œdema	532
	0.3	15	3000	0		532
	1.0	2-6	3600	30		532
	1.6-2.0	30	960	0		532
	0.3	15	125		Increased œdema after 24 hours	690
	0.3	10	460		None significant	690
	0.3	20	460		None significant	690
	0.3	30	1040		None significant	690
	0.3	60	1040		None significant	690
	0.3	10	1040		None significant	690
	0.3	15	1560		None significant	690
	0.3	60	1560		None significant	690
Dog	1.0	1-3	2400		No effect	532,1488a
	2.0	1-3	(LCT_{100})		No effect	532,1488a
Man	0.06[c]		560		No effect	532
	0.06		1400		No effect	532

[a] Subcutaneously. [b] Intraperitoneally. [c] Orally. [d] Intravenously. [e] Aerosol.

TABLE 2.8

EFFECT OF ADMINISTERING GLUCOCORTICOIDS ON PHOSGENE POISONING

Substance	Species	Dose	Time of application[a]	$COCl_2$ dose /p.p.m. min	Effect	Ref.
Dexamethasone-isonicotinate	Rat	15-30[b]	Immediately	240	Mortality down by 20%. Œdema down by 50%	532
	Mouse	6-10	Immediately	210	Œdema down by 57%	532
	Rabbit	6-10	Immediately	900	Œdema down by 57%	532
	Mouse	6-10	1-2 h	210	Œdema reduced	532
		6-10	Immediately, then periodic repeats for two hours	210	Œdema increased by up to 70%	532
	Rat			240	Œdema increased by up to 70%	532
	Rat	6.0	Immediately	360	Survival time increased 10%	532
		6.0	Immediately	240-290	Œdema down by 20%	532
		?	10 min	10000	No increase in survival time or reduction in mortality	509
		10-20[c]	10 min	1200	No effect	509
	Mouse	1.5	30 h pre-exposure	340	Mortality up by 20%	509
		10.0	30 h pre-exposure	340	Mortality down by 10%	509
		1.5	2 h	340	No effect	509
6-methyl-prednisolone	Mouse	5.0	23 h	250-340	Regression of œdema	532
		10.0	3 h	340	Mortality down 20%	532
		2x1.5	Immediately	340	Mortality down 20%	532
		2x10	Immediately	340	Mortality up 20%	532
	Rat	5.0[d]	15 min and 5 h	600	Increased mortality	532
	Mouse	20.0[c]	Immediately	1200	No effect	509
		10-20	10 min	1100	No increase in survival time. Mortality not reduced	509
Hydrocortisone	Rabbit	40[e]	30 min	1500	Increase in survival time	693a
		40	30 min	500	Œedema unchanged	693a

[a] Time, after exposure to phosgene, of glucocorticoid application. [b] Strokes of aerosol administered. [c] mg kg^{-1} administered intraperitoneally. [d] mg administered intravenously. [e] mg kg^{-1} administered intravenously.

2.6.2 Recommended treatment

2.6.2.1 First aid

The victim should be removed to an uncontaminated atmosphere (at ambient temperature) but must not be allowed to have unnecessary exertion (increased oxygen demand by the muscles can exaggerate the symptoms). Affected skin and eyes should be thoroughly washed with water and contaminated clothing must be removed [41,238,253,256,363,505,1318, 1404,1456,1893,ICI21-ICI24].

2.6.2.2 Treatment in the latent and chronic phase

Regrettably there is, as yet, no known antidote to phosgene poisoning. Consequently treatment is usually directed to the main symptom – toxic pulmonary œdema – the development of which is dose-related [1374].

Moderate doses (50–150 p.p.m. min) can produce sub-clinical pulmonary œdema, which may be prevented or alleviated by administering glucocorticoids (dexamethasone-nicotinate aerosol, 3 x 5 puffs, and prednisolone, 0.1 g intravenously) as soon as possible after exposure. If radiography reveals no sign of œdema after eight hours, the patient may be discharged. If radiography is not available, supervision should be continued for twenty-four hours.

With moderate-large doses (>150 p.p.m. min), toxic pulmonary œdema must be expected; doses of 300 p.p.m. min or greater are potentially lethal. X-ray photographs taken two hours after exposure are recommended for early diagnosis. In these cases, large amounts of glucocorticoids should be administered as soon as possible after exposure (dexamethasone-nicotinate 10.5 g as aerosol, prednisolone 0.25–1.0 g intravenously) [525].

Oxygen should be given in sufficient concentration to ensure adequate oxygenation of the blood, though care must be taken not to actuate alveolar damage or induce oxygen poisoning [525]. PEEP ventilation has proved useful, particularly in the early stages [525].

Sodium hydrogencarbonate given intravenously may be used to correct acidosis resulting from phosgene intoxication. However, this should be given with caution to avoid alkalosis and increase in œdema due to over-infusion [1359].

Sedatives may be used if the patient seems severely agitated, although the use of morphine has been discouraged because of its depressive effect on the respiratory centre.

Superinfection of damaged tissues is a recognized complication of phosgene poisoning and antibiotics (2 g ampicillin for three to four days) may be given to prevent this [505,525].

In addition to these measures, further standard treatments of pulmonary œdema may prove useful, *e.g.* aspiration.

2.7 PHOSGENE AS A PESTICIDE

Phosgene has been tested for its effectiveness as a general pesticide on several occasions [768,1493,1837] but, owing to its great toxicity to man, it is not generally used.

2.7.1 Effects of phosgene on invertebrates

The toxic action of phosgene on a variety of invertebrates is summarized in Table 2.9 [1493]. In every case tested, phosgene is less effective as a pesticide than hydrogen cyanide [1493]. Bactericidal action was noticed only when the concentration of phosgene was in excess of ten percent [1837].

TABLE 2.9

PESTICIDAL ACTION OF PHOSGENE ON INVERTEBRATES [1493]

INVERTEBRATE	CONDITIONS FOR 100% MORTALITY		
	% Conc	Time/min	Temp/°C
Ant	0.5	30	19
Aphid	1.0	30	31
Bedbug	2.0	120	26
Bedbug eggs	2.0	120	24
Body louse	3.0	120	23
Cockroach	1.5	120	27
Cockroach egg pods	3.0	120	30
Colorado potato beetle	4.0	120	30
Colorado potato beetle larvæ	4.0	120	30
Flat grain beetle	1.0	120	29
Flour weevil	4.0	120	23
Fly	0.5	7	26
Fly larvæ	3.0	120	26
Grain borers	2.0	60	29
Phyllostachys bamboo mite	1.5	30	25
Potato flea beetle	1.0	60	30
Red spiders	0.5	60	31
Rice weevils	4.0	120	26
Sawtooth grain beetle	1.0	120	28
White fly	1.0	30	22

2.7.2 Phosgene as a rabbit fumigant

Phosgene has been tested as a rabbit fumigant [768] and was found to be very toxic, not only because of its direct effects, but also because it induces secondary infection.

However, it is undesirable for field use because of its great toxicity to man and its lack of warning irritant effects.

2.7.3 Phosgene as an antifungal agent

Phosgene was found to be totally ineffective as a fungicide against *Fusarium, Penicillium, Colletotrichum* and *Ascochyta* [1493].

2.7.4 Phosgene as a water pollutant

Liquid phosgene sinks in water, and so may present a hazard if it enters water intakes. The effect of low concentrations on aquatic life is unknown [506].

2.8 THE EFFECTS OF PHOSGENE ON PLANTS, SOILS AND FOODSTUFFS

2.8.1 Effect of phosgene on seed germination and plants

The consequences of phosgene exposure for seed germination have been investigated by Neifert and Garrison (see Table 2.10). There was a deleterious effect on most seeds tested, in particular, muskmelon, wheat and millet. However, it did appear to have a slight

TABLE 2.10

EFFECT OF PHOSGENE ON SEED GERMINATION RATE [1493]

Seed type	% Change in germination rate[a] for 3% phosgene exposure	
	30 minute exposure	120 minute exposure
Alfalfa	-12	0
Carrot	-16	-9
Clover	-31	+6
Grass	- 9	+9
Lettuce	-23	-18
Millet	-24	-68
Muskmelon	-94	-100
Onion	-37	-1
Radish	- 5	-2
Wheat	-18	-59

[a] {(control rate - experimental rate)/control rate} x 100

stimulating effect, at higher doses, on clover and grass. It would seem from these results that pretreatment of seeds with phosgene as an antifungal measure would be inappropriate. This is further confirmed by phosgene's lack of toxic effects on fungi [1493].

Phosgene appears to have a generally damaging effect on plant life, the extent of the damage being mainly dependent on the temperature and levels of sunlight [831–833].

2.8.2 Effects of phosgene on soil and flour

Fuhr *et al.* [696] have investigated the absorption of phosgene by soil. The soil used had an average moisture content of 11% and the surface area exposed was approximately 1 m^2. It was found that soil absorbed more than 99%, of the phosgene introduced, within forty minutes. Similar work by Griffon du Bellay and Houdord [828] also found soil to be very absorptive and they associated this with the soil humus content. They described the reaction between soil and phosgene as being "chemical and exothermic"!

Contamination of foodstuffs by phosgene has been investigated [659,1812]. Fisher [659] found that grain or flour exposed to the vapour may be used after being thoroughly aerated. However, phosgene exposure does reduce the baking quality of flour, possibly because of hydrogen chloride formation. A U.S. Armed Forces Technical Manual [505] advises that "phosgene contamination offers little danger to food products", because it decomposes rapidly on contact with water. However, it also warns that phosgene may alter the flavour of the food!

3 INDUSTRIAL HYGIENE, ANALYTICAL METHODS AND ENVIRONMENTAL ISSUES

Preuention is so much better than healing, because it saues the labour of being sicke.
T. Adams (1618)

The preceding Chapters demonstrate that phosgene is, beyond all doubt, an insidious and highly poisonous material, albeit one against which adequate protection can be readily provided. This Chapter deals mainly with the systems necessary to prevent exposure to phosgene above the concentrations that could be envisaged as being injurious to human health. In order to achieve this, it is essential to be aware of the hygiene standards established over many years, the equipment and test methods required for its detection, personnel training, and the procedures and legislative matters that are associated with its handling, transportation, classification and labelling. In addition, this Chapter also describes the sources (and potential sources) from which phosgene can be derived, supported by real case histories, and concludes with methods for treating phosgene spillages and catastrophic emissions, followed by a discussion of the environmental problems (both local and global) raised by the presence of phosgene in the atmosphere.

3.1 INDUSTRIAL HYGIENE

Industrial hygiene is that branch of preventative medicine which deals with the safety and health preservation of industrial personnel. In order to apply the principles of this important area to the industrial usage of phosgene, it is necessary to have a detailed knowledge of its history, technology and toxicology. The toxicology of phosgene has been described in Chapter 2, and forms the basis of the industrial hygiene practice described here. Sources of phosgene emission are described in Section 3.3, and general reviews on phosgene industrial hygiene have been published [40,41,145,608,936,1484,1486,1487,1595a,1893,ICI24].

Estimates of the number of workers potentially exposed to phosgene have been given by NIOSH. In 1970, 5752 workers were potentially exposed to phosgene, as either the compound itself or its precursors [1483b]. In 1980, 2358 workers were estimated to have been potentially exposed to phosgene resulting from the manufacture or use of the compound itself [1483a]. The estimate of ten thousand potentially exposed workers in 1976 has been given by NIOSH without explanation [1484].

3.1.1 Explanations of common acronyms

The only areas more dominated by acronyms than industrial hygiene are the civil service and the international intelligence communities. However, a number of these acronyms have very specific meanings and implications, and it is worth defining these for the tyro [734a,1787]:

LC_x	When the toxicant is airborne, the term LD_x is usually replaced by LC_x.
LD_x	The Lethal Dose x (LD_x) of a substance (usually expressed as the LD_{50} or LD_{10}) indicates that quantity of a substance (usually expressed in mg per kg of body weight) required to kill x% of a specified animal population in 14 days by a specified route of entry.
LD_{LO}	LD_{LO} is the Lethal Dose Low, as defined by NIOSH. It is the lowest dose, other than the LD_{50}, of a substance introduced by any route, other than by inhalation, over any given period of time in one or more divided portions that is reported to cause death in humans or other animals.
MAC	See TLV–C
OEL	The Occupational Exposure Limit (OEL) is a general term referring to advisable exposure limits in the workplace.
PEL	NIOSH/OSHA have designated another set of terms – Permissible Exposure Limit (PEL) – to replace TLV. Most PELs have the same values as the TLV–TWA.
TLV	TLV (Threshold Limit Value) is a recommendation issued by the American Conference of Governmental Industrial Hygienists). The TLV of a compound is a term used to express tolerable concentrations. It is an estimate extrapolated from some defined damage to humans or (other) animals at higher concentrations, or by drawing analogies between similar compounds. It is based upon the assumption that some concentration does exist where no harmful effect will occur on exposure to the particular substance, no matter how often that exposure is repeated, even for every working day of a normal working lifetime. They are based on the best information available at the time and are subject to annual revision. They do not give a precise definition of a hazard/non–hazard situation, but only provide good practice guidelines.
TLV–C	TLV–C is the ceiling level concentration which must not be exceeded, even instantaneously. In some countries these are known as Maximum Allowable Concentration (MAC).

TLV-STEL	TLV-STEL is the maximum Short Term Exposure Limit to which the average (*i.e.* not hypersensitive) worker can be exposed without experiencing either irritation, irreversible tissue damage, or narcosis.
TLV-TWA	TLV-TWA is the Time Weighted Average of the Threshold Limit Value, usually expressed for an eight-hour period.

3.1.2 Potential hazards

Owing to the experience of the use of phosgene in World War I, and to the atrocities revealed from experiments on humans in World War II, more is known about the toxic effects of phosgene on man than is known for most chemicals. Nowadays, phosgene is used extensively in the chemicals industry, and exposure to the gas may result as a consequence of an industrial accident (but see Section 3.6). Hazards associated with phosgene are well documented [364,1297a,1318,1787,2198,ICI21,ICI23], and are summarized in the following paragraphs.

Phosgene is a poisonous, potentially lethal, gas, classified by the U.S. Department of Transportation as a Class A poison ("poisonous gases or liquids of such nature that a very small amount of the gas, or vapour of the liquid, mixed with air is dangerous to life") [1318,1893], and by the Environmental Protection Agency as both a hazardous substance and hazardous waste [1893]. Although other ratios have been recorded [1327a], phosgene is reported to be some five times more toxic than dichlorine [372], but often has a delayed effect before the onset of respiratory problems is apparent. It is highly volatile in the liquid state (boiling temperature ≈ 8 °C), and the vapour is heavier than air. The material is non-flammable, non-explosive, and does not deteriorate on regular storage in the absence of extraneous materials or unusual conditions. Of course, high temperatures may rupture containers as a result of increased internal pressure. Moreover, the closeness of the boiling temperature of phosgene to ambient temperatures may lead to particular hazards associated with the difficulty of purging out lines and equipment used in phosgene service [314] (as a result of the slow vaporization of the liquid). A comprehensive account of the physical properties of phosgene is given in Chapter 6.

Phosgene reacts, sometimes violently, with a large number of common inorganic (Chapter 9) and organic (Chapter 10) substances. Hazardous reactions with lithium, sodium, potassium, aluminium, lithium amide, hexa-2,4-diyn-1,6-diol, propan-2-ol, and hexafluoropropene have been mentioned specifically [1787]. Mixtures of potassium and phosgene are reported to explode when subjected to shock [1913a]. In addition, phosgene dissolves in many organic solvents. It dissociates into carbon monoxide and dichlorine both thermally (at temperatures above about 300 °C) and photolytically (Chapter 8). It is corrosive when moist, owing to the slow release of hydrochloric acid, but the relatively low solubility and slow reactivity in water enables the gas to penetrate the lungs deeply, making the material particularly insidious. Reaction with strongly alkaline solutions is exothermic and may result in the ejection of excessive amounts of the gas, particularly where the alkali is added to liquid phosgene.

Liquid phosgene attacks rubber [608], which retains the gas for a long time and eventually hardens and perishes [ICI21]. Some plastics and surface coatings may be attacked by liquid phosgene [1487]. Stopcock greases are reported to be strongly attacked by phosgene [770]. When dry, phosgene is compatible with steel, stainless steel or copper. When moist, however, the use of corrosion resistant materials such as ™Monel, tantalum, or glass-lined equipment is recommended [277].

Liquid phosgene may burn the eyes, and corneal ulceration could develop. Liquid splashes may cause a burning sensation on the skin. The gas will irritate the eyes, nose and lungs – high concentrations causing pulmonary œdema which may be delayed in onset and is occasionally fatal [1487] (see Chapter 2). Ingestion is highly unlikely during normal industrial use, and little information is available upon this mode of entry [ICI24]. However, the entry of liquid phosgene into the mouth is likely to cause burns of the mouth and throat, and will likely be accompanied by serious toxic effects owing to the inhalation of vapour.

The physiological response to various concentrations of phosgene are summarized in Table 3.1 (see Chapter 2 for more details) [40,936,1787].

TABLE 3.1

HUMAN PHYSIOLOGICAL RESPONSES TO INCREASING CONCENTRATIONS OF PHOSGENE [40,531,936,1787]

Response	Concentration/p.p.m.
Least detectable odour	0.5-1.0
Odour recognition	>1.5
Least amount required to cause immediate irritation of the throat	3
Least amount required to cause immediate irritation of the eyes	4
Least amount required to cause coughing	5
Incipient lung injury	>10
Dangerous for short exposure (30 min - 1 h)	25
Fatal for short exposure	50

3.1.3 Olfactory detection

Although pungent, stifling and unpleasant in high concentrations [2088b], at low concentrations (*ca.* 0.5 p.p.m.) the odour of phosgene in air is said to resemble that of freshly mown grass [678]. However, although the characteristic odour warns of its presence, the gas will condition the sense of smell so that it can be detected only for a brief period at the onset of exposure [1318]. This phenomenon may be a result of olfactory fatigue or adaptation, which may cause a gradually increasing concentration to go unnoticed [145].

It is well known from World War I that men suffering from phosgene poisoning quickly rejected a lighted cigarette owing to the unpleasant and persistent characteristic taste caused by the effect of phosgene on the mucous surfaces [678,1660]. It is therefore likely that a smoker would abandon their smoking material before any appreciable quantity of phosgene were inhaled. Smoking, indeed, offers one of the most sensitive early-warning tests for the presence of low concentrations of phosgene. Moreover, this effect is not confined to phosgene; it occurs also, for example, after inhaling a trace of ketene [ICI37].

The odour detection threshold has been established by NIOSH [1484]. Technically trained volunteers were exposed to increasing concentrations of phosgene until all could detect the gas by smell. The lowest detected concentration by any of the fifty-six subjects was 0.4 p.p.m.; half of the subjects reported the detection of the gas at 1.5 p.p.m. Other reports suggest 0.5 p.p.m. as the minimum concentration at which the gas can be detected by smell by people acquainted with its odour [40,145,678]. In a related study [1484], four volunteers, who were asked to identify the lowest concentration at which they could recognize the distinctive "hay-like" odour of phosgene, detected it at at 1.0 p.p.m. However, experienced, professional personnel, familiar with the odour of phosgene, have detected the gas in a concentration as low as 0.25 p.p.m. (measured by Dräger tube) [327a]. Nevertheless, the generally accepted air-dilution odour threshold for phosgene is 1.0 p.p.m. [1703], or, by taking an average of the available literature values (omitting extreme points), 0.9 p.p.m. [43]. An odour threshold for phosgene reported as 0.125 p.p.m. [1487] has failed, not surprisingly, to have met with general acceptance.

The odour index {vapour pressure (in p.p.m.)/odour threshold (in p.p.m.)} for phosgene at 20 °C is recorded as 1600000 [2112]. This dimensionless term is based on the expression of the vapour pressure in p.p.m. for which 1 atmosphere is taken as 1000000 p.p.m.

3.1.4 Occupational exposure limits

The occupational exposure limits assigned to phosgene may vary not only from country to country, but also from authority to authority. They are not only subject to change with the passage of time, but may also vary between different work environments. Some industrial companies follow their own standards, where these are more stringent than those set by the health and safety authorities [40]. Clearly, there are no sharp boundaries at which concentrations of phosgene are "safe" and at which some are "dangerous" to the human condition [917], although Cucinell [439] has suggested that the highest phosgene concentration in ambient air which is safe for all people (of all ages and states of health) to breathe for 24 hours per day is 0.0006 p.p.m. This concentration is ten times the maximum concentration recorded in a sample of ambient air [1889].

Because of its irritating effect on the respiratory tract at concentrations slightly above 0.1 p.p.m. (but from which tolerance develops), and by analogy with other œdemagenic agents of similar activity, the American Conference of Governmental Industrial Hygienists (ACGIH) have adopted a Time-Weighted Average Threshold Limit Value (TLV-TWA), since 1966, of 0.1 p.p.m. (≡ 0.4 mg m^{-3} of air) [38,40,40a,1484]. The Occupational Safety and Health Authority (OSHA) and the National Institute for Occupational Safety and Health (NIOSH) similarly recommend 0.1 p.p.m. as their respective TWA standards in air [1787,2012]. In some countries (*e.g.* Sweden, Italy and Romania), recent recommendations for the maximum allowable concentration have suggested the value 0.05 p.p.m., whilst most other countries (including France [59] and, until recently, the UK [917,917a]) have followed the American example to employ 0.1 p.p.m. as the occupational exposure limit [40,59]. The UK Occupational Exposure Limit for phosgene is now 0.08 mg m^{-3} (≡ 0.02 p.p.m. v/v) in the 1995 edition of EH40 [917b], meeting new criteria [917c]. Exposure limits for phosgene in occupational air are provided for various countries in Table 3.2.

The historical development of the recommended standard has been described [1484], but earlier values can be regarded as obsolete for all practical purposes [561,608,868,917a,1595a,2097].

"Occupational exposure to phosgene" has been defined by NIOSH [1484] as exposure above half of the recommended time-weighted average (TWA) environmental limit whilst "overexposure" is defined as known or suspected exposure above either the TWA or ceiling concentration, or any exposure which results in the development of pulmonary symptoms.

Exposure limits have been defined for land, sea and air: the National Academy of Sciences gives a 90-day atmospheric limit of 0.05 p.p.m. in submarines, and a Douglas aircraft continuous atmospheric limit of 0.04 p.p.m. [40]. These recommendations exist because of the possibility of producing phosgene as a result of the decomposition of chlorofluorocarbon refrigerants used in air-conditioning systems.

Phosgene cannot be detected by smell (see Section 3.1.3) at the generally accepted occupational exposure limit of 0.1 p.p.m. [43,1703]. Although the sense of smell undoubtedly acts as a natural safety detection warning system, the accepted odour threshold is approximately ten times the TLV-TWA. The odour safety factor (TLV/odour threshold) has been calculated as 0.11, and the material has been assigned an odour safety classification "E" to suggest that less than 10% of attentive persons can detect the gas at a concentration corresponding to its TLV [43].

To rely upon the detection of phosgene by its odour would, therefore, be hygienically undesirable. Fortunately, safe and reliable methods for its detection are available and, in particular, the extent of exposure is conveniently provided [145] by special detector badges

TABLE 3.2

COMPARATIVE NATIONAL EXPOSURE LIMITS FOR PHOSGENE IN OCCUPATIONAL AIR

Country	Exposure Limit/mg m^{-3}	Classification[a]	Year
Australia	0.4	TLV-TWA	1983
Belgium	0.4	TLV	1974
Bulgaria	0.5	MPC	1971
Czechoslovakia	0.5	MAC-TWA	1978
E. Germany	0.5	MAC-TWA	1983
	0.5	MAC-STEL	1983
W. Germany	0.4	MAC-TWA	1984
	0.8	MAC-STEL	1984
Finland	0.4	MPC-TWA	1982
Hungary	0.4	MAC-TWA	1978
	0.8	MAC-STEL	1978
Italy	0.2	TLV	
Japan	0.4	MAC	1981
Netherlands	0.4	MXL-CLV	1985
Poland	0.5	MPC-CLV	1982
Romania	0.2	MPC-TWA	1975
	0.5	MPC-CLV	1975
Russia	0.5	MAC-CLV	1977
Sweden	0.2	HLV-CLV	1985
Switzerland	0.4	MAC-CLV	1984
UK	0.08	OEL-TWA	1995
USA (OSHA)	0.4	PEL-TWA	1974
USA (ACGIH)	0.4	TLV-TWA	1995

[a] CLV = ceiling value, HLV = hygienic limit value, MAC = maximum allowable concentration, MPC = maximum permissible concentration, MXL = maximum exposure limit, PEL = permissible exposure limit, STEL = short-term exposure limit, TLV = threshold limit value, and TWA = time-weighted average.

(see Section 3.2.3.2.2). For short term laboratory work, the use of such badges may not be necessary, since other detection devices may be readily available in this environment. In addition, the gas can be simply and conveniently monitored using indicator papers, as described in Section 3.2.3.

A short-term exposure limit (ceiling value for any 15 min period) has been proposed by NIOSH as 0.2 p.p.m. [1484,1486,1893], and by HSE as 0.06 p.p.m. [917b,917c]. The long-term occupational exposure limits should not be extrapolated to their numerically equivalent concentration-time values [935]. For exposure to phosgene at the TLV of 0.1 p.p.m. for 8 h, the total exposure is 48 p.p.m. min. However, exposure to the equivalent concentration-time value of 48 p.p.m. for 1 min would be intolerable (see Section 2.4). The IDLH level (IDLH = Immediately Dangerous to Life or Health; the maximum level from which one could escape within 30 minutes without any escape-impairing symptoms or irreversible health effects) for phosgene has been set at 2 p.p.m. [1893].

Phosgene has been included in various hazard rating systems in which the actual hazard, rather than just toxicity, is evaluated [1206,1623,1957]. A vapour hazard index (a measure of the amount by which a saturated atmosphere of a material exceeds the TLV) for phosgene is estimated to be 10000. The index takes account of the volatility of the material, in addition to its toxicity; for comparison the value for dichlorine is 1000 [1623].

3.1.5 Personnel protection and safe handling of phosgene

3.1.5.1 Safety procedures for chemical processing plants

Comprehensive safety precautions are essential in facilities in which phosgene is manufactured, stored, or processed in any way. Techniques to control occupational exposure to phosgene must be assessed, and major accidents should be prevented, literally, at all costs. These requirements are enforced by legislation in most industrial nations.

Recommended standards for occupational exposure to phosgene have been published by NIOSH [1484,1486,1487]. Compliance with these standards should prevent detrimental effects of phosgene on the health and safety of workers, and they should be compulsory reading. Guidance notes for the safe handling and use of phosgene [1318] have been published by the Manufacturing Chemists Association (now the Chemical Manufacturers Association, CMA) and a code of practice has been published by ICI for both internal [ICI23] and external [364] use. Although the recommended practices are, in part and of necessity, of a general nature for working with toxic gases, it is imperative that these, or similar, practices are followed when working with phosgene. Personnel should be protected from liquid phosgene by protective clothing which is impervious to phosgene [1893], and exposure to the gas in concentrations above the recommended limits should be prevented by the use of suitable gas masks or air respirators [1486,1487,1893].

Owing to the poor warning properties of the gas to the human senses, automatic continuous monitors equipped with alarm systems are recommended [36,1486,1893], and a detailed specification for such devices has been provided [1484]. Skin and eye contact with phosgene should be avoided, but contaminated clothing should be removed immediately and decontamination effected by washing. Emergency showers should be provided [1893] in any facility in which phosgene is stored, used or manufactured.

Personnel engaged in the handling of phosgene should be trained to recognize its odour and instructed in the application of protective measures and first aid and emergency procedures [36,41,401,1486]. Eye, skin and respiratory protection equipment have been described in the NIOSH document [1484]. In particular, personnel should be made to appreciate the delayed effects following potentially lethal exposures to phosgene [1486]. Individuals with cardiac or pulmonary diseases should be precluded from any potential exposure [1318,1629] and NIOSH recommend that annual medical examinations be available to all workers to be occupationally exposed to phosgene [1484,1486], with proper medical management provided for workers who are overexposed. Records pertaining to all cases of overexposure should be maintained [1484].

The following safety measures have been described for phosgene storage and handling in the plant environment [36,1484,1488,2100]:

⊗ Phosgene storage and handling operations should be in a remote location from the rest of the plant.

⊗ Phosgene storage rooms should be provided with an inspection window to permit the area to be viewed without the need of entry.

⊗ Ventilation switches and emergency protection equipment should be located outside the storage area in easily accessible locations, which would be uncontaminated in the event of an emergency.

⊗ Where possible, phosgene should be generated on demand to avoid cylinder handling and phosgene storage (see Chapter 4).

⊗ Phosgene gas should be used in preference to the liquid material.

⊗ The phosgene storage area should be continuously vented to alkali scrubbers.

⊗ A system of automatic analysers should be employed to continuously monitor the ambient air and all phases of the operation.

⊗ Alarms (audible, visual and valve-closing) should be set to operate, automatically, when the concentration of phosgene reaches the sensored limit.

⊗ Phosgene should be piped through a double-skinned conduit, such as a pipe within a pipe. The outer pipe should be continuously monitored for phosgene. Pipes containing phosgene should be distinctively marked.

⊗ Where phosgene is stored in tanks, these should be of a double shell construction. Bulk phosgene is preferably stored underground.

- ⊗ Plant hardware which is exposed to phosgene should be composed of high quality stainless steel, or PTFE, as appropriate.

- ⊗ An extensive preventative maintenance programme should be operated to safeguard against leaks and equipment failure. Potential emission sources should be identified.

- ⊗ An extensive training program should be implemented and a Phosgene Manual should be available.

- ⊗ Dosimeter badges should be worn by personnel who work in the phosgene area.

- ⊗ An emergency/evacuation plan should be established (see Section 3.6.4) and frequent drills executed.

- ⊗ Before equipment is taken out of service, all lines must be purged of any phosgene.

Principles for the safe design and siting of phosgene plant have been recorded by ICI personnel [364,ICI23], whilst NIOSH [1484] have described recommended work practices for emergency procedures, control of airborne phosgene, storage, handling, management of work areas, waste disposal, monitoring and record keeping, and entry and inspection of confined and enclosed spaces. These recommendations and principles have not been repeated here *in toto*, but the consultation of these documents is essential for plant management involved in the handling of phosgene.

3.1.5.2 Laboratory handling

Laboratory personnel intending to use phosgene should be fully acquainted with its toxicity and reactivity, and the protective measures associated with this particular type of poisonous material. In addition, the workers' colleagues should be familiar with the hazards and the necessary rescue and first aid procedures.

Before starting laboratory work with phosgene, it is recommended that the individual is equipped with fresh-air breathing apparatus, a bottle of strong ammonia (or alternative reagents) for leak testing, and a supply of 10% aqueous ammonia solution (or 15% sodium hydroxide solution) for decontamination purposes [ICI21]. Experiments involving phosgene should be carried out only under the supervision of an experienced experimentalist [ICI21]. All operations must be carried out in a suitably effective fume cupboard – fume cupboard face velocities for materials classified as highly toxic {TLV < 0.1 p.p.m.} should be not less than 125 ft min^{-1} (38.1 m min^{-1}) – and regular checks on the fume cupboard air flows should be carried out [1942,ICI22]. It is advisable, in addition, to attach detector tapes (such as filter papers which have been dipped in an ethanolic solution of 5% 4-(dimethylamino)benzaldehyde and 5% *N*,*N*-diethylaniline) to the fume cupboard face. Any emissions of phosgene may then be noted from the characteristic colour change (see Section 3.2.3). Notices should be placed nearby to warn that phosgene is being used. All gas bubblers, or other vessels, through which phosgene has been passed should be labelled so that other workers are not exposed to the residual phosgene unwittingly [ICI21]. Flow rates of phosgene gas and amounts of liquid material should be kept to the minimum practical amount [ICI22]. An efficient way to dispose of phosgene gas is to catalyse the hydrolysis reaction on a bed of charcoal over which an excess of water is passing (Section 4.4.2). Where venting is carried out at a sufficiently low rate that the phosgene concentration is below the threshold value when diluted by the large air inflow into the fume cupboard, such scrubbing procedures may be unnecessary, but are always advisable.

Vacuum pumps, where used, should be protected by solid NaOH traps.

Low concentrations of phosgene in dinitrogen are commercially available, or alternately may be generated using a simple bubbler. Concentrations of around 0.1 p.p.m. have been produced by passing a low flow rate of dinitrogen into a 0.5% v/v solution of phosgene in hexane maintained at the temperature of dry ice, followed by further dilution with dry air and appropriate adjustment of flow rates [125]. Mixtures of phosgene in air, in the concentration range of one half to five times the value corresponding to the TLV, have been prepared using simple gas-blending procedures [1602].

For both laboratory and field testing, low accurate concentrations of phosgene have been generated using permeation tubes [116,1888,2068aa]. These are commonly constructed of standard borosilicate glass serum bottles, filled with an appropriate amount of liquid phosgene, fitted with a septum cap of permeable constitution (such as silicone rubber or PTFE). The permeation rate is calculable from the decrease in weight of the bottle or tube [116]. Accurate flow rates of the gas have been generated by passing known quantities of dry air or dinitrogen over the permeation tube at a fixed temperature [2068aa]. For a 2 cm permeation tube, a typical permeation rate of phosgene of 1 μg min^{-1} can be generated, permitting concentrations in the range of 0.025 to 1 p.p.m. to be produced [2068aa].

In the laboratory, gaseous phosgene is conveniently metered by calibrated flow meters of stainless steel construction; electronic mass flow meters are commercially available where accurate readings are required [255]. It has been found that flow meters suitable for use with chlorine may also be used, after calibration, to meter phosgene [1764].

Liquid phosgene remaining from experimental work should be allowed to vaporize, in a controlled manner, through ethanolic solutions of ammonia or sodium hydroxide [534,2042]. Aqueous solutions of phosgene should be treated in the fume cupboard with an excess of 10% aqueous ammonia (or 15% sodium hydroxide solution), and allowed to stand until all the phosgene has been neutralized before running to drain. Solutions of phosgene in water-immiscible solvents should be destroyed with ethanolic ammonia. Decontamination of rubber tubing should be carried out by immersion into aqueous ammonia before disposal into sealed plastic bags.

3.1.5.3 Cylinder and drum handling

Phosgene is most readily obtained as a liquified gas stored under pressure, in steel cylinders of various sizes. The pressure, under normal conditions, may vary between about 1–2 bar depending upon the ambient temperature (see Chapter 6) and the type and concentration of impurities (see Chapter 4). In the United Kingdom, the smaller 3 lb (1 kg) and 9 lb (4 kg) cylinders are painted black with blue and yellow bands at the shoulder (see Fig. 3.1).

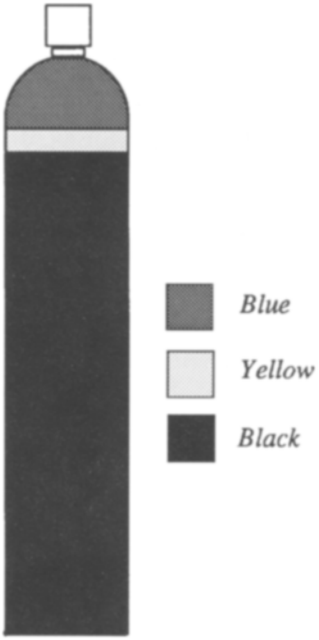

Fig. 3.1 **A cylinder of phosgene.**

These cylinders tend not to have a dip pipe fitted, so that delivery of gas is obtained from the cylinder in the upright position; for the delivery of liquid material, these cylinders need to be turned upside down [ICI21]. The larger 64 lb (29 kg) cylinder, again painted black with the blue and yellow bands on the shoulder, also has no dip tube, and is designed to deliver gas only, whereas the same size cylinder having no yellow band contains a dip pipe for the ready delivery of liquid [ICI21]. Some examples of a larger size, 130 lb (59 kg), cylinder are still in existence [364,ICI23] – the manufacturer's literature should be consulted for technical details.

For most laboratory work, the smallest available size of cylinder (*e.g.* lecture bottles) should be employed. This should be operated in a cool place, inside the fume cupboard. If the valve of a new cylinder is difficult to open, the cylinder should be cooled in ice to suppress the pressure before continuing the effort to open the valve. If undue force would be necessary to open the valve, then the cylinder should be rejected. As in standard laboratory practice, adequate bunding† should be provided. Suck-back into a phosgene cylinder should be avoided; pressure release devices should be provided next to the cylinder to avoid the build-up of pressure in the event of a blockage. Guides to the safe handling of compressed gases in general [1347], and phosgene in particular [254,255], have been published by Matheson, who suggest that, in an experiment, respirators or gas masks should be available for use in an emergency.

It is recommended that the cylinder temperature should never exceed 122 °F (50 °C) [1318,1347,1486]. The cylinder valve should be closed after use, and when the cylinder is empty. Cylinders may be heated by warm air or warm water to facilitate the removal of the contents or transfer of the material in gaseous form. Indeed, phosgene may be vaporized directly from the cylinder by immersion, up to the cylinder shoulder, in a tank of hot water maintained at a suitable temperature, depending upon the rate of delivery required. This rate is not constant, however, and the rate of vaporization tends to tail off as the level of liquor in the cylinder falls [ICI83]. The rate of vaporization of phosgene at a particular temperature, and for a particular cylinder size, may be readily determined experimentally or calculated from a knowledge of the heat transfer coefficients. Heating of phosgene cylinders by the use of steam, boiling water or direct flame is not to be recommended owing to the resulting corrosion of the cylinder which may lead to container failure [1318].

Specifications for phosgene cylinders have been described [1318] and should be constructed according to regulatory standards, such as British Standard 5405 [277a]. Recommendations for the design, construction, testing, filling and maintenance of containers (>0.5 l) for conveyance by road of low pressure liquefiable gases ($T_c > 70$ °C) are covered by the British Standard 5045 [277a].

For usage in excess of about 25 kg day^{-1}, drums of phosgene are employed in preference to cylinders. Drums are painted black with blue and yellow bands at each end of the container [364,ICI23]. For manufacture in the United Kingdom, nett weights are 863 kg (for use in temperate climates) and 813 kg (for tropical conditions). Drum manufacture for phosgene containment must be in accordance with the appropriate regulatory standards. All containers should be registered and a comprehensive system of documentation established to control and record periodic testing, maintenance, and movement – inside and outside the works [ICI23]. The manufacturer's recommendations on such procedures as storage, filling, and making and breaking connections, must be followed rigorously.

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†A system of containment for catching liquid spillage.

Valves for both cylinders and drums may be composed of a ™Monel metal spindle, PTFE gland packing and lead outlet–washer on the cover nut.

If a cylinder is to be disconnected and transferred to storage for later use, the valve must be closed and the adaptor or control valve must be disconnected. The valves, and any associated equipment, should be flushed with nitrogen, and the outlet of the cylinder blown clear. The cylinder blanking screw should then be refitted before storage.

3.1.6 Legislation

Legislative matters concerning hazardous materials are, strictly, beyond the scope of this work and a comprehensive account of the directives provided by the various regulatory bodies has not been attempted. However, any book dealing with industrial hygiene would be incomplete if the legal implications were not considered. These legal aspects are currently in a state of transition throughout the world and, in addition, the laws controlling chemical substances are (by definition) of an evolutionary nature. Thus, this Section deals with the philosophy behind, rather than the letter of, the law. Of one thing we can be certain – the restrictions on the use of bulk quantities of phosgene will increase, and not decrease, with time. In answer to a recent written question concerning the principle of banning phosgene [1734a], the Commission of the European Communities replied that, given the economic importance of phosgene and the stringency of the current regulations, the Commission does not envisage the banning of phosgene production.

Although there are over seventeen countries with their own chemical control laws of various types, the interested reader is directed primarily to the recent Toxic Substances Control Act (TSCA) of the United States, and the various National Laws based on the EEC Sixth Amendment (Dangerous Substances). The legislation and codes of practice affecting compressed gases in general (for the United Kingdom) have been described by the British Compressed Gases Association [277].

3.1.6.1 Classification

Phosgene was listed in the EEC Core Inventory (ECOIN) [602] as number 006–002–00–8 [602], and is now included in the European inventory of existing chemical substances (EINECS) [602a] as 200–870–3. The Registry of Toxic Effects of Chemical Substances (RTECS) lists its accession number as SY5600000, and the U.S. Department of Transportation Identification No. is UN 1076 [1347,1893,2012]. The CAS registry number is [75–44–5], the (UK) Hazard Identification No. is 266, and the Hazchem code is 2XE [277].

For manufacturing and industrial use, phosgene is defined in the draft directive on the Control of Industrial Major Accident Hazards [916] as a dangerous substance at quantities in excess of 20 ton, and manufacturers and users of the material have an obligation to take all measures necessary to prevent major accidents.

Other laws and regulations currently affecting phosgene use in the UK include the Notification of Installations Handling Hazardous Substances Regulations 1982 (applies to sites with 2 ton or more of phosgene), the Control of Industrial Major Hazards Regulations 1984 (applies to phosgene in quantities of 20 ton or more) [916], and the Control of Substances Hazardous to Health Regulations. The most recent amendments of the Control of Industrial Major Accident Hazards Regulations (1988) for Great Britain [916a] impose that sites using, or proposing to use, phosgene in a total quantity of greater than or equal to 750 kg must make that information publicly notified.

The U.S. Environmental Protection Agency (EPA) legislates for the control of acute hazardous wastes such as phosgene. It is subject to handling, transport, treatment, storage and disposal regulations, and permit and notification requirements. The EPA, in addition, legislates for emissions of phosgene into water under the various Water Pollution Control Acts. Recommendations regarding the transport, labelling and packaging of phosgene (Hazard Class 2) are given by the United Nations, and for marine purposes, by the International Maritime Organisation.

Standing instructions for dealing with discharges of phosgene have been prepared by the United States Coast Guard [506].

Owing to the absence of sufficient animal data on the carcinogenic behaviour of phosgene, the material has not been classified according to the EPA's guidelines for carcinogenic risk assessment. It is therefore considered as a "class D " material for these purposes.

3.1.6.2 Labelling

Wherever phosgene is used, stored, handled or generated, a label must accompany the appropriate container or area. According to NIOSH [1484,1486], containers must bear the following legend, in addition to labels required by other statutes or regulations:

> **CONTAINS PHOSGENE; EXTREME HEALTH HAZARD** - Harmful or fatal if inhaled, may cause delayed lung injury. Do not breath gas. Do not get liquid in eyes, on skin, or on clothing. Use only with adequate ventilation and/or in closed systems. Open containers with care. Have respiratory protection available for emergency.
>
> **FIRST AID; CALL A PHYSICIAN IMMEDIATELY** - In case of inhalation, remove victim to uncontaminated atmosphere. If breathing stops, administer artificial respiration. Do not allow victim to walk or exercise. In case of liquid contact, immediately flush skin or eyes with water. Remove contaminated clothing without delay and dispose of liquid properly.

Areas in which phosgene may be encountered must additionally be equipped with a sign describing the location of available respiratory protection, and warning unauthorized persons to keep out. Foreign language considerations should be taken into account.

Pipes containing phosgene should be plainly labelled in accordance with the appropriate National Standards. Shut–off valves should be conspicuously labelled, and containers which are in use should be suitably marked.

In the UK and EEC, the Classification, Packaging and Labelling Regulations 1984 [1936a] require phosgene to be labelled for supply and conveyance. The supply classification is "Toxic", although in fact the substance should be called "Very Toxic", and this change will be made sometime in the future. The "Toxic" supply symbol (a black death's head on an orange background) must be shown on the label, together with the risk phrase:

R26	Very Toxic by Inhalation

and the safety phrases:

S7/9	Keep container tightly closed and in a well ventilated place
S24/25	Avoid contact with skin and eyes.
S45	In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible)

Finally, the label must show the UN diamond symbol "Toxic Gas" as the conveyance hazard symbol, and the UN number 1076.

Technically, phosgene can be exempted from the supply labelling regulations, because it is a "compressed/liquified gas". However, in view of its extreme toxicity and hazardousness, this exemption cannot be recommended [327a].

Because of the comparative rarity with which phosgene gassings occur, it is essential to have instructions of the appropriate diagnosis and treatment in order to avoid any unnecessary delay. The Chemical Industries Association (CIA) Works Safety Committee have instituted a scheme by which casualties are escorted to hospital along with a suitable label which sets out details of the first aid treatment already received, and suggesting any further treatment that might be suitable. For phosgene, the mode of treatment is similar to that required following exposure to nitrogen(IV) oxide or phosphorus(V) oxide trichloride, all of which are dealt with in Label No. 18, available from the Chemical Industries Association, London [363].

3.1.6.3 Transportation

In the United Kingdom, when packages of phosgene (cylinders, *etc.*) are carried on vehicles, the latter and their drivers become subject to the Road Traffic (Carriage of Dangerous Substances in Packages, *etc.*) Regulations 1986. These require the driver to carry the phosgene Tremcard in the cab, in addition to defining a number of other requirements governing the operation of the vehicle, training of the driver, and so on.

If conveyed by road in road tankers, phosgene is subject to the Dangerous Substances (Conveyance by Road in Road Tankers and Tank Containers) Regulations 1981. These regulations require the display of the orange "Hazchem" plate on the vehicle, with the UN Number 1076, the Emergency Action Code 2XE, and the UN "Toxic Gas" warning diamond. The driver, also, must carry the phosgene Tremcard.

In the United Kingdom, transportation of phosgene by road tanker is limited to a maximum payload of 13 ton. The vehicles in use for this purpose must conform rigidly to regulatory specifications. The product name, payload and working pressure are displayed on each side of the barrel unit and at the rear, and each vehicle must carry two eyewash bottles, first aid equipment and a fire extinguisher. In addition, the vehicle driver has a personal issue of goggles, gloves and a respirator [ICI23]. Prescribed routes are laid down for phosgene tankers, and detailed procedures must be followed for the loading and unloading of containers. The phosgene tanker driver is obliged to receive training on the hazards of phosgene, first aid treatment of phosgene gassing casualties, and other safety, emergency, and regulatory procedures [ICI23]. For transportation by rail in the United Kingdom, phosgene can be supplied by 14–20 ton rail tanks for discharge into stock tanks.

For marine transportation, phosgene has been defined (by HMSO, 1978) as Class 2 dangerous goods - prohibited from carriage on ships with more than twenty-five passengers, or more than one passenger per 3 m of overall length, which ever is the greater.

Most phosgene that is produced is used captively. Where any bulk transportation is required, it may be necessary to report the intention to the relevant Authority, and to comply with the required regulatory codes. However, importation and exportation of phosgene is likely to be of low volume. Regulations governing shipment in cylinders and tank cars in the United States have been specified [1318].

Phosgene is subject to specific regulations regarding its transportation by the US DOT [1347]. This authority specifies the following classifications:

DOT Shipping Name:	Phosgene
DOT Hazard Class:	Poison A
DOT Label Required:	Poison Gas
DOT Identification No:	UN 1076

The International Civil Aviation Organization (ICAO) publishes technical instructions for the safe transport of dangerous goods by air [1010a]. For these purposes, phosgene is classified in Category 6.1 (a poisonous gas, liable to cause death or injury or to harm human health if swallowed, inhaled or brought into contact with skin). The transportation of phosgene (normally forbidden on passenger or cargo aircraft) is allowed "only with the prior approval of the appropriate authority of the State of Origin under the written conditions established by the Authority". For passenger aircraft, where ICAO have been notified that prior approval is required under the Special Provision, approval must also be obtained from the States of transit, overflight and destination, and of the State of the operator, as appropriate [1010a]. In each case, a copy of the document(s) of approval, showing the quantity, and packing and labelling requirements, must accompany the assignment [1010a].

3.2 ANALYTICAL METHODS FOR THE DETERMINATION OF PHOSGENE

Quantitative analytical procedures for the determination of phosgene are necessary for hygienic and environmental purposes, in addition to those methods required for its commercial production and use. The required analytical range of concentrations may thus vary from the p.p.t. level to virtually 100%. In particular, the 1995 UK low exposure limit value for phosgene in air of 0.02 p.p.m. (see Section 3.1.4) emphasizes the requirement of sensitive, reliable and specific methods for its detection in the work environment.

A variety of methods are known for the analytical determination of phosgene ranging from simple titrimetric procedures to sophisticated spectroscopic and electrochemical techniques. Comparisons of modern methods for the detection, quantification and monitoring of phosgene have been reported [1116,2068aa] and some general reviews have appeared [458a,884,885,996, 1255,1913a]. A review of the recent advances in the determination of trace quantities of phosgene has focused upon methods based upon spectrophotometry, chromatography, electrochemistry and automatic colorimetry [1513a]. The appropriate analytical method to use depends on such factors as the effect of potential interfering materials, the concentration range, the duration of the test, and the required degree of accuracy. In the field, rapid identification of low concentrations of the gas was of primary importance, and systematic tests for the differentiation of the more common war gases were developed based on distinctive colour effects [2243].

Virtually any physical, chemical, or spectrometric property of phosgene could in principle be utilized for its analytical determination, and it is expected that new methods will evolve alongside general technological advancement. In this Section, a summary of the established analytical methods for the determination of phosgene will be given, classified according to technique. Many of these methods (especially volumetric and argentiometric procedures) are not specific to phosgene, and rely upon some secondary property of the phosgene molecule, such as the generation and subsequent analysis of chloride ion.

Methods for the sampling and assay of bulk phosgene are considered in Section 4.6.

3.2.1 Volumetric methods

3.2.1.1 Acidimetry

Phosgene may be determined by simple acid–base titration methods, using standard indicators [1255,2091]. When passed into aqueous alkali solutions, both carbonate and chloride ions are produced, consistent with equation (3.1). The phosgene can thus be determined by a double–indicator titration, or by determining the chloride content of the solution [1694]. As mentioned above, acidimetry is not specific to phosgene, and the results of such procedures will be distorted by the presence of acid impurities (particularly hydrogen chloride). This problem can be circumvented to some extent by dual determinations, involving both acidimetry and the application of some other technique. For example, phosgene and HCl have been determined in admixture [1914]. Alternatively, absorption trains can be employed to remove interfering contaminants: water [268] or granular pumice impregnated with silver(I) nitrate [649b] has been used to remove HCl; metallic antimony [1496], or powdered antimony(III) sulfide interspersed on glass wool [649b], have been used to remove dichlorine. The phosgene remaining was then absorbed into alkali solution and the resulting chloride was determined by standard methods.

$$COCl_2 + 4[OH]^- \longrightarrow 2Cl^- + [CO_3]^{2-} + 2H_2O \qquad (3.1)$$

An alternative method for the determination of phosgene in the presence of Cl_2 and HCl is based on the reaction of phosgene with an excess of 1-azacycloheptane, $(CH_2)_6NH$, followed by back-titration of unreacted material (after removal by distillation from alkaline solution) with standardized acid [2017a]. Dichlorine and hydrogen chloride can additionally be removed with a filter containing potassium iodide and silver(I) nitrate [297]. The removal of dichlorine, moisture and hydrogen chloride from a stream of phosgene can also be affected by passage of the gases into each of three towers placed in series. The first tower contains a mixture of mossy zinc, mossy tin and tin amalgam, the second tower contains the same ingredients, but with added calcium chloride and powdered mercury(II) sulfide, and the third tower contains a wad of absorbent cotton, together with a layer of small marble pieces and a further mixed layer of calcium chloride and mercury(II) sulfide [1600].

3.2.1.2 Iodometry

Phosgene is an oxidising agent, and iodometric techniques, based upon equation (3.2), have been employed for its determination [425,1148,1255,1357,1604]. The reaction must be carried out under anhydrous conditions (commonly in propanone or methyl ethanoate [1604]), and the iodine determined by conventional procedures, such as by titration with $[S_2O_3]^{2-}$. Although the usual starch indicator cannot be used in propanone solution, the colour of the generated diiodine affords a reasonably sharp end-point [1560]. In addition, indications of very small quantities of phosgene are indicated by the reddish-yellow colour of the liberated diiodine, so that the method can be applied for the trace determination of the gas [1560].

$$COCl_2 + 2I^- \longrightarrow CO + 2Cl^- + I_2 \qquad (3.2)$$

Modifications have been developed which are claimed to avoid side reactions, such as those between phosgene and propanone (see Chapter 10) [1357]. Iodometric methods for the determination of phosgene in the presence of chlorine [445,1168,1627] and of HCl [2216] have been established.

3.2.2 *Gravimetric methods*

Gravimetric methods for the determination of phosgene [425,518,1127,1168,1233,1521, 2231] are based on the quantitative precipitation of 1,3-diphenylurea (dpu) from the passage of the phosgene-containing gas into a cold, saturated, aqueous solution of aniline, according to equation (3.3). An excess of aniline must be ensured in this determination, otherwise phenyl isocyanate is formed instead of dpu (see Section 10.2.1.1) [1126]. Phosgene concentrations as low as 10 p.p.m. have been determined using this procedure [1127], although the method suffers from interference by halogens [1126,1529] and hydrogen halides [1562], which must be separated from the phosgene prior to precipitation. Indeed, the mass spectrum of the precipitate obtained from the passage of vinyl chloride combustion gases into aqueous aniline solutions showed that not even a trace of dpu was formed: the precipitate consisted of materials that resulted from the oxidative coupling of aniline, owing to the high concentration of HCl in the combustion gases [1562]. The aniline method is therefore inadequate for determining phosgene in the presence of large amounts of HCl.

$$COCl_2 + 4PhNH_2 \longrightarrow (PhNH)_2CO + 2[PhNH_3]Cl \qquad (3.3)$$

Diphenylurea has a solubility of 5.5 mg in 100 cm^3 of saturated aniline solution [1560], and for improved accuracy in phosgene determinations it is recommended that phosgene is passed into the aniline solution until a small amount of precipitate is formed. This is then filtered off, and the clear filtrate (now saturated with diphenylurea) is subsequently used for the phosgene determination [1560]. Although traces of phosgene can be readily detected by the appearance of slight turbidity in diphenylurea-saturated aniline solutions, the filtration and weighing of such precipitates is impractical, and the method is not as accurate as the iodine titration method (Section 3.2.1.2) [1560].

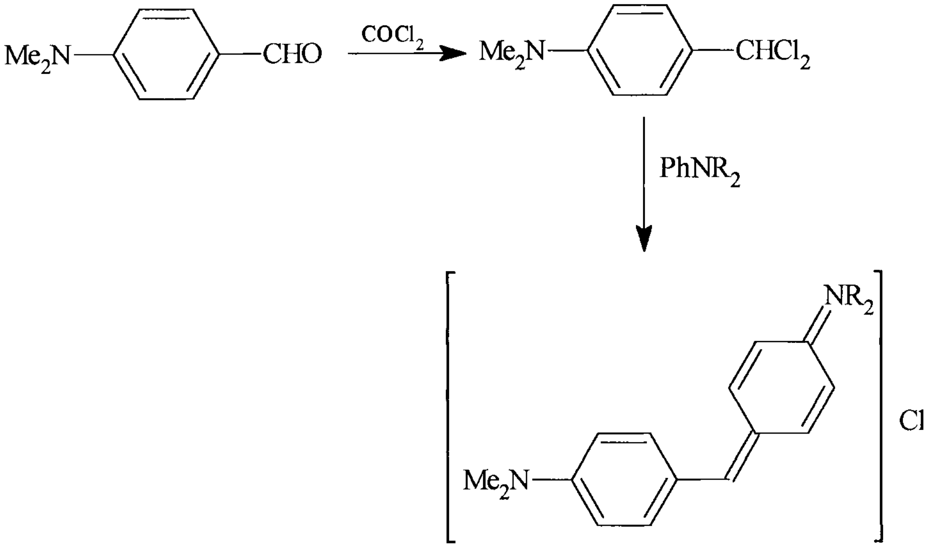
3.2.3 *Colorimetric methods*

The colour reactions of phosgene constitute the most widely published methods for its determination. They are frequently reliable, and are often amenable to continuous monitoring of effluents and the workplace environment [1255]. The earliest methods based on colour changes of reagents were developed for the rapid detection of phosgene when used as a war gas [187b,642,643,1107,2024,2243].

3.2.3.1 Non-automatic colorimetry

3.2.3.1.1 Wet techniques

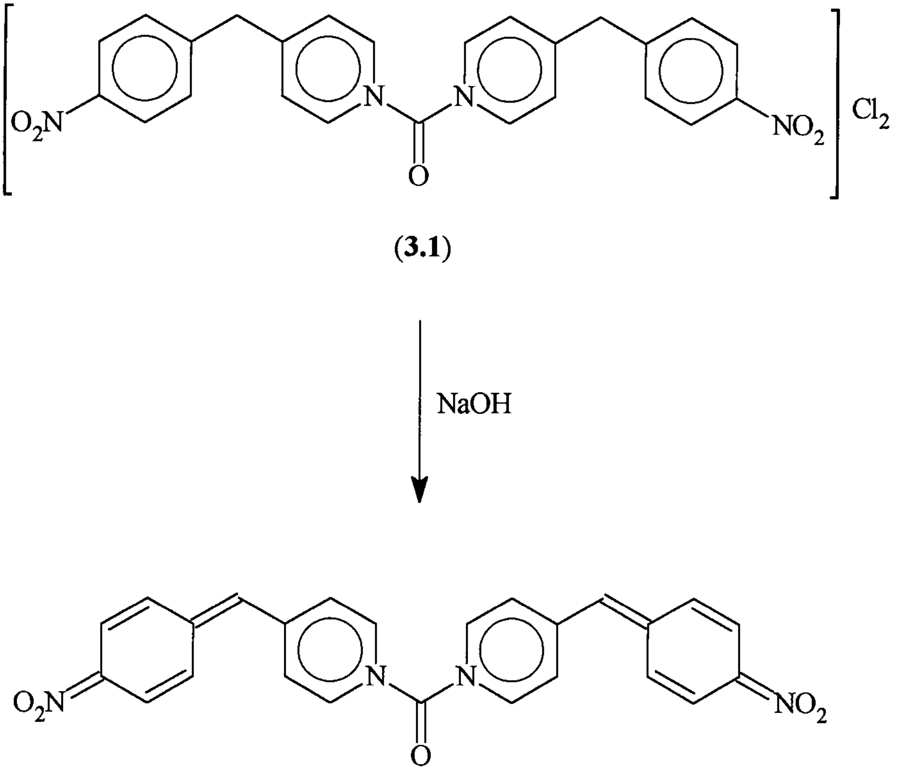
Harrison's reagent (a mixture of non-aqueous solutions of 4-(*N*,*N*-dimethylamino)-benzaldehyde and diphenylamine) yields a yellow, orange, or brown colour on contact with phosgene, according to concentration [165,1742]. A more marked colour change (yellow to blue) is observed when *N*,*N*-dialkylanilines are coupled to the above aldehyde, and exposed to phosgene [1255]:



Similarly, an intense blue-violet colour is generated when phosgene is exposed to 4-(*N*,*N*-dimethylamino)benzaldehyde and the resulting aryldichloromethane is reacted with 3-(*N*,*N*-dimethylamino)phenol [1928].

The one-time recommended standard (NIOSH) for the analysis of phosgene in air was based upon the use of a mixture of 4-(4'-nitrobenzyl)pyridine and *N*-benzylphenylamine in diethyl 1,2-benzenedicarboxylate solution, to produce a brilliant red colour on exposure to phosgene [125,1484]. The absorbance of the sample solution is usually determined spectrophotometrically at a wavelength of 475 nm [688,1202,1484,1526,2030] and as little as 5 μg has been detected in a 250 l air sample, corresponding to 5 p.p.b. [2030]. The method suffers from interference by sulfate esters, and other acid chlorides or chloroformates, which must be removed from the sample [17,1484,2030], but the reagent is highly sensitive to phosgene, resistant to humidity, produces a stable colour, and is unaffected by HCl, Cl_2, ClO_2, and halocarbons in concentrations commonly encountered [1525]. The rate constant for the reaction of phosgene with this reagent has been determined from absorbance-time curves [17], and the principal drawback of the method is that it does not have a sufficiently fast response time for field evaluation [2068aa].

Mixing of ethereal solutions of phosgene and 4-(4'-nitrobenzyl)pyridine results in the formation of a precipitate (3.1), which gives a violet product (3.2) on addition of an alkali [1202]:



(3.1)

(3.2)

Other, less important, colour tests for phosgene have been based upon the following reagents: *N*-benzylaniline [838], Michler's ketone {4,4'-bis(*N*,*N*-dimethylamino)benzophenone} or its corresponding diethyl derivative [1255], 2-(4'-aminobenzenesulfamido)thiazole [171], 5-(*N*,*N*-dimethylamino)-2-nitrosophenol [1255,1521], 2,4-dinitrophenylhydrazine [ICI38], rosaniline or methyl violet dyes [1665], anabasine {2-(3-pyridyl)piperidine} [668a], resorcinol/vanillin [33], pyridine/ethanoic acid [170], 2-methoxyaniline [1304], indole [1304] and PhMgBr [758]. The sensitivities of some of these reagents have been reported [1913a].

Colorimetric methods have been developed for the detection of phosgene in trichloromethane or tetrachloromethane [33,52,425,1360b,1504,1815]. A sensitive visual test involves the addition of an excess of phenylhydrazine (usually as its *trans*-3-phenylpropenoate salt), which reacts with phosgene according to equation (3.4) [52,425]. The diphenylcarbazide so formed reacts with aqueous copper(II) ions to generate a red-violet copper complex [52,425].

$$\mathrm{PhNHNH_2 + COCl_2 \longrightarrow PhNHNH(CO)NHNHPh + 2HCl} \qquad (3.4)$$

3.2.3.1.2 Dry techniques

Impregnation of many of the above reagents onto suitable adsorbents has been employed as a convenient means of detecting or analysing phosgene. An early standard method [55,980,1145,1260,1974,2093,2146,2198,ICI39,ICI40] used a paper disc impregnated with Harrison's reagent (a mixture of non-aqueous solutions of 4-(*N*,*N*-dimethylamino)benzaldehyde and diphenylamine): a sample of the test atmosphere is drawn through the prepared paper at a prescribed rate until a standard coloration is produced. The sensitivity of the test is increased ten-fold, to about 50 p.p.b., by using the reagent deposited on powdered glass [1260,ICI39]. This reagent (as a test paper) was also recommended as part of a military kit for the systematic identification of phosgene [2243]. A yellow to orange coloration was taken to indicate the presence of phosgene, dichlorine or chloracetophenone. Whilst the lack of a colour change on exposure to paper freshly moistened with anilinium chloride indicated the absence of dichlorine, the formation of a green colour on further exposure of the gas to filter paper freshly moistened with equal parts of 4-(*N*,*N*-diethylamino)-2-nitrosophenol and 3-diethylaminophenol solutions indicated the presence of phosgene [2243].

Filter papers impregnated with a mixture of 4-(*N*,*N*-dimethylamino)benzaldehyde and *N*,*N*-dimethylaniline constitute a rapid [1761] and sensitive [1446] test for phosgene, although the test is not specific [2146] since, for example, both dichlorine and hydrogen chloride also act upon the paper (which must also be protected from sunlight). However, it has been noted that even in the presence of ten-to-twelve times the corresponding concentration of Cl_2 or CCl_3NO_2 (chloropicrin), these papers were capable of detecting 10 mg of phosgene per cubic metre of air (2.4 p.p.m.) [1446]. With *N*-ethyl-*N*-(2-hydroxyethyl)aniline, rather than the *N*,*N*-dimethyl derivative, detection sensitivity is reported to be of the order of 1 mg of $COCl_2$ per litre in a 0.5 l sample of air. A related reagent (using *N*,*N*-diethylaniline as the co-additive) constitutes the active component of the commercially available "Dräger" tube (*ex* Drägerwerkes, Lübeck, West Germany), Fig. 3.2, and is specific for the detection or determination of phosgene [678,1223,1223a]. In this system, the number of strokes of a hand pump through which the sample is drawn is related to the phosgene concentration, measurable in the ranges of about 0.05 to 1.5 p.p.m. (Type 0.05/a) or 0.25 to 15 p.p.m. (Type 0.25/b). The pumping action is continued until the blue-green colour of the stain matches that of the reference stain. Although it is suggested that dichlorine and other acid halides must be absent during the determination [678], the detector is reported not to suffer from interference from hydrogen chloride [1223]. However, a pre-scrubber containing mossy zinc has been recommended for the removal of HCl in the 2-10% concentration range [ICI38]. Other commercially-available detector tubes specific to phosgene have been evaluated, but the Dräger tube is described as the most promising [1913a].

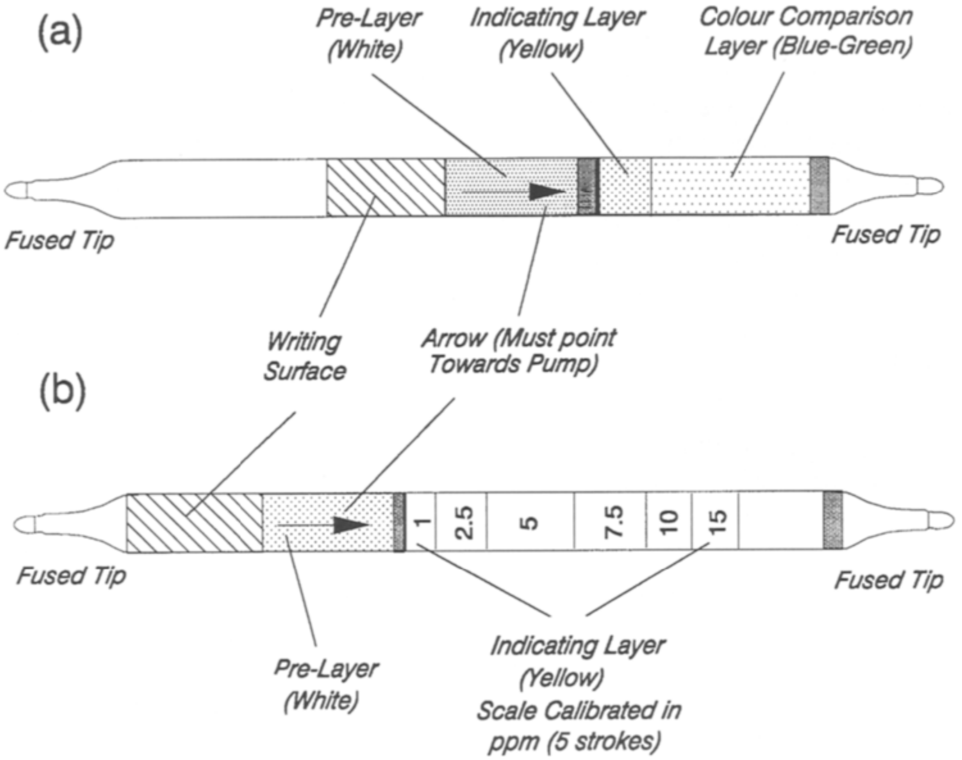


Fig. 3.2 **Phosgene Dräger tubes: (a) Type 0.05/a for 0.04 to 1.5 p.p.m. (v/v) (b) Type 0.25/b for 0.25 to 15 p.p.m. (v/v) [1223,1223a].**

Test papers impregnated with 4-(4'-nitrobenzyl)pyridine and *N*-benzylphenylamine constitute the once Government-recommended method for the detection of phosgene in air [56,539,2027a]. A specified volume of air is drawn through the paper at a specified rate, and the exposed paper is compared with a printed colour chart; the effective range is 0.05–0.4 p.p.m. The concentrations of interfering agents have been established for this method [539,880], and a concentration of 500 p.p.m. hydrogen chloride is reported not to interfere [539]. Detector crayons, suitable for marking a variety of surfaces, have been produced from a recipe based upon this reagent [2204]. A red colour becomes distinguishable at a concentration-time of 0.03 mg min m^{-3}, equivalent to detecting 8 p.p.b. in one minute. Indicator papers impregnated with 4-(4'-nitrobenzyl)pyridine for the detection of phosgene are commercially available (*ex* Rimon Laboratories Ltd., Church Gate Works, Waterloo Rd., Stockport, England). These should be stored away from sunlight, and have a recommended shelf life of 3 months.

3.2.3.2 Automatic colorimetry

3.2.3.2.1 Paper tape monitors

Automatic methods of analysis for phosgene gas have been based upon chemically treated paper tapes [16,260,504,711,729,987,1108,1322,1488,ICI41-ICI43] and several instruments are commercially available [517,1216,2093a], frequently providing an audible or visual alarm. The principle of measurement of the paper tape monitoring technique may be based upon the decrease of light transmission through the paper resulting from exposure to the test sample [729], or the intensity of the colour may be measured *in situ* spectrophotometrically [1216a,ICI41-ICI43] with reference to unexposed tape. Rapid, reliable and sensitive detection methods have been undoubtedly facilitated in recent times by the incorporation of modern photo-optic techniques and microprocessor control.

3.2.3.2.2 Passive dosimetry

The inhalation of phosgene can be fatal, and the type of medical treatment required following an exposure depends upon both the concentration to which the victim has been subjected and to the length of time of the exposure (see Chapter 2). It is therefore necessary not only to have methods which permit the determination of phosgene in air generally, but also to have the facility to monitor the duration of the exposure by the individual.

In recent times [528-530,1346,1430,1431,1506], phosgene dose indicator badges (known as passive dosimeters) have been developed, usually based upon the 4-(4'-nitrobenzyl)pyridine reagent, using acid acceptors, such as *N*-benzylphenylamine, to increase the sensitivity and colour stability. The badges are usually light-weight and disposable and designed to be worn externally on the clothing (or headgear) of personnel who may potentially come into contact with the gas. Rapid estimation of the degree of exposure is possible within the range 1 to 300 p.p.m. min, depending on the intensity of the red colour developed. These badges have been used on a routine daily basis in the plant environment [1430].

3.2.4 Argentiometric methods

Argentiometric procedures cut across the classification boundaries to some extent, in that volumetric, gravimetric or colorimetric methods may be applied to the analysis of particular silver salts. However, the argentiometric methods for the determination of phosgene are specific to the chloride ion, and as such are susceptible to other chloride impurities (especially dichlorine or hydrogen chloride). The details of these methods have been reviewed elsewhere [1255], and since they are neither specific to phosgene, nor in any obvious way amenable to automation, they will not be reviewed here.

3.2.5 Chromatographic methods

3.2.5.1 Gas chromatography

Gas chromatography (g.c.) has proven to be particularly useful for the analysis of phosgene in a wide range of concentrations. A katharometer (thermal conductivity) detector is most frequently employed for routine use (down to about 200 p.p.m. [1339]), but very low concentrations in air, in the p.p.b. [563,598,1039,1663,1887] or even sub-p.p.b. range [448,1886] have been analysed using an electron capture detector [98a,1253,2025]. For such very low concentrations of phosgene, it is usually necessary to precondition the column with several larger doses of phosgene before performing the analysis [1886]. Other detector systems used in phosgene analysis include a Hall electrolytic conductivity detector [1698], a thermionic detector [15], and an argon plasma detector [1179].

Pulsed-flow coulometry has been used for the absolute determination of phosgene in air in the p.p.b. range [1887]. No significant gas phase phosgene-water reactions were observed, but the kinetics for the heterogeneous decomposition of phosgene in the g.c. column (didecyl 1,2-benzenedicarboxylate/ Chromosorb P) and on the glass surfaces were shown to be first-order at low concentrations (<167 p.p.b.). From a knowledge of the kinetics, this method corrects for column sorption by extrapolating to zero retention time. G.c. procedures have been employed for the separation and analysis of phosgene in a range of mixtures, including the gases produced from the combustion of vinyl chloride [1562] or other chlorine-containing organic materials [658], the products of methane chlorination [1339], the oxidation products of dichloroethyne [1698], waste gases from a municipal incinerator [334], the products resulting from phosgene decomposition reactions (CO_2, CO, and CCl_4) [ICI44-ICI46], the chlorination products of petroleum coke [1856], the products of the reductive chlorination of metal-containing ores [13,101,1394], and admixtures with $SiCl_4$, $SnCl_4$ or $TiCl_4$ [2188].

Methods have been published for the gas chromatographic analysis of phosgene in $TiCl_4$ [15], BCl_3 [19], CH_3Cl [1016], $SiCl_4$ [512], benzoyl chloride [835], or propanoyl chloride [1109].

A variety of stationary phases and chromatographic supports have been employed in analyses for phosgene, depending upon the components and their respective concentrations in the particular system. Some of these are summarized in Table 3.3. A range of columns for the detection of phosgene in air has been evaluated [598]: recently, a fused-silica capillary column has detected phosgene at 7 p.p.t. (v/v) in 1 litre of ambient air [98a].

A good working g.c. analytical system for the analysis of phosgene in the presence of other carbonyl dihalides consists of a Porapak P column using helium carrier gas, with a temperature programme operating at 70 °C for 2 min followed by about 40 °C min^{-1} to 130 °C [84a].

A disadvantage of using g.c. analysis for the determination of phosgene results from frequent degradation of the column owing to the corrosive nature of the gas, particularly in the presence of water. For this reason, the column, packing and other parts may be

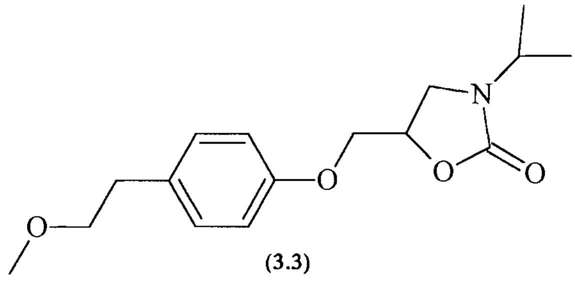
TABLE 3.3

GAS CHROMATOGRAPHIC ANALYSIS OF PHOSGENE-CONTAINING MIXTURES

System or Mixture	Stationary Phase	Solid Support	Ref.
Combustion products of vinyl chloride	Safflower oil or silicone oil	"Chromosorb" W	1562
Waste gases from a municipal incinerator	Hexadecane	"Chromosorb" R	334
Products of phosgene disproportionation	Tritolyl phosphate	Celite	ICI45
Phosgene in CH_xCl_{4-x}	Dinonyl phthalate	Firebrick	1339
Phosgene in air	Didecyl phthalate	"Chromosorb" P	1886,1887
Phosgene in CH_3Cl	Dibutyl decanedioate	Insen brick	1016
Phosgene in CCl_4	Silicone oil	"Chromosorb" W	ICI46
Phosgene in $SiCl_4$	Silicone E 301	"Chromatron"	512
Phosgene in $TiCl_4$	Polmethylsiloxane	"Spherochrome" 1	15
Phosgene/Cl_2/$SiCl_4$	"Kel-F" 10	"Chromosorb" T	137
Phosgene/Cl_2/HCl	-	Zeolite	1394
Phosgene/CO_2/Ar	-	Silica gel	812
Phosgene/CO/CO_2/Cl_2/HCl	"Arochlor" 1232	"Chromosorb" T	101

composed of fluorinated polymers or other corrosion resistant materials [1179,1759].

Phosgene has been used as a derivatizing agent in g.c. separations [856,856b,1152], and this procedure may be employed as an indirect method for its analysis. Thus the oxazolidine derivative (3.3), formed by the reaction of phosgene with the β-blocking drug metoprolol, was analysed by gas chromatography using nitrogen-selective detection. This reaction was used for the analysis of both metoprolol [856] and of phosgene [855]. Similarly, $COCl_2$ in CH_2Cl_2 was determined by reaction with 2-aminophenol [855] (see Section 10.3.1.5).

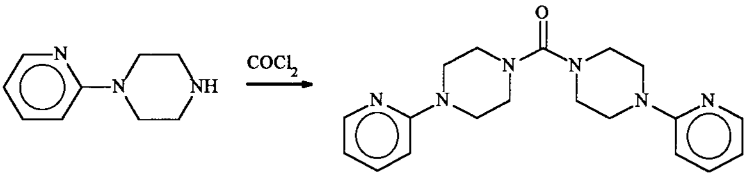


(3.3)

3.2.5.2 High performance liquid chromatography

Phosgene contaminated with large amounts of interfering gases, produced by the combustion of vinyl chloride, was determined by passage into an aqueous solution of aniline to convert it into 1,3-diphenylurea (*cf.* Section 3.2.2). The diphenylurea was separated from aniline (and other derivatives produced by the interfering gases) by h.p.l.c. [982]. The limit of detection using a u.v. detector was reported to be 0.55 p.p.m. [982]. However, in view of the observation [1562] that the formation of 1,3-diphenylurea is greatly retarded in the presence of large amounts of HCl, this method must be treated with suspicion.

When a solid sorbent tube is coated with 1-(2-pyridyl)piperazine, it reacts with airborne phosgene (at concentrations as low as 5 p.p.b. in 20 litres of air) according to:



The resulting urea derivative is desorbed with CH_3CN, and determined by reversed-phase h.p.l.c., using a u.v. detector [1680a].

3.2.6 Optical methods

3.2.6.1 Spectrometry

3.2.6.1.1 Infrared spectroscopic methods

Infrared spectrometric methods for the determination of phosgene [598,1261,1307,2104, 2151] are particularly amenable to continuous monitoring at concentrations below the currently established threshold limit value, and have been applied to the analysis of process gas streams [598,1307]. Measurements of low concentrations (1-10 p.p.m. [104], >30 p.p.b. [1991], >96 p.p.b. [1805], and 25-500 p.p.b. [598]) of phosgene have been facilitated in recent times by the development of long path (20 m) compact sample cells using fixed wavelength peak measurements, particularly those based on ν_4 {the ν_{as}(CCl) stretch at 849 cm^{-1}; see Table 7.2} [598]. Water, carbon dioxide and hydrogen chloride do not interfere [598], and instruments suitable for the detection of phosgene are commercially available [1991,2068aa,2093a].

Measurements of phosgene in the upper troposphere and lower stratosphere have been made [2196a], using a matrix isolation Fourier-Transform infrared spectroscopic technique involving the cryogenic trapping of air samples at a temperature of 87 K, thus freezing out mainly carbon dioxide and water, and subsequently measuring the i.r. absorption of $COCl_2$ (ν_4) in the CO_2 matrix.

The feasibility of using infrared laser beams for the monitoring of phosgene in and around the plant has been described [ICI47-ICI49]. Phosgene has strong absorption bands at 849 (ν_4) and 1827 cm^{-1} (ν_1), but the combination band at 1011 cm^{-1} ($\nu_2+\nu_5$), is less than one thirtieth of the intensity of the 1827 cm^{-1} band. The absorption data, appropriate to

TABLE 3.4

INFRARED ABSORPTION DATA FOR PHOSGENE

ν/cm^{-1} [a]	Absorption Coefficient $/\mathrm{Pa}^{-1}\ \mathrm{m}^{-1}$	% Absorbance [b]	Ref.
1833.5	4.59×10^{-2}	8.9	1805
1010.0	1.40×10^{-3}	0.3	1615
847.5	8.06×10^{-2}	15.1	1615

[a] Laser frequencies. [b] For a 20 m path length at 1 p.p.m. phosgene concentration.

infrared laser monitoring, are summarized in Table 3.4 (see also Section 7.2). The band at 849 cm^{-1}, whilst accessible with a semiconductor diode laser, is considered to be out of reach of the CO_2 lasers, but the bands at 1827 and 1011 cm^{-1} are conveniently within the tuning ranges of the CO and CO_2 lasers, respectively. The absorption of atmospheric water vapour in the 1833 cm^{-1} region would tend to rule out the use of a CO laser, but the 800–1100 cm^{-1} region, by contrast, is virtually free of absorption of water vapour or other atmospheric constituents [ICI48]. Since the 1010 cm^{-1} band for phosgene is rather weak, it would require a very stable laser monitoring system in order to observe very small changes in concentration [ICI47]. For this reason, the feasibility of using a CO_2 laser to drive an ammonia laser tuned to the stronger 849 cm^{-1} band has been considered [ICI47].

A method for the estimation of phosgene in commercial chlorine is based on a knowledge of the apparent extinction coefficient of the carbonyl stretching band in a high pressure cell designed to contain liquid chlorine [1664].

3.2.6.1.2 Ultraviolet spectroscopic methods

Although the u.v. absorption of phosgene, at around 39,420 cm^{-1} (253.7 nm), is rather weak {absorption coefficient of $(1.65\pm0.02)\times10^{-3}$ Pa^{-1} m^{-1} in the temperature range 218–313 K [1427,1964]}, ultraviolet analysers for monitoring phosgene in the atmosphere [2093a] and for its determination in mixtures with hydrogen chloride [765] have been developed for operation in the p.p.m. range. It is more common, however, to find reports describing the indirect determination of phosgene by the u.v. analysis of its reaction product with aniline [191,366,430,431,1126,1127]. The diphenylurea precipitated from aqueous solution (*cf*. Section 3.2.2) is dissolved into methanol [430], or pentan-1-ol/hexane mixtures [431], and the absorbance of the resulting solution recorded at 39,290 cm^{-1} (254.5 nm) [430] or 38,910 cm^{-1} (257 nm) [431]. The limit of detection for this method is reported to be 0.05 mg $COCl_2$ per litre of air (12.2 p.p.m.) [431].

Related methods utilizing the reactions of phosgene with ammonia in Me_2CHOH [2063], or of phosgene with piperidine [1535] have also been described.

3.2.6.1.3 Interferometry

Methods for the analysis of phosgene in the presence of HCl have involved interferometric techniques [1235,1967]. In one example, the refractive index of the gas mixture was measured by use of an interferometer, in order to calculate the composition of the mixture [1967]. In another example, a rapid method for the continuous analysis of phosgene (in the off-gases from the production of alkyl isocyanates) involved an interferometric technique in which the number of interference lines were correlated as a function of phosgene concentration [1235].

3.2.6.2 Light scattering and particle detection

Low concentrations of phosgene (>0.1 p.p.m.) in non-reactive gases can be determined by firstly passing the gas through a filter, and then reacting it with ammonia (or, alternatively, hydrazine or another amine) to form solid particles of ammonium chloride and urea. Water vapour is condensed onto the particle and the degree of light scattering is measured with a nuclei detector [730].

Phosgene concentrations in the range of 0–10 p.p.m. can be monitored on the principle that a marked change in ionization current is produced by the formation of sub-micron size particulate matter in a gas stream. The number of particles formed from contact of phosgene with dimethylamine [2138] or diethylamine [1381] was correlated with the phosgene concentration using an automatic analyzer [2138].

3.2.7 Electrical methods

3.2.7.1 Electrochemical methods

Various cells are available for the detection of phosgene. In one example [2093a], the test gas is fed into a solution of potassium iodide, and the liberated iodine reduced at the cathode (*cf*. Section 3.2.1.2). Ion-selective electrodes have also been adapted for the detection of phosgene in air [697–699,1609]: an electrochemical cell having a polarographic device with cyanide ion-selective electrodes, for example, depends upon the formation of HCN from the reaction of phosgene with methanamide, equation (3.5). The limit of detection of $COCl_2$ by this method is a few parts per billion [1609]. An electrochemical sensor, used for continuous monitoring of phosgene, similarly detects cyanide produced from the reaction of phosgene with certain oximes [125].

$$COCl_2 + HCONH_2 \longrightarrow CO_2 + 2HCl + HCN \qquad (3.5)$$

Other, indirect, methods for the electrochemical determination of phosgene are based upon the measurement of chlorine as a result of pyrolysis [1174,2093a].

3.2.7.2 Electrical conductivity methods

Electrical conductivity methods for the determination of phosgene are particularly amenable to automation, and several potentially suitable gas analysers have been described [2093a].

Phosgene may be detected by the variations in the electrical resistance of a heated wire of palladium–silver alloy surrounded by the gas [1706]. Methods based upon the electrical conductance of solutions, however, depend upon the production of ionic compounds for their measurement [1173,2093a], and are particularly susceptible to interference from hydrogen chloride.

3.2.8 Miscellaneous methods

A piezoelectric crystal coated with methyltrioctylphosphonium dimethylphosphate has been recently described as a good detector for phosgene in air [1976]. The sensitivity of this device is in the range of 1–35 p.p.m.

An indirect method for the analysis of phosgene in phosgene/carbon dioxide mixtures involves passage of the gases over metallic silver at 800 °C. This induces decomposition according to equation (3.6), and the phosgene is estimated by analysing for the CO [1375].

$$COCl_2 + 2Ag \longrightarrow CO + 2AgCl \qquad (3.6)$$

Quantitative analysis of a mixture of HCl and $COCl_2$ has been achieved by condensing the mixture onto solid diphenylmercury(II): the HCl is converted quantitatively to benzene [464].

In one commercially-available gas analyser [2093a], $COCl_2$ is determined after its thermal hydrolysis to HCl in a small furnace, at temperatures in excess of 700 °C. Although capable of measuring phosgene concentrations in the sub-p.p.m. region, many other gases interfere in this technique [2093a].

Phosgene in a mixture with NOCl and Cl_2 can be analysed by gas pressure measurements following exposure of the mixture to mercury. Dichlorine reacts and is completely absorbed by mercury; NOCl yields an equimolar amount of nitrogen(II) oxide; and phosgene is inert to the metal [1939]. Condensation of the phosgene in a suitable refrigerant permits measurement of the NO pressure, whilst measurement of the total pressure of the combined gases at room temperature permits the partial pressure of phosgene to be calculated.

When air contaminated with phosgene is passed into a burner flame in contact with a copper gauze, a green colour is imparted to the flame in concentrations of phosgene as low as 5 p.p.m. [1099]. This arrangement, referred to as the "telltale lamp", has been employed in the field with alcohol being used as the preferred fuel when testing for the presence of phosgene [2146].

3.2.9 Overview

Clearly, the preferred method to use for the analysis of phosgene depends upon the particular application to hand. For routine use in the laboratory, for monitoring the ambient air, impregnated paper strips and Dräger tubes can be recommended as both reliable and easy to use. On the plant, automatic methods for continuous analysis would be appropriate, and one of the electrical or automated spectroscopic techniques would be suitable. For accurate measurement of very low (p.p.b.) concentrations however, a gas chromatographic procedure using one of the special detectors is most suitable.

3.3 SOURCES OF PHOSGENE EMISSION

Emissions of phosgene most commonly arise as a result of its release during manufacture and use, its formation from the decomposition of chlorinated hydrocarbons, and its formation from the photochemical oxidation of air-borne chlorinated organic materials, particularly the C_1 and C_2 chloroalkanes, and chloroethenes. The location and estimation of air emissions from sources of phosgene have been described by the US Environmental Protection Agency [2088b]. Catastrophic emissions and accidental spills and leaks are discussed in Section 3.6.

Despite the careful precautions always taken in the handling of phosgene during its manufacture and subsequent use, releases of the material are inevitable. From engineering estimates [1099a], an emission factor of 0.01 g kg^{-1} (500 kg in a 50 kt unit) for phosgene has been reported for phosgene manufacture from CO and Cl_2. Emissions from the disposal of waste are believed to be at a similar level [1099a]. Control of the releases of significant amounts has to be carefully monitored, not only to maintain a high standard of occupational hygiene at the site of use or production, but also to prevent the exacerbation of the quality of the environmental air.

This Section is concerned with the emissions of phosgene arising from the decomposition of chlorinated hydrocarbons and related materials, and is conveniently separated into those areas which concern occupational or industrial hygiene, and those which raise wider environmental, or pollution, issues. Emission of and exposure to phosgene is, or has been, a potential risk in pharmaceutical, dyestuff and insecticide/herbicide/pesticide manufacture, welding and brazing, ceramics and glass production, aluminium chloride production, cleaning, degreasing, and paint removing processes, municipal waste incineration, firefighting, fuel production, water purification and other related chemical or engineering processes [241,334,747,873,874,1015,1239,1369,1372,1484,2102,2156].

Chlorinated hydrocarbons, and other halogenated materials containing chlorine, can decompose to more toxic substances when subjected to heat or electromagnetic radiation in the presence of air or moisture [201,586]. The products of decomposition may include chlorine, hydrogen chloride and phosgene, *inter alia*, and it is clearly important, in view of the widespread commercial uses of the various halogenated hydrocarbons as solvents, refrigerants, aerosol propellants, fire extinguishants, monomers and anæsthetics, to assess the concentrations of these break-down products and to determine the conditions under which they are formed.

Decomposition to phosgene can be caused by contact of the chlorinated hydrocarbon vapours with hot surfaces (especially metals), a lighted cigarette, a flame, sunlight, or the radiation emitted from a welding arc. However, there is considerable debate concerning the rôle of phosgene as the cause of intoxication from some of these sources, a discussion which is not helped by sensational, scaremongering newspaper headlines (not just in the tabloids) and magazine articles, bearing titles which relate to its use as a war gas.

The oxidation of various chlorinated hydrocarbons, either by air or other means, has been used as a method of synthesizing phosgene; this is discussed in detail in Chapter 5.

3.3.1 From fire extinguishers

3.3.1.1 Tetrachloromethane

Although the employment of tetrachloromethane (carbon tetrachloride) in fire extinguishers has now largely been superseded by more efficient and inherently safer materials, this type of extinguisher is undoubtedly still in use, despite the fact that phosgene is a major product of its oxidative thermal decomposition.

The extinguishment of fires using CCl_4 in enclosed spaces has been reported to lead to deaths as a result of phosgene poisoning [649b]. The first recorded example of this was reported in 1919, when a fire on board a submarine at a naval base was extinguished by two crewmen using a CCl_4-containing extinguisher. Both men were poisoned, and died within a few days of the incident from symptoms resembling phosgene poisoning [649b]. In other cases, however, the reports are considered to be in error [1894], and the quantity of $COCl_2$ that may be formed in extinguishing fires with the CCl_4 type of extinguisher may be small, relative to the quantity of other toxic compounds in the atmosphere surrounding the fire [1559a,2123]. The main hazard under normal conditions is considered to be the potential exposure to the CCl_4 vapour itself, and the presence of harmful amounts of other gases is considered to be largely academic [586]. Thus, CCl_4-based fire extinguishers should not be used when ventilation is inadequate [875], irrespective of whether phosgene is formed in any appreciable concentrations.

Although phosgene is undoubtedly a product of combustion of tetrachloromethane [649b, 950,1356,1529,2231], it is largely decomposed at about 800 °C into CO (and hence CO_2 in air) and chlorine [1912]. At high temperatures, phosgene combines rapidly with water vapour and, in addition, may be absorbed by enclosing walls or ceilings [1912]. The main product of the fire decomposition of tetrachloromethane under most conditions is hydrogen chloride [1912], and analytical methods have been developed for the determination of $COCl_2$ and other chlorinated products resulting from the decomposition of CCl_4 in air [1526].

In "real-fire" situation experiments, in which commercial CCl_4 extinguishers were used to extinguish fires contained in closed rooms (28 m^3 capacity), phosgene is said to be generated in lethal concentrations [649b]. At the industrial threshold limit concentration of

10 p.p.m., tetrachloromethane vapours were thermally decomposed in the presence of air to give hazardous compounds ($COCl_2$, ClO_2 and HCl) far in excess of their respective TLVs. $COCl_2$, the most hazardous of these products, was produced with a maximum concentration of 10 p.p.m. [1527]. Phosgene concentrations were noted to increase with the increase of decomposition of the CCl_4 up to completion; on further heating, the concentration of $COCl_2$ decreased, probably as a result of dissociation [1527]. In the presence of water, pure phosgene decomposes at a greater rate than phosgene formed from CCl_4 decomposition, indicating that tetrachloromethane, or its decomposition products, inhibit phosgene decomposition [1527].

In the high temperatures of a carbon monoxide flame (up to 1730 °C), CCl_4 vapours in dry air were completely decomposed, but only a low concentration of $COCl_2$ (0.07 p.p.m.) was detected [1527]. Higher concentrations of $COCl_2$ were obtained when CCl_4 was poured onto a red-hot iron block [649b], or onto burning magnesium [1600].

Experiments conducted with pure CCl_4 in dry air at 800 °C indicated that phosgene is formed according to [649b]:

$$2CCl_4 + O_2 \longrightarrow 2COCl_2 + 2Cl_2$$

In real fire situations, phosgene may also result from the thermal hydrolysis of tetrachloromethane [649b]:

$$CCl_4 + H_2O \longrightarrow COCl_2 + 2HCl$$

The thermal decomposition of tetrachloromethane in the presence of air is enhanced when it is in contact with metal [191,432,1616,1894,2189], metal chlorides [191,762,1894] or ceramic surfaces [201]. Phosgene yields from the decomposition of tetrachloromethane are the highest amongst the chlorinated hydrocarbons [1894], and in the presence of copper(II) chloride the yield can rise to 25% [1894] at 250 °C. At this temperature, the passage of a mixture of dry air and CCl_4 through a tube charged with anhydrous iron(III) chloride and pumice resulted in a yield of up to 45% of theoretical [762]. The yield of phosgene when CCl_4 vapour is passed over heated iron at 335 °C in the presence of air is 27.5%; this yield drops to 3.6%, however, when heated copper is substituted at a temperature of about 240 °C [432]. Only slight decomposition occurs over zinc, brass, aluminium, or (surprisingly) steel (cold-roll 1045) [432], at temperatures up to *ca.* 350 °C.

The kinetics of the thermal oxidation of CCl_4 in the presence of silica have been analysed between 300 and 480 °C. The process proceeds *via* the formation of phosgene, according to [201]:

$$CCl_4 + \tfrac{1}{2}O_2 \longrightarrow COCl_2 + Cl_2$$

and its ensuing destruction according to:

$$COCl_2 + \tfrac{1}{2}O_2 \longrightarrow CO_2 + Cl_2$$

The rate of formation of phosgene is given by:

$$\frac{d[COCl_2]}{dt} = \frac{k_1[CCl_4]^2[O_2]}{[Cl_2] + k_2[O_2]} - \frac{k_3[COCl_2]^2[O_2]}{[Cl_2] + k_4[O_2]}$$

and the following mechanism was proposed [201]:

$$\begin{aligned}
2CCl_4 &\underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2(CCl_3)_{ads} + Cl_2 \\
2(CCl_3)_{ads} + O_2 &\xrightarrow{k_3} 2COCl_2 + Cl_2 \\
2COCl_2 &\underset{k_5}{\overset{k_4}{\rightleftharpoons}} 2(COCl)_{ads} + Cl_2 \\
2(COCl)_{ads} + O_2 &\xrightarrow{k_6} 2CO_2 + Cl_2 \\
(COCl)_{ads} + (CCl_3)_{ads} + O_2 &\xrightarrow{k_7} CO_2 + COCl_2 + Cl_2
\end{aligned}$$

Various materials have been examined for their effect of suppressing $COCl_2$ formation in CCl_4 decomposition. Curiously, bromomethane was noted to increase the yield of $COCl_2$ when CCl_4/air mixtures were passed over iron(III) chloride/pumice heated to 250 °C, whilst 1,2-dibromoethane reduced the yield of phosgene [762]. A small proportion of coconut fat or other suitable oil or fat added to the extinguisher mixture (typically comprising CCl_4, anhydrous NH_3 and alkyl or aryl phosphate) is also claimed to suppress $COCl_2$ formation [618]. Other phosgene-inhibiting compounds which have been added to CCl_4-based extinguishers include ammonia-based compounds [192], quinones, sulfur, maleic anhydride (and its alkyl-substituted derivatives), and nitroaromatic compounds [1365].

3.3.1.2 Bromochlorodifluoromethane

The concentration of phosgene resulting from the breakdown of bromochlorodifluoromethane (BCF; $CBrClF_2$) extinguisher compositions has been measured using Dräger indicator tubes [ICI50-ICI52]. Different fuels were noted to give different $COCl_2$ concentrations, which were also found to be dependent upon the extinction time [ICI52]. The decomposition products resulting from the extinguishment of heptane fires with $CBrClF_2$, under a variety of fire conditions, were noted to contain trace quantities of phosgene, especially where the time taken to extinguish the fire was deliberately prolonged [ICI51]. No phosgene (*i.e.* <0.2 p.p.m. v/v) was detected from heptane-fuelled fires contained in a 0.1 m^2 metal tray (lorry-cab simulation) for which the extinction time was one second [ICI50]. Similarly, for a crude naphtha-fuelled (8 l) fire contained in a 70 m^3 test room, no phosgene (*i.e.*

<0.2 p.p.m. v/v) was detected at several points in the room, for an extinction time of one second [ICI50].

3.3.2 From chemical smokes and explosives

Chemical smoke ("smoke bomb") formulations based on powdered zinc and highly chlorinated organic compounds, such as CCl_4 or C_2Cl_6, when raised to reaction temperature, are known to produce phosgene in varying quantities. A formulation known as the Berger mixture produces at least 1 mg of $COCl_2$ per gram of starting material [599,600]. Chemical analysis of hexachloroethane smoke mixtures (containing equal quantities of C_2Cl_6 and ZnO, with 10% calcium silicide) produced in an enclosed gas chamber show traces of $COCl_2$ ($<15\ \mathrm{mg\ m^{-3}}$). The smoke constituent most likely to be harmful, however is considered to be zinc chloride [440]. In chemical smokes of this kind, phosgene is understood (from d.t.a. measurements) to be formed from the following series of reactions:

$$CaSi_3 + 3C_2Cl_6 \longrightarrow CaCl_2 + 2CCl_4 + 2C_2Cl_4 + 3Si$$
$$6ZnO + 2CCl_4 \longrightarrow 2(2ZnO.ZnCl_2) + 2COCl_2$$

However, the initiation temperature of the ensuing reaction, equation (3.7), between phosgene and zinc oxide (which also results in the formation of oxide chloride, see Section 9.5.7) is sufficiently low (*ca.* 220 °C) compared to the temperature of the burning composition that the concentration of phosgene in the smoke cloud is low [1033].

$$6ZnO + 2COCl_2 \longrightarrow 2(2ZnO.ZnCl_2) + 2CO_2 \qquad (3.7)$$

Deflagration of 1,3,5-trichloro-2,4,6-trinitrobenzene on heating to 340-350 °C at constant pressure (1 atm) gave a gas mixture consisting of only 0.3% $COCl_2$. Detonation at constant volume in a bomb, however, under a pressure of 10-50 atm of inert gas, gave an explosive mixture containing 12-15% $COCl_2$ upon cooling [1371,1814].

3.3.3 From chlorinated hydrocarbon solvents

Owing to their low flammability and excellent degreasing properties, the chlorinated hydrocarbons are commonly used as solvents in the laboratory, office and industrial workplaces. These materials, however, are particularly susceptible to thermal or photochemical decomposition to phosgene in normal environments.

3.3.3.1 By thermal oxidation

Phosgene is produced when chlorinated hydrocarbons are heated in the presence of air to temperatures generally in excess of 400 °C [1260]. At these temperatures (>400 °C), air containing vapours of CCl_4, $CHCl_3$, CH_2Cl_2, $CHCl_2CHCl_2$, CH_2ClCH_2Cl, $CCl_2{=}CCl_2$, $CHCl{=}CCl_2$, *cis*-CHCl=CHCl or *trans*-CHCl=CHCl was noted to generate phosgene when passed through a silica tube [1260]. Enhanced decomposition to $COCl_2$ has been observed when the vapours of chlorinated hydrocarbons, in an excess of air, were exposed to metals, including iron, copper, aluminium or zinc [1894]. Results in which the contact metal is steel are shown in Table 3.5 [1894]. Phosgene is generated from tetrachloromethane at temperatures as low as 100 °C when in contact with steel, whilst at least 300 °C is required for other chlorinated hydrocarbons [1894]. Above 500 °C, a marked increase in phosgene formation was noted in most cases, whilst at 600 °C hardly any phosgene was formed (owing to its thermal dissociation into CO and Cl_2) [1894].

TABLE 3.5

THERMAL OXIDATION OF CHLORINATED HYDROCARBONS IN AIR,[a] OVER STEEL [1894]

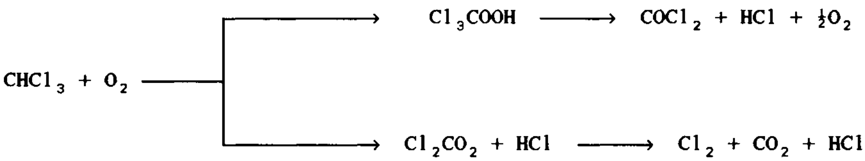
Compound	$T/°C$ [b]	Yield of $COCl_2$ [c]
CCl_4	350	287
$CHCl_3$	450	115
CH_2ClCCl_3	500	42
$CHCl_2CCl_3$	500	14
CH_2ClCH_2Cl	450	6
CCl_3CCl_3	500	4
$CCl_2{=}CCl_2$	500	3

[a] Chlorinated hydrocarbons mixed with an excess of air. [b] Temperatures corresponding to maximum phosgene production. [c] Measured in mg of $COCl_2$ per g of chlorinated hydrocarbon.

Small quantities of phosgene were noted when the vapours of many chlorinated hydrocarbons were passed over glowing charcoal, but no phosgene could be detected when 1,2-dichloroethane was used [1894]. Similarly, small amounts of phosgene (0–11 mg $COCl_2$ per g of compound) were formed when chlorinated hydrocarbon–air mixtures were passed into a propane/butane/oxygen flame [1894].

It is generally believed that cigarette smoking in atmospheres contaminated with chlorinated solvents results in the formation and inhalation of phosgene [1260,2189]. Tetrachloromethane and trichloroethene are reported to be partly oxidized to $COCl_2$ in contact with burning tobacco [2189]. However, no phosgene (<1 p.p.m.) was detected in the exit gas from a cigarette, or in the vicinity of the glowing tip, when smoked in air contaminated with chlorinated hydrocarbons [1260]. Indeed, when phosgene was added to the atmosphere in a concentration of 1 p.p.m., it was destroyed when passed through a burning cigarette. It is considered that the phosgene chemically combines with the basic organic substances in the tar [1260]. However, the passage of air containing 0.1–1.0% trichloroethene over glowing tobacco ash at 600–750 °C results in the formation of phosgene in a concentration proportional both to the original concentration of solvent, and to the temperature [ICI37].

Thermal oxidation of trichloromethane, $CHCl_3$, in the presence of air results in the formation of peroxide intermediates which ultimately decompose to give phosgene [356]:



The decomposition of $CHCl_3$ to $COCl_2$ has been noted as a result of exposure to a gas flame [1529]. Trichloromethane oxidation is also considered to be responsible for the generation of phosgene following the addition of trichloroethanoic acid in flame photometric procedures [1219]:

$$CCl_3COOH \longrightarrow CHCl_3 + CO_2$$
$$CHCl_3 + \tfrac{1}{2}O_2 \longrightarrow COCl_2 + HCl$$

The addition of a small quantity of thymol (10 p.p.m.) to crude $CHCl_3$, exposed to air and mild steel for a week, prevented the production of phosgene by inhibiting the formation of the precursor peroxides [ICI53].

Under certain conditions, dichloromethane (often the major constituent of chemical paint removers) can be converted into phosgene [238,747]. Tobacco smoke, exhaust gases from oil-fired furnaces or petrol engines, and hot metal surfaces are all reported to have a 'catalytic' effect on the reaction [238]:

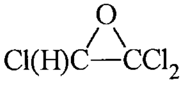
$$CH_2Cl_2 + O_2 \longrightarrow COCl_2 + H_2O$$

However, in the case of oil-fired stoves, it is more likely that dichloromethane vapour is mixed with the air used for the burning of the oil, and the vapour therefore passes through the flames and comes into contact with carbon monoxide. Chlorine, formed by decomposition of CH_2Cl_2, then reacts with the CO to form phosgene, and in ill-ventilated rooms dangerous concentrations of $COCl_2$ can accumulate [747].

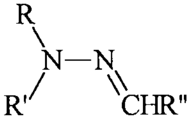
At 1000 °C, 1 g of CH_2Cl_2 in air was found to produce 18 mg of $COCl_2$ [1178]. Exposure to a gas flame results in the transformation of dichloromethane into $COCl_2$ [1529]. The low temperature solvent, CH_3Cl, is similarly decomposed in a gas flame [1529] or on a hot ceramic surface in air [976]. 1,1,1-Trichloroethane is decomposed to phosgene in relatively small quantities (0.74 mg $COCl_2$ per 1 g CH_3CCl_3) when the chlorinated hydrocarbon vapour is passed over heated iron at 335 °C. Over heated copper at temperatures above 315 °C, 0.3 mg of phosgene are formed per gram of CH_3CCl_3 [432]; only slight decomposition occurs in contact with zinc, brass, aluminium or steel at temperatures up to 350 °C [432]. The formation of phosgene was noted when 1,1,1-trichloroethane was exposed to a naked flame, but no quantitative measurements were made [1700].

Chloroethane is decomposed on exposure to a flame to produce some phosgene [1527]. The decomposition of tetrachloroethene (commonly known as "Per") on a steel hot plate ($>$300 °C), in the presence of air, resulted in the formation of a small quantity of phosgene, and the addition of water (0.1%) was noted to enhance the decomposition to $COCl_2$ [ICI54].

Fatalities involving trichloroethene (commonly referred to as "Tri") have been traced to phosgene poisoning as a result of thermal oxidation [2053]. The oxidation of trichloroethene with oxygen at 45–70 °C was found to give dichloroethanoyl chloride {a material believed to arise from the epoxide, (3.4)}, phosgene, carbon monoxide and hydrogen chloride [1364]. The thermal decomposition of $CHCl{=}CCl_2$ and formation of $COCl_2$ is inhibited by the addition of a small amount of a hydrazone, (3.5) [1873] or other stabilizing materials.



(3.4)



$R,R' = CH_3,\ C_2H_5$ or C_3H_7,

$R'' = H$ or CH_3

(3.5)

The addition of phosgene to mixtures of trichloroethene and air or oxygen is found to have an insignificant effect upon ignition limits [1871]. Tests for the detection of phosgene in atmospheres containing trichloroethene should be performed at temperatures above 120 °C, at which temperature phosgene is said to be actively liberated [1726]. Dichloroethene (unspecified isomer) is partially decomposed to phosgene on exposure to a gas flame [1529].

3.3.3.2 By photochemical oxidation

Phosgene may be formed when chlorinated hydrocarbons are exposed to ultraviolet radiation in the presence of air [627]. Dichloromethane was found to contain trace quantities of phosgene after storage for a few days in clear glass flasks, despite being protected from exposure to direct sunlight [855]. Trichloromethane decomposes photooxidatively in a similar way to that described for its thermal oxidation (Section 3.3.3), the process differing in the reaction rate, and in the yields of the peroxide intermediates [356]. Methanol or ethanol are normally added to $CHCl_3$ in order to inhibit its decomposition to phosgene [133,2169].

Although stable in the absence of u.v. radiation [1836], tetrachloroethene can be decomposed photooxidatively into $COCl_2$. In the chlorine-sensitized oxidation of CCl_2CCl_2, approximately 20% of the starting material is converted into $COCl_2$ (the remaining 80% of the tetrachloroethene is transformed into CCl_3COCl, trichloroethanoyl chloride). The following scheme was proposed to account for the products [1813]:

$$\begin{aligned}
Cl_2 &\longrightarrow 2Cl\cdot \\
C_2Cl_4 + Cl\cdot &\longrightarrow [C_2Cl_5]\cdot \\
[C_2Cl_5]\cdot + O_2 &\longrightarrow [C_2Cl_5O_2]\cdot \\
[C_2Cl_5O_2]\cdot &\longrightarrow CCl_3COCl + [ClO]\cdot \\
[ClO]\cdot + C_2Cl_4 &\longrightarrow CCl_3COCl + Cl\cdot \\
[ClO]\cdot + C_2Cl_4 &\longrightarrow COCl_2 + [CCl_3]\cdot \\
[CCl_3]\cdot + \tfrac{1}{2}O_2 &\longrightarrow COCl_2 + Cl\cdot
\end{aligned}$$

In the presence of NO_2, the chloroethenes, $CH_2{=}CCl_2$, $CHCl{=}CCl_2$ and $CCl_2{=}CCl_2$, are photo-oxidized by air and u.v. radiation to give phosgene in addition to other degradation products [725]. Chloroethene (vinyl chloride) and 1,2-dichloroethene were extensively photo-oxidized under these conditions but without the formation of phosgene [725]. A reaction sequence was proposed which involves the photolysis of NO_2 to ozone, which in turn reacts with the C=C moiety to give an unstable epoxide; rearrangements of the epoxide result in phosgene production.

Solvents containing $CCl_2{=}CCl_2$ as the major chemical constituent have been shown to be responsible for causing eye and throat irritations in the employees of a publishing company [228], following the introduction of a mercury-vapour lamp into the factory, which was shown to induce breakdown of the tetrachloroethene into $COCl_2$ and HCl [228].

Phosgene was detected, by g.c.-m.s. and n.m.r. spectroscopy, in a commercial solvent mixture of trichloroethene and tetrachloroethene (80:20) [1254]. Such contamination is likely to arise as a result of photochemical decomposition. The primary product of the oxidation of trichloroethene under ultraviolet radiation is trichloroepoxyethane {*cf.* the thermal decomposition product, structure (3.4)}, which rearranges to dichloroethanoyl chloride and chloral. Secondary decomposition of one of these compounds occurs to give CO, CO_2, HCl and $COCl_2$ [ICI55].

Phosgene in ambient air, derived from the photooxidation of C_2Cl_4 and C_2HCl_3 [1886], is discussed in Section 3.7.

Photo-oxidation of chlorinated ethanes (in the presence of Cl_2) produces $COCl_2$ along with a variety of other chlorocarbonylated derivatives, see Table 3.6 [1926]. Chlorine atoms (generated by the photodissociation of Cl_2) initiate the oxidation of the chlorinated ethenes. A hydrogen atom is abstracted (simulating hydroxyl attack in the ambient atmosphere) and

TABLE 3.6

CONCENTRATIONS OF REACTANT CHLOROETHANES AND PHOSGENE AFTER U.V. IRRADIATION [1926]

$C_2H_xCl_{6-x}$[a]	t/min[b]	Δc/p.p.m.[c]	$[COCl_2]$/p.p.m.[d]
Chloroethane	5.0	2.5	0.0
1,1-Dichloroethane	2.0	5.5	0.1
1,2-Dichloroethane	4.0	4.0	0.0
1,1,1-Trichloroethane	6.0	2.0	2.0
1,1,2-Trichloroethane	2.5	4.5	0.1
1,1,2,2-Tetrachloroethane	2.0	3.5	0.5
1,1,1,2-Tetrachloroethane	3.0	2.0	1.5
Pentachloroethane	6.0	3.0	0.5

[a] Initial concentrations of 10 p.p.m. for each reactant and 4 p.p.m. of chlorine were irradiated; 10 p.p.m. of Cl_2 was used for 1,1,1-trichloroethane, diluted to 1 atm pressure with dry air. [b] Irradiation time; irradiation was performed at room temperature in a cylindrical 9 x 3.0 m glass cell surrounded by 96 u.v. fluorescent lamps (72 with I_{max} near 3650 Å; 24 with I_{max} at 3100 Å). [c] Decrease in chloroethane concentration. [d] Concentration of phosgene formed.

dioxygen then attacks to form the peroxy radical. Phosgene is the major carbon–chlorine reaction product for CCl_3CH_3 and CCl_3CHCl_2. The trace of $COCl_2$ formed from irradiation of $CHCl_2CH_3$ results from the stepwise reaction of the peroxy radical, $CHCl_2O_2\cdot$, involving the formation of the oxy radicals, $CHCl_2O\cdot$, followed by abstraction of the hydrogen atom to form $COCl_2$. Phosgene is the only chlorocarbon product from irradiation of CCl_3CH_3:

$$Cl_2 \longrightarrow 2Cl\cdot$$

$$CCl_3CH_3 + Cl\cdot \longrightarrow [CCl_3CH_2]\cdot + HCl$$

$$[CCl_3CH_2]\cdot + O_2 \longrightarrow [CCl_3CH_2O_2]\cdot$$

$$[CCl_3CH_2O_2]\cdot \longrightarrow [CCl_3]\cdot + CO + H_2O$$

Phosgene is then formed from the trichloromethyl radicals.

The photochemical oxidation of chlorinated hydrocarbons into phosgene has been the subject of particular concern for the welding workshop [679,2217]. Solvent residues from degreasing procedures may remain on the part to be welded, particularly in cracks and cavities where the solvent may have been drawn by capillary action [627]. Upon exposure to the heat of the welding arc, the residues vaporize and although some thermal oxidation will then occur, it is photochemical action which appears to give rise to the major phosgene contamination problems. Moreover, degreasing baths in the vicinity of the workshop may generate a background concentration of chlorinated solvent vapours which are then photolytically oxidized in the presence of the short-wave radiation emitted by the welding arc.

For a solvent to be considered safe in connection with welding practice, the condition must be satisfied that the solvent-contaminated air (at or below the threshold limit value of the solvent) must not give rise to decomposition products whose respective OELs are then exceeded in the vicinity of the welder [447]. This is particularly apposite for phosgene, which is probably the most toxic of the products arising from the decomposition of the most common chlorinated hydrocarbon solvents. Procedures for the control of fumes and gases (including phosgene) generated in the welding environment have been described thoroughly elsewhere [678,2099].

Analytical determinations of phosgene and stabilized 1,1,1-trichloroethane have been performed for aluminium, stainless steel and carbon steel welding. The commonly accepted OEL for CH_3CCl_3 is far greater than that for phosgene, but owing to the decomposition of 1,1,1-trichloroethane into phosgene during welding, the OEL of the former material has been considered to be unacceptably high in this situation [447]. Of the commoner chlorinated hydrocarbon solvents, 1,1,1-trichloroethane is considered to give rise to least phosgene during welding. Welding in air contaminated with tetrachloroethene is considered to be particularly hazardous, owing to the high quantum yield of phosgene in the photooxidation reaction [50]. Light absorption of tetrachloroethene is stronger at the longer wavelengths, where the emission from welding arcs is usually most intense [50], and six times more phosgene is said to be produced from tetrachloroethene than from trichloroethene under similar conditions [678]. The main product of the photooxidation of trichloroethene, induced by the u.v. radiation emitted from a welding arc, is dichloroethanoyl chloride – formed in a concentration of about five times that of phosgene [449]. Since a concentration of 10 p.p.m. of this acid chloride is sufficient to cause immediate irritation to the eyes and throat, and is not endurable for a prolonged time, an exposure to a concentration of phosgene in excess of about 2 p.p.m. for longer than a few minutes is considered to be unlikely [449]: exceeding the OEL of phosgene during welding will thus be avoided by paying attention to the smell of the dichloroethanoyl chloride. Welding in an atmosphere exceeding 10 p.p.m. of trichloroethene is not recommended [449], and for inert gas welding of aluminium or stainless steel, even this concentration must be regarded as too high [449].

Wavelengths of less than 220 nm are considered to be important for the generation of phosgene from trichloroethene. The short-wave band of the ultraviolet spectrum is present to a much larger extent in welding with argon (or carbon dioxide) than when covered electrodes are used [678], but the use of helium in the welding torch has been shown to decrease the phosgene concentrations considerably relative to those generated using argon (see Table 3.7) [646]. Shielding of the arc by means of a pyrex glass funnel was shown to practically eliminate the decomposition effect [646].

TABLE 3.7

DECOMPOSITION OF TRICHLOROETHENE VAPOUR IN THE VICINITY OF AN INERT WELDING ARC[a] [646]

Inert Gas	$[CHCl=CCl_2]$/p.p.m.[b]	$[COCl_2]$/p.p.m.[c]
Argon	0-15	45
Argon	60	140
Argon	100	180
Argon	140	280
Helium	30	6
Helium	30	4

[a]Standard inert arc holder and power source.; DC, straight polarity; tungsten electrode/copper block; 10 A, 0.09375 inch electrodes; trichloroethene source positioned 30 cm from arc. [b] Initial concentrations of trichlorethene. [c]Relative values of generated phosgene concentrations, not directly related to the trichloroethene concentrations.

TABLE 3.8

DECOMPOSITION OF CHLORINATED HYDROCARBONS IN AN ELECTRIC ARC [1035]

Formula	Compound	Phosgene[a]	α[b]
CCl_4	Tetrachloromethane	Yes	4
$CCl_2=CCl_2$	Tetrachloroethene	Yes	2
$CCl_2=CCl-CCl=CCl_2$	Hexachlorobutadiene	Yes	1.5
$CCl_2=CHCl$	Trichloroethene	Yes	1
$CHCl_2CHCl_2$	1,1,2,2-Tetrachloroethane	Yes	1
C_6HCl_5	Pentachlorobenzene	Yes	0.66
$C_{12}H_2Cl_8$	Octachlorodiphenyl	Yes	0.5
$C_6H_2Cl_4$	Tetrachlorobenzene	No	0.33
$C_{12}H_4Cl_6$	Hexachlorodiphenyl	No	0.17
$CHCl_2CH_2Cl$	1,1,2-Trichloroethane	No	0
$C_6H_3Cl_3$	Trichlorobenzene	No	0

[a]Phosgene detected. [b]Defined in Equation (3.8).

In a study of a variety of chlorinated hydrocarbons (CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4, $ClCH_2CH_2Cl$, CH_3CCl_3, $CHCl{=}CCl_2$, $CCl_2{=}CCl_2$ and Cl-2-C_4H_4Cl) exposed in turn to three common forms of arc welding in a glove-box containing concentrations of the vapours corresponding to their respective OELs - only $CHCl{=}CCl_2$ and $CCl_2{=}CCl_2$ were noted to produce potentially hazardous concentrations of $COCl_2$; the other materials were found to generate little or no phosgene [1719]. An electric arc (generated by AC; 10–12 A, 220 V) burning in liquid highly-chlorinated hydrocarbons into which air is injected can result in the formation of phosgene [1035]. The decomposition of these materials (which are potentially non-flammable dielectric liquids for transformation) is governed by the ratio α, defined in equation (3.8) {where the number of atoms refer to the molecular formula}, and this is illustrated in Table 3.8. When $\alpha > 0.4$, phosgene is likely to form: if $\alpha < 0.35$, neither phosgene nor chlorine is likely to be generated [1035].

$$\alpha = \frac{\{(\text{No. of chlorine atoms}) - (\text{No. of hydrogen atoms})\}}{(\text{No. of carbon atoms})} \tag{3.8}$$

3.3.4 *From refrigerants, aerosol-propellants and anæsthetics*

Although many refrigerants, propellants and anæsthetics are non-toxic, in the presence of a flame or on contact with very hot surfaces, phosgene may be produced as one of the toxic decomposition products. The chlorofluorocarbons, CCl_3F (CFC-11), CCl_2F_2 (CFC-12) and $C_2Cl_2F_4$ (CFC-114), when exposed to a gas flame, all generate phosgene as one of the decomposition products. Tests have also shown that CCl_2F_2, if allowed to leak and come into contact with a burning fire, also generates phosgene [2092]. $COCl_2$ was also detected, but to a lesser degree, when vapour-air mixtures of these compounds were exposed to oil or wood fires.

Trace amounts of $COCl_2$ were detected when CCl_3F, CCl_2F_2 and $C_2Cl_2F_4$ were decomposed in the presence of hot metal surfaces [1099,1529]. Moreover, $CFCl_3$ and CF_2Cl_2 decompose to $COCl_2$ on a hot ceramic surface in the presence of excess air, at temperatures above 300 °C [976,1099]. HCl is a major constituent of the decomposition, and is formed in amounts far in excess of the phosgene concentration [976]. At about 1000 °C in air, 1 g each of trichlorofluoromethane, dichlorodifluoromethane and *sym*-dichlorotetrafluoroethane produce 7.0, 2.4 and 12.00 mg of $COCl_2$, respectively. Although HCl is generated in larger quantities, the dangers associated with phosgene generation should not be underestimated [1178].

Aerial oxidation of trichloromethane (chloroform), on storage, results in the contamination of the material with phosgene. Early concerns, at the time when chloroform was commonly used as an anæsthetic, have been recorded [134].

As an example of the ludicrous extremes to which phosgene has been held responsible for deaths and injuries, an article published as recently as 1976 [1863] under the sensationalist title "The Phosgene Proposition" was published in which phosgene was said to be responsible for the deaths caused by Legionnaire's Disease (so called because of a case of over 175 deaths and hospitalization resulting from a Legion Convention held in the Bellevue Stratford Hotel, Philadelphia in the summer of 1976). The article argued that the symptoms displayed by the victims of Legionnaire's Disease were said to be strikingly similar to the symptoms of phosgene gas poisoning, and that phosgene gas can be a derivative of a refrigerant sold commercially for use in air-conditioning systems, CCl_3F. CCl_3F, in the presence of heat and moisture decomposes into HF, HCl and $COCl_2$, according to equation (3.9). It was speculated that a

$$CCl_3F + H_2O \longrightarrow COCl_2 + HF + HCl \qquad (3.9)$$

leak in the air-conditioning system could have resulted in the circulation of the gas into the convention room. The tip of a lighted cigar or cigarette at 1200–1400 °F was then said to be enough to convert the chlorofluorocarbon into phosgene. Alternatively, the leaking refrigerant could have contacted hot spots such as an overheating motor (600–800 °F) in the air-conditioning system, so that phosgene gas itself could have been released through the duct system. *A little learning is a dang'rous thing* (Alexander Pope). Whilst it is known that CCl_3F can be decomposed into $COCl_2$ gas [1178], it seems most unlikely that a disease associated with bacterial origins could be attributed to phosgene poisoning. Indeed, it would be a slight on the competence of the pathologists associated with this case if the symptoms of gas poisoning were not recognized relative to those attributed to a bacterial infection. The reader will be relieved to learn that phosgene has been studied by the Environmental Protection Agency (EPA) and found not to be the cause of Legionnaire's Disease [1893].

"Fluothane", $CF_3CHClBr$, at 60–70 °C, is reported to produce phosgene (0.002–0.02 p.p.m.) and hydrogen chloride, 300 μg gas per 10 cm^3 of "Fluothane". Although the mucous membranes of the human eye and nose were irritated by these gases, no other toxic effects were observed. Young rats exposed to the gas showed no change in lung, trachea and bronchi [2066].

3.3.5 From chlorinated monomers and polymers

Although several chlorinated monomers and polymers [281,1139,1360a,1562,1139] are known to decompose in a thermal oxidative fashion to give $COCl_2$, by far the most important industrial chlorine-containing monomer is chloroethene (vinyl chloride; $CH_2{=}CHCl$) and several studies have been carried out on the thermal oxidation of this material [976,982,1178,1562, ICI38]. Phosgene is a minor combustion product of chloroethene: on burning the monomer in oxygen, only 40–200 p.p.m. of the combustion product is determined as $COCl_2$, although conversion to hydrogen chloride can be almost quantitative [ICI38]. In a typical analysis of the combustion gases from the burning of chloroethene in the absence of an external fuel, the following composition was determined; HCl, 27000; CO_2, 58100; CO, 9500; $COCl_2$, 40 p.p.m. [1562]. In a room of 50 m^3 capacity, 100 g of CH_2CHCl at 100 °C was calculated to generate a phosgene concentration of 0.05 p.p.m., whereas the concentrations of HCl and of

TABLE 3.9

THERMAL DECOMPOSITION OF CH_2=CHCl IN A CH_2=CHCl/AIR MIXTURE [1178]

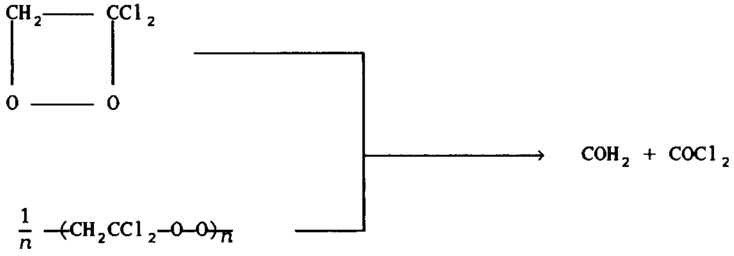
$T/°C$	$COCl_2/\mu g$[a]
100	0.3
200	0.81
300	2.2
400	17
500	34
600	50
750	64
900	92
1000	110

[a] Weight of phosgene produced from 1 g of vinyl chloride.

CO were estimated at 126 and 63 p.p.m., respectively [1178]. The quantity of phosgene formed from the thermal decomposition of 1 g of CH_2=CHCl in a CH_2=CHCl–air mixture between 100 and 1000 °C is illustrated in Table 3.9 [1178]; phosgene generation would therefore not be an important factor in a road tanker fire [ICI38].

Photo-oxidation of CH_2=CHCl in air by u.v. irradiation, and in the presence of NO_2, did not result in the formation of phosgene [725].

When pure 1,1-dichloroethene (vinylidene chloride) is exposed to oxygen, it develops a sharp odour as a result of the formation of a peroxide, which decomposes to phosgene and formaldehyde [1360a]. The peroxide precursor has been formulated as having either a cyclic or a polymeric structure:



Many hazardous materials may be produced during the burning of plastics in fires, incinerators, *etc.*, and it is necessary to determine the risk, to fire fighters in particular, resulting from the generation of toxic substances, and to assess the appropriate decontamination procedures. The thermal decomposition of chlorinated plastics, including chlorinated poly(methyl methacrylate) {45% C, 27% Cl}, poly(vinyl chloride)–poly(vinylidene chloride) copolymer {61% Cl}, and various forms of stabilized and unstabilized poly(vinyl chloride), have been examined in a static chamber between 300 and 1000 °C. The quantities of phosgene generated from the heating or combustion of these materials was regarded as unimportant relative to the concentrations of other toxic gases (*e.g.* HCl and CO) generated.

There has been considerable debate concerning the possible formation of phosgene from the burning of poly(vinyl chloride) [202,281,402,815,1008,1572]. In a closed (static) system, in which the surfaces of the vessel were maintained at room temperature, yields of up to 1.6 mg of $COCl_2$ per gram of poly(vinyl chloride) were obtained by Brown and Birky [281]. Smaller yields (<0.25 mg g^{-1}) were obtained by Coleman and Thomas [402], whilst larger amounts (up to 3.5 mg g^{-1}) were found by Baltaitis *et al.* [109a]. In flow experiments, however, where prolonged contact between the gases and the heat source was absent, no phosgene could be detected in the gas phase [202], although Imoto [1008] found that burning poly(vinyl chloride) in air gave combustion mixtures containing 1 mg of phosgene per gram of poly(vinyl chloride). Although the formation of large amounts of phosgene is possible thermodynamically below 850 K, the rates of the reactions involved are very slow at, and below, these temperatures [202]. These rates, however, may be strongly enhanced if the evolved gases from poly(vinyl chloride) combustion come into contact with copper, iron or carbon [202]. Phosgene is considered to be formed through secondary reactions during the burning of poly(vinyl chloride): HCl is oxidized to molecular chlorine, equation (3.10), which then combines with carbon monoxide as illustrated in equation (3.11) [281]. It is thus not surprising that the formation of phosgene may be enhanced in the presence of copper – the chloride salt of which is a catalyst for the reaction (the Deacon reaction) represented by equation (3.10) – and of carbon, which is a catalyst for the reaction represented by equation (3.11). In addition, copper(II) chloride is a catalyst for the oxychlorination of carbon monoxide to phosgene, equation (3.12) [85], representing the overall reaction of equations (3.10) and (3.11).

$$2HCl + \tfrac{1}{2}O_2 \longrightarrow Cl_2 + H_2O \qquad (3.10)$$

$$Cl_2 + CO \longrightarrow COCl_2 \qquad (3.11)$$

$$CO + 2HCl + \tfrac{1}{2}O_2 \longrightarrow COCl_2 + H_2O \qquad (3.12)$$

In view of the fact that poly(vinyl chloride) is frequently used in copper conduit, and that carbonaceous material is invariably formed during the combustion of plastics, then the co–combustion of poly(vinyl chloride), carbon and copper must constitute a commonly occurring situation. The thermal decomposition of poly(vinyl chloride) (electrical wire formulation) was examined by four methods [281]:

(a) thermal degradation in a resistively heated furnace,

(b) electrical overloading of a poly(vinyl chloride)–clad wire,

(c) electrical arcing between electrodes partially covered with poly(vinyl chloride), and

(d) electric arc initiated flaming combustion in a cup furnace.

Whilst small quantities of $COCl_2$ were generated by all of these methods, the electric arc decomposition generated 10–20 times more phosgene {$\leqslant$1.6 mg of $COCl_2$ per 1 g of poly(vinyl chloride)} than the combustion methods. It was postulated that a high intensity electrical discharge could produce vapours of copper and copper(II) chloride in the presence of poly(vinyl chloride), as precursors to phosgene formation in electrical fires [281]. A phosgene hazard is thus more likely when the combustion involves poly(vinyl chloride)–clad electrical wires or cables. Incineration of poly(vinyl chloride) in municipal waste, for example, where the poly(vinyl chloride) concentration constitutes only a few percent of the total, does not constitute a significant hazard since the prevailing conditions are either unfavourable for its formation, or favourable for its destruction through oxidation, equation (3.13), or hydrolysis, equation (3.14) [202].

$$COCl_2 + \tfrac{1}{2}O_2 \longrightarrow CO_2 + Cl_2 \tag{3.13}$$

$$COCl_2 + H_2O \longrightarrow 2HCl + CO_2 \tag{3.14}$$

On the basis of theoretical equilibrium studies, phosgene formation from the burning of poly(vinyl chloride) is considered most favourable when the polymer combustion takes place in a limited excess of oxygen in an intermediate temperature region (with a lower limit of 800 K), and the gases of combustion are maintained between 600 and 850 K for the longest possible period [202].

Two modes of decomposition have been found to exist for the oxygen–vinylidene chloride copolymer [1722]. In the initial and rapid mode, the chief volatile decomposition products at 170 °C were phosgene, formaldehyde, CO and HCl in the ratio of 15:(7.5–15):5:1. In the secondary process, polymerization of vinylidene chloride in the presence of oxygen causes part of the monomer to oxidize to polyperoxide, which itself undergoes the rapid decomposition:

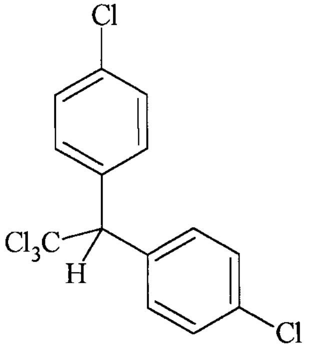
$$\sim\!\sim\!\sim CH_2CCl_2\text{-}O\text{-}O\text{-}CH_2CCl_2 \sim\!\sim\!\sim \longrightarrow 2 \sim\!\sim\!\sim CH_2\text{-}CCl_2\text{-}O\cdot$$

$$\sim\!\sim\!\sim CH_2CCl_2\text{-}O(OCH_2CCl_2O)_n \longrightarrow \sim\!\sim\!\sim CH_2CCl_2O\cdot + nCOH_2 + nCOCl_2$$

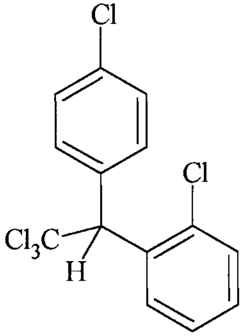
$$COCl_2 + H_2O \longrightarrow 2HCl + CO_2$$

3.3.6 From other chlorinated compounds

A report [64] that phosgene had been evolved when a horticultural dust, containing DDT, (3.6), was mixed with copper(II) oxide chloride was shown to be unfounded [579]. Rather severe conditions (not likely to be encountered in agricultural practice) are necessary in order to generate phosgene from DDT. Thus, DDT or its component isomers (3.7) and (3.8), when heated with potassium dichromate(VI) – sulfuric acid mixtures, gave 30–40%, 5–10%, and 1–5% of the theoretical yields of phosgene, respectively [579], based on the formation of one mole of $COCl_2$ per mole of substance.



(3.6)



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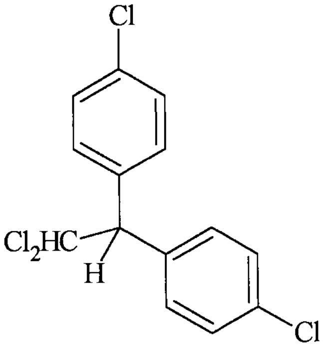

(3.8)

Sugar beet, treated with the organochloride pesticides, hexachlorocyclohexane and sodium trichloroethanoate, results in the contamination of the plantation with dust containing residual amounts of the pesticides. The maximum amount of phosgene produced was associated with the maximum u.v. radiation occurring between hours of strong sunlight [834].

3.4 TREATMENT OF LIQUID PHOSGENE SPILLAGES

Comparatively little information is available in the open literature on the correct procedures for handling large liquid phosgene spillages. Effective methods for retarding the rate of vaporization of liquid phosgene have been developed at ICI [364,ICI56], and are based upon dissolution into an inert hydrocarbon or chlorinated hydrocarbon solvent, followed by coverage with an inert barrier to reduce the rate at which the gaseous phosgene reaches the atmosphere. The phosgene which is gradually released may then be mopped up by the addition of solid alkali or adsorbent (such as coconut charcoal) [ICI56].

Four principles for the treatment of phosgene spillages have been investigated [ICI56]:

- Adsorption (*e.g.* charcoals, Fuller's earth, activated alumina, molecular sieve 13X, silica gel)
- Insulation (*e.g.* sand, sawdust, PTFE powder)
- Reaction (*e.g.* soda ash, soda lime, methanol, ethylene glycol, triethylamine)
- Solution (*e.g.* 1,2-dichlorobenzene, perchloroethylene, C_{14}–C_{17} paraffins, derv, kerosine).

Direct addition of alkaline material to a phosgene spillage cannot be recommended [ICI56], owing to the violent reaction which ensues and which results in an enhanced evaporation rate. Similarly, the addition of an otherwise inert material possessing a significant heat capacity per unit volume increases the rate of phosgene evaporation. Indeed, the addition of any material which reacts exothermically may substantially increase the rate of evaporation, and any material which adsorbs phosgene and has a significant enthalpy of adsorption may initially increase the rate of vaporization, although the total amount of phosgene evaporated may be ultimately less [ICI56].

The addition of any paraffin(ic) material was found to significantly reduce the rate of phosgene evaporation [ICI56]. The addition of a linear-chain paraffin (C_{14}–C_{17}) or kerosine (2 parts of solvent to 1 part of liquid phosgene) reduces the rate of evaporation to 20% of that of an untreated pool. The addition of an inert filler (dried sawdust) impregnated with paraffin was found to be as effective as adding the paraffin, but acted also as a filling material. If this is followed by the addition of an excess of hydrated lime (calcium hydroxide), as a surface layer, it provides an effective remedy for the treatment of a phosgene spillage, destroying 90% of the original material [ICI57]. The direct addition of the hydrated lime to a liquid kerosine/phosgene mixture, however, resulted in the vaporization of >80% of the phosgene, owing to the ensuing exothermic reaction [ICI57]. Ignition of phosgene/kerosine mixtures does not result in significant thermal decomposition of the $COCl_2$, and cannot be considered as a potential method for the destruction of phosgene [ICI57].

A recommended sawdust/kerosine mixture is prepared by thoroughly drying sawdust and mixing with 1½ times its own weight of kerosine. The resulting material should be stored in sealed waterproof containers in a total quantity equal to twice the maximum envisaged phosgene spillage [ICI56,ICI57]. The weight of hydrated lime to be stored should be approximately equal to six times the weight of the likely spillage [ICI23]. A perlite/paraffin oil mixture, however, when used in combination with calcium hydroxide was noted to give a rate of phosgene evaporation equal to about half of that of the corresponding sawdust/paraffin/calcium hydroxide treatment [ICI58], and may constitute an improvement over the previously recommended remedy [ICI58].

Trichloroethylene (trichloroethene) was found to be as effective a solvent as any for the dissolution of phosgene, and has the additional advantage of being both non-flammable and readily available [ICI58]. The addition of trichloroethylene (one part) to liquid phosgene (two parts) contained in a 50 mm diameter glass beaker, followed by Hycar (a synthetic nitrile rubber powder) to solidify the mixture, resulted in only about 20% weight loss after one hour, compared to 50% for untreated phosgene. If an excess of "Limbux" (calcium hydroxide) was spread on top of the phosgene/trichloroethylene/Hycar mixture, the loss was reduced to almost 10% after one hour [ICI58]. Although the last mentioned treatment appears to be the most effective in terms of reducing the phosgene vaporization rates, it does involve an additional procedure (which includes the addition of a liquid solvent) relative to the inert filler/paraffinic type of treatment.

Union Carbide workers [1900] have examined methods for retarding the evaporation rates of liquid phosgene. Their most effective method was to cover the surface of the spillage with a paraffin-based oil (Texaco Regal F), in conjunction with an inert chlorinated hydrocarbon solvent such as chloroform. The chloroform was added to make the resulting phosgene solution sufficiently dense that the oil would cover the surface. When the recommended oil (one part) was added to an equivolume chloroform solution of phosgene (six parts), the evaporation rate was reduced from 106 to 4 g min^{-1} m^{-2} on a 0.0768 m^2 surface. When the mixture was thoroughly stirred the evaporation rate increased to 72 g min^{-1} m^{-2}. Without the chloroform, the oil was not very effective (evaporation rate, 85 g min^{-1} m^{-2}) [1900].

Small spillages of liquid phosgene inside a fume cupboard should be treated with 10% ammonia solution, and allowed to evaporate so that any residual phosgene is removed by the fan [ICI21].

3.5 CASE REPORTS OF PHOSGENE POISONING

It has been estimated (although without substantiation) [1484] that some ten thousand workers were potentially at risk to occupational phosgene exposure during its manufacture or use in 1976. In addition, exposure to phosgene can result from the decomposition of various chlorinated organic materials as described in Section 3.3. Risks to the populace, as a result of catastrophic emissions, are described in Section 3.6.

The observations on two thousand cases of exposure to war gases (186 of which were attributed to phosgene gassings) were reported shortly after the end of World War I. These studies, performed on the survivors of gas shell attacks, were limited only to clinical findings [1766]. In contrast, outside of war time, ten cases of phosgene gassings (including only one fatality) were reported to the United Kingdom Factory Inspectorate during the period 1932-1937 [2189]. These latter figures should be compared with those reported for other industrial, toxic materials. For example, more than 450 gassings (including fifty fatalities) were reported in this period resulting from carbon monoxide poisoning in the power, coal, steel and related industries. About 900 reports of gassings (including ninety fatalities) were received in this reporting period from the chemical and related industries [2189]. Details of many individual case histories of phosgene gassings have been summarized by NIOSH [1484].

Although phosgene poisonings are comparatively rare, they do appear from time-to-time, and are occasionally fatal, Table 3.10. However, even though exposure may be apparently severe, complete recovery is frequently encountered [605,764,1186,1902a,1940,2020] with little evidence of long term effects. An analysis of 109 phosgene inhalation cases during the twelve year period 1955-1966 at the BASF AG revealed that in only three of 31 cases in which X-ray studies were performed did the poisonings cause serious consequences (including one fatality), illustrated by the characteristic pulmonary œdema; two cases were regarded as being clinically insignificant [2020]. Similar studies at BASF have been carried out for the periods 1955-1972 [2020a] and 1980 [2020b].

TABLE 3.10

SOME FATAL INCIDENTS RESULTING FROM PROBABLE PHOSGENE POISONINGS

Exposure Source	Additional Comments	No of Fatalities	Ref
$COCl_2$ storage tank	Demobilization stocks in city location	11	220,920
CCl_4 extinguisher	Decomposition by fire in confined space	2	649b
$COCl_2$-containing brick dust	Replacement of reactor furnace lining which had been exposed to $COCl_2$ ($AlCl_3$ manufacture)	1	2020
CH_2Cl_2 in paint remover	Vapours exposed to oil-fired stove, ill-ventilated room	1	747
$CHCl{=}CCl_2$ ("Tri") vapour degreaser[a]	Excessive heating of solvent	1	1932
$COCl_2$	Exposure during experimental research	1	732
$COCl_2$	Exposure resulting from a fire to which a $COCl_2$ cylinder was exposed	1	221

[a] Non-fatal accidents of a similar nature have been reported [1368,1727].

In 1973, in Czechoslovakia, the release of about 400 kg of phosgene from a damaged valve of a steel pressure vessel resulted in the medical treatment of 82 workers. Of these, 52 were diagnosed as having phosgene poisoning but pulmonary œdema was manifest in only three of the effected persons [1186], none of whom died. The poisonings from this incident occurred within 200 m of the site of the accident.

Owing to the number of other hazardous materials which may be generated in accidental fires, direct proof of poisoning by phosgene is inevitably lacking [1828]. Although many deaths have been associated with carbon tetrachloride fire extinguishers, it is unlikely that these have arisen in every case as a result of phosgene poisoning [1828]. In another case, phosgene exposure has apparently resulted from photochemical decomposition of trichloroethene during arc welding (see Section 3.3.3) [764].

3.6 CATASTROPHIC EMISSIONS

Although toxic releases, in general, are not the principal cause of major accidents (relative to fire and explosion) associated with the chemical industry, they are a just cause of "considerable public apprehension" [1327a]. This concern has been compounded by an event which occurred in Bhopal, India in December 1984, in which over 2500 people were killed by a single toxic release of methyl isocyanate.

In the UK, carbon monoxide causes more deaths than any other toxic gas [1327a], although Marshall does not consider this to be a major chemical hazard, since deaths involving this material usually take place in confinement, generally involving only one person.

Phosgene is one of the few materials used in industry for which its poisonous nature is well documented, primarily because it was used as a chemical warfare agent. The subject of major chemical hazards has been competently treated by Marshall [1327a], and the reader is directed to that source for the comprehensive treatment of this subject in terms of the control, quantification and legislation of major chemical hazards.

Catastrophic releases of phosgene have arisen both deliberately (see Chapter 1) and accidentally. This Section is concerned with accidental releases of disastrous, or potentially disastrous, proportions, simulation studies of such releases, and the emergency procedures necessary to minimize the hazards.

Phosgene is said to be probably the most poisonous gas used in industry† [1768] and an attempt has been made [1327] to derive a "mortality index" for phosgene based upon an analysis of data from explosions, releases of flammable gases, and from toxic releases of

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†Hydrogen selenide is probably a more poisonous gas and methyl isocyanate is certainly a more poisonous vapour (b.pt. ≈ 39 °C). Bis(chloromethyl)ether is more poisonous in the chronic sense (OEL = 1 p.p.b.). Phosgene might, therefore, be more correctly described as the most poisonous gas used in any significant volume in industry.

accidental or military origin. This index was determined for each source in terms of mean fatalities per ton, for any given size of incident. For phosgene {using data based on the Hamburg disaster of 1928 (see Section 3.6.1), in which the release of *ca.* ten tons of phosgene resulted in ten fatalities}, the mortality index of 1 is very close to that for conventional explosives. For comparison, the mean of thirty incidents involving chlorine releases gave a mortality index of 0.5 [1327].

These figures, however, are overshadowed by the Bhopal incident, in which some 2500 deaths were caused by a release of about fifteen tons of methyl isocyanate. Based on this scheme, methyl isocyanate would have a mortality index of about 167, a figure that is clearly disproportionate relative to the toxicities of the materials considered, and reveals the inherent deficiency in this index. The magnitude of the tragedy that occurred in Central India was more to do with the fact that an estimated 12000 people lived in close proximity to the plant.

A spill hazard ranking system for toxic chemicals has been proposed based upon the derived equation (3.15):

$$x \simeq 1.02\{PA/\mathrm{CT}\}^{\frac{1}{2}} \qquad (3.15)$$

where x is the "downwind" distance (in m), P is the liquid vapour pressure (in Pa; taken at the limit of atmospheric pressure for phosgene), A is the area covered by the spill (in m^2) and CT is the Threshold Limit Value of the chemical.

Logically, the equation illustrates that the toxic area is proportional to the vapour pressure of the substance and the area of the spill, and is inversely proportional to the TLV. For phosgene, the toxicity index (for a 1 m^2 spill) is 1000, compared to a value for dichlorine of 316, and for cyanogen of 100 [1957].

3.6.1 The Hamburg disaster

In Hamburg, West Germany, on the Sunday afternoon of 28th May, 1928, the cover of a tank filled with about 10 m^3 of liquid phosgene was ejected with a loud bang. Within a short time, approximately 8 m^3 (11 t) of phosgene escaped. A light North-Easterly wind of only 2–3 m s^{-1} prevailed, and 300 people were poisoned at distances of up to 10 km from the source; 17 were severely injured, 10 of whom eventually died [920]. Most of the animals in the area died, vegetation yellowed; a distance of approximately 14 km marked the limit of perceptibility [939].

Despite having been previously tested at 22 atm (2.2 MPa), the container (one of three), reputedly pressurized to only 1.5–1.8 atm (0.15–0.18 MPa), ruptured at the welded seam on the main head dome after less than eleven months of storage. No excessive pressure was said to be generated in the container, since the shed of corrugated metal in which the containers were stored showed no signs of impact damage. Although the welded seam showed defects ascribed to the expansion of the metal [220], it has been speculated that the probable escape of gas at a small leaky point on the tank lead to the evolution of HCl, which eventually caused corrosion and failure of the riveted dome [920].

A total of 80 tons of liquified phosgene gas (originating from military demobilization stocks) was thus stored within a populated city, without the deployment of any particular safety precautions. Had the gas release occurred on any day other than Sunday, the fatalities would surely have been considerably higher. Marshall's mortality index would then no doubt have been disproportionate to the actual toxicity of the chemical – more a reflection of the absurdity of locating a major chemical hazard close to a populated region than of the intrinsic toxicity of the gas.

Because gas masks suitable for protection against phosgene were not available to the emergency services, five of the fire brigade personnel and eight policemen suffered phosgene poisoning of varying severity [920]. Again, there are serious lessons to be learned from this incident.

3.6.2 Simulation studies

Simulated accidents involving the escape of phosgene have been examined by the Swedish Armed Forces Research Establishment [557]. The dispersion of the gas, and its possible toxic effects at different distances from the accident source, have been estimated on the basis of two model accidents which might conceivably result in a maximum emission of material. The effects of climatic changes upon the gas dispersion were assessed and calculations performed at two different ambient temperatures, and for two types of weather conditions. The studies (based upon the discharge of a 900 kg containment of phosgene at a particular location in Sweden) indicate that serious injuries could be caused to people (assumed to be out-of-doors) in a small, wedge – shaped area within a range of about 2 km under unfavourable weather conditions. From an analysis of the weather statistics for the locality, the probable direction of the gas cloud was estimated, and the frequency of unfavourable weather conditions was determined. Despite the high toxicity of phosgene, it was concluded [557] that the material presents no greater risk than chlorine, which is used and stored in much larger quantities.

When phosgene is liberated, about 90% is effective in forming the cloud [590], and observations [939] from the Hamburg disaster (Section 3.6.1) revealed that the gas cloud formed a semi-cone, the apex of which coincided with the origin. The cloud was noted to spread about 15° in all directions, as far as about 50 m from the source.

The relationship between the physiological effect of phosgene exposure and the corresponding hazard category has been assessed [ICI59] from extrapolation of information contained in the published literature. The results, expressed as straight line plots of phosgene concentration *versus* exposure time, are represented in Fig. 3.3, and may be considered broadly to indicate the likely effects of exposure upon an adult of average fitness.

Leakage rates for gaseous and liquid emissions of phosgene have been estimated for holes of different sizes [ICI60]. The gas leak from a ¼" (6 mm) hole at 20 °C is calculated to be 142 kg h^{-1}; from a 1" (25 mm) hole, leakage is 2300 kg h^{-1}. For a liquid leak at

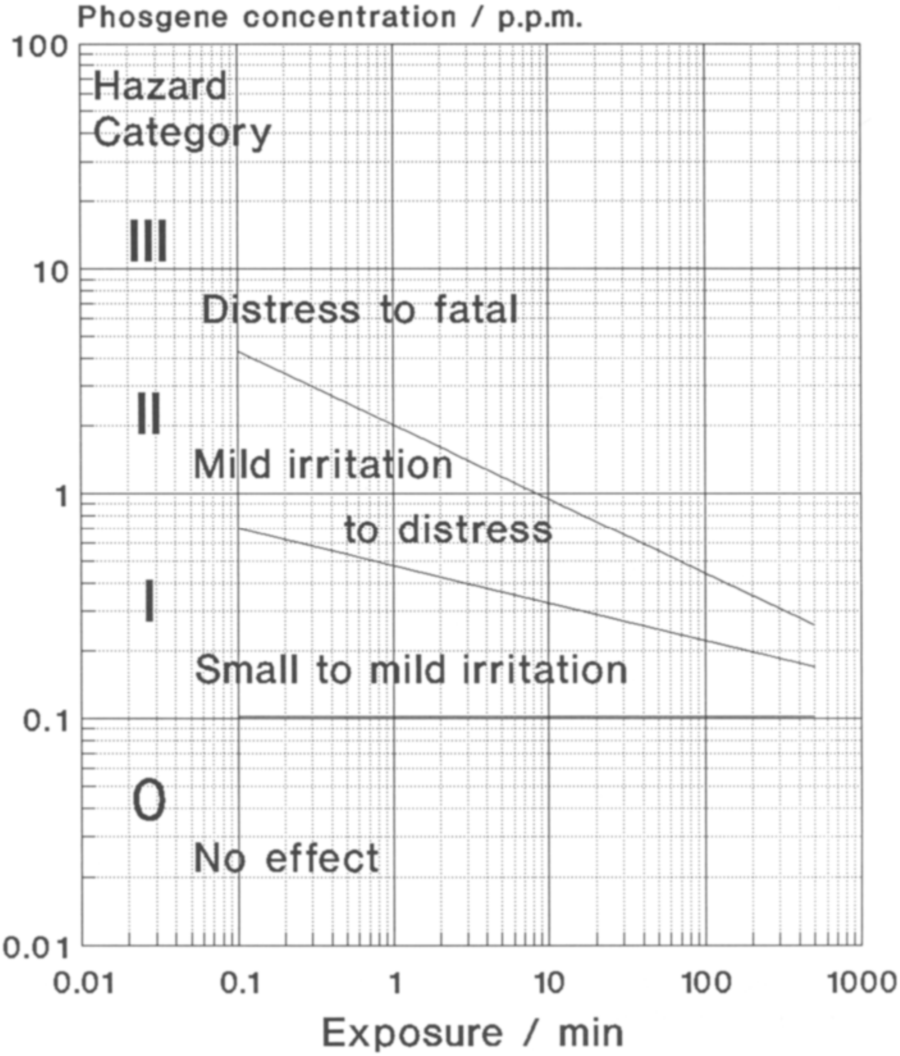


Fig. 3.3 Hazard categories for the effects of phosgene exposure [ICI59].

20 °C, a ¼" (6 mm) hole would give a leakage rate of 3600 kg h^{-1}, whilst a 1" hole would provide 57500 kg h^{-1} [ICI60].

3.6.3 Description of the vaporization process

The gas-forming processes resulting from the discharge of a large quantity of liquid phosgene can be summarized as follows:

(a) Adiabatic evaporation for $T > T_b$

(b) Aerosol formation and gradual gasification of droplets

(c) Boil-off from the underlying surface

(d) Evaporation resulting from vapour diffusion

Adiabatic vaporization of phosgene occurs when the temperature of the discharged liquid is above its boiling temperature (8.3 °C). The amount of liquid that is vaporized depends upon the temperature at which the liquid was held before its discharge (Table 3.11) [557].

Owing to the relative closeness of the boiling point of phosgene to ambient temperatures, phosgene has a low adiabatic vaporization compared, say, to chlorine. However, although the total quantity of gas generated by this process is small, the emission is rapid and can give rise to high concentrations of the gas within a short period of time [557,ICI61]. The adiabatic flashing fraction at 20 °C is about 5% (see Table 3.11).

Following the discharge, the temperature of the liquid falls to the boiling point. Depending upon the outflow rate and the shape of the orifice from which the discharge occurs, a varying quantity of droplets of different sizes is formed. The smaller of these droplets may be carried on the prevailing wind as an aerosol. Generation of vapour in accordance with processes (a) and (b) occurs at a constant rate, as long as liquid is discharging from the container.

The liquid remaining after adiabatic vaporization and aerosol formation will form a pool of liquid on the surface of the ground adjacent to the leak. If the temperature of the surface is in excess of the boiling temperature of phosgene, then the liquid will start to boil. The amount of material then vaporized depends upon the nature of the surface and the area of the liquid pool – which in turn depends upon the slope, the ground roughness and porosity, and the presence of embankments or other obstacles. When heat is supplied from the ground, gradual cooling of the underlying surface takes place and boil-off eventually ceases when temperature equilibrium is established. The degree of vaporization by this process depends upon the ground temperature. Since there is usually only a small difference between the ground temperature and the boiling temperature of the phosgene, the average boil-off is low at ambient temperatures, Table 3.12 [557], compared to that for more volatile materials.

TABLE 3.11

THE EFFECT OF TEMPERATURE UPON THE ADIABATIC VAPORIZATION OF LIQUID PHOSGENE [557].

T/°C [a]	Extent of Vaporization / %
8.3	0
10	0.7
15	2.7
20	4.7
25	6.7

[a]Temperature of liquid prior to discharge.

Generation of gas by this method provides a long-lasting source of emission, which reaches a maximum rate immediately following the discharge. Obviously, if the pool comes into contact with a hot surface, such as an item of operating plant equipment, then gasification can be enhanced considerably. If the ground temperature is below 8.3 °C, or when boil-off stops, vaporization of the pool still occurs, as a result of air flowing over the pool surface, by the heat supplied by the atmosphere, and by direct radiation. Gas generation resulting from evaporation by vapour diffusion/dispersion at 0 °C and with a wind velocity of 5 m s^{-1} is comparable with that resulting from boil-off with the ground temperature at

TABLE 3.12

AVERAGE BOIL-OFF RATES FOR PHOSGENE FROM UNDERLYING CONCRETE [557]

	Average Boil-Off Rate/kg m^{-2} min^{-1}		
	Time Interval		
Ground temperature/°C	0-2 min	2-10 min	10-60 min
10	0.037	-	0.008
15	0.154	0.073	0.033

15 °C at the start of the process [557].

The continuous rate of evaporation of the pool remaining after initial flashing (in the absence of any spillage treatment) has been estimated [ICI61] to be about 50 kg min^{-1} (28.6 kg m^{-2} h^{-1}) for a ten ton spillage at an ambient temperature of 15 °C, if the assumption is made that the roughness of the ground corresponds to an average depth of 7 cm. Evaporation rates for phosgene from a 6" (15 cm) deep pool at an ambient temperature of 20 °C have been estimated as a function of the time lapsed following the spillage for two wind speeds, Fig. 3.4 [ICI60].

3.6.4 Emergency procedures

Toxic gas emissions in the Works and at the Works' boundary, strictly, are beyond the scope of this book, since their analyses are more far-reaching than those exemplified by a single toxic material. However, it must be emphasized that any facility which handles a sizeable quantity of toxic gas, such as phosgene, should have detailed knowledge of the hazard frequencies for all operations in which the material is involved, and these should be within the currently acceptable levels.

Detailed studies of this kind have been performed in ICI [ICI23,ICI61–ICI64], in which the potential causes, frequencies, and effects of phosgene emissions have been analysed during manufacture, storage, or transportation of the material. It would be inappropriate, however, to describe the detailed results from any one particular installation.

The advanced formulation of emergency procedures has been recommended by NIOSH [1486], and broad measures for dealing with phosgene emissions have been described by the MCA [1318]. Participation in periodic emergency drills has been suggested [1484].

Although major liquified gas emergencies, leading to the emission of toxic gases in quantities likely to affect the public beyond the Works' boundary, have a low order of probability they are not, nor could they be expected to be, impossible. Even the best-managed Works are subject to "Acts of God" – such as floods, storms of unprecedented magnitude, or an aeroplane crash resulting in impact damage to, say, containers of stored material – and to "Acts of Man" – such as terrorist attack.

In the event of a major incident, well-planned emergency procedures should be brought into action involving, as necessary, Police, Fire, Ambulance and Medical Services, coordinated by the Works' Emergency Management, with the primary objective of minimizing casualties [364,ICI23,ICI65,ICI66].

When a large phosgene leak occurs, a white vapour cloud forms which tends to keep towards ground level, owing to the high density of phosgene vapour relative to air. The heavier phosgene vapour gives rise to trapped pockets of the gas in sheltered areas, and although the affected area will be determined initially by the wind direction and the location of the emission source, accurate definition of the contaminated area will only be possible from qualitative observations and from tests carried out by trained personnel. Their responsibilities would be to report their results to a plotter to record the results onto maps of the area, for

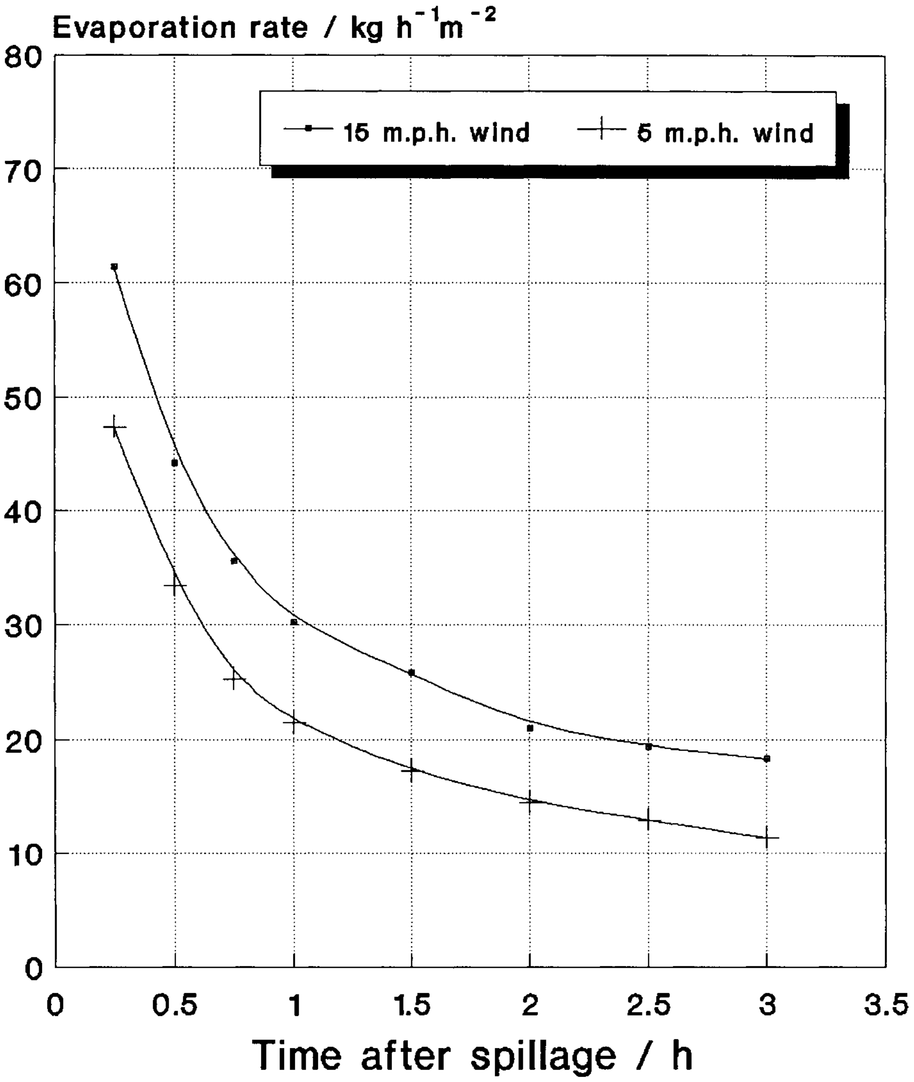


Fig. 3.4 Estimated evaporation rates for phosgene from a 6" (15 cm) deep pool at an ambient temperature of 20 °C as a function of the time lapsed following the spillage for two wind speeds [ICI60].

use by the emergency services whose rôles should be pre-defined. Stocks of emergency equipment, such as civilian respirators, should be held in the event of an evacuation being necessary [ICI65,ICI66].

The behaviour of phosgene gas clouds has been analysed, and recommendations of action made on the basis of these and other gas cloud releases [939]. Flight at right angles to the wind direction is considered to be a reasonable evasive action if out of doors, and it is advisable to install a wind sock or weather vane in a prominent location [1318]. Deep breaths should not be taken and, if indoors, the shutting of doors and windows can provide adequate protection. Phosgene cloud lengths and widths (defined for a tolerable limit of 5 p.p.m.) have been correlated as a function of the emission rate (both sudden and steady) for a series of wind speeds and atmospheric conditions (sunny, neutral, or inversion), following a simulated spillage of 150 tons of phosgene at 20 °C [ICI60].

3.7 ENVIRONMENTAL CONSIDERATIONS

This section is mostly concerned with the presence of phosgene in the atmosphere, its formation and removal in both the troposphere (lower atmosphere) and stratosphere (upper atmosphere) and its possible effects on that part of the stratosphere known as the ozone layer.

3.7.1 Phosgene in ambient air

The following discussion considers the sources of formation of phosgene, and its removal, in the lower atmosphere, a subject which has been recently reviewed by Helas and Wilson [932b].

Although constituting a significant indoor problem, direct emissions of phosgene are unlikely to present a significant contribution to environmental concentrations. Whilst mass incineration of chlorinated hydrocarbons and polymers, for example in waste incinerators, may contribute somewhat to the atmospheric burden (Section 3.3.5), photochemical oxidation of chloroalkanes, particularly $CHCl_3$ and CH_3CCl_3, and chloroethenes, particularly C_2Cl_4 and $CHCl{=}CCl_2$, is of much greater significance. Other sources of phosgene emission have been described in Section 3.3, and accidental releases have been described in Section 3.6. Probably the most direct, natural source of phosgene in the troposphere arises from volcanic activity [1990a], although calculations show that the dominant chlorine-containing species in volcanic gases is HCl, and that the phosgene concentration is at least 15 orders of magnitude lower than this. It is considered unlikely that phosgene is generated from fluorine-containing halocarbons (such as CFC-11 and CFC-12), as a result of the stronger C-F bond relative to the C-Cl bond, which leads invariably to the preferential cleavage of such molecules into chlorine atoms [932b,2196a].

Although phosgene is undoubtedly a photolysis product of a number of commodity chlorinated hydrocarbons, the quantity of phosgene formed in the atmosphere, and the relative importance of the various sources, is difficult to assess [2088b]. Phosgene is likely to be formed in the lower atmosphere from the attack of [OH]· radicals on $CHCl_3$, CH_3CCl_3, C_2Cl_4, $CHCl{=}CCl_2$ and CH_2Cl_2 (with a smaller source arising from the transport of stratospheric air through the tropopause) [932b]. Although such reactions take place throughout the troposphere, maximum reaction rates will occur near to the Earth's surface where higher temperatures prevail. Tetrachloromethane is tropospherically stable [36a] and does not contribute to phosgene formation in that part of the atmosphere (see Section 3.7.2). An attempt to quantify the contributions to these various sources has been made, and possible formation pathways for phosgene from both CH_3CCl_3 and $CHCl{=}CCl_2$ have been proposed [932b]. The relatively slow reaction rate of [OH]· with the chloroalkanes results in residence times sufficiently long for material to be transferred into the stratosphere, and leads to even distribution throughout the troposphere, thus acting as a non-localised source of phosgene.

In Darmstadt, Germany, phosgene concentrations in the urban air were noted to vary between about 50 and 500 p.p.t. (v/v) [695a]. Daily maxima and night-time minima were realised. Later studies in the same locality revealed the concentrations of phosgene in air to be in the range of 8 to 87 p.p.t., with night-time concentrations determined to be up to 143 p.p.t. [98a]. Measurements (over 24 h) of the ambient phosgene concentration at four Californian locations (urban and non-urban) have been carried out using gas chromatographs equipped with electron-capture detection [1886,1889]. The mean concentration of phosgene for the (clean air) rural areas was 21.7 p.p.t., whilst for the urban areas the average was 31.8 p.p.t. The maximum value recorded by the researchers (61.1 p.p.t.) was measured within urban Los Angeles. In a related study [1890], at a further Californian location, a phosgene concentration of 50 p.p.t. was measured. This concentration was calculated to be equivalent to a daily dose rate of about 5 μg for a human male of 70 kg weight. It has been suggested that the photo-oxidation of the chloroethenes, C_2Cl_4 and C_2HCl_3 (see Section 3.3.3.2), is most probably responsible for the presence of phosgene in air, since these materials are commonly emitted in urban areas. The relatively small difference (about 50%) in phosgene concentrations between the urban and rural sites compared to a large (twenty-fold) difference in chloroethene concentrations was taken as an indication of the relative stability of phosgene in the troposphere, permitting the wide distribution of the precursor materials in the atmosphere before appreciable photo-oxidation can occur. It has also been suggested that, under adverse atmospheric conditions, high concentrations of phosgene could be encountered around urban centres [1889]. From an estimated release of 1.5×10^6 tons of chloroethenes per year, phosgene formation could amount globally to an annual total of 300,000 tons [1886]. Other estimates, which include sources based upon $CHCl_3$, CH_3CCl_3 and CH_2Cl_2, in addition to $CHCl{=}CCl_2$ and $CCl_2{=}CCl_2$, arrive at a total annual source strength of 1.2×10^6 tons of phosgene. It has been suggested that tobacco smokers may face an additional exposure risk to phosgene, particularly in urban areas, since chloroethenes can be thermally decomposed to $COCl_2$, and are often present at concentrations of up to 200 times the ambient phosgene concentration (see Section 3.3.3.1, however) [1886].

Data concerning the environmental distribution of phosgene are not available.

However, phosgene is a gas at temperatures above about 8 °C, and it has a density similar to air; it is also relatively stable and it may therefore be expected that phosgene can be transported over considerable distances in the environmental air. From the knowledge of the kinetics of hydrolysis of gaseous phosgene (see also Section 9.10.3.1), carried out in the temperature range of 260–350 °C, the rate constant for reaction (3.16):

$$COCl_2 + H_2O \longrightarrow CO_2 + 2HCl \tag{3.16}$$

was found to be given by the Arrhenius expression [313]:

$$k = 9192\exp(-7140/T)\ \mathrm{l\ mol^{-1}\ s^{-1}}$$

Although this hydrolysis study is far removed from conditions relevant for the atmosphere, and interpolation to ambient temperature cannot be regarded as reliable, the half-life of phosgene (at a concentration of 1 p.p.b.) at sea level (25 °C; 1 atmosphere) calculated from this equation was estimated to be 113 years [313,1913]. Another source estimates the residence time of phosgene in the troposphere as a few days [932b], although this figure increases considerably above the cloud layer. Yet another source has estimated the tropospheric lifetime of phosgene as being a few months [98a]. It must be concluded that the half-life of phosgene in the atmosphere, or its atmospheric lifetime, is not known with any certainty. Whatever the precise value, it is unequivocal that the rate of hydrolysis of gaseous phosgene in the atmosphere is low. Thus, in the absence of its removal in the lower atmosphere, it was concluded that phosgene could constitute a potentially detrimental effect on the stratospheric ozone layer (but see below) [313,1913]. Under the typical stratospheric conditions of 220 K, 6.67 kPa and 1 p.p.m. water vapour, the half-life of phosgene at the 1 p.p.b. concentration level is estimated to be 8.2×10^{10} years [1913].

Phosgene is removed only slowly from the atmosphere, and tropospheric removal of phosgene through gas-phase hydrolysis, photolysis, or from gas-phase reactions involving $O\cdot$ or $[OH]\cdot$ radicals are clearly insignificant: electronically excited oxygen atoms $O(2\,^1D_2)$ are quenched by phosgene with an absolute second-order rate constant (at 300 K) of 7.1×10^{-10} $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ [660]. However, the principal atmospheric sinks for phosgene [1886] are heterogeneous decomposition (through contact with surfaces) and liquid phase hydrolysis (particularly within clouds). The first of these sinks is confirmed by the observation that phosgene in low concentrations could not be measured in indoor spaces. The second sink was indicated by the observation that overnight rain causes a 20% reduction in the average phosgene concentrations. Slow dissolution into water sources, followed by hydrolysis, is therefore a significant sink for ambient phosgene. Measurable amounts of phosgene have not been found in water, because of its ultimate irreversible hydrolysis following dissolution. For similar reasons, phosgene is not expected to be present in detectable quantities in soil, sediments, plants or animals. However, a reduction of amenities results from the detection of a faint odour in water at a concentration of 4.4 mg m^{-3} [2112].

Because of the existence of these tropospheric sinks, phosgene is unlikely to have a detrimental effect on the stratosphere [1889], such as the depletion of the ozone layer (but see Section 3.7.2). However, the precise fate of phosgene in the troposphere is closely linked to the water cycle, particularly the presence of clouds and their type of behaviour.

3.7.2 Phosgene in the stratosphere

An understanding of the sources and ensuing reactions of chlorine-containing compounds in the stratosphere is essential for the evaluation of their impact on the ozone layer. Whilst phosgene should be largely removed in the troposphere, it is anticipated that only slow photolysis will occur in the stratosphere.

The two most probable loss processes of phosgene in the stratosphere are photolysis, and transport into the troposphere. Phosgene can be formed *in situ* in the stratosphere [36a], and indeed it is one of the main photo-oxidation products in the upper troposphere and lower stratosphere from the breakdown of chlorinated hydrocarbons (of both natural and anthropogenic origin). For example, the relatively inert tetrachloromethane accumulates in the air, but can photodissociate in the stratosphere according to:

$$CCl_4 + h\nu \longrightarrow [CCl_3]\cdot + Cl\cdot$$

$$[CCl_3]\cdot + O_2 \longrightarrow COCl_2 + [ClO]\cdot$$

$$COCl_2 + h\nu \longrightarrow CO + 2Cl\cdot$$

It is likely that this dissociation takes place in a region where the resulting chlorine atoms are effective in depleting the ozone. Since phosgene absorbs u.v. light more strongly than CCl_4, the ensuing photolysis of the phosgene means that all four of the chlorine atoms originally present in the CCl_4 are released into the stratosphere in the location of the initial photolytic dissociation [36a]. Although CCl_4 has a marked effect as a pollutant on atmospheric ozone, it does not pose a considerable threat because emission rates of CCl_4 are relatively small compared to those for chlorofluorocarbons [36a], and it is now a regulated substance under the terms of the Montreal Protocol.

Recent measurements [2196a] taken during several flights between Germany (50° N) and Spitzbergen (78° N) showed an average concentration of phosgene of 17 p.p.t. in the upper troposphere and 22 p.p.t. in the lower stratosphere. These values, although comparable with those found in rural areas in ambient air (see Section 3.7.1), are substantially larger than those estimated with a model that only considered the formation of phosgene *via* the photolysis of tetrachloromethane [432a], indicating, perhaps not surprisingly, that other reactive chlorocarbons (such as $CHCl_3$, CH_3CCl_3, $CHCl{=}CCl_2$ and $CCl_2{=}CCl_2$) or their oxidation products may take part in supplying chlorine to the lower stratosphere, or that processes (such as hydrolysis) which could be considered to act as a sink for phosgene removal, are not sufficiently effective to stop the transport of phosgene into the stratosphere. Based upon these observations [2196a], it was considered that other chlorocarbon species such as CCl_3CHO, CCl_3OONO_2, $CCl_3C(O)OONO_2$, CCl_3OOH and CCl_3CH_2OOH might also be present in the lower stratosphere [2196a]. These compounds are anticipated photo-oxidation products of CH_3CCl_3.

Abstraction of a hydrogen atom from the trichloromethane molecule by [OH]· radicals results in the formation of a $[CCl_3]\cdot$ radical, which reacts with dioxygen to form phosgene and [ClO]· [36a,1926a]. This process is considered to occur in those regions of the atmosphere where there is little ozone available for destruction, so that before ozone is properly encountered the [ClO]· will be reduced to Cl·, which will be converted to HCl by abstracting a hydrogen atom from, say, methane. Less is understood about the fate of the phosgene generated from $CHCl_3$, however. If it were to migrate to a region of the atmosphere where the ozone concentration is high, then its ensuing photodissociation would contribute to ozone destruction [36a].

Phosgene is the main oxidation product of dichloromethane, resulting from the abstraction of the molecule's two hydrogen atoms. Further photolysis could lead to chlorine atoms being produced in the atmosphere [36a, 1926a]. Further research in this area is clearly warranted.

The photo-oxidation of trichloroethene and of tetrachloroethene to phosgene, in addition to other compounds, has been demonstrated experimentally (see also Section 5.2) [49,72,725]. Photo-oxidation in air, by ultraviolet radiation in the presence of NO_2, resulted in the conversion of 66% C_2HCl_3 and 7% C_2Cl_4 after 140 min of u.v. exposure to give phosgene concentrations of 0.47 and 0.12 p.p.m. (see Section 3.3.3.2) [725]. A combination of phosgene and NO was noted to increase the photochemical decomposition rate of $CHCl{=}CCl_2$ [533]. Phosgene is also formed as a minor product from the attack of oxygen atoms, hydroxyl radicals or ozone molecules on the double bond of tetrachloroethene [36a]: the major oxidation product is trichloroethanoyl chloride. Owing to the long lifetime of C_2Cl_4, it is possible that the material may reach the tropopause and cross over into the stratosphere, permitting the oxidation products to possibly reach the ozone-rich regions, where they could break down into chlorine atoms [36a]. In contrast, trichloroethene has a half-life of less than a day in the troposphere. Dichloroethanoyl chloride and phosgene are the principal oxidation products, and the ultimate effect upon the ozone layer will depend upon how quickly these can be removed [36a].

The main pathway for the removal of phosgene in the stratosphere is expected to be *via* its photolysis, ultimately to ClO_x and CO_2 [2196a]. Some u.v. spectroscopic studies [1444] indicate that this reaction occurs at lower energies than those required for the dissociation of CFCs, suggesting that phosgene photolysis can occur at a lower stratospheric altitude. In this region of the spectrum, it was concluded [2196a] that phosgene (formed as a reactive intermediate) is probably the largest (and a significant) source of $[ClO_x]\cdot$ (x = 0, 1 or 2) radicals, which are involved in ozone destruction cycles.

It is anticipated that further environmental research will lead to a satisfactory resolution of the seemingly conflicting statements in the literature concerning the effect of phosgene on the ozone layer.

4 INDUSTRIAL MANUFACTURE AND USES

Phosgene is a well established article of commerce. This Chapter deals with the synthesis of this compound on the multi-ton scale, and includes a treatment of its subsequent purification and storage: effluent treatment is highlighted, and other commonly used engineering practices are discussed. In addition, the process technology currently available for license [64,64a] is described, along with typical product specifications. The Chapter concludes with an overview of the most common industrial uses, providing a guide to both current and future areas of application.

4.1 INDUSTRIAL MANUFACTURE

The earliest methods for the manufacture of phosgene were based upon John Davy's original procedure of exposing a mixture of carbon monoxide and dichlorine to sunlight [577]. Later methods (used to a limited extent in Italy and France during World War I) involved the oxidation of tetrachloromethane or hexachloroethane with sulfur(VI) oxide or fuming sulfuric acid (see Chapter 5) [577,1778]. Alternative methods proposed for the manufacture of phosgene, but which have not been commercialized, are described in Chapter 5.

The modern industrial preparation of phosgene has not changed significantly since the 1920s. It is based on the reaction:

$$CO(g) + Cl_2(g) \longrightarrow COCl_2(g); \qquad \Delta H \hat{=} -108 \text{ kJ mol}^{-1}$$

Basic patents for the manufacture of phosgene from CO and Cl_2 have thus long since expired, and current commercial process design is based on proprietary information, although process improvement patents may still be in force. General reviews of the industrial manufacture of phosgene can be found in Kirk-Othmer's Encyclopædia of Chemical Technology [884,885], Ullmann's Encyclopædia of Technical Chemistry [2215], and elsewhere [1768], whilst early industrial manufacture is described adequately by Sartori [1778]. Different plants operate different variations of the same process, so in this Chapter operations are described that are common to most manufacturing methods. No attempt is made to consider the economics of phosgene production, which will vary enormously from manufacturer to manufacturer, not least depending upon the available source of carbon monoxide, and the purity of product required.

The process comprises the preparation and purification of the raw materials, carbon monoxide and dichlorine, the metering and mixing of these materials, the reaction of the

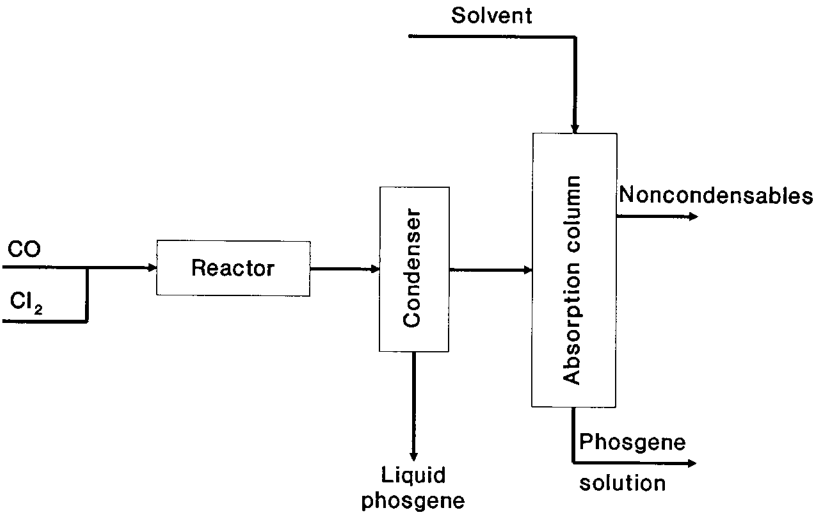


Fig. 4.1 **A flow diagram for the manufacture of phosgene from carbon monoxide and dichlorine [885].**

mixed gases over activated charcoal, and the purification and condensation of the phosgene product. A flow diagram of the process is illustrated in Fig. 4.1. Early, now obsolete, methods of carrying out these processes are described elsewhere [577,1291].

The process is normally operated on a continuous basis, employing a high degree of automation. Owing to the toxicity of phosgene, extensive safety features are an integral part of the plant design.

4.1.1 Raw materials for phosgene production

4.1.1.1 Carbon monoxide

Carbon monoxide may be prepared in a variety of ways, for example by the reduction of carbon dioxide over coal, by the controlled oxidation, or steam reforming, of hydrocarbon fuels (such as natural gas or naphtha), or by the controlled air oxidation of coke [884,885]. The carbon monoxide for phosgene preparation must be of a high degree of purity, and the last method of CO production (from producer gas), in which the CO concentration is fairly low, cannot now be regarded as suitable for a modern process, although it formed the basis of an early method of manufacture of phosgene, referred to as the "dilute" process [ICI72].

Carbon dioxide is removed from CO streams by amine (*e.g.* ethanolamine) scrubbing, and high concentration CO for $COCl_2$ manufacture can be obtained from absorption of CO-containing streams into ammoniacal copper(I) solutions under pressure. The CO is recovered by then reducing the pressure and heating the copper liquor [ICI67]. Alternatively, CO and H_2 can be separated cryogenically.

In particular for liquid phosgene production, noncondensable impurities should be avoided, since their presence causes poor condenser efficiency and difficulties in recovering phosgene [577,663,885]. In addition to the above methods, the carbon monoxide used for phosgene manufacture may be a by-product of other manufacturing processes. One early method, for example, utilized CO generated from the manufacture of calcium carbide (carbide furnace gas) [ICI64].

Water must be eliminated from the carbon monoxide (for example by passage over molecular sieve adsorbers) prior to its entry to the reactor, in order to avoid the hydrolysis of the phosgene and the formation of corrosive hydrochloric acid [555]. The concentration of dihydrogen and of hydrocarbon in the CO should be kept to a minimum, since reaction of these materials with dichlorine could ignite a reaction between dichlorine and the mild steel construction of the primary reactor, in addition to forming hydrogen chloride and chlorinated hydrocarbon impurities (methane, for example, forms tetrachloromethane). Other impurities may poison the catalyst (causing it to become irreversibly inactive). Sulfide impurities should be excluded, owing to the potential of generating undesirable sulfur chlorides; these compounds produce objectionable odours in some of the phosgene derivatives such as the organic carbonates [ICI69]. Sulfur-based stenching agents added deliberately to the carbon monoxide (to permit the detection of leaks) can be used, but only at such low concentrations that they contribute little by way of contamination to phosgene and its end products [ICI70].

A typical specification analysis for carbon monoxide for use in a modern phosgene plant is given in Table 4.1 [311a].

TABLE 4.1

A TYPICAL SPECIFICATION FOR CARBON MONOXIDE SUITABLE FOR PHOSGENE SYNTHESIS [311a]

Compound	Concentration/% vol
CO	99.0
CH_4	0.1
CO_2	0.4
H_2	0.5

4.1.1.2 Dichlorine

The dichlorine used for phosgene manufacture must be of a high degree of purity (*ca.* 99.8% [823b]). In particular, it must be dry and free of dihydrogen (to prevent corrosion), and free of dioxygen (to prevent burning of the carbon monoxide or the charcoal catalyst)

[ICI68,ICI71]. Interestingly, no hydrogen chloride was produced below 70 °C, when dihydrogen was present in the carbon monoxide, although the yield of HCl increased greatly at 90 °C [89].

Manufacture of dichlorine is generally by the electrolysis of brine, although electrolysis of aqueous HCl or catalytic oxidation of dry HCl may be employed [2165]. As mentioned above, complete reaction of the dichlorine must be ensured, as this is an undesirable impurity in the phosgene product [437,1488], particularly where the material is to be used for high specification polycarbonates or isocyanates.

Substantial removal of dichlorine from phosgene can be accomplished by adsorption onto activated carbon. The Cl_2 (adsorbed onto the carbon in quantities of up to 16% at about −5 °C) may then be recovered, and re-used by regenerating the adsorber with hot carbon monoxide for phosgene recycle to the process stream [499]. One patent describes the removal of dichlorine from phosgene by contacting the liquid product with a hydroxyaryl compound, such as 4,4'-dihydroxydiphenyl, at temperatures below about −10 °C. Phosgene, substantially free from dichlorine, can then be separated by vaporization [239a].

4.1.2 Mixing and metering

The metering operation is considered to be critical with regard to the economics of the plant. If the metering of the reactants is not controlled within precise limits, then excess of carbon monoxide must be used to prevent dichlorine contamination of the final product. This is wasteful not only of carbon monoxide, but also of phosgene product in the condenser off-gas stream, which additionally places an increased load on the scrubbing system [1032]. Metering equipment is considerably simplified if the reactants are dry and free of suspended solids. Drying and filtering equipment are routinely available.

The mixing ratio of the reactants is either analysed constantly, or regulated manually or automatically. However, since the CO quality may vary within limits, it is recommended that the CO excess in the phosgene be monitored continuously, for example by infrared analysis. The measured variable may then be employed to automatically correct the mixing ratios.

The mixing of the reactant gases can be easily and efficiently carried out using a small cylinder containing two or three diaphragms in series, and perforated with a number of holes, as illustrated in Fig. 4.2 [1291]. Alternatively, the gases can be mixed by passing over a coke-packed tower [ICI69], or simply over stoneware Raschig rings.

4.1.3 Reactors

Carbon monoxide and dichlorine are mixed in stoicheiometric proportions, but the CO may be employed in slight excess, to ensure complete reaction of the dichlorine: the unreacted CO may be recycled to the reaction zone [1533].

After mixing, the gases are passed to the primary reactor (usually of steel or lead-lined construction) containing the activated charcoal catalyst. In normal circumstances,

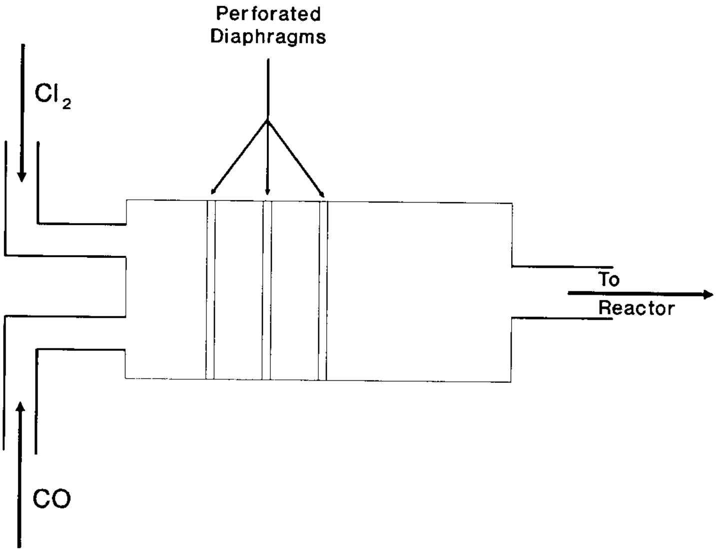


Fig. 4.2 Simple gas mixing equipment [1291].

better than 99% of the dichlorine is converted to phosgene at this stage of the process. Gas leaving the primary reactor then passes to a secondary reactor, whose purpose is to complete the conversion of CO and Cl_2 into phosgene. The secondary reactor, also containing activated charcoal, is commonly uncooled, since much less heat is generated at this stage owing to the relatively small concentrations of remaining reactants.

The converters used for phosgene production are normally of simple design, consisting of tubular heat exchangers to remove the heat formed from the reaction. The reaction normally operates at atmospheric pressure, although at higher pressures (2–12 atm) smaller reaction vessels may be used, liquefaction for shipment is unnecessary, and the output for a given mass of catalyst is increased [285].

The temperature profile along the reactor bed may range from a maximum 500 °C close to the reactor inlet, down to around 150 °C at the exit to the catalyst bed: hot-spot temperatures can reach 600 °C [ICI68]. The exit gas temperature may reach up to 200 °C [ICI69]. The cooling water flow rate is carefully monitored, since its failure could result in severe corrosion as a result of temperature runaway. A temperature alarm, fitted to the jackets, is employed, and is commonly set at around 40 °C.

4.1.4 Scrubbers

The gaseous phosgene product is condensed, and the uncondensed material is solvent-scrubbed to remove the remaining phosgene (although for subsequent "in-line" operations, uncondensed gaseous phosgene can be employed). Where the phosgene is scrubbed with solvent, the resulting solution can be used in the subsequent process. Alternatively, unconsensed $COCl_2$ may be passed into activated charcoal adsorbers; preferential adsorption of phosgene occurs and the inerts pass to the destruction system [ICI69]. When saturated, the adsorbers are regenerated by heating with high pressure steam, and the gases are pumped off through a filter packed with quicklime to trap moisture and charcoal dust [ICI69].

Finally, the product gases remaining after condensation and absorption are scrubbed to destroy any remaining phosgene (see Section 4.4.2). Process emissions of phosgene during its manufacture are routinely routed to a caustic scrubber, where the material is destroyed quickly and completely. The sodium hydroxide concentration should be maintained at between 3 and 8% w/w, care being taken not to allow the product sodium chloride and sodium carbonate to precipitate and clog the scrubber [1116].

Estimations of phosgene emissions have been made for a large hypothetical plant producing 200 Mlb (90718 tons) per year [2088b]. The total phosgene emission of about 210–3150 kg comprises 136 kg arising from the process vents, 54–2994 kg from fugitive emissions (for example from leaks in the various valves, pumps and other equipment) and 23 kg resulting from process upsets. These figures give a phosgene emission factor of 0.002–0.034 g kg^{-1} [2088b]. Similar estimates have been made for the phosgene released during TDI (0.0012–0.014), polycarbonate (0.00055–0.0062), and herbicide and pesticide manufacture (0.00055–0.0064 g kg^{-1}) [2088b]. As expected the major source of phosgene emission is during its production rather than in its utilisation.

4.1.5 Catalysts for the industrial manufacture of phosgene

Carbon monoxide and dichlorine do not combine together unless the reaction is activated by some external agent such as ultraviolet radiation (see Chapter 5) or a suitable catalyst. Early manufacture of phosgene was carried out by passing the CO and Cl_2 reactants into enormous glass balloons exposed to the sun but, owing to the generally impractical nature of employing sunlight or other sources of UV radiation in industrially operated processes, catalysts are now universally employed for phosgene manufacture [515].

According to Atkinson *et al.*, highly active charcoal effects the conversion of a mixture of CO and Cl_2 at a temperature below 50 °C [89]. Other workers, however, have found that commercial charcoals, supplied for phosgene manufacture, do not catalyse the CO/Cl_2 reaction, even at temperatures as high as 100 °C. After treatment with dichlorine the catalyst was active above 80 °C [ICI72].

Catalysts for the large-scale industrial synthesis of phosgene are invariably composed of activated charcoal of high adsorptive capacity [885], and there is usually no need to treat the material with metallic salt or other commonly used activating substances in order to improve its adsorptive efficiency. The activation treatment may be achieved with an oxidising gas at elevated temperature, resulting in the removal of a fractional portion of the material, to leave behind a highly porous surface of high surface area. The phosgene manufacturing process is normally and advantageously operated by passing the mixed gases over a fixed bed [515] of material, so that the charcoal is normally in the form of granules to allow the flow of gases to be uninhibited. The purity of the feed gases should be such that the catalyst is not readily poisoned, and under these circumstances a high catalyst efficiency can be obtained. Indeed, the catalyst charge will usually convert efficiently (for example, 2–5 tons of phosgene generated for 1 kg of catalyst consumed) until the feed gas impurities render it chemically inactive, or physically block the free passage of reactants and product [1032,ICI64]. Much larger conversions may be obtained where pure feeds are employed [89]. In a modern plant the usage of catalyst may correspond to as little as 80 g of catalyst per ton of phosgene, and the reaction can be made virtually quantitative when suitable flow rates of carbon monoxide and dichlorine are used. In addition, if the dichlorine contains an appreciable quantity of dioxygen, as may be the case for liquid chlorine tail gas, the catalyst may burn under the process operating conditions [ICI71,ICI73]. Iron(III) chloride contamination is a common cause of catalyst fouling [ICI69]. Catalyst performance is commonly monitored by analysis of the exit gases for dichlorine [ICI69], and when the activity of the catalyst is sufficiently decreased it can be reactivated by heating to 550–630 °C [2215,ICI69].

The reaction between carbon monoxide and dichlorine over activated charcoal is very fast (see Chapter 5) and generates a large amount of heat (*vide supra*). Because the granular charcoal catalyst is a poor conductor of heat, phosgene tends to be formed faster than the heat can be removed. Unless this heat is removed sufficiently rapidly (for example, by diluting the catalyst with an inert and conducting filler, such as graphite, or by diluting the reactant gases with an inert gas, the phosgene will tend to dissociate to the starting materials [1032].

Charcoals of various origin (vegetable [2008] or animal [25]) may be employed as catalysts for the production of phosgene. These include, *inter alia*, coal, wood, peat, coconut, and bone charcoal. Coconut charcoal is a particularly favoured and readily available material, although the final choice of catalyst will depend on local factors best known to the particular manufacturer. Their activation (*vide supra*) generates material of high surface area (commonly 1000–1200 m^2 g^{-1} [1765]), and it is this large surface for gas contact that gives the charcoal such high catalytic activity. Fresh charcoal must be dried before operation, and the charcoal is then conditioned for a period of time by slow passage of reactants into the reactor. The manufacture of charcoals suitable for phosgene production has been well described [1025], and will not be repeated here.

The sorption properties of phosgene on charcoals has been described in Section 4.4.

Other materials proposed to effect the reaction of Cl_2 with CO include a catalyst prepared from the heating of natural magnesite (magnesium carbonate) at 400–500 °C [689].

4.1.6 Plant operating requirements

Operating requirements typical of those required for the production of phosgene in a modern plant are given in Table 4.2 [311a]. In addition, the modern phosgene plant will require manpower provided by shift operators, maintenance workers, laboratory chemists and supervisors.

TABLE 4.2

TYPICAL MODERN PLANT OPERATING REQUIREMENTS [311a,823b]

Raw Material	Quantity (in tons) per ton of phosgene
Consumables	
Carbon Monoxide	0.306
Dichlorine	0.732
Charcoal	0.00008
Sodium hydroxide	For emergency use only
Utilities	
Steam (inc. distillation)	0.15-0.3
Process Water	2-5
Cooling Water[a]	50-60
Power/Refrigeration[a]	150 kW h

[a] The cooling water requirement is reduced, and the refrigeration load is eliminated, if phosgene is fed directly from the reactor without condensation or further purification.

4.1.7 Experimental (model) studies

Catalyst and process optimization studies have been carried out using a laboratory model flow reactor [438]. The optimal temperature, and the temperature gradient, of the reactor were determined for two particular charcoal catalysts and, for given space velocities, the minimum CO excess required for preparation of dichlorine-free phosgene was determined. The flow reactor was filled with charcoal catalyst and surrounded by a thermostatted jacket. Temperature was monitored by thermocouples at different locations of the reactor. The reactor off-gases were analysed by gas chromatography (suitable for the simultaneous determination of dichlorine, carbon monoxide and phosgene, see Section 3.2.5) to determine the reactant conversions under the various conditions.

The dichlorine content of the product gas was noted to decrease with increasing CO excess, and to increase with increasing space velocity. The optimal thermostat temperature to give least dichlorine content (for any particular $CO:Cl_2$ molar ratio, or space velocity) was 150 °C. The Cl_2 content increased with increase in concentration of inert gas, requiring a greater CO excess to obtain the dichlorine-free product. A similar effect is observed when air is added to the reactant mixture, although the temperature is raised (indicating that the carbon catalyst undergoes oxidation, and to a minor extent that CO is oxidized to CO_2). More than 1 or 2% of added dioxygen is considered to induce an unacceptable degree of catalyst loss for an industrial process [438].

4.2 PURIFICATION OF COMMERCIAL PHOSGENE

Phosgene of technical quality can be further purified by repeated fractional distillation [1614]: this procedure removes most of the volatile impurities, notably, dichlorine, and sulfur compounds. Cl_2 can be removed from $COCl_2$ by adsorption onto charcoal (see Section 4.1.1.2) or by contacting with mercury over 24 h [1614]. Alternatively, removal of dichlorine can be achieved using a column containing metallic antimony [998]. Other methods for the removal of small quantities of Cl_2 have employed copper amalgam, or mercury [1964]. For larger (>2%) quantities of dichlorine - ethene, ethyne or 1,3-butadiene may be introduced in the presence of ultraviolet radiation or metallic salt catalysts to scavenge the Cl_2 [781].

In addition, phosgene can be dried by passage over charcoal [614], since the material acts as a hydrolysis catalyst (see Section 9.10.3.1):

$$COCl_2 + H_2O \longrightarrow CO_2 + 2HCl$$

Phosgene may also be dried using the following procedure [770,774]. The technical grade $COCl_2$ is passed through concentrated sulfuric acid, and over phosphorus(V) oxide, before condensing into an ice-salt bath. To remove the volatile impurities, about one-fifth of the condensate is allowed to evaporate and the residue is fractionated under high vacuum until all fractions have the same vapour pressure, corresponding closely to that of pure phosgene (see Section 6.2.1). Phosgene may also be dried using Linde 4A molecular sieve, followed by vacuum distillation [343].

To remove hydrogen chloride from phosgene, the gas is passed at a rate of 2 l h^{-1} through a column containing silver(I) sulfate.

4.3 STORAGE

Phosgene is transported and stored in steel cylinders conforming to rigid design specifications (see also Sections 3.1.5.3 and 3.1.6.3). Suitable cylinders are those that have undergone special hydrostatic testing at 5.5 MPa, with extension rings incorporated to protect the valves. Excessive filling of the cylinders is to be avoided, with allowance made for a suitable vapour space (ullage). After filling, the cylinders must be tested for leaks.

Phosgene may be stored for essentially indefinite periods without loss of quality. Contamination with water should be strictly avoided, however, since this can induce corrosion and generate excessive pressures leading to tank rupture (see Section 3.6.1). The ingress of moisture into storage tanks, or other parts of the plant, such as from a leak in a heat exchanger, can be detected immediately by exposing a zinc wire to the medium. Phosgene is hydrolysed at the wire, and the HCl produced reacts with the zinc causing a change in the electrical resistance of the wire, which is continuously monitored [1265].

Bulk phosgene is kept in underground storage tanks of double shell construction in some facilities [1488]. This provides containment in the event of a leak from the inner wall, and protection from mechanical damage to the outer wall. If the outer shell also develops a leak then the surrounding earth would prevent a large scale release of gas [1488].

Engineering principles for the design of phosgene storage tanks (>1 ton capacity) have been adequately described elsewhere [364]. A typical precautionary measure is to store the liquid phosgene in two pressurized steel tanks, each of which is filled to less than half of their respective capacities. This arrangement permits the transfer of phosgene to either tank in the event of the development of a leak in one of the tanks, or its associated pipework [2088b].

4.4 TREATMENT OF PHOSGENE EFFLUENTS

Owing to its high toxicity, phosgene waste-gas must be recycled, destroyed or, in some way, removed to prevent environmental contamination or hazards to personnel. This Section is concerned with the main methods for chemically removing phosgene from gaseous effluents, the extent to which phosgene is taken up and retained by various sorbents, and the effect of time, temperature, pressure and moisture on the sorption.

NIOSH have recommended the following regulations and procedures for the disposal of waste phosgene [1486]:

- ⊗ Disposal of waste phosgene shall conform to all applicable local, state and federal regulations.
- ⊗ Phosgene shall not be allowed to enter drains or sewers.
- ⊗ Appreciable discharges of phosgene shall be passed through an adequate decomposition system, such as a scrubbing tower utilizing sodium hydroxide or aqueous ammonia solution, or through a sorbent system.
- ⊗ Solid sorbents should be chosen so that desorption of phosgene is unlikely. Heating of solid sorbents should be avoided.

The burning of phosgene is not recommended except as a short-term emergency measure [1318].

4.4.1 Sorption

Various solid adsorbents have been screened for their efficiency in retaining phosgene vapour from a flow of the gas in a dinitrogen/air mixture through a tube packed with the sorbent material [125,1485]. Carbon-based substances, such as activated carbon or carbon fibre, were found to be particularly effective, although certain commercially-produced aluminas or gas chromatographic packing materials (such as Porapak S) were also noted to work well [125,1485]. Phosgene was shown to be effectively retained on an ordinary sand filter [107]. Coked titanium(IV) oxide-containing briquettes have been employed on the semi-technical scale for removal of $COCl_2$ (and Cl_2) from flue gases. An effective composition suitable for the absorption of phosgene (especially in gas masks) has been prepared by mixing hydrated soda-lime, kieselguhr, copper(II) carbonate (or zinc(II) oxide) and sodium hydroxide solution to form a paste, which was then dried, granulated, and screened to size [470,471].

The adsorbents silica gel, alumina, CaX zeolite and activated carbon were examined for their activity to adsorb phosgene [264]. Of these, the zeolite and the activated carbon were noted to be most effective. The carbon material was reported to completely adsorb small traces of phosgene from 1,1,1-trichloroethane upon stirring both adsorbent and solvent at room temperature for about 3 h [264]. Zeolite 13X is recommended for removing phosgene from trichloromethane (chloroform) [302].

Copper-impregnated activated carbon has been noted to be effective for removal of phosgene from air [1620], and activated charcoal impregnated with sodium hydroxide or potassium hydroxide may be used in gas masks as a protection against phosgene [406]. The adsorptive capacity of KOH-impregnated active charcoal for phosgene increases as the loading of KOH increases up to 25%, and then falls off again with increased loadings [452,952]. When water is present in addition to the KOH, the adsorptive capacity is much more marked and there is no falling off after reaching a maximum [952], possibly as a result of improved dispersion of the impregnant over the charcoal surface.

The collection of phosgene onto solid sorbents is not regarded as a satisfactory monitoring method for industrial hygiene applications, since the molecule is not always readily desorbed as the intact entity owing to its high reactivity in the adsorbed state [125,1485]. Indeed, at low pressures, the adsorption isotherm of phosgene on an activated charcoal sample showed some deviation from the desorption isotherm owing to chemisorptive effects [370], and it was observed experimentally that the original carbon weight could not be completely regenerated after adsorbing phosgene at temperatures as high as 350 °C under vacuum. At this temperature, about 1% of the phosgene was firmly retained on the carbon. Strong chemisorption effects were noted for phosgene on other carbon samples [370]. In particular, a sample of activated carbon impregnated with Cu^{2+}, Ag^{+}, and $[CrO_4]^{2-}$ ions was noted to retain 10% of the exposed phosgene after outgassing [370]. This shortcoming, however, does not detract from the use of solid sorbents for the removal of phosgene in protective masks, or related equipment, and most work has been carried out using charcoals, of various origins, since these materials are used both as phosgene synthesis catalysts (Section 4.1.5) and as conventional hydrolysis catalysts. Cardboard-type filtration pads for the removal of phosgene have been prepared containing activated carbon as one of the absorbing components [1661].

Equilibrium sorption of phosgene by Beechwood charcoal was investigated at 18 and

100 °C [298]. The sorption is rapid, with almost all of the gas represented by any particular equilibrium being sorbed within a few minutes. The results of experimentation agree with the Freundlich sorption formula:

$$\frac{x}{m} = ap^{1/n}$$

in which x is the weight of phosgene adsorbed (in g), p is the saturation pressure (in mm Hg), and m is the weight of charcoal employed (in g). The constants a and n have the values 0.235 and 4.33 at 18 °C, and 0.038 and 2.05 at 100 °C, respectively [298]. Equations for the sorption isotherms for phosgene by activated sugar charcoal have been given as follows [74]:

$$a_{20} = \frac{12.529p}{(1+0.0483p)}$$

$$a_{30} = \frac{10.349p}{(1+0.0409p)}$$

$$a_{40} = \frac{8.440p}{(1+0.0345p)}$$

where a_t is the amount sorbed (in mg per g of charcoal) at t °C, and p is the equilibrium pressure (in mm of mercury, between 50 mm Hg and atmospheric pressure) [74]. The sorptive capacities at room temperature and pressure of a range of coconut shell-derived charcoals for phosgene were found to be between 397 and 643 mg of phosgene per g of charcoal [1851]. Isotherms were determined for the sorption of phosgene by an activated coconut shell charcoal in the temperature range of −39 to 200 °C, Fig. 4.3 [ICI74]. The heat of sorption was found by calorimetry to be approximately 420 J g^{-1} for both unused and regenerated material, with an average enthalpy of adsorption, over the stated temperature range of 456 J g^{-1}. At 20 °C, the charcoal initially takes up its own weight of phosgene; the weight of phosgene sorbed, however, gradually increases to its equilibrium value [ICI74].

Room temperature isotherm data for phosgene on activated carbon, and on a series of impregnated activated carbons, have been plotted in the form of the Dubinin-Polanyi equation [370]. The derived experimental and theoretical affinity coefficients were compared in order to assess the degree of chemisorption and physisorption on the various adsorbents [370]. The sorption of flowing phosgene in air has been examined over activated wood charcoal impregnated with zinc(II) chloride [547]. Rates of adsorption and desorption were determined, to aid in engineering design considerations, as a function of charcoal bed length, bed cross-sectional-area, flow rate, influent concentration, temperature, and relative humidity [547]. No marked decrease in phosgene adsorptive power was noted after subjecting active carbon to

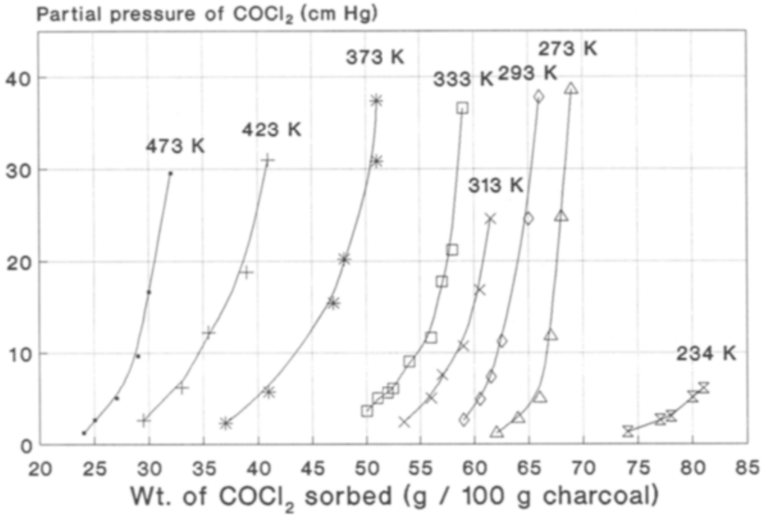


Fig. 4.3 **Isotherms for the sorption of phosgene by an activated coconut shell charcoal [ICI74].**

temperature variations varying from −20 to +60 °C, three times a day, for up to twenty-five days [1675].

Although carbon is especially effective for the sorption of phosgene, periodic replacement of the carbon is necessary, since it has a limited capacity (perhaps due to modification of the carbon surface [867a]). It can be regenerated thermally and then reused, but the regenerated carbon bed has a lower capacity than fresh material, owing to deactivation. For example, fresh, dry bone phosphate of lime (osteolite) carbon was found to have a breakthrough capacity for phosgene of 153.2 mg g^{-1} at 5 °C under a superficial linear air velocity of 17 cm s^{-1}. After eighteen adsorption/desorption cycles, the capacity of the carbon was progressively reduced to 44.6 mg g^{-1}, 35% of the fresh carbon capacity [2164a].

The effect of moisture on the adsorption properties of phosgene on activated charcoal has been examined [115,591,951]. Three phenomena are exhibited during the process; adsorption, capillary condensation, and hydrolysis [115]. The degree to which each are involved varies with water concentration.

The rate of adsorption of phosgene has been examined over a high surface area (1500 m^2 g^{-1}) charcoal. Diffusion to the most accessible part of the surface was reported to occur faster than the observed rate, but more slowly to the less accessible areas of the surface. Both diffusion and surface reaction mechanisms of adsorption are involved in the actual adsorption process [546]. At 25 °C, the observed adsorption rate constant, k_{ads}, is 7.62×10^{-20} cm^3 s^{-1} for the rate equation:

$$\frac{dn}{dt} = k_{ads}c(n_0-n)$$

where dn/dt is the rate of adsorption, c is the concentration, and (n_0-n) is the available free surface of charcoal [546].

4.4.2 Scrubbing

In the direct reaction of phosgene with water, it is usually difficult to achieve the intimate mixing required for effective nullification [1318]. However, phosgene, in a concentration of 25% in air, was reduced to a final concentration of <0.1 p.p.m. using a bubble column water scrubber, in which the bubble diameter was 4–6 mm; the mean gas residence time was 25 s per metre of reactor length, and the liquid:gas volume ratio was equal to, or in excess of, 8:1 [1945]. Alternatively, phosgene may be hydrolysed by bringing it into intimate contact with water through a submerged porous material, such as fritted glass of average pore size 40–60 μm [960].

Leaking phosgene gas can be destroyed by spraying the contaminated zone with large volumes of water. Although the reaction is slow, the excess of water helps to suppress dispersion [1318]. Water should not be sprayed directly onto phosgene cylinders, however, since this may increase the size of the leak as a result of the formation of corrosive HCl [1318,1486].

Phosgene gas may be conveniently destroyed with water in a column packed with activated alumina, activated carbon granules, molecular sieves or anion exchange resins [2206,ICI21]. Hydrolysis of phosgene over a packed bed of activated charcoal is a particularly efficient and economic method of disposal, one volume of activated charcoal being capable of decomposing about 40–70 volumes of phosgene per hour [615,2207]. Sufficient water must flow through the catalyst bed that the concentration of HCl formed by hydrolysis does not exceed 10%, since higher concentrations inhibit the reaction [615,2207]. Active carbons impregnated with NaOH or KOH are effective for phosgene hydrolysis [406], but the consumption of alkali renders this process uneconomic for most industrial purposes [615,2207].

Small quantities of phosgene (*e.g.* <1%) may be conveniently removed from inert gas streams by saturating with water vapour and passing through a column of high surface area active carbon at 25 °C [565aa].

The destruction of phosgene may be accomplished by passage of the gas into a solution of sodium hydroxide in ethanol; the products formed are diethyl carbonate and sodium chloride [2042]. In addition, phosgene has been neutralized by solutions of ammonia or hmt [534], and by aqueous solutions of aniline [327a], but large amounts of phosgene in air are most usually destroyed with aqueous solutions of sodium or calcium hydroxide, or of sodium carbonate [511]. Sodium carbonate solutions have also been used for decontaminating containers used for transporting phosgene [2023].

Traces of phosgene remaining in plant tail gases leaving the scrubbing towers can be destroyed by using 2–2½ times the quantity of gaseous ammonia [ICI75], and some manufacturers are reported to store one ton of anhydrous ammonia for each ton of phosgene [235,318].

Liquid phosgene remaining from experimental work should be allowed to vaporize slowly through solutions of one of the above-mentioned materials [ICI21]. Aqueous solutions of phosgene (*e.g.* from gas bubblers) should be treated in the fume cupboard with an excess of 10% aqueous ammonia (or 15% sodium hydroxide solution), and allowed to stand until all the phosgene has been neutralized before running to drain. Alternatively, it is recommended that phosgene or its solutions can be destroyed by treatment with 15% sodium hydroxide solution and stirring for about one hour at room temperature [1458a]. Following neutralization with hydrochloric acid, the effluent can be disposed to drain.

Solutions of phosgene in water-immiscible solvents should be destroyed with ethanolic ammonia [ICI21]. Decontamination of rubber tubing may be carried out by immersion into aqueous ammonia before disposal [ICI21].

Industrial phosgene waste is handled most effectively by scrubbing with these alkali solutions in a packed column [885], often employing the use of recirculating caustic solution, as illustrated in Fig. 4.4 [2068aa]. However, whilst these materials tend to have a low cost, this procedure has the disadvantage that the alkali is ultimately neutralized and has to be replaced with fresh material. By contrast, one volume of charcoal in the catalysed hydrolysis process is capable of destroying many volumes of phosgene.

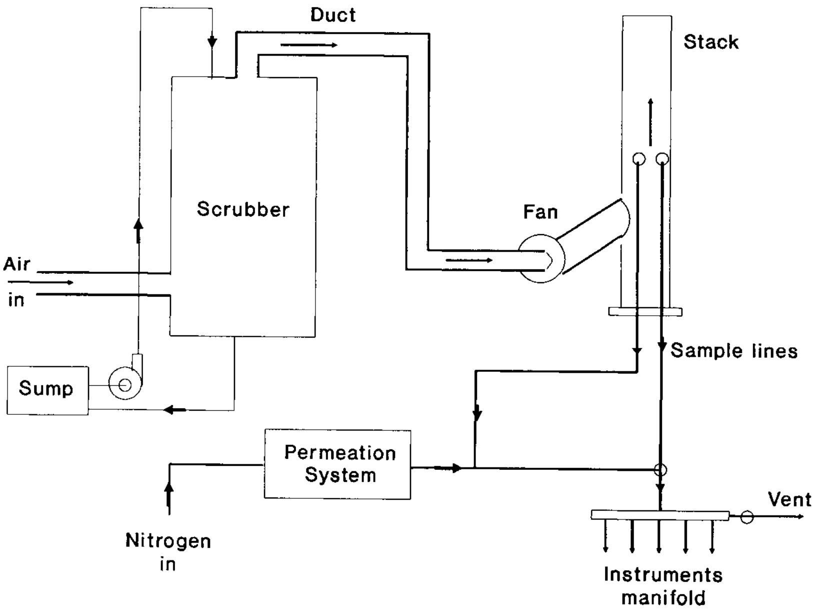


Fig. 4.4 **A scrubber design for the control of phosgene emissions [2068aa].**

It is recommended that any plant which makes or uses phosgene in large quantities should be provided with two separate scrubber systems. A fume scrubber (to handle low phosgene concentrations diluted with a large volume of inerts) and a caustic scrubber (to handle higher phosgene concentrations). The fume scrubber is a general suction service for handling routine, minor leaks. This scrubber is coupled to a ducting system which has feeds from all sections of the plant. The caustic scrubber is an emergency requirement. The capacity must be sufficient to neutralize the contents of the plant, including pipework, other than storage material [ICI23].

The design, testing and performance of a caustic scrubber system for the control of phosgene emissions has been described [1115,1116]. Two counter-current towers, packed with plastic pall rings, were arranged in series, and aqueous sodium hydroxide solution (3-8%) was circulated through the towers using separate pumps. Removal of phosgene was in the range 99.86-99.99%. This design has been employed for the disposal of >1000 tons of phosgene, stockpiled for anticipated military use [1115,1116]. Emergency phosgene destruction plants have also been described in which the phosgene is sucked by ventilators through a tower into which ammonia and steam are simultaneously injected [2215].

Phosgene, dichlorine and hydrogen chloride in waste-gases from the manufacture of aluminium chloride (also see Section 9.4.3) were completely removed by treatment with aqueous acidified iron(II) chloride solution in the presence of activated carbon [1571].

Chlorinated organic solvents can also be used to remove phosgene. In the manufacture of tetrachloroethene by the chlorination of 1,2-dichloroethane, either of these solvents (particularly the dichloroethane) may be used to scrub HCl in order to remove impurity phosgene, as the solvent has a much greater affinity for $COCl_2$ than for HCl [347]. Phosgene is also a common contaminant in by-product HCl resulting from isocyanate manufacture [ICI76,ICI77]. This HCl is frequently used for feeding to other processes, and may require purification, depending upon its intended use. Hydrogen chloride containing >1% phosgene is unacceptable for chloroethene (vinyl chloride) production *via* the reaction of HCl with ethyne (acetylene), since the phosgene acts as a poison to the $HgCl_2$-charcoal catalyst [ICI77]. However, more than 5% of phosgene in HCl can be tolerated in the catalytic oxychlorination of ethene to give 1,2-dichloroethane [ICI76].

The chemical engineering features of the use of organic scrubbing liquids (usually toluene, xylene, chlorobenzene, or 1,2-dichlorobenzene) for phosgene waste-gas scrubbing have been described in terms of the amount and temperature of scrubbing liquid required, the height of the absorber, and the amount of polluting material remaining in the regenerated scrubbing fluid [206].

4.5 ENGINEERING PRACTICES

A code of principles for the siting, safe design, construction and use of phosgene plant has been produced by ICI plc, and published by the Chemical Industries Association [364]. Thus, no attempt will be made here to repeat the details of this Code of Practice, other than in a superficial way. An assessment of engineering controls to reduce worker exposure to phosgene by the use of on-line continuous monitoring equipment has been given by NIOSH [1488]. Five MDA Scientific Model 7020 continuous phosgene monitors (paper tape colorimetric detection, see Section 3.2.3.2.1) were installed at a phosgene – methyl isocyanate production facility, and their effectiveness for the monitoring of phosgene in ambient air was evaluated. Leaks occur during normal operation of the plant units, and the system is designed to sound an alarm in the control room when one of the monitors senses more than 0.05 p.p.m. of phosgene. An assessment of the leak size is then made before further action is taken by the control room personnel. This system was considered to be simple, reliable, phosgene-specific and easy to maintain. The fast response time of the detection method made it particularly suitable for this application.

The chemical engineering features of phosgene waste-gas disposal have been alluded to in Section 4.4.2.

The extensive physical data available on both reactants and products allows engineering calculations to be performed to a high degree of precision, and calculations of the size and efficiency of the equipment required have been performed for a production facility of 50 [1024] and of 200 [1291] tons per week. The detailed design of a phosgene plant will depend upon the local requirements of the manufacturer in terms of quantity needed, source of raw materials, and their likely impurities. Detailed descriptions of the currently employed processes are proprietary information.

4.5.1 Control of hazards

Unquestionably, safety is the most important design criterion of a phosgene manufacturing plant. Phosgene plants are usually designed as outdoor installations incorporating facilities for neutralization, and appropriate equipment for dealing with emergencies. Where installations are under a roof, process employees should operate from a pressurized control room supplied with fresh air from an area remote from the plant [1318].

The design of an inherently safe phosgene plant has been described by workers at

TABLE 4.3

LICENSORS OF PHOSGENE PROCESS TECHNOLOGY [64,64a]

Licensor	Process Characteristics
EniChem	Gas phase catalytic oxidation
BUSS	Small industrial plant (200-600 kg/h), no storage
John Brown	High purity, low cost, safe operation
Ventron	Continuous low inventory process
Zeneca	High turndown, low inventory, tubular bed reactor

Ciba–Geigy [36,1573a,1696] (see Section 4.5.2). The process is based on the production of phosgene according to actual needs, thus avoiding long–term storage.

4.5.2 Process technology available for licensing

A number of licensors offer the process technology for phosgene plant, all based on the catalysed reaction of carbon monoxide and dichlorine [64,64a]. The predominant companies are listed in Table 4.3.

Licensors will normally provide their licensees with comprehensive information regarding detailed engineering, equipment design specification, fabrication requirements, operator training, consultation during the engineering and construction phases, start–up assistance, *etc.* The scope of the technology package should include the following:

- Process Flow Diagrams, with energy and material balances, indicating flows, temperatures, pressures and compositions
- Detailed piping and instrumentation diagrams
- Plant layout plans
- Equipment and instrument lists with item numbers
- Equipment specifications
- Instrument sizing
- Piping specifications
- Operating manuals, comprising:
    - Detailed process description
    - Pre–commissioning instructions
    - Initial start–up procedure
    - Normal operating instructions
    - Emergency and normal shut–down procedures
- Analytical manuals, comprising:
    - List of necessary laboratory equipment
    - Sampling and testing procedures
    - Sample schedules
    - Plant control tests
- Raw material requirements and specifications
- Utilities requirements

- ⊗ Physical and chemical property data for:
    - Raw materials
    - Intermediates
    - Products
- ⊗ Safe working practices and procedures
- ⊗ Consultation during the engineering phases of the project
- ⊗ Visits to existing plant operating with similar technology
- ⊗ Operations training at plants practising similar technology
- ⊗ Continuing technology exchange for process improvements and product developments

The Swiss-based company BUSS AG offer a small capacity phosgene generating plant, developed by Ciba-Geigy, that is probably the most technologically advanced of its kind [823b,1573a,1696], developed to reduce storage, transportation and handling of phosgene by captive production as required by the downstream unit. The principal features of this system are as follows:

- ⊗ Phosgene generation is automatically controlled by the downstream demand, with a turn-down ratio of 15:1 (production range of 40-600 kg h^{-1}).
- ⊗ Storage, condensation and evaporation of phosgene are eliminated, with no harmul waste products.
- ⊗ Start-up and shut-down of the plant are achieved within minutes.
- ⊗ Plants are offered with maximum capacity ranges of *ca*. 300-5000 tons per year.
- ⊗ Preconstructed units are supplied, equipped with instrumentation and alarms.
- ⊗ Low maintenance costs

The process flow system and associated safety absorption system are reproduced {with permission} in Figs. 4.5 and 4.6 [823b].

Carbon monoxide (97%) and dichlorine (99.8%) are metered, mixed and completely converted in the catalytic reactor to phosgene (an on-line analytical control system guarantees maximum yield, and the reactor temperature is regulated to maintain favourable equilibria, prevent phosgene condensation, and prevent corrosion of the reactor tubes by hot dichlorine). The gas (the quality of which is largely dependent upon the feedstock purity) is then directly

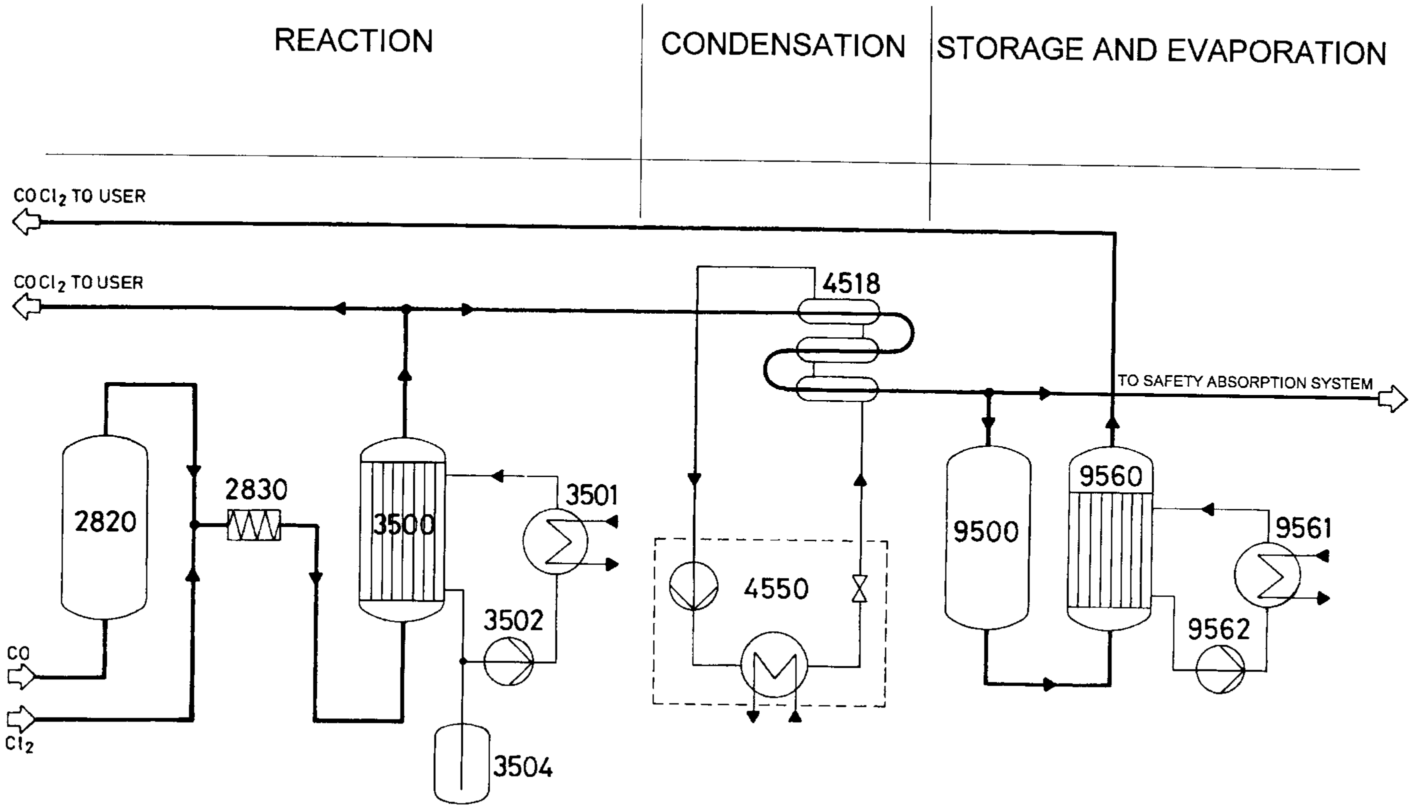


Fig. 4.5 **The process flow system for the BUSS small-capacity phosgene plant [823b]: 2820, pressure vessel; 2830, in-line mixer; 3500, reactor; 3501, cooler; 3504, reservoir; 4518, condenser; 4550, refrigeration unit; 9500, storage; 9560, evaporator; 9561, heat exchanger; 9562, forced circulation pump.**

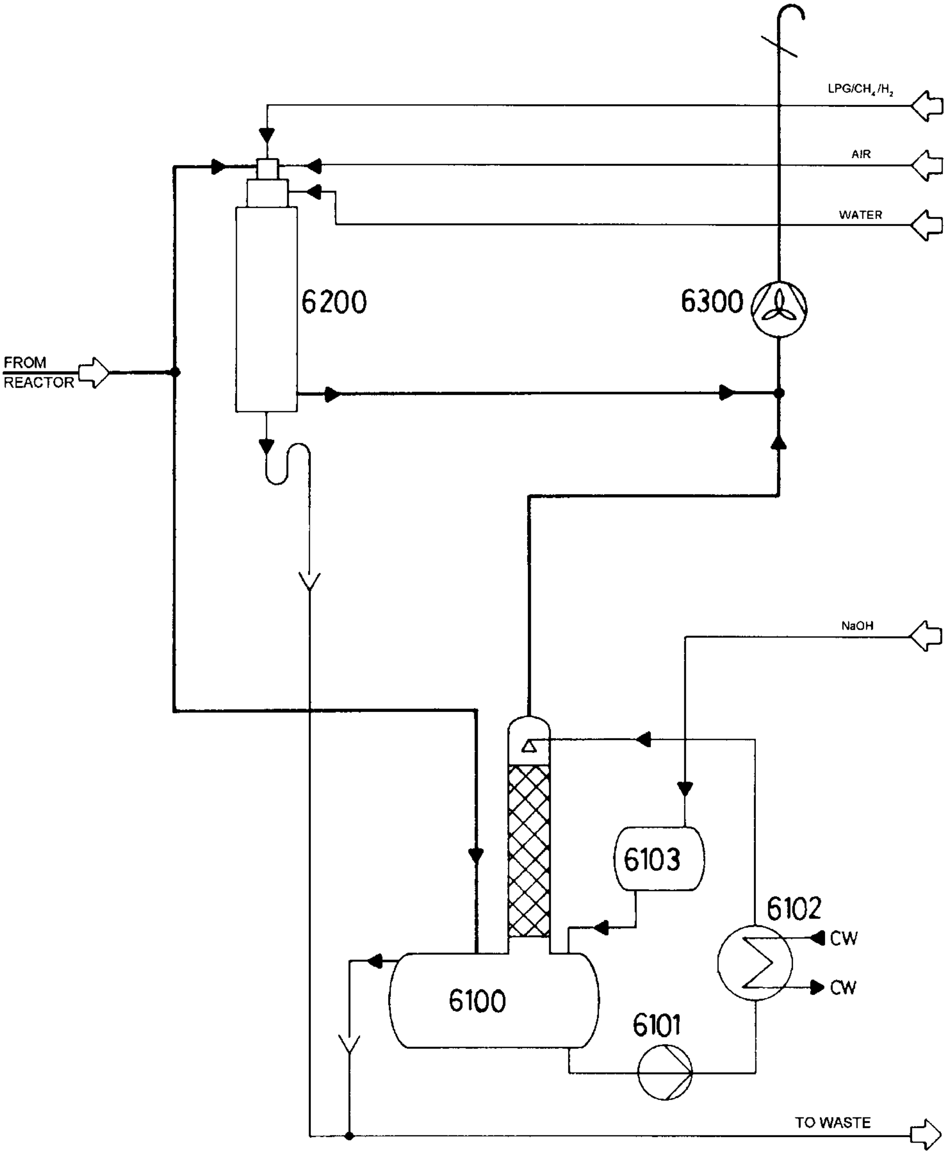


Fig. 4.6 The safety absorption system for the BUSS small-capacity phosgene plant [823b]: 6100, scrubber; 6101, caustic pump; 6102, cooler; 6103, caustic buffer; 6200, incinerator; 6300, fan.

piped to the consumer plant, monitored by an interface control unit to adjust and control the phosgene production rate according to demand. In an emergency, surplus phosgene is absorbed by a circulating caustic solution. The expected product quality of the BUSS installation (details of which are available from BUSS AG, Pratteln, Switzerland) is: phosgene, $\geqslant$97.5 wt %; CCl_4, $\leqslant$0.1%; CO, N_2, O_2, CO_2, and HCl, $\leqslant$2.5%; Cl_2, $\leqslant$0.035%.

4.6 ASSAYING

Specifications for the analysis of phosgene will depend upon the end-use application, but a typical analysis of the liquid commercial product may be as given in Table 4.4 [ICI69,ICI78]. Military specifications for use in munitions ($COCl_2$, $\geqslant$98%; free Cl_2, $\leqslant$1%; acid (HCl), $\leqslant$0.5%; residue, $\leqslant$0.5%) also exist [1394a], and the analysis of phosgene for isocyanate manufacture (for polyurethane production) has been described in detail [458a].

TABLE 4.4

A TYPICAL ASSAY OF COMMERCIAL LIQUID PHOSGENE[a]

Component	Composition/% (w/w)
Phosgene	99.5
Carbon Dioxide	0.10
Iron	0.05
Free Chlorine	0.03
Acidity (as HCl)	0.04
Residue on evaporation	0.03
Sulfur (volatile, *e.g.* COS or SO_2)	0.0039
(non-volatile)	0.0005

[a] Normally appears as a clear, pale yellow liquid.

The pale yellow or yellowish-green appearance of commercial phosgene samples is a result of the presence of dichlorine impurity although a yellowish-grey appearance may result from the presence of iron(III) chloride [1168].

The principles of the methods for the analysis (assaying) of commercially produced phosgene are described in the following Sections [458a,ICI91-ICI93]. A sample cooled to about −10 °C is normally taken for the quantitative analyses of phosgene. At this temperature, the solubility of Cl_2 is 3.9–4.3%, that of CO or of CO_2 is <0.1%; the solubility of HCl is 1.6–2.2% at 0 °C, and 4% at −12 °C (see also Section 11.3) [1168].

4.6.1 Phosgene

The sample of liquid phosgene is vaporized and the vapour absorbed into dilute sodium hydroxide solution:

$$COCl_2 + 4OH^- \longrightarrow [CO_3]^{2-} + 2Cl^- + 2H_2O$$

The resulting chloride is determined by titration with standardized silver nitrate solution, according to established methods (*cf.* Sections 3.2.1.1 and 3.2.4), to provide the total phosgene composition. In most cases, this method is sufficiently accurate, because free dichlorine and hydrogen chloride, which would interfere with the test are present in only low concentration. If, however, free dichlorine or HCl are present (see below), the dichlorine equivalent is deducted from the total chlorine and the difference calculated to the percentage value of phosgene.

A military specification [1394a] suggests the determination of phosgene by reaction of phosgene with a solution of sodium iodide in propanone, and titration of the liberated iodine with sodium thiosulfate (see Section 3.2.1.2), correcting for any free chlorine present.

4.6.2 Total chlorine

Total chlorine may be determined in bulk phosgene by treating an aliquot of the basic solution (Section 4.6.1) with hydrogen peroxide, to reduce any hypochlorite to chloride, followed by titration with silver(I) nitrate solution as above.

4.6.3 Free chlorine

A portion of the alkaline absorbing solution (Section 4.6.1) is treated with sodium, potassium or cadmium iodide in acid solution, and the liberated iodine is titrated with standardized sodium thiosulfate solution, according to the established procedures (*cf.* Section 3.2.1.2). If the concentration of iodide is in excess of 0.1%, iodine may also be released as a result of the interaction between I^- and $COCl_2$ [487,1168]. Alternatively, phosgene may be dissolved in 3% aqueous KI solution, and the liberated iodine immediately titrated with aqueous $Na_2[S_2O_3]$ solution [458a,1394a].

The determination of Cl_2 in $COCl_2$ may also be performed by passage of the gas over mercury(II) iodide at room temperature. $COCl_2$ does not react, whereas Cl_2 reacts to release iodine [1335]. Concentrations of dichlorine in phosgene in the 50–1000 p.p.m. range have been determined using a biamperometric method, based upon the liberation of iodine from potassium iodide in the presence of free dichlorine [ICI79]. Analysis of Cl_2 down to 30 p.p.m. in $COCl_2$ has been accomplished by measurement of the UV absorption of dichlorine at 30490 cm^{-1} (328 nm) [ICI78], and analysis of dichlorine in the range of 0–1000 p.p.m. can be accomplished by means of an automatic galvanic analyser, based on the reduction of dichlorine to chloride on the electrode at the expense of the oxidation of the silver electrode to silver chloride [2152].

4.6.4 *Hydrogen chloride*

The simplest determination of HCl in phosgene involves measurement of the volume of phosgene before and after treatment with water. The difference in volume approximately represents the quantity of hydrogen chloride present in the sample. Any hydrolysis of the phosgene can be ignored, since this generates an equal volume of carbon dioxide [1778].

A method for the determination of small quantities of HCl in phosgene involves the slow passage of phosgene gas over dry mercury(II) cyanide [491]:

$$Hg(CN)_2 + 2HCl \longrightarrow HgCl_2 + 2HCN$$

The liberated HCN is absorbed then into sodium hydroxide solution, and titrated with standardized silver nitrate solution.

When phosgene has been determined with sodium iodide in propanone (Section 4.6.1), acid content may be determined by titrating (phenolphthalein indicator) the resultant solution with standard aqueous sodium hydroxide solution [1394a].

4.6.5 *Iron*

Iron impurities (arising from equipment corrosion) in the residues obtained from the evaporation of a known quantity of phosgene are dissolved in hydrochloric acid, and the iron determined colorimetrically with thioglycollic acid, according to standard procedures.

4.6.6 *Total sulfur*

The method for the determination of sulfur in phosgene is based on the absorption or hydrolysis of sulfur compounds in an excess of sodium hydroxide solution, followed by reduction to H_2S using hydriodic acid and subsequent determination of sulfide ion by the methylene blue method.

4.6.7 *Chlorinated hydrocarbons*

Tetrachloromethane and hexachloroethane in phosgene are determined following their extraction into tetrachloroethene. The phosgene is destroyed using aqueous sodium hydroxide, and the tetrachloroethene layer separated prior to analysis by gas–liquid chromatography.

4.6.8 *Carbon dioxide and carbon monoxide*

CO_2 and CO in phosgene are most readily determined by gas chromatography (*cf*. Section 3.2.5.1) [458a].

4.6.9 *Water*

Water may be determined in phosgene by selectively absorbing onto a silica gel column at room temperature from the gas stream. The water is then desorbed by heating and simultaneously purging with dry dinitrogen into an anhydrous pyridine/methanol mixture, followed by titration with Karl Fischer reagent. This method is capable of detecting as little as 0.8 mg of water.

4.6.10 Residue on Evaporation

Non-volatile impurities in phosgene are determined by allowing a known quantity of the phosgene sample to evaporate and weighing the residue [458a,1394a]. Analysis of the residue obtained from the evaporation of the commercial samples of phosgene has revealed the presence of hexachloroethane, chloroformates, and various sulfur-containing organochlorine compounds.

4.6.11 Vapour composition

Owing to the nature of the impurities described from commercial samples of phosgene, the vapour phase composition of a sample of phosgene obtained, from a cylinder say, may be considerably different from that indicated by analysis of the liquid. As an example, consider the vapour phase composition at room temperature of a sample of phosgene having the analytical composition indicated in Table 4.5.

TABLE 4.5

VAPOUR-LIQUID EQUILIBRIUM COMPOSITION OF A TYPICAL COMMERCIAL SAMPLE OF PHOSGENE

Component	Composition/% w/w	
	Liquid Phase	Vapour Phase
Phosgene	99.69	86.7
Hydrogen chloride	0.10	1.9
Carbon dioxide	0.10	11.2
Chlorine	0.06	0.22
Bromine	0.05	0.07

In particular, it should be noted that a phosgene sample containing only 0.1% of carbon dioxide, as measured in the liquid phase, would produce a vapour containing more that 11% CO_2, owing to the higher volatility of CO_2 relative to $COCl_2$. This CO_2, and other very volatile contaminants, can be removed by distillation or by simple "bleeding" of the phosgene cylinder.

TABLE 4.6

VAPOUR PRESSURE DATA FOR A TYPICAL COMMERCIAL SAMPLE OF PHOSGENE [ICI78]

Temperature/°C	Vapour Pressure/bar	
	Commercial sample	Pure sample [649]
11.7	1.58	1.17
14.0	1.72	1.28
19.1	2.07	1.53
27.6	2.76	2.05
34.6	3.45	2.58

In addition, it should be noted that the vapour pressure of commercial samples of phosgene will differ from those recorded for the pure material (see Chapter 6). The vapour pressure corresponding to the sample instanced in Table 4.5 is illustrated in Table 4.6 as a function of temperature [ICI78].

4.7 INDUSTRIAL USES

Phosgene is a reagent that may be used to affect a very large number of chemical transformations. In particular, its organic chemistry is vast (see Chapter 10) reflecting the compound's versatility and general usefulness. Owing to its notorious reputation, however, many industrial users appear to be sensitive to their use of the material being made common knowledge. In addition, the growing trend (particularly in the United States) for the material to be used captively means that many of the material's applications remain undisclosed. This Section has been prepared with these limitations in mind. It is not therefore a comprehensive review of all the possible applications for phosgene, but rather represents the general areas in which phosgene is, or has been, employed commercially.

Although employed, at one time, primarily as a war gas, phosgene is now an important chemical intermediate for the synthesis of a large number of commercial materials. Worldwide, it is used mainly in the manufacture of isocyanates (for urethane polymers and organic intermediates), polycarbonates (for speciality polymers), and monomeric carbonates and chloroformates (largely for the synthesis of pharmaceuticals and pest control chemicals). The established large-scale, commercial applications of phosgene are summarized in Fig. 4.7.

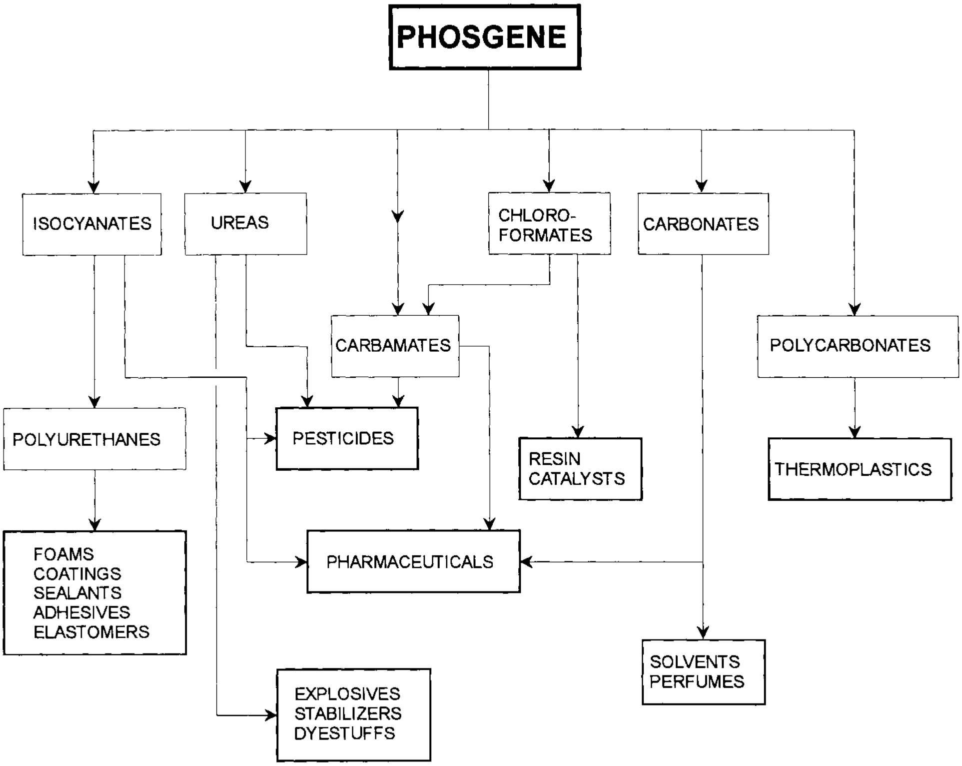


Fig. 4.7 **The principal commercial applications of phosgene.**

The largest scale uses are thus based on the reactions of phosgene (or its direct derivatives) with either alcohols or amines.

According to a recent source [885], over 85% of the world phosgene output (about 2.7 million tons p.a. [1804a]) is consumed in polyurethane production whilst some 6% is employed for polycarbonate manufacture. Fine chemical (such as pharmaceutical and agricultural) applications account for most of the remaining amount. The reported consumption of phosgene in North America (for which most information is available) is represented in Figs. 4.8 and 4.9 for the period 1965–1981. The growing importance of phosgene as a commercial reagent can be clearly seen, as can the rising importance of polycarbonates. These historical trends are realised in the more recent 1989 global data [1804a], presented in Figure 4.10. The merchant market for phosgene, *per se*, is only a very small proportionation of the total production, and this area is expected to fall as a result of transportation legislation. The manufacture and handling of phosgene thus tends to be restricted to specialized businesses, and custom synthesis is becoming common practice.

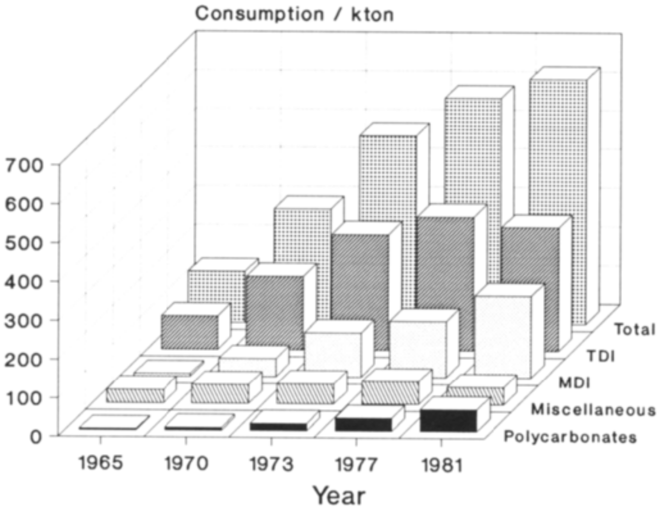


Fig. 4.8 Consumption of Phosgene (North America, 1965–1981).

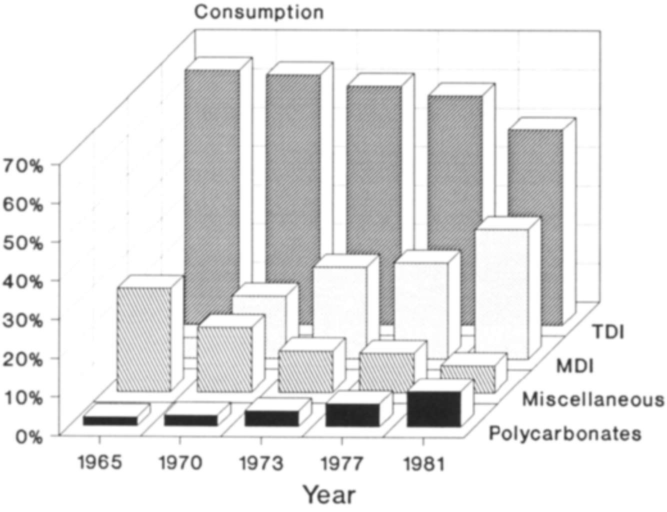


Fig. 4.9 Percentage of phosgene consumed in the major product areas (North America, 1965–1981).

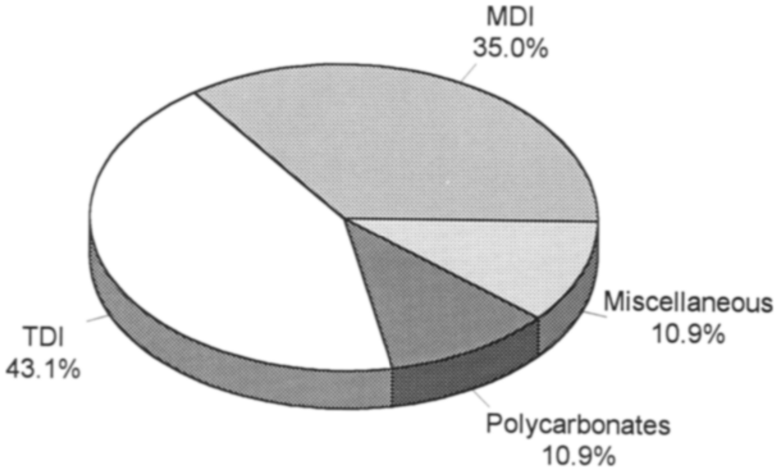


Fig. 4.10 Percentage of phosgene consumed in the major global product areas (1989) [1804a].

4.7.1 Isocyanate and urethane manufacture

Di- and poly-isocyanates are mainly used in the production of polyurethane rigid or flexible foams (for insulation and in furniture), adhesives, sealants, surface coatings, elastomers and fibres [2007,2072,2165], whilst mono-isocyanates are employed in the synthesis of substituted ureas and carbamates (Section 4.7.3) for medicinal, agricultural and other applications [2072].

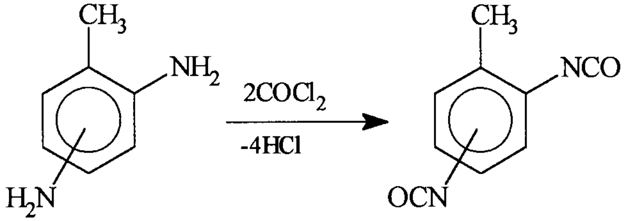
4.7.1.1 Isocyanates

Although other routes have been proposed, most economic manufacture of the commercially important isocyanates are based upon the reaction of phosgene with amines, Equation (4.1), first described by Hentschel in 1884 (see Section 10.2.1.1) [945a]. Processing details vary depending upon the particular isocyanate, but the overall approach is the same [351,1684]. The first stage of the reaction is very fast (*e.g.* for the reaction of phosgene with aniline, the half-life at 0 °C is 0.3 s), whilst the second stage of the reaction proceeds at a moderate rate. In order to achieve a satisfactory yield, hydrogen chloride must be removed and side reactions inhibited.

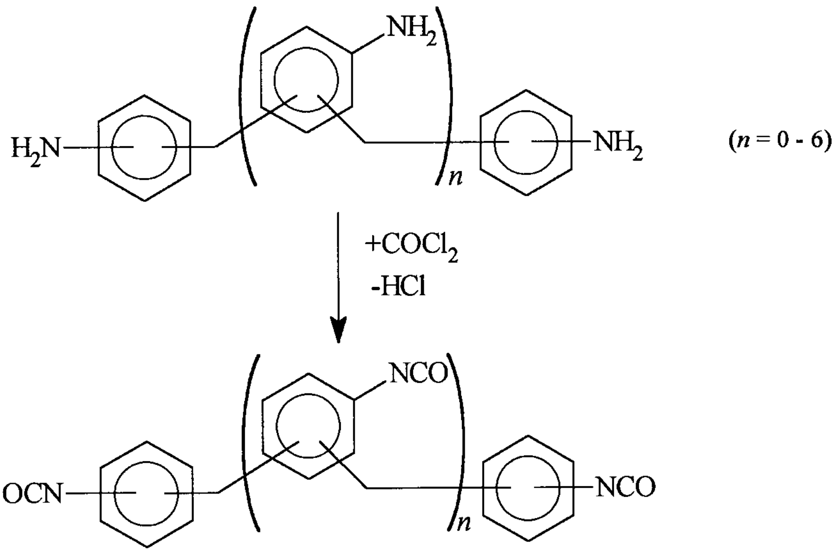
$$RNH_2 + COCl_2 \longrightarrow RNHC(O)Cl + HCl \longrightarrow RNCO + 2HCl \qquad (4.1)$$

Many isocyanates are presently manufactured in this way but by far the most important materials, in terms of volume, are toluene diisocyanate (TDI), Equation (4.2), the increasingly important diphenylmethane-4,4'-diisocyanate (MDI; also commonly known as

4,4'-diisocyanatodiphenylmethane) and polymeric MDI {PMDI; made by the reaction of phosgene with polyamine mixtures, Equation (4.3)}, produced by a wide range of manufacturers. Details of the manufacturing routes [392,1078,2165] and of the process chemistry [2072] of these materials have been presented elsewhere, and a kinetic model for TDI synthesis has been developed [1302] in order to calculate the yields of the reaction as a function of the conditions.

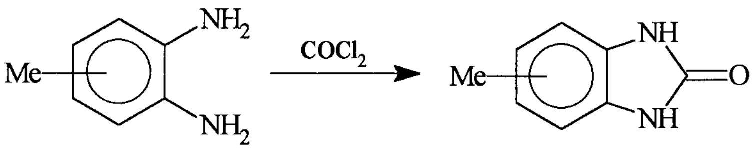


(4.2)



(4.3)

TDI is commonly sold as a mixture of isomers. For example 80/20 TDI is a mixture of 80% 2,4- and 20% 2,6-toluene diisocyanate, whilst 65/35 is a mixture of 65% 2,4- and 35% 2,6-isomer [2165]. The amine groups of the starting material are therefore in 1,3-positions relative to each other. However, a small quantity of impurity in which the amine groups are in 1,2- positions relative to each other can give a disproportionate loss in yield, as a result of the cyclization reaction illustrated in Equation (4.4) [1282]; the cyclic urea is volatile and distills with TDI, crystallizing from it and contributing to a loss in quality.



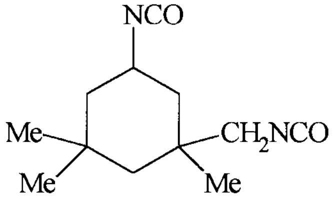
(4.4)

The choice of solvent in this system can have an important influence on the reaction yield [58,2072]. The most commonly used solvents are probably chlorobenzene and 1,2-dichlorobenzene, although the employment of diethyl carbitol (the diethyl ether of diethylene glycol) has been disclosed to give higher reaction efficiencies whilst being, surprisingly, unreactive towards the HCl co-product [58]. For the more usual solvents, it is suggested that phosgene can be readily removed from TDI by bubbling dinitrogen through the solution at a temperature 10 °C lower than the boiling point of the solvent [2064].

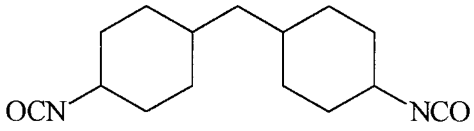
MDI has now substantially overtaken TDI as the industry's major isocyanate [104a]. It is available in a wide variety of forms, based upon monomeric and polymeric materials, to serve the numerous applications of the polyurethanes industry [2209a].

A number of aliphatic isocyanates find a variety of market niches in polyurethane resin and coating components. The largest volume aliphatic isocyanate is probably hexamethylene diisocyanate (HDI; 1,6-diisocyanatohexane; *ex.* Bayer), used as an intermediate in the production of, for example, polyurethane coatings for automobile refinishing, where it is particularly favoured for its resistance to chipping.

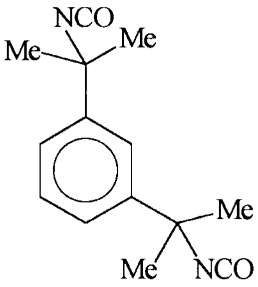
Other high growth aliphatic isocyanates currently in production include: isophorone diisocyanate {IPDI; (**4.1**); *ex.* Hüls}, hydrogenated MDI {HMDI; (**4.2**); *ex.* Mobay}, tetramethyl xylene diisocyanate {TMXDI; (**4.3**) and (**4.4**); *ex.* American Cyanamid} and 3-isopropenyl dimethylbenzyl isocyanate {TMI; (**4.5**); *ex.* American Cyanamid} [63a]. The latter two



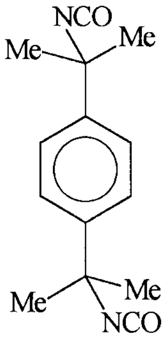
(**4.1**; IPDI)



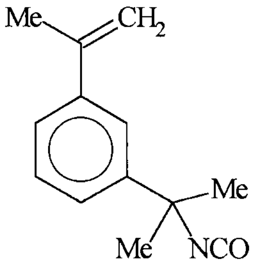
(**4.2**; HMDI)



(**4.3**; TMXDI)



(**4.4**; TMXDI)



(**4.5**; TMI)

TABLE 4.7

SOME SMALL-VOLUME COMMERCIAL ISOCYANATES MANUFACTURED FROM PHOSGENE

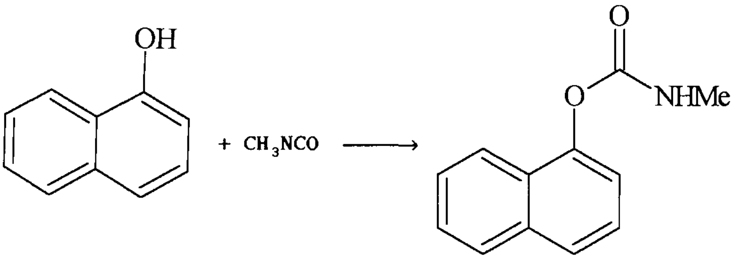
Commercial name	Manufacturer/Supplier
Allyl isocyanate	Carbolabs
Benzenesulfonyl isocyanate	Carbolabs
4-Bromophenyl isocyanate	Carbolabs
n-Butyl isocyanate	BASF; Bayer
t-Butyl isocyanate	Bayer; Carbolabs
2-Chloroacetyl isocyanate	Carbolabs
2-Chloroethyl isocyanate	Carbolabs
2-Chloro-4-methylphenyl isocyanate	Carbolabs
3-Chloro-4-methylphenyl isocyanate	Bayer; Hoechst
3-Chlorophenyl isocyanate	Bayer; Hoechst
4-Chlorophenyl isocyanate	STPC; Bayer; Hoechst
Chlorosulfonyl isocyanate	Lonza
3-Chloro-4-tolyl isocyanate	Bayer
4-Cyanophenyl isocyanate	Carbolabs
trans-1,4-Cyclohexane diisocyanate	Akzo; Du Pont
Cyclohexyl isocyanate	Bayer
2,6-Dichlorophenyl isocyanate	Carbolabs
3,4-Dichlorophenyl isocyanate	STPC; Bayer; Hoechst
3,5-Dichlorophenyl isocyanate	STPC; Chuo Kaseihin; Carbolabs
2,4-Difluorophenyl isocyanate	Carbolabs
2,6-Dimethylphenyl isocyanate	Orgamol; Carbolabs; SNPE
Ethyl isocyanate	Carbolabs
2-Fluorophenyl isocyanate	Carbolabs
4-Fluorophenyl isocyanate	Carbolabs
Isopropyl isocyanate	STPC; Bayer
4-Isopropylphenyl isocyanate	STPC
Methyl isocyanate	Bayer; Du Pont; Rhône Poulenc; Carbolabs
Naphthyl-1,5-diisocyanate	Bayer; Mitsui Toatsu
1-Naphthyl ethylisocyanate	Norse
1-Naphthyl isocyanate	Bayer
4-Nitrophenyl isocyanate	Carbolabs
Octadecyl isocyanate	Bayer; Hoechst; Hodogaya; Olin; Vanchem
3-Phenylene diisocyanate	Carbolabs
4-Phenylene diisocyanate	Du Pont
2-Phenylethyl isocyanate	Norse
Phenyl isocyanate	STPC; Nippon Soda; Bayer
4-Toluenesulfonyl isocyanate	Vanchem
2-Tolyl isocyanate	Bayer
3-Tolyl isocyanate	Bayer; Hoechst
4-Tolyl isocyanate	Hoechst; Carbolabs
4-Trifluoromethoxyphenyl isocyanate	Bayer
3-Trifluoromethylphenyl isocyanate	STPC; Bayer; Hoechst
4-Trifluoromethylphenyl isocyanate	Bayer; Carbolabs
Trihydroxyethyl isocyanate	BASF
Trimethylhexamethylene diisocyanate	Hüls
Triphenylmethane-4,4',4"-triisocyanate	Bayer
1,3-Xylylene diisocyanate	Takeda

compounds, recently introduced by American Cyanamid, have the distinction of being produced using proprietary technology which avoids the use of phosgene [73a], although this technology is considered to be not transferable to other commercially important isocyanates [2032e].

Some other isocyanates that are manufactured on a lesser scale than those described above, and used for a variety of purposes, are listed by their common names, together with the corresponding supplier, in Table 4.7. Additionally, many materials, such as tri-(4-isocyanatophenyl)thiophosphate and halogenated varieties of MDI or TDI, have been produced at least in experimental quantities [2072]. The unsaturated isocyanates, 3- and 4-$CH_2{=}CHC_6H_4NCO$ have also been prepared from the reaction of phosgene with the corresponding amines [1172].

Methyl isocyanate, widely known because of its tragic implication in the Bhopal disaster, is used for the manufacture of several insecticides and herbicides {including the carbamate insecticide "Sevin", (4.6), Equation (4.5); produced by Union Carbide} and accounts for about three-quarters of all monoisocyanates manufactured [351].

$$CH_3NH_2 + COCl_2 \longrightarrow CH_3NCO + 2HCl$$



(4.5)

(4.6)
"Sevin" (or "Carbaryl")

The toxicity of isocyanates is a complex subject which is mostly beyond the scope of this monograph. Although the 8 h TLV-TWA for diisocyanates has been assigned as 5 p.p.b. [351], the relative hazards associated with these materials is a function, mainly, of their volatility and the temperature at which the material is handled. Polymeric MDIs, for example, under normal industrial conditions, are handled at room temperature, where the vapour pressure is so low that the TLV-TWA is unlikely to be exceeded. The handling and health and safety aspects of isocyanates used in polyurethanes manufacture have been competently dealt with elsewhere [2209a].

The more volatile isocyanates (such as the monoisocyanates) are inherently hazardous [651] and it makes little sense, in most cases, to invent or evaluate non-phosgene routes to these compounds on the grounds of toxicity considerations alone. However, isocyanate production from phosgene results in the formation of large quantities of hydrogen chloride, and the isocyanate products may be contaminated with chlorine compounds which are difficult to separate [701]. In addition, the possibility exists that the transportation of phosgene could be inhibited by legislation so that new routes to the commercially important isocyanates might then be desirable [ICI63] in a situation where phosgene is not used captively.

A large number of patents have been concerned with the description of non-phosgene routes to isocyanates, indicating the considerable research effort that has been undertaken in this area [ICI80]. Of particular note is the so-called ARCO process, in which nitrobenzene is reductively carbonylated to phenyl isocyanate (as part of a route to MDI), whilst in another development MDI is prepared from aniline, carbon monoxide, dioxygen and aqueous methanal [351]. Similar non-phosgene routes to TDI (Mitsui) and IPDI (Daicel) have been proposed, although these developments are not expected to make a large influence on phosgene demand [885]. Indeed, despite numerous publications, spanning more than 30 years, the fact remains that no alternative route to any of the major isocyanates, which avoids the use of phosgene, has been commercialised. All of the proposed methods have been found to give rise to major technological problems, which despite indications to the contrary, have not been resolved [2032e].

4.7.1.2 Urethanes

Reaction of an isocyanate with an alcohol gives the corresponding urethane. This reaction, which forms the basis for the important polyurethane manufacture, is illustrated in its simplest form in Equation (4.6). For polyurethane manufacture the alcohol (or polyol) and isocyanate reactants must of course contain, respectively, at least two functional groups.

$$\mathrm{RN{=}C{=}O + R'OH \longrightarrow RNHC(O)OR'} \qquad (4.6)$$

The chemistry and associated background to polyurethane manufacture and usage has been recently covered in The ICI Polyurethanes Book [2209a].

4.7.2 Carbonate and chloroformate manufacture

Phosgene reacts with alcohols or phenols (or their simple salt derivatives) to give two types of compound, chloroformates {ROC(O)Cl; Equation (4.7)} and carbonates {ROC(O)OR; Equation (4.8)}, see Section 10.3.1. Carbonates are generally derived from the further reaction of the alcohol or phenol with the chloroformate.

$$\mathrm{COCl_2 + ROH \longrightarrow ROC(O)Cl + HCl} \qquad (4.7)$$

$$\mathrm{ROC(O)Cl + R'OH \longrightarrow ROC(O)OR' + HCl} \qquad (4.8)$$

Hundreds of chloroformates and carbonates have been prepared, and reviews of the chemistry and chemical technology of both types of material can be found in the literature [3,676,1358]. In general, it may be said that the potential availability of a particular chloroformate or organic carbonate is essentially limited only by the availability of the precursor alcohol. Indeed, only recently has the selective synthesis of the potentially important 1-chloroethyl chloroformate been reported (from phosgene and acetaldehyde [322], Section 10.3.3.1), since the precursor alcohol $CH_3CH(OH)Cl$ is not synthetically attainable. Similarly, the selective synthesis of vinyl chloroformate, $CH_2=CHClOC(O)Cl$, has been achieved only recently (from phosgene and the mercury chloride acetaldehyde compound, $ClHgCH_2CHO$; also see Sections 9.9.2 and 10.3.3) [1917]:

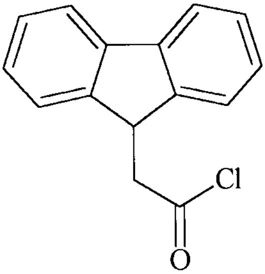
$$ClHgCH_2CHO + COCl_2 \longrightarrow HgCl_2 + CH_2{=}CHOC(O)Cl$$

Several new polymers have been prepared by polymerization of vinyl chloroformate derivatives, or by chemical modification of the reactive polymer [1917]. Such materials are marketed by SNPE in France.

4.7.2.1 Chloroformates

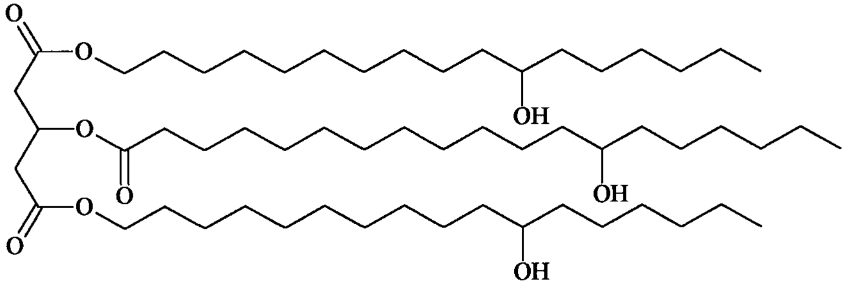
Alkyl chloroformates are generally prepared by reaction of anhydrous alcohols with a stoicheiometric excess of dry phosgene in a corrosion-resistant reactor. For the lower alcohols, temperatures are maintained at 0-10 °C, in order to minimise the formation of carbonates, and the phosgene is most usually added to the alcohol. Higher alcohols may require temperatures up to 60 °C. Acid acceptors are frequently used in this process to remove HCl as it is formed, but in this procedure the alcohol is added to an excess of liquid phosgene to inhibit the production of the corresponding dialkyl carbonate. Unreacted phosgene is removed from the product by gas purging or vacuum stripping [3]. Although chloroformates are traditionally produced in batch processes, methods for continuous production have been described [ICI81]. The use of acid acceptors is more important in the preparation of aryl chloroformates, since phenols tend to be unreactive towards phosgene at temperatures below about 75 °C [1358].

Apart from being intermediates for organic carbonate synthesis, chloroformates are also intermediates for a variety of other commercially important materials, including pesticides, dyes, perfumes, polymers and drugs. Chloroformates, such as $Me_3COC(O)Cl$, $PhCH_2OC(O)Cl$ and 1-(9-fluorenyl)methyl chloroformate, (4.7), are used for the protection of amino and



(4.7)

hydroxyl groups in the synthesis of complex organic compounds such as peptide-based pharmaceuticals, and artificial sweeteners [1841a]. In pharmaceutical applications, chloroformates are also used to prepare carbamates which, in turn, are used to prepare tranquillizers, antihypotensives and local anæsthetics [3]. Chloroformates in general, but 1-chloroethyl chloroformate in particular, are useful and selective reagents for the *N*-dealkylation of tertiary amines (an important step in some drug syntheses) [1559ab]. A number of pesticides have been patented based on the use of thiol chloroformates [885,2036], and the chloroformate derivative of hydrogenated castor oil, (4.8), reacts with ammonia to give the corresponding carbamate, which has been used as an intermediate in the preparation of a wool anti-shrink agent.



(4.8)

The chloroformates listed in Table 4.8 are available in bulk quantity, but many other mono- and di-chloroformates can be obtained in amounts suitable for experimental purposes. Technical data sheets are available from PPG Industries (Chicago, Illinois) and from SNPE (Paris).

4.7.2.2 Carbonates

Symmetrical carbonates are produced by a similar method to that described for chloroformates in either a two-stage {Equations (4.7) and (4.8)} or one-stage process {Equation (4.9)}. For the one stage process, longer reaction times, higher temperatures, and extra quantities of alcohol are normally required relative to the preparation of the chloroformate [3].

$$2ROH + COCl_2 \longrightarrow (RO)_2CO + 2HCl \tag{4.9}$$

Diaryl carbonates are made from the reaction of phosgene with two molar equivalents of the particular sodium phenolate [3]. However, the direct conversion of phenols can be achieved by reaction of phosgene in the presence of quaternary ammonium salts, or acid acceptors (such as pyridine), at ambient temperatures [2016]. The three dihydroxybenzenes

TABLE 4.8

COMMERCIAL APPLICATIONS OF SOME CHLOROFORMATE INTERMEDIATES [3,1841a]

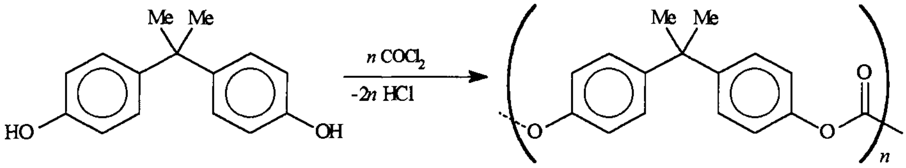
Precursor	Application
Methyl chloroformate	Pharmaceuticals
	Pesticides
Ethyl chloroformate	Ore flotation agents
Isopropyl chloroformate	Blowing agents
	Oprical lenses
	Selective herbicides
Propyl chloroformate	Polymerization initiator
	Cross-linking agent
Allyl chloroformate	High impact-resistant optical lenses
Ethylene bis(chloroformate)	Polyurethanes
Diethylene glycol bis(chloroformate)	High impact-resistant optical lenses
	Polymerization catalyst
Cholesteryl chloroformate	Liquid crystals
1-(9-Fluorenyl)methyl chloroformate	Amino-protecting reagent

(hydroquinone, resorcinol and catechol) react with phosgene in pyridine [676]: resorcinol (1,3-dihydroxybenzene) reacts with phosgene to produce an amorphous polymer (melting at about 200 °C), hydroquinone (1,4-dihydroxybenzene) reacts to give a crystalline, intractable polymeric material, and catechol (1,2-dihydroxybenzene) produces a cyclic carbonate, see Section 10.3.1.4.

Although other (non-phosgene) methods [676] can be employed to prepare carbonates, these will not be described here.

As with chloroformates, carbonates (particularly diethyl carbonate) are used as synthetic intermediates for pharmaceuticals, dyes, and agricultural chemicals. Di-*t*-butyl carbonate, $Me_3COC(O)OCMe_3$, is a widely used reagent for the protection of amino groups in organic syntheses [1841a]. Carbonates can be used for the manufacture of so-called "pro-drugs". These have properties which are different to the parent drug, but produce the same physiological effect after hydrolysis *in vivo* [884]. Dimethyl carbonate, most simply prepared from phosgene and methanol, has been proposed as an anti-knock additive for gasoline. In addition, liquid carbonates can be used as solvents for natural or synthetic resins, and long-chain organic carbonates can be viscous liquids with a low flash point, used as lubricants and synthetic resins themselves. The cyclic ethylene carbonate (dioxolone-2), prepared from the interaction of ethylene glycol with $COCl_2$ can be used to prepare dialkyl carbonates [3]. Dialkyl peroxydicarbonates, ROC(=O)OOC(=O)OR, are employed as polymerization initiation catalysts; the doubly unsaturated material diethylene glycol bis(allyl carbonate), $O(CH_2CH_2OCOOCH_2CH=CH_2)_2$, can be polymerized to give tough, optically clear castings used in safety glasses and for lightweight lenses in spectacles [3].

The so-called bisphenol A polycarbonate constitutes the largest outlet for the carbonate-based materials. It is prepared by reaction of phosgene with bisphenol A in an organic solvent (or in a two-phase system [1294,1295]), as illustrated in Equation (4.10) [1228,1520,1952].



(4.10)

The polymerization reaction in pyridine (or aqueous caustic) solutions is readily carried out at room temperature. The pyridine functions as both catalyst and HCl acceptor, but in addition is a solvent for the polymer, permitting high molecular weight material to be obtained. The polymer is ultimately obtained by precipitation in methanol [1228,2016]. Although almost any dihydroxy compound is amenable to this reaction, only bisphenol A polycarbonate has achieved commercial importance. This is probably a result of the low monomer costs (bisphenols are commonly used in epoxy resins and are easily prepared) and the particularly good properties (high impact strength, thermal stability, self-fire-extinguishing, high hardness and malleability, and transparency) of the polymer [676,1952]. This material is thus used in a wide variety of manufactured articles requiring these particular properties (such as gear wheels, refrigerator parts, electrical components, *etc.*).

As with the chloroformates, a large number of carbonates (*e.g.* diethyl carbonate, dimethyl carbonate, and diphenyl carbonate) are commercially available. Manufacturers of chloroformates are usually also manufacturers of carbonates.

4.7.3 Urea and carbamate derivatives

The reactions of phosgene with ammonia lead, depending upon the conditions, to the formation of the useful materials: urea, biuret ($NH_2CONHCONH_2$), cyanuric acid (1,3,5-triazine-2,4,6-triol), and successive products of ammonolysis up to melamine $H_2NCN(NH_2)NC(NH_2)N$ (see Section 9.10.2.1) [718a]. Urea is usually manufactured from ammonia and carbon dioxide, but a useful fertilizer mixture can be produced by injecting ammonia into gaseous phosgene in the ratio of 4:1 respectively [1439]. Urea and ammonium chloride are formed as indicated in Equation (4.11), although this simple equation has no mechanistic implications, and many side reactions occur.

$$COCl_2 + 4NH_3 \longrightarrow CO(NH_2)_2 + 2[NH_4]Cl \qquad (4.11)$$

4.7.3.1 Explosives Stabilizers

Powder stabilizers for the explosives industry are frequently composed of substituted ureas prepared from phosgene, as illustrated in Equation (4.12).

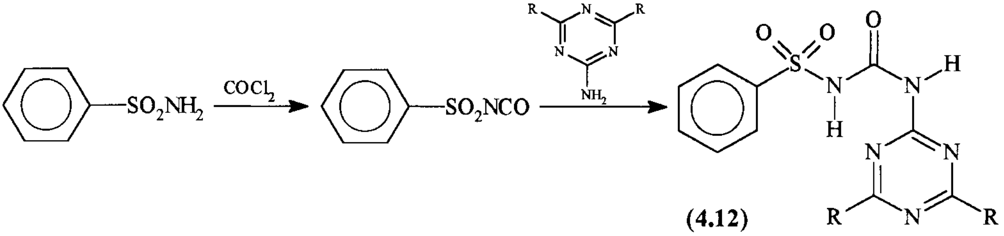
$$COCl_2 + RR'NH \longrightarrow RR'NC(O)NRR' + 2HCl \qquad (4.12)$$

Examples of such materials include *N*,*N*'-diphenylurea (R = H, R' = Ph), *N*,*N*'-diethyl-*N*,*N*'-diphenylurea (also known as diethyl centralite, centralite I, or carbamite; R = Et, R' = Ph), *N*,*N*'-dimethyl-*N*,*N*'-diphenylurea (also known as centralite II; R = Me, R' = Ph), and *N*,*N*,*N*',*N*'-tetraphenylurea (R = R' = Ph) [718a]. Stabilizers derived from urethanes are also employed in the explosives industry [718a]. These materials are prepared either from the corresponding carbamoyl chloride or chloroformate, both of which are derived from phosgene. Examples include methyl phenyl urethane {EtO(CO)NMePh}; ethyl phenyl urethane {EtO(CO)NEtPh} and diphenyl urethane {EtO(CO)NPh$_2$}.

4.7.3.2 Pesticides

The pesticides derived from phosgene also commonly belong to the class of substituted ureas or carbamates. The substituted ureas are mainly used as herbicides (see Fig. 4.11), and the carbamates (see Fig. 4.12) as insecticides and acaricides. It is said that 93% of all carbamates and 92% of all urea-based herbicides in the US market are commercially synthesized with phosgene. Of the substituted ureas, monuron, (**4.9**), and diuron, (**4.10**), are the most important pesticides in volume terms, and of the carbamates, carbaryl (**4.6**; "Sevin") is the predominantly important chemical [718a]. Eptam (**4.11**; *S*-ethyl-*N*,*N*-dipropylthiocarbamate) represents an example of a range of selective thiocarbamate herbicides derivable from phosgene. These products are made in a two-stage process by reacting phosgene with a thiol to give a thiochloroformate, which is then combined with an amine.

The sulfonyl urea herbicides, such as (**4.12**), are prepared from phosgene by the following sequence of reactions [1841a]:



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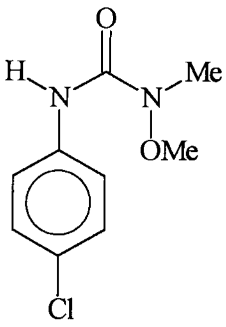
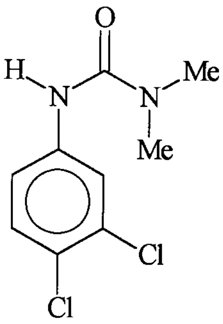
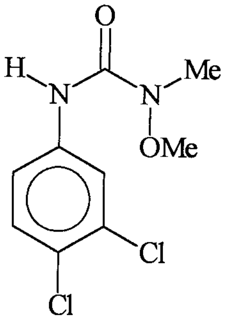


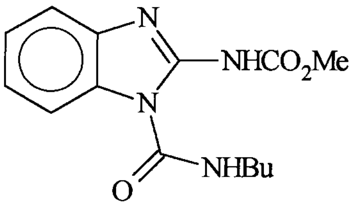
Monuron **(4.9)**



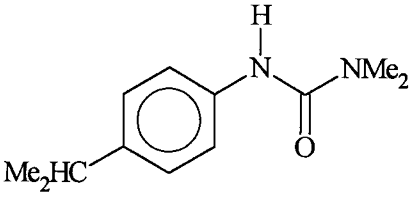
Diuron **(4.10)**



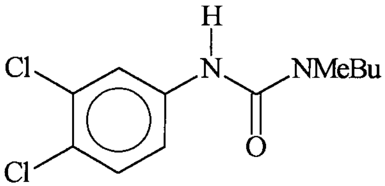
Linuron



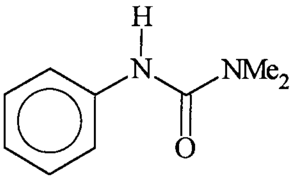
Benomyl



Isoproturon

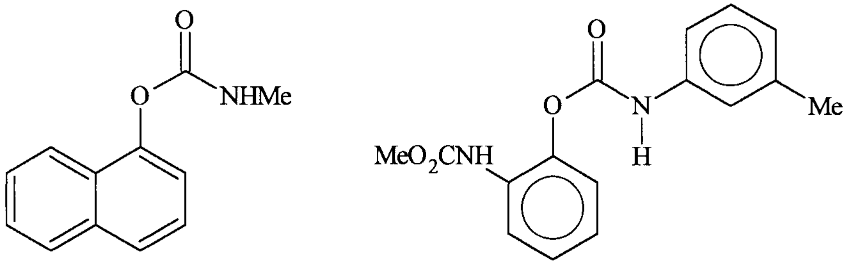


Neburon



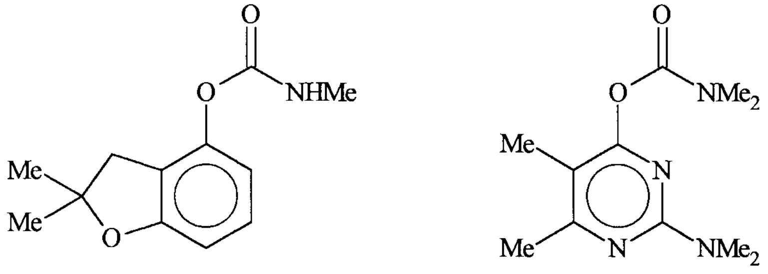
Fenuron

Fig. 4.11 Selected substituted urea herbicides.



Carbaryl

Phenmedipham



Carbofuran

Pyrimicarb

Propham

Cycloate

Eptam (**4.11**)

Butylate

Pebulate

Vernolate

Fig. 4.12 **Selected carbamate and thiocarbamate herbicides.**

4.7.3.3 Pharmaceuticals

Phosgene is employed in the synthesis of drugs for the treatment of diabetes. The hypoglycemic sulfonyl ureas have the general formula R"HNC(O)NHSO$_2$R' (R_1 = Me–4–C_6H_4, Cl–4–C_6H_4, or NH_2–4–C_6H_4; R_2 = Ph, Bu, or HO–2–C_6H_4) [718a].

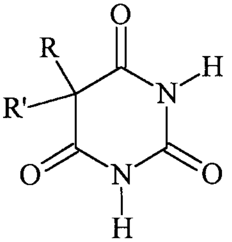
Carbamic acid derivatives of phosgene form the basis of a series of sedatives and hypnotics. Such materials are to be found in "Aponal", "Hedonal", "Euferina", "Termodina", "Neurodina", *etc.* [718a]. The simple urethane, $CO(NH_2)OEt$ (prepared from the reaction of ethyl chloroformate with aqueous ammonia, or by treatment of ammonium chloride with phosgene to give carbamoyl chloride, NH_2COCl, followed by reaction with ethanol) is a mild, but important, narcotic [577]; it has been employed in the treatment of chronic leukæmia [718a]. "Hedonal" {$CH_3CH_2CH_2CH(CH_3)OCONH_2$} is about twice as strong as urethane [577]; it is prepared by firstly reacting phosgene with pentan–2–ol, in the presence of *N*,*N*–dimethylaniline, to give the corresponding chloroformate, which upon treatment with aqueous ammonia gives a good yield of "Hedonal", Equation (4.13) [577].

$$\begin{aligned} CH_3CH_2CH_2CH(OH)CH_3 + COCl_2 &\longrightarrow CH_3CH_2CH_2CH(CH_3)OC(O)Cl + HCl \\ CH_3CH_2CH_2CH(CH_3)OC(O)Cl + NH_3(aq) &\longrightarrow CH_3CH_2CH_2CH(CH_3)OC(O)NH_2 + HCl \end{aligned} \qquad (4.13)$$

The barbiturate series of hypnotics are easily and cheaply made from phosgene [577]. Typically, a dialkyl malonic ester is treated with strong aqueous ammonia to give the diamide of the substituted malonic acid, Equation (4.14). This substance is then heated in an autoclave with phosgene for several hours at about 100 °C to give the corresponding dialkyl barbituric acid [577].

$$RR'C(CO_2CH_2CH_3)_2 + 2NH_3(aq) \longrightarrow RR'C(CONH_2)_2 + 2CH_3CH_2OH$$

$$RR'C(CONH_2)_2 + COCl_2 \longrightarrow$$

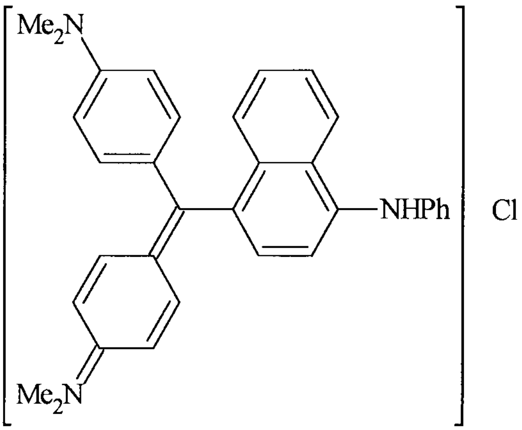


+ 2HCl (4.14)

4.7.4 Dyestuffs

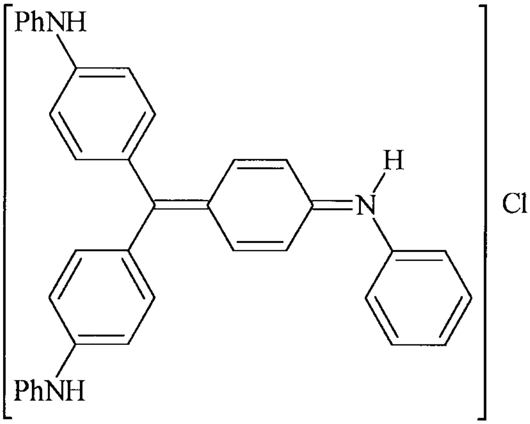
Phosgene has been commonly employed as an intermediate for the dyestuffs industry [577,718a,1003], and the treatment of aminoazo dyes with phosgene in aqueous solution, to give symmetrical urea azo dyes, has been practiced since the end of the last century [99a,99b].

When phosgene is combined with *N*,*N*-dimethylaniline in the presence of aluminium(III) chloride, Michler's ketone, 4,4'-bis(dimethylamino)benzophenone, is produced (see Section 10.2.1.1), which undergoes further reaction with *N*,*N*-dimethylaniline (also in the presence of aluminium(III) chloride or $POCl_3$) to give the colouring material "crystal violet", used in the production of methyl violet indicator paper. When Michler's ketone is warmed with *N*-phenyl-1-naphthylamine in the presence of $POCl_3$, Victoria blue (**4.13**) is formed, which is used as a dye for natural fibres [718a].



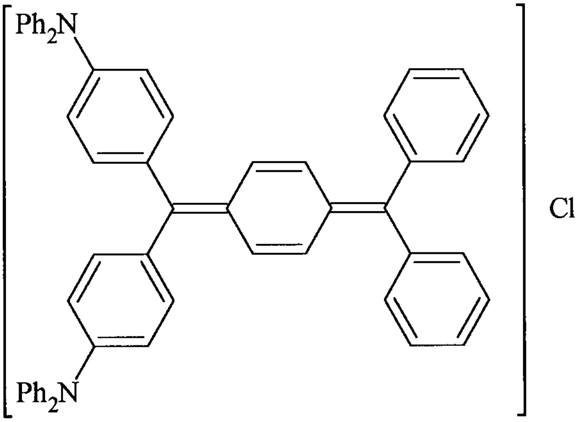
(**4.13**)

Treatment of *N*-phenylaniline with $COCl_2$ in the presence of aluminium(III) chloride gives diphenylamine blue, (**4.14**) [577]. Similarly, triphenylamine reacts with phosgene to form



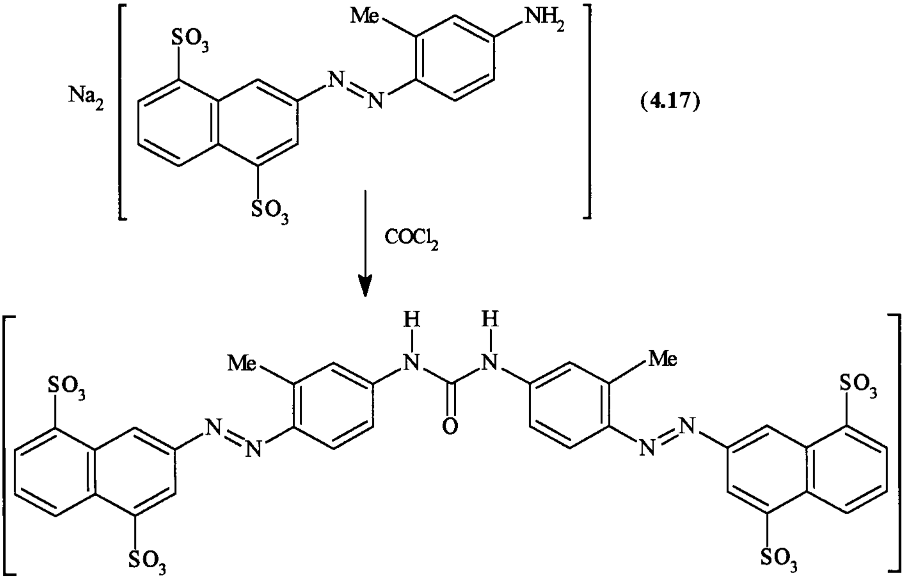
(**4.14**)

hexaphenylrosaniline, (**4.15**), a dark insoluble dye [577].



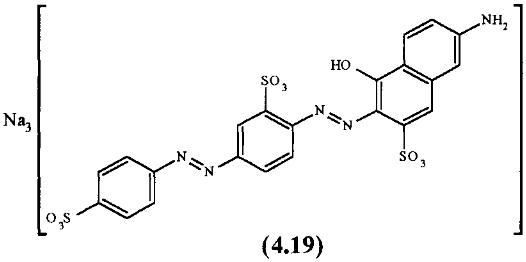
(4.15)

The commercially important Direct Yellow 50 (**4.16**; C.I. No. 29025) is obtained by treatment of two molar equivalents of the aminoazo compound (**4.17**) with phosgene [992a]:

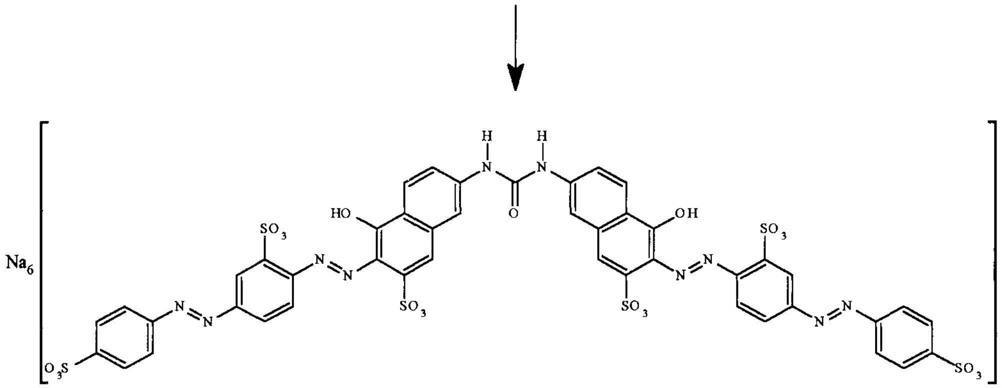


(4.16)

Disazo and trisazo dyes (containing two and three azo groups, respectively) can be treated with $COCl_2$ to give mostly red or brown shades. For example, Direct Red 80 (**4.18**; C.I. No. 35780) is prepared by treating (**4.19**) with phosgene [992a]:

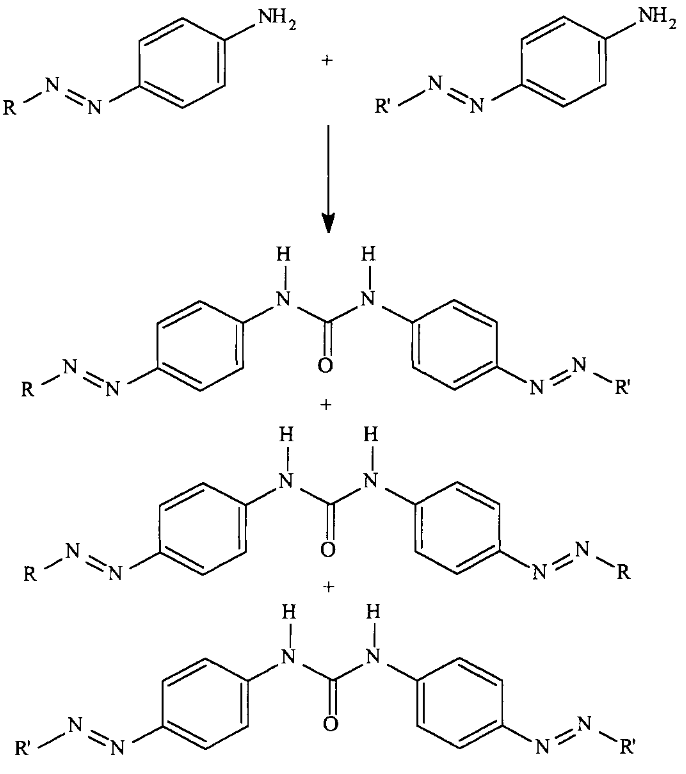


(4.19)



(4.18)

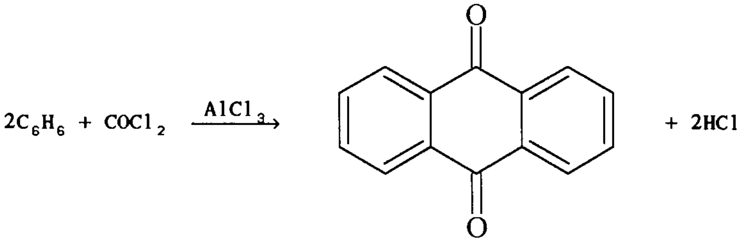
Mixing of two different aminoazo compounds, followed by reaction with phosgene, gives the asymmetrical urea, in addition to the two symmetrical products [992a]:



Other commercially important azo dyes which have been prepared using phosgene as a coupling agent are illustrated in Figure 4.13.

In addition to those mentioned above, phosgene has been used as a reagent in making the following commercial dyes [825]: Benzo Fast Orange, Benzo Fast Red, Benzo Fast Scarlet, Benzo Fast Yellow, Brilliant Sulphon Red B, Cotton Yellow, Ethyl Violet, Helindon Yellow, Chlorazol Fast Scarlet and Chlorazol Fast Orange.

One method for the preparation of 9,10-anthraquinone (used as the basis for many textile dyes) involves the catalysed reaction between phosgene and benzene [823a]:



The phosgene cyclization derivative, benzimidazalone (2-hydroxybenzimidazole), is also employed in dyestuffs manufacture, and phthalonitrile (used in the preparation of copper phthalocyanine) has also been prepared by the dehydration of phthalamide using phosgene.

4.7.5 Miscellaneous and potential uses

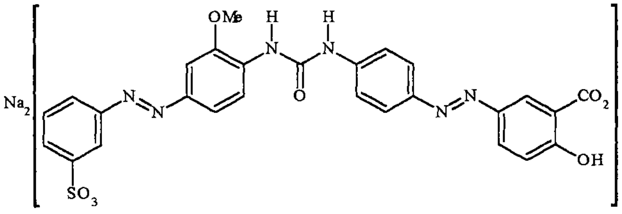
4.7.5.1 Polymers

Many patents describe the potential uses of phosgene for a wide variety of applications [885] but the singularly most important use for phosgene is in the preparation of polymeric materials. Apart from the polymers alluded to in Sections 4.7.1 and 4.7.2, phosgene may be used to prepare polymers *via* the C=O linkage, such as polyketones, polyureas, *etc.* Whilst not involving any new chemistry (as far as phosgene is concerned), the scope for preparation of new polymeric materials is enormous, if not infinite. In addition, phosgene can be employed in the modification of polymers although, curiously, much of this type of work has centred upon the reactions with materials such as bitumen, lignin and asphalt, derived directly from coal, wood, or petroleum [885].

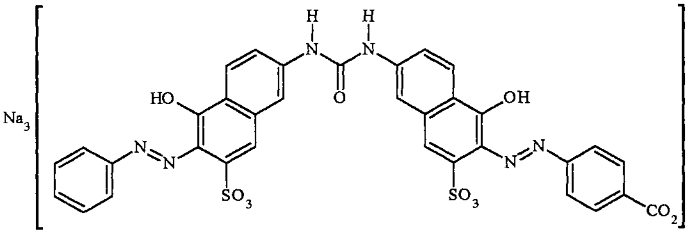
4.7.5.2 Phosgene as a reagent in organic syntheses

It is not the intention here to review the organic chemistry of phosgene (that is exhaustively covered in Chapter 10), but the scope for its use as an industrial synthetic reagent is apparent.

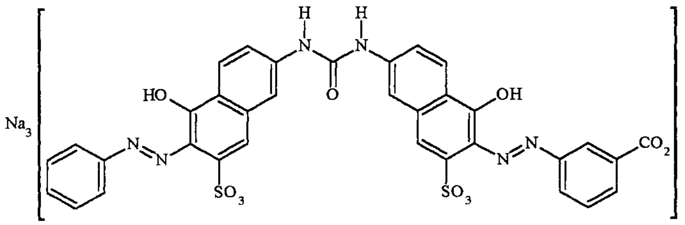
Phosgene has many uses and potential uses as a synthetic intermediate. It reacts with aromatic compounds in the presence of aluminium(III) chloride to give mostly acid chlorides, although the passage of phosgene into benzene at 50 °C, in the presence of aluminium(III) chloride, produces benzophenone as the final product [1415a]. 4,4'-Diphenoxybenzophenone, (**4.20**), is prepared from diphenyl ether and phosgene under similar conditions; it is used



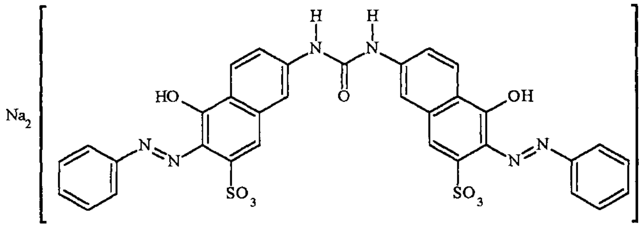
Direct Yellow 44
C.I. No. 29000



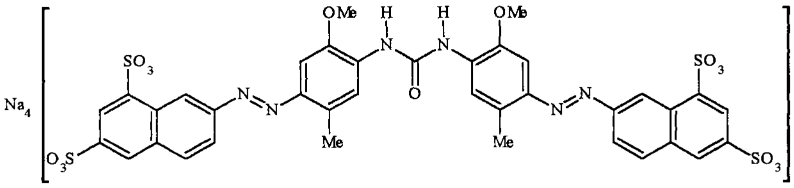
Direct Orange 102
C.I. No. 29156



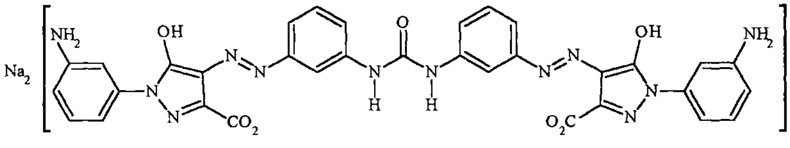
Direct Orange 29
C.I. No. 29155



Direct Orange 26
C.I. No. 29150

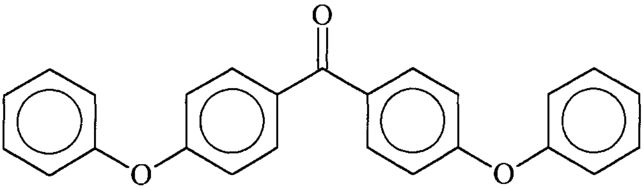


Direct Orange 72
C.I. No. 29058



Direct Orange 73
C.I. No. 25200

Fig. 4.13 **Some commercial dyes commonly prepared from phosgene [346a,992a].**

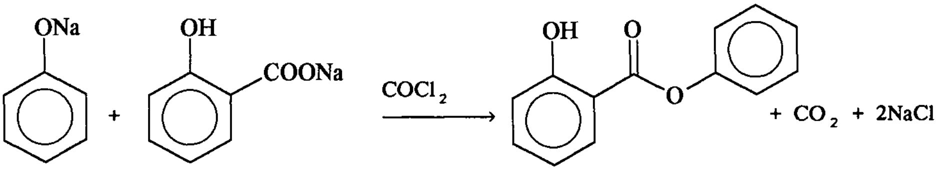


(4.20)

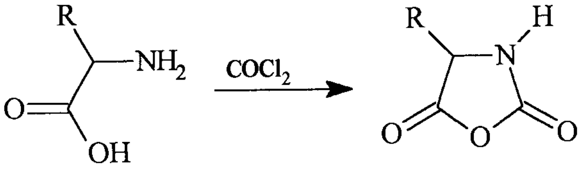
in the production of high-performance plastics that have long-term heat resistance and fire-extinguishing properties [11873a,2027b]. A particularly interesting reaction is that of phosgene wiht fluorobenzene, in the presence of HF and BF_3, to give 4,4'-difluorobenzophenone (BDF; see Section 10.1.5), a precursor for the high-performance thermoplastic, Victrex® PEEK [509a].

Phosgene can also be used to convert acetic acid to its anhydride [92], and the addition of phosgene to propene, followed by treatment with methanol and dehydrochlorination of the ester (see Section 10.1.2) results in the production of methyl methacrylate [1699]. Despite their simplicity, neither of these routes have been developed commercially. However, the use of phosgene with carboxylic acids to form acid chlorides has many advantages over the use of PCl_5 or $SOCl_2$, in that the by-products (CO_2 and HCl) are readily removed, leaving a high purity product: this is especially important in the synthesis of acid chlorides of fatty acids, which resist distillation [1841a]. Isophthaloyl dichloride and terephthaloyl dichloride are both produced commercially by the action of phosgene on their respective acids [1804a].

Phosgene may be used as a condensing agent. For example, the antiseptic and general chemical, phenyl salicylate, may be prepared by mixing sodium phenate, sodium salicylate and phosgene in an autoclave; phenyl salicylate is formed quantitatively [577]:

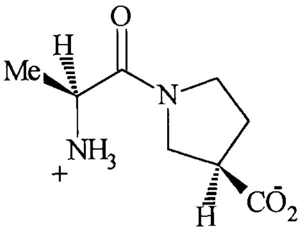


The cyclization reactions of phosgene are described in detail in Chapter 10; these transformations represent important routes to many intermediates in the food, pharmaceutical and agricultural industries. For example, *N*-carboxyanhydrides, of type (**4.21**), are formed from the reaction of phosgene with 1-amino acids:



(4.21)

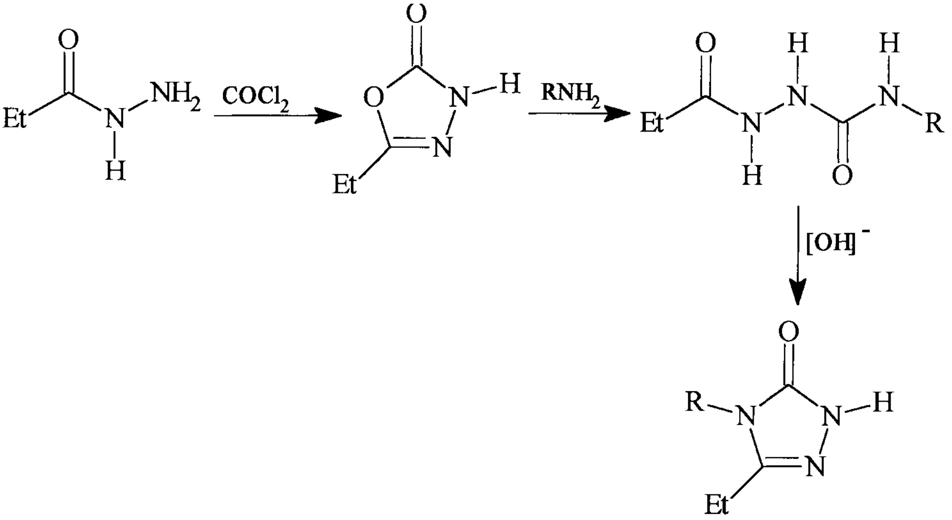
The compound (**4.21**; R = $CH_2C(O)OMe$) is a precursor of the nutritive sweetner, aspartame (see Section 10.3.4.5) [2045a]. Related carboxyanhydrides can be used in the preparation of dipeptides, such as L-alanyl-L-proline (**4.22**) [202a]:



(4.22)

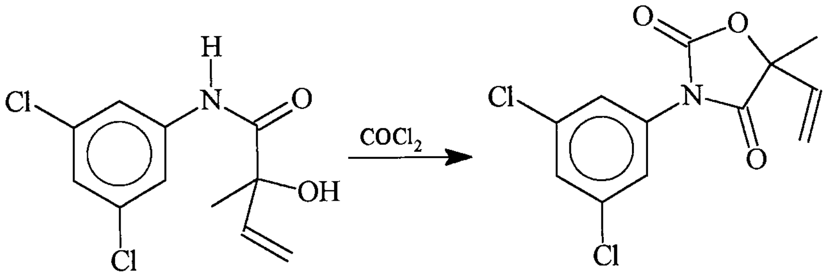
N-Carboxyanhydrides are also used in the production of polyamino acid artifical skin [1841a].

Hydrazides cyclize to oxadiazolinones on treatment with phosgene, to give compounds with important applications in both the pharmaceutical and agricultural industries. For example, "Etoperidone" (**4.23**; R = Et) and "Nefazodone" (**4.23**; R = $PhOCH_2CCH_2$) can be prepared as follows [1841a]:



(4.23)

Finally, in this Section, it is noted that the hydroxyamide (**4.24**) cyclizes on addition of phosgene to give the fungicide 1,3-oxazolidine-2,4-dione, "Vinclozolin", (**4.25**) [1841a]:



(4.24) (4.25)

4.7.5.3 Phosgene as a reagent in inorganic syntheses

Miscellaneous uses of phosgene include precious metal–recovery operations [90,231,261] and anhydrous metal chloride manufacture (see Sections 9.4 and 9.5) [97,577,962]. The conversion of PuO_2 to $PuCl_3$ with phosgene has been used as part of a plutonium recovery process (see Section 9.6.2) [234]. Reaction of phosgene with metal silicates gives the metal chloride and silicon dioxide, useful for the breaking down of silicate minerals (Section 9.4.4) [120,577,884] and for the de-alumination of zeolites (Section 9.4.3) [638]. The ash content of natural graphite can be considerably reduced by treatment with phosgene at high temperatures [814]. Phosgene has been used as a bleaching agent in treating sand for making fine glass [825], and in admixture with HF, phosgene is reported to catalytically crack hydrocarbon oil [1256].

Phosgene has been employed in the modification of the surfaces of cellulose–acetate membranes used for water desalination and waste water treatment [1450]. Similarly, phosgene has been used to surface-modify porous diaphragms for electrolytic cells [324]. Aluminium and aluminium-based alloys can be etched at a high rate when $COCl_2$ is used in a mixed gas plasma [1004], as can semiconductors (see Section 9.12).

In the manufacture of $SOCl_2$ from phosgene [ICI82], sulfur dioxide and phosgene are combined over a charcoal catalyst at about 170 °C (see Section 9.4.6) [ICI10,ICI32]. This process at one time formed the basis for manufacture of thionyl chloride ($SOCl_2$) in ICI.

The reaction of phosgene with cadmium sulfide is said to be a good method for the preparation of COS (see Section 9.5.7) [885], used in the manufacture of organic thio compounds, whilst reaction of $COCl_2$ with iron(III) phosphate at 300–350 °C has been proposed as a synthetic method for $POCl_3$ (see Section 9.4.5) [885].

Phosgene can be used as the starting material for the preparation of other potentially useful carbonyl halides and carbonyl pseudohalides. Reaction of phosgene with fluorspar, for example, gives COClF (see Section 9.1.1 and Chapter 16). With aluminium(III) bromide, $COBr_2$ is formed (Section 9.1.2.6). Reaction of $COCl_2$ with HF gives COF_2 (see Section 9.10.4 and Chapter 13), reaction with silver cyanide gives carbonyl dicyanide, $CO(CN)_2$ (Section 9.1.7), whereas reaction with a mixture of sodium fluoride and HCN gives the mixed carbonyl halide pseudohalide, COFCN (Section 9.1.7 and Chapter 13). The chemistry of these simple phosgene derivatives is largely unexplored yet each offers considerable potential for the synthesis of many important compounds (see Chapters 13, 14 and 16).

4.7.6 Phosgene as a chlorinating agent

The applications of phosgene as a carbonylating agent, an acylating agent, a dehydrating agent, a condensing agent, a cyclizing agent and a chloroformylating agent have all been described above. Curiously, only rarely has phosgene been employed industrially as a chlorinating agent. Indeed, in most of the commercial reactions alluded to above, the chlorine atoms of phosgene are downgraded into hydrogen chloride, sodium chloride or the like, and even where chloroformates are prepared from phosgene, the subsequent reactions normally result in the loss of the remaining chlorine atom from the molecule.

A possible exception to the foregoing statement is the so-called "disproportionation" of phosgene (see Chapter 8). This process, Equation (4.15), has been proposed as an efficient method for the manufacture of tetrachloromethane, although in the present feedstock situation this process would not be economical. Indeed, at the current prices commanded for phosgene, and with the perceived availability of carbon tetrachloride, it would be more beneficial to be able to derive phosgene from CCl_4, for example by oxidation or hydrolysis.

$$2COCl_2 \longrightarrow CCl_4 + CO_2 \qquad (4.15)$$

Interestingly, since tetrachloromethane may be readily interconverted into tetrachloroethene, a synthetic route to the C_2 chlorinated hydrocarbons appears feasible [ICI1].

The advantages of phosgene over dichlorine, hydrogen chloride or other chlorinating agents become clear when the reactions with oxides or oxygenates are considered [ICI1]. Consider, initially, the reaction of phosgene with aluminium(III) oxide to produce aluminium(III) chloride (a process used for its large-scale production [2215]):

$$Al_2O_3(s) + 3COCl_2(g) \longrightarrow [Al_2Cl_6](s) + 3CO_2(g); \qquad \Delta G^{\circ}_{298} = -150 \text{ kJ mol}^{-1}$$

This reaction takes place at around 400 °C and has an equilibrium yield lying well over to the right hand side of the equation; it is driven by the large negative value of the free energy associated with the formation of the thermodynamically stable CO_2. The reaction of alumina with hydrogen chloride, however, is not thermodynamically favourable (ΔG°_{298} = +80 kJ mol^{-1}) unless much higher temperatures are employed. The reaction of dichlorine with alumina suffers from the disadvantage that no oxygen scavenger is inherent in the system (the addition of carbon is necessary to produce an acceptable yield). Thus, phosgene has a higher thermodynamic reactivity than HCl and, unlike dichlorine, phosgene can act as an oxygen scavenger [ICI1]. Other examples for the preparation of the anhydrous chlorides from the refractory metal oxides are provided in Table 4.9 (see also Sections 9.5 and 9.6) [577].

TABLE 4.9

PREPARATION OF METAL CHLORIDES FROM METAL OXIDES AND PHOSGENE [577]

Metal Oxide	T/ °C [a]	Product
V_2O_5	350	VCl_4
WO_3	350	WO_2Cl_2
Ta_2O_5	400	$TaCl_5$
TiO_2	400	$TiCl_4$
ZrO_2	400	$ZrCl_4$
UO_2	450	UCl_4
Cr_2O_3	600	$CrCl_3$ [c]
CeO_2	600	$CeCl_4$
Y_2O_3	600	YCl_3
La_2O_3	600	$LaCl_3$
ThO_2	650	$ThCl_4$
PuO_2	850	$PuCl_3$ [b]

[a] Reaction temperature. [b] [234]. [c] [282].

Coal is poised to eventually replace oil as the primary industrial feedstock [862a]. In the way that oil is cracked to produce ethylene, coal (or other organic material, such as natural gas) may be converted to synthesis gas. A large number of oxygenates are derivable from synthesis gas, some of which (such as ethanoic acid and methanol) are already in full commercial production. In conventional (ethylene-based) technology, dichlorine is normally employed to produce the commercial chlorinated hydrocarbons such as vinyl chloride, 1,1,1-trichloroethane, and trichloroethylene. If synthesis gas is to eventually displace ethylene, and if the chlorinated hydrocarbons are still in demand, then an alternative chlorinating agent will be required in order to manufacture these materials economically. Consider, as an example, the reactions of the four chlorinating agents - Cl_2, HCl, $COCl_2$ and $SOCl_2$ - with acetaldehyde (an oxygenate derivable from synthesis gas) to produce 1,1-dichloroethane (a potential key intermediate in the chlorinated hydrocarbons industry) [ICI1,ICI84].

4.7.6.1 The reaction between dichlorine and acetaldehyde

In the reaction of acetaldehyde with dichlorine (Equation 4.16), hydrogen atoms are substituted for chlorine atoms to give mono-, di-, and trichloroacetaldehyde (chloral); chlorine does not displace the oxygen atoms.

$$CH_3CHO + Cl_2 \longrightarrow ClCH_2CHO + HCl \text{ (+ other chlorinated aldehydes)} \qquad (4.16)$$

4.7.6.2 The reaction between hydrogen chloride and acetaldehyde

This hypothetical reaction (Equation 4.17; $\Delta G^\circ_{298} = -19.2$ kJ mol^{-1}) is thermodynamically unfavourable at higher temperatures. For example, at 227 °C and atmospheric pressure, $\Delta G^\circ_{500} = +65.3$ kJ mol^{-1}, corresponding to an equilibrium yield of only 0.1%.

$$CH_3CHO + 2HCl \longrightarrow CH_3CHCl_2 + H_2O \qquad (4.17)$$

4.7.6.3 The reaction between phosgene and acetaldehyde

This reaction (Equation 4.18; $\Delta G^\circ_{298} = -127.4$ kJ mol^{-1}) is highly favourable at temperatures at which it may be expected to occur in a practical sense (see also Section 10.3.3.1). The equilibrium yield is in excess of 99% at temperatures up to 750 °C.

$$CH_3CHO + COCl_2 \longrightarrow CH_3CHCl_2 + CO_2 \qquad (4.18)$$

4.7.6.4 The reacton between thionyl chloride and acetaldehyde

The energetics of the reaction of acetaldehyde with $SOCl_2$ are not favourable at reasonable reaction temperatures. Unlike CO_2 (which is much more stable than $COCl_2$), SO_2 is only marginally more stable than $SOCl_2$. There is thus a much smaller thermodynamic driving force for the $SOCl_2$ reaction compared to that for $COCl_2$. The reaction of $SOCl_2$ with CH_3CHO (Equation 4.19; $\Delta G^\circ_{298} = -6.4$ kJ mol^{-1}) is feasible only at low temperatures (<100 °C) within the limitations described, and in fact the preferred reaction product at low temperatures is bis(1-chloroethyl) ether, $(CH_3CHCl)_2O$.

$$CH_3CHO + SOCl_2 \longrightarrow CH_3CHCl_2 + SO_2 \qquad (4.19)$$

The reactions of acetaldehyde with phosgene to produce 1,1-dichloroethane [ICI84], and of formaldehyde with phosgene to produce dichloromethane [1765,ICI84], have been demonstrated by employing active charcoal catalysts. Other possible conversions of oxygenate materials (derivable, or potentially derivable, from synthesis gas) to commercially important chlorinated hydrocarbons are listed in Table 4.10 [ICI1,ICI84–ICI86]. Although most of these reactions are as yet untried, their importance may increase as petroleum-based materials become prohibitively more expensive and synthesis gas becomes increasingly more attractive as the chemical industries major synthesis building block [ICI87].

TABLE 4.10

POTENTIAL ROUTES TO C_1 AND C_2 CHLORINATED HYDROCARBONS [ICI1]

Oxygenate	Chlorinated Hydrocarbon
CH_3OH	CH_3Cl
CH_2O	CH_2Cl_2
CH_3CH_2OH	CH_3CH_2Cl
$CH_2(OH)CH_2(OH)$	CH_2ClCH_2Cl
CH_3CHO	CH_3CHCl_2
CH_3COOH	CH_3CCl_3
$CH_2{=}C{=}O$	$CH_2{=}CCl_2$
$CH_3(CO)OCH_3$	CH_3CCl_3, CH_3Cl
$CH_3CH(OCOCH_3)_2$	CH_3CCl_3, CH_3CHCl_2
$CH_2{=}CH(OCOCH_3)$	CH_3CCl_3, $CH_2{=}CHCl$

There is thus considerable scope for further examination of the reactions of phosgene with a wide variety of alcohols, diols, aldehydes, hydroxy-aldehydes, epoxides, esters, acids and anhydrides to produce the desired range of chlorinated organic materials. The analogous reactions of COF_2 and of COClF will be described in Chapters 13 and 16, respectively.

4.7.7 Overview

Phosgene can be regarded, in many ways, as an activated form of carbon monoxide. The attached chlorine atoms are good leaving groups and confer high reactivity to phosgene, particularly towards active hydrogens. Although most phosgene is used captively, within the plant boundary, its wide application as a synthetic intermediate means that at least some of the material is employed at locations remote from the site of manufacture. Despite its toxicity, then, phosgene is an indispensable starting material for a variety of commercially important materials. Indeed, the primary reaction products of phosgene (isocyanates, chloroformates, carbonates, carbamates and ureas) are in themselves useful synthetic intermediates. Other isocyanates and chloroformates, in particular, will be required for new products as they are developed, and phosgene will be the obvious material to affect the required chemical transformations.

For the more distant future, there is no doubt that the full potential of phosgene as a useful chemical intermediate has not yet been fully realized. It appears to be the obvious intermediate *en route* from carbon monoxide (or synthesis gas) feedstocks to those important large-scale C_1 and C_2 chlorocarbons and hydrochlorocarbons which will ultimately survive legislative phase-out. In addition, the reaction of phosgene with calcium fluoride (fluorspar) to give carbonyl chloride fluoride (Sections 9.1.1 and 16.1.4) and the facile way in which it can be converted into COF_2 (see Chapter 13) permits a new system for the preparation of a wide range of fluorochemicals and CFC alternatives.

5 SYNTHESIS AND FORMATION OF PHOSGENE

It is rarely necessary, nowadays, to prepare phosgene in the laboratory since cylinders and lecture bottles are generally readily available (see Section 3.1.5.3). The purpose of this Chapter is threefold:

(1) to demonstrate the synthetic methods which are available, or which could be developed, for the production of phosgene,

(2) to highlight the known reactions which can result in the formation of phosgene as a by-product, and

(3) to review the published methods available for the synthesis of labelled phosgene.

Thus, we have concentrated in this Chapter not only upon those reactions which constitute an efficient synthesis of phosgene or labelled phosgene, but also (owing to the exceptional toxicity of the compound) on those reactions which generate even comparatively low yields and which could be conceivably problematical in the chemical plant environment, and in both the organic and inorganic laboratory.

Sources of industrial emission of phosgene have been described in Sections 3.3 and 3.6, and its environmental formation has been dealt with in Section 3.7. Useful reviews concerning the synthesis or formation of phosgene have appeared [578,781,996,1019,1378,1379,1464], and the manufacture and purification of phosgene is the subject of Chapter 4.

The manufacture of any large-scale, industrially important compound is susceptible to changes in the availability of raw materials, the economic climate, legislative constraints, and the particular manufacturer's local considerations. There is little doubt, at the present time, that (under the vast majority of conditions) the synthesis of phosgene from carbon monoxide and dichlorine, catalysed by activated charcoal, constitutes the most favourable method in economic terms.

However, those chemical manufacturers (particularly the smaller contract manufacturer) who may not be sited near to a CO (or Cl_2) producing facility may need to have alternative means of generating phosgene at their disposal, for their various processes (see Section 3.1.6). Indeed, in view of the anticipated legislation in Europe, the U.S.A., and elsewhere to control, or prohibit, the transportation of phosgene, those processes which depend upon phosgene (where it is not locally available) could be severely prejudiced in the absence of such alternatives.

This Chapter is therefore structured bearing such important considerations in mind. At the same time, we have not disregarded the need for alternative syntheses of phosgene in the research laboratory, where budgetary or bureaucratic constraints can result in lost research capability.

5.1 SYNTHESIS OF PHOSGENE FROM CARBON MONOXIDE

The importance of carbon monoxide for the synthesis of phosgene has been exemplified in Chapter 4: this material, along with dichlorine, constitutes the basis for most, if not all, modern phosgene manufacture. This Section deals with the various means of activating the reaction between CO and Cl_2, or other chlorinating agent, by photochemical, thermal, catalytic, or electrochemical means, and ends with a special Section dealing with the generation of phosgene from the reaction of CO with inorganic chlorides.

5.1.1 Photochemical synthesis

The historical significance of the photochemically-induced reaction between carbon monoxide and dichlorine has been described in Chapter 1; notably, investigation of this system led to the discovery and christening of phosgene ("produced by light") by John Davy [467]. Although, as expected, most studies use u.v. light to promote reaction, visible light will also initiate the reaction [190].

In 1907, Weigert [2162] showed that the effect of light upon the equilibrium between CO, Cl_2 and $COCl_2$ was purely catalytic, and did not effect the position of final equilibrium. The importance of truly anhydrous conditions had been highlighted as early as 1923 [2048]. Although a later investigator [1818] found that the presence of small amounts of water did not alter, appreciably, the measured reaction kinetics, the seminal work of Bodenstein clearly emphasizes (perhaps not surprisingly) the importance of really dry reagents and apparatus [211,219].

The first serious studies of the kinetics of photochemically induced phosgene formation were made by Bodenstein and his collaborators, who published two rather concise reviews of their own research [212,213]; this work was also reviewed by other, independent, groups [1114,2013]. At room temperature, the rate of reaction was given by [211]:

$$d[COCl_2]/dt \quad = \quad kI^{\frac{1}{2}}[Cl_2][CO]^{\frac{1}{2}}$$

where I = intensity of absorbed light

Dioxygen was found to inhibit this reaction, CO_2 being formed in a dichlorine-sensitized photocatalytic reaction [210,215,219,272,1546,2068], and experiments at low pressures indicated that chlorine atoms were recombining at the vessel walls, thus slowing down the reaction [217,1114]. The effect of added CO_2 was also examined [344,345]. At 260–300 °C, however, simpler kinetics were followed, and the inhibition effect of O_2 was eliminated (no CO_2 was formed) [211,219]:

$$d[COCl_2]/dt = kI[Cl_2][CO]$$

At 400 °C, photochemical and thermal formation of phosgene start to compete with each other, but the equilibrium position is unaffected [219]:

$$d[COCl_2]/dt = [Cl_2]^{\frac{1}{2}}\{k_1[Cl_2][CO]^{\frac{1}{2}} - k_2[COCl_2]\}$$

The mechanism for the photochemical formation of phosgene has evolved with time. The production of the $[COCl]\cdot$ radical was first proposed by Christiansen [387], and the simplest mechanism at ambient temperature and normal pressures for the photochemical formation of phosgene is that proposed by Bodenstein, Lenher and Wagner [212,217,1819]:

$$\begin{aligned} Cl_2 + h\nu &\longrightarrow 2Cl\cdot \\ Cl\cdot + CO &\longrightarrow [COCl]\cdot \\ [COCl]\cdot &\longrightarrow CO + Cl\cdot \\ CO + Cl\cdot + Cl_2 &\longrightarrow COCl_2 + Cl\cdot \\ [COCl]\cdot + Cl\cdot &\longrightarrow CO + Cl_2 \end{aligned}$$

An alternative mechanism [387], involving the formation of $[Cl_3]\cdot$ as the chain carrier (*cf.* Section 5.1.2), gained its proponents [346,1735,1736,1737], but was soon discounted by Bodenstein and coworkers [212,214,215a]. More recent studies have confirmed the key role of the $[COCl]\cdot$ radical [308,674,705], whilst highlighting the importance (both experimentally and theoretically) of third-body collisions, and collisions with the reactor wall [1528].

Surprisingly, under the conditions of flash photolysis, no detectable photochemical reaction is induced between CO and Cl_2, although almost complete dissociation of phosgene can be induced under identical conditions [1523,1647a]: this has been ascribed to the very high radical concentrations present, and the high instantaneous temperatures which are generated [1523].

Although it was recognized by Bodenstein *et al.* in 1929 [217] and Lenher and Rollefson in 1930 (*pace* later disagreements concerning the involvement of $[Cl_3]\cdot$) [1226] that the reaction of chlorine atoms with CO was a key step in the photochemical formation of phosgene:

$$Cl\cdot + CO \longrightarrow [COCl]\cdot$$

it was not until 1965 [1023] that the $[COCl]\cdot$ radical was observed experimentally, trapped in a matrix of either argon or CO at 14 K. Chlorine atoms (formed by the photolysis of HCl, Cl_2, $COCl_2$ or $\{C(O)Cl\}_2$) were shown to react with CO with essentially zero activation energy, to generate bent [COCl]·, which shows fundamental vibrations at 1880, 570 and 281 cm^{-1} [1023]. Interestingly, [COCl]· shows no absorption bands in the region 450–250 nm, and the CO bond appears to be stronger than that in phosgene [1023]. The reaction between CO and Cl_2 under thermal conditions can now be used as a source of [COCl]· radicals. For example, the reaction between [COCl]· and NO_2 has been studied between 381 and 473 °C [2027]:

$$[COCl]\cdot + NO_2 \longrightarrow CO_2 + NO + Cl\cdot$$

The full, currently accepted, mechanism for the photochemical (and thermal) formation of phosgene is given below [308,781], and is supported by both photochemical [1964] and thermal [1965] studies using ^{14}CO and $^{12}COCl_2$ (see also Section 5.8.3):

I	$Cl_2 + h\nu$	$\longrightarrow$	$2Cl\cdot$
II	$Cl_2 + M$	$\rightleftharpoons$	$2Cl\cdot + M$
III	$Cl\cdot + CO + M$	$\longrightarrow$	$[COCl]\cdot + M$
IV	$[COCl]\cdot + M$	$\longrightarrow$	$CO + Cl\cdot + M$
V	$[COCl]\cdot + Cl_2$	$\longrightarrow$	$COCl_2 + Cl\cdot$
VI	$COCl_2 + Cl\cdot$	$\longrightarrow$	$[COCl]\cdot + Cl_2$
VII	$[COCl]\cdot + Cl\cdot$	$\longrightarrow$	$CO + Cl_2$
VIII	$Cl\cdot$	$\xrightarrow{wall}$	$\frac{1}{2}Cl_2$

Each step will now be considered in turn, so that its contribution under differing conditions may be assessed.

I This step represents the photochemical initiation of the reaction. The quantum yield (366 nm) for the formation of phosgene has been determined as 6244 at 25 °C [308], and its dependence on light intensity and reactant pressure investigated [674]. Similar behaviour is obtained if the reaction is initiated with α–particles (from radon) instead of photons, and the same form of kinetic dependence is found [37]: the photochemical yield per quantum is approximately equal to the radiation yield per ion pair [37].

II This equilibrium is often represented by K_{Cl_2}:

$$K_{Cl_2} = \frac{[Cl\cdot]^2}{[Cl_2]}$$

The forward process is responsible for the thermal initiation of the reaction; the reverse process represents a termination step.

III This step represents the primary generation of [COCl]· radicals, the chain propagator.

IV This step is the reverse of step III. Under conditions where step **V** is supressed, steps III and IV are in equilibrium, usually represented by K_{COCl}:

$$K_{COCl} = \frac{[CO][Cl\cdot]}{[\{COCl\}\cdot]}$$

$$= \frac{k_{IV}}{k_{III}}$$

K_{COCl} is very temperature dependent [308]:

$$K_{COCl} = 639.7\ \exp(-3175/T)\ \text{mol l}^{-1}$$

This gives values of K_{COCl} of 0.13, 2.5, 10.5 and 25.5 mol l^{-1} at 100, 300, 500 and 700 °C, respectively.

V This step represents an important propagation reaction. Its rate constant is given by [308]:

$$k_V = 2.512 \times 10^9 \exp(-1490/T)\ \text{l mol}^{-1}\ \text{s}^{-1}$$

VI This step, the reverse of **V**, represents termination above *ca.* 350 °C, and has a relatively high activation energy.

VII This step represents termination below 250 °C; it is ineffectual at higher temperatures because of the relatively low concentrations of [COCl]· radicals. Its rate constant is given by [308]:

$$k_{VII} = 3.981 \times 10^{11} \exp(-418/T)\ \text{l mol}^{-1}\ \text{s}^{-1}$$

VIII This step represents termination at low pressure. The recombination coefficient (*i.e.* the ratio of the number of Cl· atoms recombining at the walls to the total number of Cl· atoms colliding with the walls) is 5 x 10^{-5} [1528].

Dainton's observations [450] that the reaction is inhibited by the presence of NOCl are completely in keeping with this scheme, with two new termination steps added [309,450]:

$$\mathrm{Cl\cdot} + \mathrm{NOCl} \longrightarrow \mathrm{NO} + \mathrm{Cl_2}$$

$$[\mathrm{COCl}]\cdot + \mathrm{NOCl} \longrightarrow \mathrm{NO} + \mathrm{CO} + \mathrm{Cl_2}$$

The presence of tetrachloromethane inhibits the formation of phosgene, and this has been ascribed to its action as an inert third body for the recombination of chlorine atoms to form dichlorine, thus inhibiting both the formation of [COCl]· and its reaction with Cl· [1328]:

$$2\mathrm{Cl\cdot} + \mathrm{CCl_4} \longrightarrow \mathrm{Cl_2} + \mathrm{CCl_4}$$

There have been a number of reports of convenient laboratory syntheses of phosgene based upon the photochemical reaction between CO and Cl_2. Thus, passage of a 1:1 mixture at 4.7 l h^{-1} through CCl_4 (200 cm^3) at 0–5 °C, irradiated with a mercury lamp, produced 16.7 g of $COCl_2$ h^{-1} (92% yield) [1150].

In an interesting study of the formation of phosgene from CO and Cl_2 under γ-irradiation (from a ^{60}Co source), the rate of phosgene formation was given by [1204]:

$$\mathrm{d[COCl_2]/d}t \quad \alpha \quad (1 - 0.01T)(p_{\mathrm{CO}}I)^{\frac{1}{2}}p_{\mathrm{Cl_2}}$$

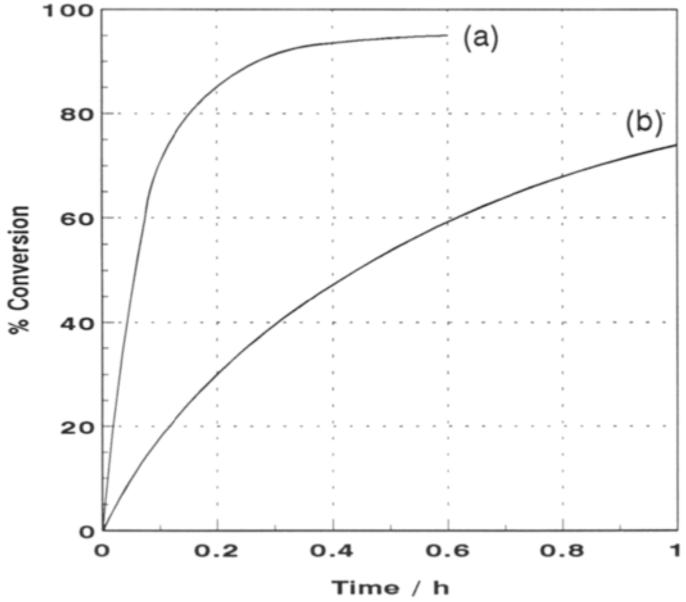


Fig. 5.1 Comparison of the reaction of CO and Cl_2 (a) in the presence of a carbon catalyst, and (b) under γ-irradiation [1204].

where p_X is the pressure of X, T is the temperature in °C and I is the radiation intensity. The presence of O_2, or a large surface-to-volume ratio, retarded the reaction; the presence of inert gases had no effect. Although this reaction is attractive, Fig. 5.1 illustrates that it does not, as yet, compete effectively with conventional technology. However, a low temperature plant (−20 °C) to produce liquid phosgene (at the rate of one million pounds per year) has been proposed (see Fig. 5.2), and merits serious attention, as it would operate using cheap nuclear waste.

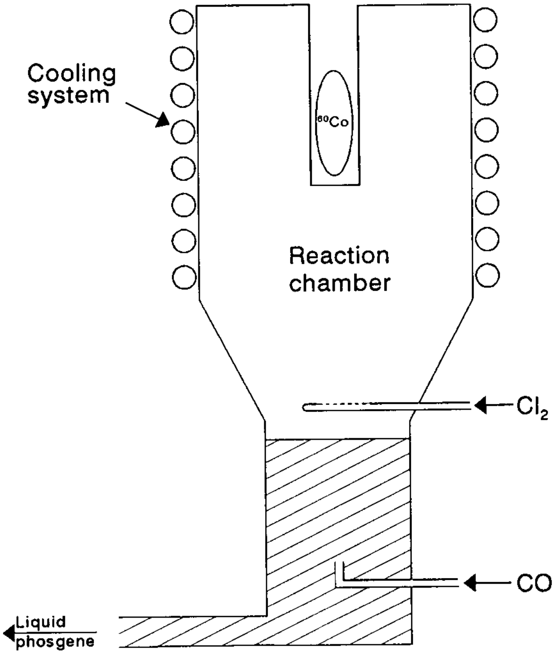


Fig. 5.2 **Proposed industrial reactor to produce liquid phosgene from nuclear waste [1204].**

5.1.2 Thermal synthesis

The thermal synthesis of phosgene involves the reaction of carbon monoxide with dichlorine {Equation (5.1)} induced by purely thermal, as opposed to catalytic (Section 5.1.3), means.

$$CO + Cl_2 \rightleftharpoons COCl_2 \qquad (5.1)$$

Since this reaction involves a reduction in pressure, investigations of the thermal equilibrium are usually based upon measurements of pressure in static systems. Owing to the slow rate of reaction, thermal equilibria can only be measured normally at temperatures above about 350 °C [212]. However, in studies extending over several months, the thermal formation of phosgene, *via* reaction (5.1), has been perceived at temperatures as low as 160 °C [1818a]. In one patent [2175], it is claimed that phosgene can be prepared by allowing CO to saturate liquid dichlorine at a temperature of below −34 °C (the boiling point of dichlorine) or at higher temperatures, under sufficient pressure to maintain the Cl_2 in the liquid state.

The extent of thermal dissociation of phosgene at 0.5, 1.0 and 10 bar pressure (0.05, 0.1 and 1 MPa, respectively) has been calculated [1764] based on the accepted ideal gas thermodynamic values [359aa], and is illustrated in Fig. 5.3, whilst the enthalpy of formation for this reaction has been based on actual measurements of the equilibrium constant in the temperature range of 645–725 K by heating together carbon monoxide and dichlorine [218], see Section 6.1. The equilibrium reaction depicted in Equation (5.1) has been measured experimentally both by dissociation of phosgene and by association of carbon monoxide and dichlorine [216]. At 603, 553 and 503 °C, the dissociation was found to be 91, 80 and 67%, respectively, in reasonable agreement with the values based on the ideal gas calculations illustrated in Fig. 5.3. At temperatures above 800 °C, the dissociation is essentially complete [216].

Even at temperatures as high as 503 °C, however, the thermal reaction between carbon monoxide and dichlorine is far from instantaneous, as illustrated in Fig. 5.4, which indicates the time required for the close attainment of equilibrium for both the formation (upper curve) and dissociation (lower curve) of phosgene [216].

Between 349–452 °C, at an initial total pressure of about one atmosphere, the rate of formation of phosgene from CO and Cl_2 under thermal, equilibrium, conditions is given (using the useful notation developed in Gmelin [781]) by the expression [218]:

$$d[COCl_2]/dt = x_1[CO][Cl_2]^{3/2} - x_2[COCl_2][Cl_2]^{\frac{1}{2}}$$

$$\text{where } x_1/x_2 = K = [CO][Cl_2]/[COCl_2]$$

The mechanism for the formation of phosgene was represented originally by the following steps, in which the Cl_2 dissociation reaction is initiated thermally, and the $Cl\cdot$ and $[Cl_3]\cdot$ radicals are the chain carriers for the process [218]:

$$Cl_2 \xrightleftharpoons{K_1} 2Cl\cdot$$

$$Cl\cdot + Cl_2 \xrightleftharpoons{K_2} [Cl_3]\cdot$$

$$[Cl_3]\cdot + CO \xrightarrow{k_3} COCl_2 + Cl\cdot$$

$$Cl\cdot + COCl_2 \xrightarrow{k_4} [Cl_3]\cdot + CO$$

$$[Cl_3]\cdot + Cl\cdot \xrightarrow{k_5} 2Cl_2$$

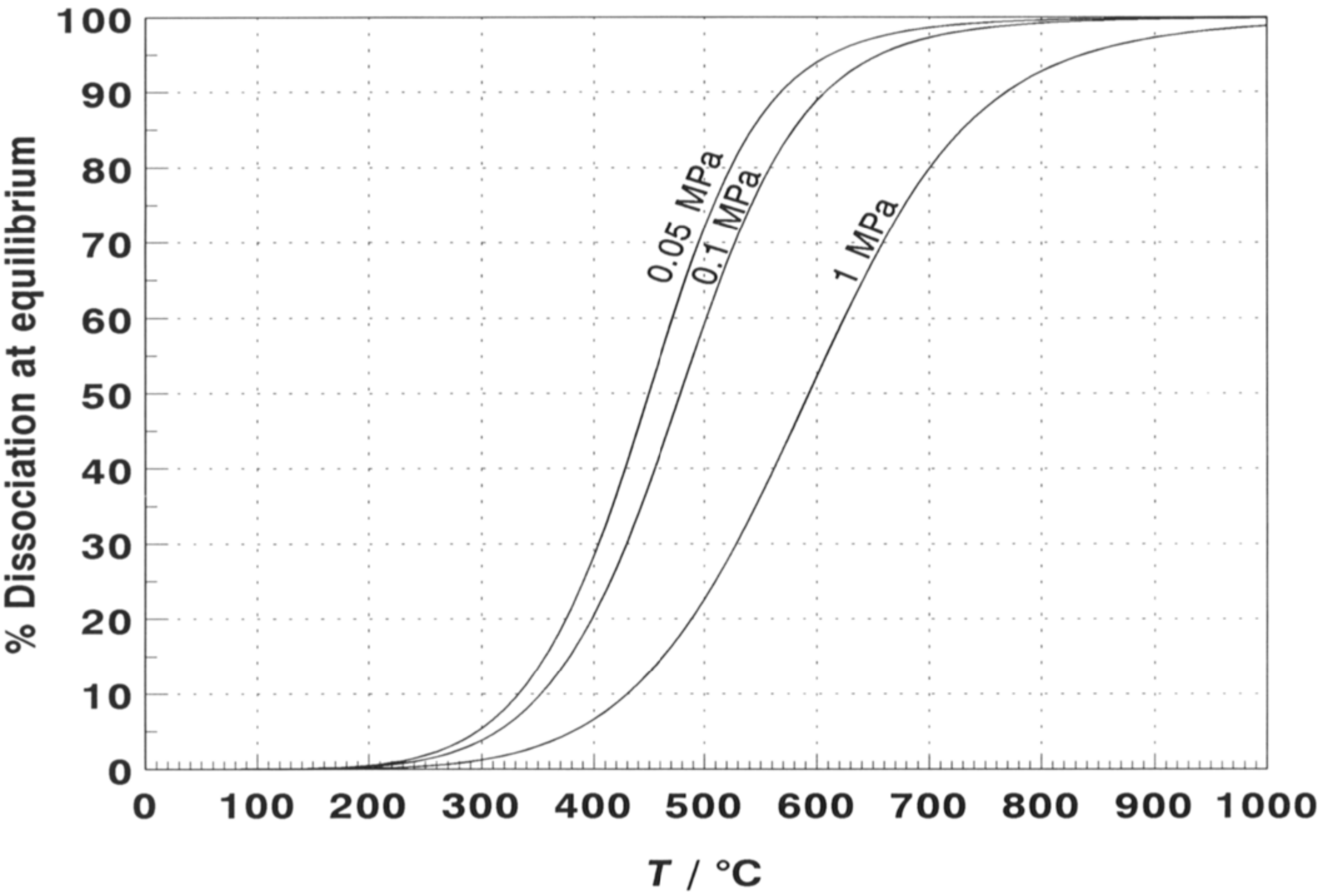


Fig. 5.3 The calculated thermal dissociation of phosgene at equilibrium at 0.05, 0.1 and 1 MPa as a function of temperature [1764].

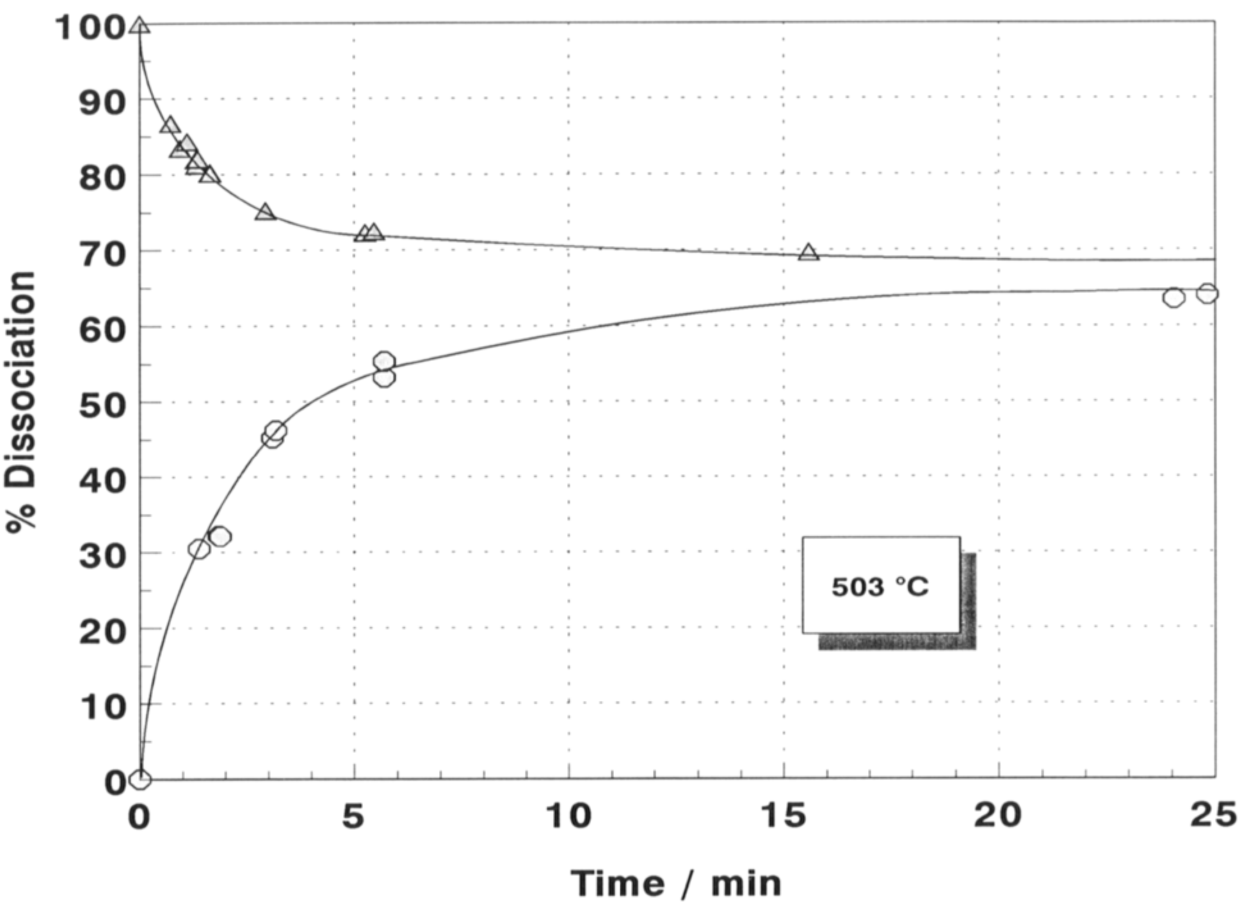


Fig. 5.4 The time dependence of the approach of reaction (5.1) to equilibrium at 503 °C [216].

For this mechanism:

$$x_1 = k_3K_2K_1^{\frac{1}{2}}$$

$$x_2 = k_4K_1^{\frac{1}{2}}$$

As described in Section 5.1.1, this mechanism was soon abandoned in favour of one in which Cl· and [COCl]· are the chain carriers:

$$\begin{array}{rcl}
\mathrm{Cl_2} & \overset{K_1}{\rightleftharpoons} & \mathrm{2Cl\cdot} \\
\mathrm{Cl\cdot + CO} & \overset{K_6}{\rightleftharpoons} & \mathrm{[COCl]\cdot} \\
\mathrm{[COCl]\cdot + Cl_2} & \xrightarrow{k_7} & \mathrm{COCl_2 + Cl\cdot} \\
\mathrm{Cl\cdot + COCl_2} & \xrightarrow{k_8} & \mathrm{[COCl]\cdot + Cl_2} \\
\mathrm{[COCl]\cdot + Cl\cdot} & \xrightarrow{k_9} & \mathrm{CO + Cl_2}
\end{array}$$

For this mechanism, then:

$$x_1 = k_7K_6K_1^{\frac{1}{2}}$$

$$x_2 = k_8K_1^{\frac{1}{2}}$$

The equilibrium constants calculated from rate measurements are in agreement with those obtained directly from equilibrium measurements [218]. For the decomposition of phosgene, a similar rate law is given with the signs reversed [387]. The full mechanism is essentially similar to that developed for the photochemical reaction (apart from initiation), and is discussed in more detail in Section 5.1.1.

For low conversions of carbon monoxide, under conditions where the dissociation reaction can be ignored, the above rate equation reduces to [1779,2027]:

$$\mathrm{d[COCl_2]}/\mathrm{d}t = k\mathrm{[CO][Cl_2]}^{3/2}$$

Under these conditions, the reaction obeys the Arrhenius equation, $k = \mathrm{A}\exp(-E/\mathrm{R}T)$, with $\mathrm{A} = 5.0 \times 10^{7}\ \mathrm{l\ mol^{-1}\ s^{-1}}$ and $E/\mathrm{R} = -12700$ K ($E = 105.6$ kJ mol^{-1}).

Phosgene may be a significant constituent of flames in the region of 1000–3000 K when carbon, oxygen, and chlorine are present [799]. The equilibrium composition of a gas mixture in the carbon–chlorine–oxygen system has been calculated for the temperature range of 400–800 K (127–527 °C). The composition is dependent upon the temperature, pressure, and concentration conditions. The percentage formation of $COCl_2$ in the equilibrium state is given in Table 5.1 for a range of temperatures and Cl:O ratios. The remaining gases consist of O_2, CO, Cl_2, and CO_2 [1144].

TABLE 5.1

EQUILIBRIUM PHOSGENE CONCENTRATION IN FLAMES [1144]

		Phosgene Concentration/%		
T/K	$O_2:Cl_2$ =	1:1	1:2	1:3
400		15.6	40.0	32.8
500		33.2	38.1	36.5
600		59.9	30.2	10.2
700		2.1	15.0	2.3
800		3.3	3.4	3.5

5.1.3 Catalytic synthesis

5.1.3.1 From carbon monoxide and dichlorine

5.1.3.1.1 Gas phase processes

The process that forms the basis of the commercial production of phosgene is the activated carbon-catalysed, gas-phase reaction of carbon monoxide with dichlorine (see Section 4.1). In the laboratory, phosgene can be readily prepared by passage of equimolar flows of the mixed reactants at atmospheric pressure through a glass tube filled with granulated charcoal. It is often not necessary to heat the reactor since the reaction can be initiated at room temperature. More than 20 kg of phosgene can be generated from as little as 10 g of wood charcoal without any noticeable reduction in catalyst activity [89], and even at quite high flow rates, virtually complete conversion of the reactants can be expected.

A laboratory Liebig's condenser can be conveniently used as the reactor, since water cooling is necessary to remove the heat from the reaction which is highly exothermic ($\Delta H \approx -108$ kJ mol^{-1}). Since the thermal dissociation of phosgene (Fig. 5.3) becomes perceptible at above 200 °C, it is desirable to regard this temperature as a ceiling for the temperature of the bulk catalyst. The principal function of the charcoal catalyst is believed to be the activation of the Cl_2 [1053], and if dichlorine is adsorbed onto the activated carbon before admission of the CO/Cl_2 mixture, much less heat is liberated from the operation and the temperature of the reactor bed is more easily controllable [1650].

At temperatures below 70 °C, any dihydrogen impurity in the carbon monoxide does not react (in the dark) with the Cl_2 to form HCl [89,1650]. This observation may be significant in connection with the manufacture of phosgene from carbon monoxide containing unseparated H_2. And, by using a 2.5% molar excess of CO in the temperature range of 50–200 °C, the phosgene product, formed in a yield of 90–97%, can be made substantially free of Cl_2 [89,1590a].

The kinetics of the carbon–catalysed formation of phosgene from CO and Cl_2 have been reported [1847,1848,1849]. Earlier work [1650] gives the experimental reaction rates, r_m, between 31 and 99 °C, in moles of $COCl_2$ per gram of catalyst per hour as:

$$r_m = \frac{kK_{CO}\,K_{Cl_2}\,p_{CO}\,p_{Cl_2}}{(1 + K_{Cl_2}\,p_{Cl_2} + K_{COCl_2}\,p_{COCl_2})^2}$$

in which the partial pressures, p, are in atmospheres and the equilibrium constants, K, refer to the adsorption of the components on the catalyst surface [1650]. Surface reaction between adsorbed Cl_2 and carbon monoxide is the controlling mechanism [1650]. A re–examination of the data showed that rates could be expressed more simply in the form [2165a]:

$$r_m = k\,p_{CO}\,p_{Cl_2}{}^{\frac{1}{2}}$$

where k is the rate constant per unit weight of catalyst [1781]. This simplified expression does not, however, account for the retarding influence of phosgene.

Under conditions close to those used in industrial practice, the reaction rate for commercial activated carbon catalysts is given by Equation (5.2) [1847,1848]:

$$r_m = k\,p_{CO}\left[\frac{p_{Cl_2}}{(Ap_{CO} + p_{COCl_2})}\right]^m \qquad (5.2)$$

where k and A are constants, with $m = \frac{1}{4}$; and p_{CO}, p_{Cl_2}, and p_{COCl_2} are the partial pressures of carbon monoxide, dichlorine and phosgene, respectively. At 100 °C, $A = 0.02$ and $k = 0.0625$ mol g^{-1} h^{-1} atm^{-1}. For 1 ton of catalyst and a 0.1 molar stoicheiometric excess of CO at atmospheric pressure, the maximum output corresponds to 13000 mol h^{-1} (*ca.* 10000 ton of phosgene per ton of catalyst per year). The equation is based on the reaction scheme:

$$Z + CO \longrightarrow ZCO$$

$$ZCO + Cl_2 \rightleftharpoons Z + COCl_2$$

in which Z represents the active site on the carbon surface [1847,1848].

At low partial pressures of Cl_2, the kinetics are described by an equation which represents a transition between medium and high surface coverages of CO on the catalyst surface [1849]. This corresponds to Equation (5.2) in which $m = 1$.

The effects of γ-irradiation on active carbon catalysts has been examined [1780,1781]; the rate constant of the irradiated catalyst was noted to be smaller than that for unirradiated material. The radiation is considered to destroy the π-electron system in the carbon, through bond ruptures, resulting in the corresponding activity decrease.

The gas phase reaction between carbon monoxide and dichlorine catalysed by gold(III) chloride or transition metal complexes is discussed in Section 5.1.5.4.

5.1.3.1.2 Liquid phase processes

Although the conventional process has remained essentially unchanged for over 60 years, a potential new (liquid phase) process route to phosgene involves the reaction of CO with Cl_2 using organophosphine chloride catalysts in an inert solvent to give a rapid and quantitative yield of product [1342,2074,2075,2077] at moderate temperatures (typically 60–120 °C) and pressures. The phosgene is recovered by heating the solution or by reducing the pressure. Alternatively, depending upon the requirements of subsequent processes, the solution of phosgene, in tetrachloromethane or chlorobenzene say, may be used directly.

The liquid phase process conveys the advantages of better heat transfer characteristics relative to the traditional gas phase chemistry, which is prone to developing hot spots, resulting in depressed yields. In addition, the phosgene is more readily separated from unreacted gases and, providing an excess of CO is used, the amount of residual dichlorine in the solution is negligible. The disadvantages are that the process uses more costly and difficult-to-handle catalysts and that solvent make-up is required. This process does not yet appear to have been commercialized, but typical organophosphine chloride catalysts include materials based on the following formulations, or their precursors (such as the corresponding phosphine oxides), in which R, R', R", R"' and R"" represent a wide variety of alkyl or substituted alkyl groups [1342,2075,2077]:

$RR'R''PCl_2$ $\qquad$ $RR'PCl_2{-}PCl_2R''R'''$

$RR'PCl_2(CH_2)_nPCl_2R''R'''$ $(n = 1{-}6)$ $\qquad$ $R'PCl_2{=}R''''$

Alternatively, phosphine sulfides and/or phosphine selenides have been screened as active catalysts for phosgene synthesis from CO and Cl_2 [2076]. In one example, a mixture of liquid dichlorine, CCl_4, and PH_3S (0.5%, based on the solvent) was loaded into an autoclave under a CO pressure of about 3 MPa. The reaction, maintained at 10 °C for 3 h, resulted in a yield of phosgene of 97%.

5.1.3.2 Oxychlorination methods (using HCl/O_2)

Since phosgene is used in industry mainly as a carbonylating agent, as opposed to a chlorinating agent, this results in the chlorine atoms of phosgene being downgraded, in an industrial and thermodynamic sense, into HCl. For example, in the production of the high-capacity MDI (Section 4.7.1.1), used in polyurethane manufacture, four moles of HCl are released per mole of product. Similarly, in the manufacture of bisphenol A polycarbonate (Section 4.7.2.2), all of the chlorine from phosgene is again degraded to by-product HCl [85].

By-product HCl is by far the major source of hydrogen chloride world-wide, and outlets for this material are usually limited. It is therefore often reconverted at the site of its production into dichlorine by one of a number of established processes [85]. However, HCl may also be used directly as a chlorinating agent, and the most widely used example of this is the catalytic oxychlorination of ethene to 1,2-dichloroethane, which is used as an intermediate in the manufacture of chloroethene (vinyl chloride) [2165]. In view of the trend to use phosgene captively, to avoid its bulk transportation, phosgene production by CO oxychlorination could provide the opportunity for the manufacturer to recycle by-product HCl without the need to produce dichlorine and then to further convert the dichlorine, in a separate process, to phosgene [85,ICI102].

The oxychlorination of carbon monoxide to phosgene has been accomplished, Equation (5.3), over a catalyst composed of copper(II) chloride supported upon a low surface area titania, containing caesium chloride and lanthanum chloride co-impregnants [85,ICI102].

$$CO + 2HCl + \tfrac{1}{2}O_2 \longrightarrow COCl_2 + H_2O \qquad (5.3)$$

Using stoicheiometric feeds of CO, HCl, and O_2 in a flow system at 393 °C and atmospheric pressure, a selectivity to phosgene of 57.2% was obtained with a conversion of CO corresponding to 42%. The only significant by-product in this reaction is carbon dioxide which is formed principally from the reaction of the product phosgene with the copper catalyst in its oxychloride state. The overall catalytic scheme is illustrated in Fig. 5.5.

Copper(II) chloride is reduced to copper(I) chloride with carbon monoxide to produce phosgene. The CuCl is then oxidised to copper(II) oxychloride (represented by $CuO.CuCl_2$ in Fig. 5.5), which can combine both with HCl, to complete the catalytic cycle, and with the product $COCl_2$ to form CO_2 [85,ICI14,ICI102].

The co-production of water in CO oxychlorination has been given as a reason for the disbelief that such a process could be feasible [455,456,457]. Although the hydrolysis of phosgene is highly favoured thermodynamically, the rates of reaction are found to be slow even at elevated temperatures, unless the reaction is suitably catalysed (see Section 9.10.3.1) [615,2207]. Indeed, the gas phase hydrolysis of phosgene has been studied [708] and extrapolation of the results of this study to the conditions under which CO is amenable to oxychlorination reveals that the degree of hydrolysis of phosgene should be less than 1% [1754].

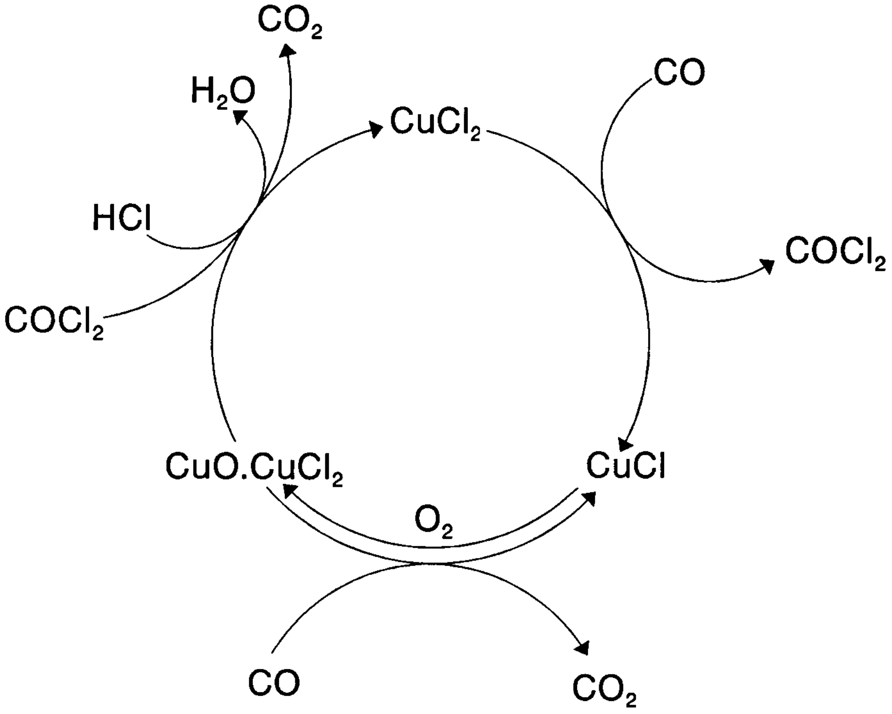


Fig. 5.5 **Mechanistic scheme for the catalytic oxychlorination of carbon monoxide [85].**

The production of phosgene from hydrogen chloride has been accomplished in a two-reactor system [455,456,457,803] in which carbon monoxide is firstly chlorinated by supported copper(II) chloride:

$$2CuCl_2 + CO \longrightarrow 2CuCl + COCl_2$$

$$\Delta G^{\circ}\ (375\ ^{\circ}C) = -2.5\ kJ\ mol^{-1}$$

and then the resulting copper(I) chloride is re-oxidised to $CuCl_2$, in a second process using a mixture of dioxygen and HCl:

$$2CuCl + \tfrac{1}{2}O_2 + 2HCl \longrightarrow 2CuCl_2 + H_2O$$

A similar process, based on molten copper chloride salt mixtures, has been recently described by the Lummus Company [1712]. The salt, rich in the higher oxidation state copper(II) chloride, is contacted with CO at 426–510 °C to produce phosgene. The molten mixture, then rich in the lower oxidation state CuCl, is contacted with HCl and air at 398–510 °C to become re-oxidised.

Molten salt mixtures of copper(II) chloride and copper(II) oxychloride have also been claimed to produce phosgene in a yield, per pass, of 10% from carbon monoxide at 460 °C [174]. Again, in this process, the depleted copper(II) salts are regenerated in a second reactor with a mixture of air and hydrogen chloride.

The commercialization of phosgene processes based on hydrogen chloride, rather than dichlorine, would permit, for example, isocyanate plants to be sited at locations not dependant on chloralkali-producing facilities or large chlorine-consuming (*e.g.* vinyl chloride) plant. However, it is not known for certain whether any of these processes are currently commercially operated.

5.1.4 Electrochemical synthesis

Phosgene has been produced at a gas diffusion anode when a sodium chloride solution was electrolysed whilst supplying carbon monoxide to the anode [2065].

5.1.5 Reactions with inorganic chlorides

Carbon monoxide combines with a variety of inorganic chloride-containing compounds to generate $COCl_2$ in various yields, Table 5.2. Several of these reactions could conceivably constitute a high-yield synthetic procedure and, although the remaining reactions do not constitute practical synthetic routes to phosgene, it is convenient to group these reaction types together.

5.1.5.1 Reactions with Group 13 chlorides

Although the early literature describes the catalytic formation of $COCl_2$ from CO and Cl_2 at 30-35 °C in the presence of a solution of aluminium(III) chloride in $CHCl_3$ [1628], this reaction was found to occur only in the presence of light [326]. Indeed, the presence of aluminium(III) chloride has been found to have no intrinsic effect on the generation of phosgene from CO and Cl_2 when these gases are passed into trichloromethane or 1,1,2,2-tetrachloroethane in the presence of light [1589b].

5.1.5.2 Reactions with Group 14 chlorides

The reaction of CCl_4 with CO is reported to result in the formation of considerable quantities of phosgene [1824a], and it is interesting to speculate upon the carbon monoxide behaving as a thermodynamic sink for dichlorine in the well-known and industrially operated reaction [2165]:

$$2CCl_4 \rightleftharpoons C_2Cl_4 + 2Cl_2$$

The reaction of carbon monoxide with lead(II) chloride is illustrated in Table 5.2 [168]. Thermal decomposition of the lead salt to give dichlorine, followed by reaction with carbon monoxide, could be responsible for the phosgene formation [781].

TABLE 5.2

REACTIONS OF CARBON MONOXIDE WITH INORGANIC CHLORIDES

Chloride	Reaction	T/°C	Ref.
CCl_4	$2CCl_4 + 2CO \longrightarrow COCl_2 + C_2Cl_4$	350	1824a
NOCl	$2NOCl + CO \longrightarrow 2NO + COCl_2$	350	2192
SCl_2	$2SCl_2 + CO \longrightarrow COCl_2 + S_2Cl_2$	60-100	142
$SbCl_5$	$SbCl_5 + CO \longrightarrow SbCl_3 + COCl_2$	*ca.* 140	972a
$PbCl_2$	$PbCl_2 + CO \longrightarrow Pb + COCl_2$	650-750	168,787a
$NiCl_2$	$NiCl_2 + CO \longrightarrow Ni + COCl_2$	450-550	168
CuCl	$2CuCl + CO \longrightarrow 2Cu + COCl_2$	450-550	168
AgCl	$2AgCl + CO \longrightarrow 2Ag + COCl_2$	650-750	168,787a
$AuCl_3$	$AuCl_3 + CO \longrightarrow AuCl + COCl_2$	50-110	1100a,1313
AuCl	$2AuCl + 2CO \longrightarrow 2Au + CO + COCl_2$	75/95	1100a,1313
$RuCl_3$	$2RuCl_3 + CO \longrightarrow 2\text{"}RuCl_2\text{"} + COCl_2$	270	1313
$PtCl_2$	$PtCl_2 + CO \longrightarrow Pt + COCl_2$	150-225	1287c
$PtCl_4$	$PtCl_4 + CO \longrightarrow PtCl_2 + COCl_2$	140	1313
$RhCl_3$	No Apparent $COCl_2$ Formation	90-140	1313
$PdCl_2$	No Apparent $COCl_2$ Formation	45	1313
$OsCl_3$	No Apparent $COCl_2$ Formation	270	1313

5.1.5.3 Reactions with Group 15 chlorides

The reaction between CO and NOCl is catalysed by activated charcoal at temperatures of 100–250 °C [2192], Equation (5.4). In the absence of a catalyst, no reaction occurs at 200 °C, but the reaction represented by Equation (5.4) is reversible at temperatures above 400 °C [1607]. In contrast, even a small amount of NOCl inhibits the room temperature photochemical formation of phosgene from CO and Cl_2 (see Section 5.1.1).

$$2NOCl + CO \longrightarrow COCl_2 + 2NO \qquad (5.4)$$

5.1.5.4 Reactions with Group 16 chlorides

In the reaction of sulfur(II) chloride with carbon monoxide, the co-product S_2Cl_2, formed in addition to phosgene, may be reconverted using dichlorine into active SCl_2 [142], so that the overall reaction corresponds to the reaction of Cl_2 with CO:

$$\begin{array}{lcl} 2SCl_2 + CO & \longrightarrow & COCl_2 + S_2Cl_2 \\ S_2Cl_2 + Cl_2 & \longrightarrow & 2SCl_2 \\ \hline CO + Cl_2 & \longrightarrow & COCl_2 \\ \hline \end{array}$$

5.1.5.5 Reactions with transition metal chlorides

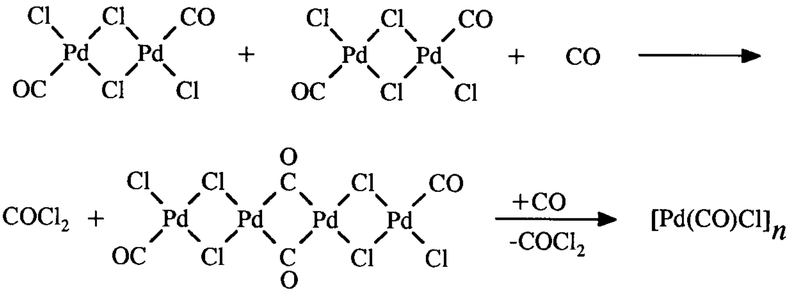
Phosgene is formed from the reaction of $PdCl_2$ with CO in ethanoic anhydride, according to Equation (5.5) [498]:

$$PdCl_2 + 1.5CO \longrightarrow 1/n[Pd(CO)Cl]_n + \tfrac{1}{2}COCl_2 \qquad (5.5)$$

The dimeric chlorocarbonyl complex, $[Pd_2(CO)_2Cl_4]$, formed also from the reaction of CO with $PdCl_2$, can react further with CO as exemplified in Equation (5.6) [498]. The formation

$$\tfrac{1}{2}[Pd_2(CO)_2Cl_4] + \tfrac{1}{2}CO \;\rule{2em}{0.4pt}\; 1/n[Pd(CO)Cl]_n + \tfrac{1}{2}COCl_2 \qquad (5.6)$$

of the polymeric palladium complex can be visualized to result from the polymerization of $[Pd_2(CO)_2Cl_4]$ by elimination of $COCl_2$ [498]:



The reaction of $PtCl_4$ with carbon monoxide is very marked at 140 °C [1313] and $PtCl_4.nH_2O$ reacts with carbon monoxide in sulfinyl chloride at 110 °C under autogenous pressure according to Equation (5.7) [495]:

$$PtCl_4.nH_2O + 3CO + nSOCl_2 \longrightarrow 2nHCl + nSO_2 + COCl_2 + cis\text{-}[PtCl_2(CO)_2] \qquad (5.7)$$

In the reactions of carbon monoxide with copper(II) chloride, nickel(II) chloride or silver(I) chloride, thermal decomposition of the salts to give dichlorine, followed by the subsequent reaction with CO to give $COCl_2$, cannot be ruled out [781]. However, the apparent lack of phosgene formation when rhodium(III) chloride, osmium(III) chloride or palladium(II) chloride (*cf.* behaviour in solution, *vide supra*) are exposed to CO is believed to be a result of subsequent catalytic decomposition [1313], since the evolution of dichlorine from these salts is initiated at appreciably lower temperatures in the presence of CO, relative to dinitrogen. This account is confirmed by the observation that phosgene is rapidly decomposed over anhydrous $OsCl_3$ or $RhCl_3.H_2O$ [1313]. In contrast, $RuCl_3$ does not eliminate dichlorine at 270 °C in a dinitrogen atmosphere, whilst traces of phosgene are generated in carbon monoxide [1313].

Early studies [517a] revealed that gold(III) chloride was decomposed into metallic gold and phosgene when heated in a stream of carbon monoxide. Later experiments showed that both gold(I) chloride or gold(III) chloride gave the same compound when heated with carbon monoxide [1100a]; gold(III) chloride is reduced to AuCl at around 100 °C; and reaction of gold(I) chloride with carbon monoxide at 110 °C occurs to generate phosgene according to Equation (5.8) [1100a]:

$$2AuCl + 2CO \longrightarrow 2Au + CO + COCl_2 \qquad (5.8)$$

The reaction of CO with AuCl also gives the gold(I) chlorocarbonyl species, Au(CO)Cl, and decomposition of this material proceeds according to equation (5.9) [1100a]:

$$2[Au(CO)Cl] \longrightarrow 2Au + CO + COCl_2 \qquad (5.9)$$

Reaction of carbon monoxide with gold(III) chloride [493,497] (or $HAuCl_4.3H_2O$ [494]) in $SOCl_2$, however, occurs at room temperature and atmospheric pressure according to Equation (5.10) [493,497]:

$$Au_2Cl_6 + 4CO \longrightarrow 2[Au(CO)Cl] + 2COCl_2 \qquad (5.10)$$

Similarly, a solution or suspension of gold(III) chloride in tetrachloroethene at 100–140 °C reacts with carbon monoxide to produce a high yield of phosgene in agreement, overall, with Equation (5.7) [1100a]. The gold(III) chloride was initially reduced to AuCl, with the liberation of phosgene, and further reaction of the AuCl with CO gave the carbonyl complex [1100a]. Addition of gold(III) chloride to a benzene solution of [Au(CO)Cl] resulted in the formation of gold(I) chloride and $COCl_2$ [1100a], consistent with:

$$Au_2Cl_6 + [Au(CO)Cl] \longrightarrow 3AuCl + COCl_2$$

Passage of a mixture of CO and Cl_2 over gold(III) chloride, at 100 °C, results in abundant phosgene formation. Only a very small amount of [Au(CO)Cl] was detected [1100a], although in complete contrast other workers have recommended the simultaneous passage of CO and dichlorine over the gold chloride in the preparation of the carbonyl complex [1312a]. In this latter work no mention is made of the formation of phosgene.

The catalytic cycle, based on gold, is thus verified to be as follows [326]:

$$Au_2Cl_6 + 4CO \longrightarrow 2[Au(CO)Cl] + 2COCl_2$$

$$2[Au(CO)Cl] + 4Cl_2 \longrightarrow Au_2Cl_6 + 2COCl_2$$

$$CO + Cl_2 \longrightarrow COCl_2$$

This reaction is able to produce at least 60 mol of phosgene per mol of gold at atmospheric pressure and room temperature in the dark [326]. The catalytic efficacy of metal complexes in phosgene formation from CO and dichlorine in sulfinyl chloride decreases in the order: $[Au(CO)Cl] > [Pd(CO)Cl_3]^- > [Pt(CO)Cl_3]^-$ [326,496]. Under similar conditions, CuCl, $CuCl_2$ and $FeCl_3$ were found to be inactive [326].

5.2 SYNTHESIS OF PHOSGENE FROM HALOGENATED HYDROCARBONS

The formation of phosgene by the aerial oxidation of chlorinated organic compounds is of considerable industrial interest and has been considered, in its proper context, in some detail in Section 3.3, whilst the *in vivo* and *in vitro* formation of phosgene from organochlorine compounds has been discussed in Section 2.5.4. Only those reactions which might constitute a synthetic procedure will be considered here.

The action of air on the chlorinated hydrocarbons tetrachloromethane, trichloromethane, trichloroethene, 1,2-dichloroethane, tetrachloroethane, pentachloroethane or hexachloroethane, heated in the presence of metals, charcoal or in an open flame, has been reported by Sjöberg [1894].

5.2.1 Tetrachloromethane

Tetrachloromethane is relatively cheap and abundantly available, and it can be converted to phosgene by a variety of methods. The oxidation or hydrolysis of CCl_4 is potentially attractive on the large scale, whilst the historic method of reaction with sulfuric acid constitutes a convenient laboratory synthesis.

5.2.1.1 Oxidation by sulfuric acid, sulfur(VI) oxide or other sulfur(VI) derivatives

A convenient laboratory preparation of phosgene involves the oxidation of tetrachloromethane with oleum (or strong sulfuric acid with an SO_3 content less than 45%) according to Equation (5.11) [829,1231]:

$$H_2S_2O_7 + CCl_4 \longrightarrow COCl_2 + 2ClSO_3H \qquad (5.11)$$

If an excess of tetrachloromethane is used in the preparation, phosgene is also generated according to Equation (5.12) [829]:

$$2ClSO_3H + CCl_4 \longrightarrow COCl_2 + S_2O_5Cl_2 + 2HCl \qquad (5.12)$$

Reaction of CCl_4 with SO_3, or with fuming sulfuric acid with an SO_3 content of greater than 45%, proceeds according to Equation (5.13) [1591,1231]:

$$2SO_3 + CCl_4 \longrightarrow COCl_2 + S_2O_5Cl_2 \qquad (5.13)$$

CCl_4 and SO_3 react over silica at 250–560 °C to give phosgene with yields of 40–87% and a selectivity of 70–100% [1238]. For example, at 435 °C, phosgene was produced at a

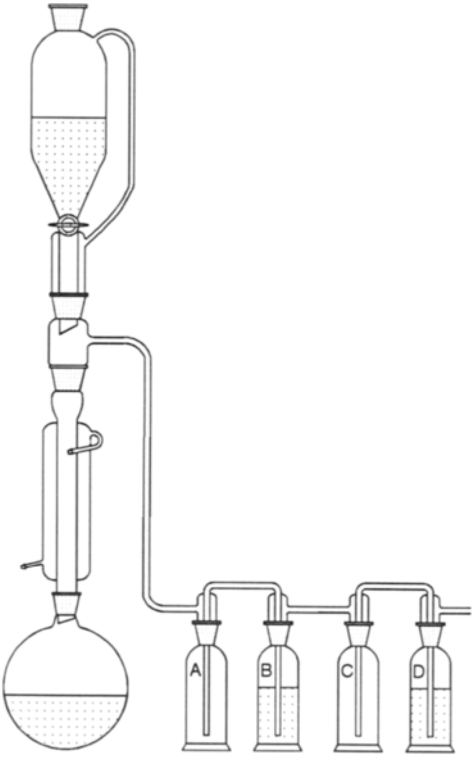


Fig. 5.6 Apparatus for the preparation of phosgene solutions on a laboratory scale; B contains toluene and D contains 20 % aqueous sodium hydroxide solution [704a].

conversion of 65% and a selectivity of 98%. Under these conditions, the reaction is best represented by Equation (5.14):

$$SO_3 + CCl_4 \longrightarrow COCl_2 + SO_2 + Cl_2 \qquad (5.14)$$

Diatomaceous earth is also reported to catalyse the reaction between oleum and CCl_4 [1464]. The reagents are slowly mixed at 90 °C, and the phosgene escapes from the reaction vessel leaving behind a mixture of sulfuric and chlorosulfonic acids. However, ordinary concentrated sulfuric acid may be used to react with tetrachloromethane in the presence of diatomaceous earth at 150–160 °C, according to Equation (5.15) [829]:

$$2H_2SO_4 + 3CCl_4 \longrightarrow 3COCl_2 + S_2O_5Cl_2 + 4HCl \qquad (5.15)$$

The reaction rate increases as the reaction proceeds, since the $S_2O_5Cl_2$ co-product improves miscibility between the reactants and can itself react further with CCl_4.

The preparation of toluene solutions of phosgene based on this method has been described [704a]. Referring to Figure 5.6, tetrachloromethane contained in the dropping funnel is slowly dripped into the reaction flask containing hot (120–130 °C) concentrated sulfuric acid to which has been added 2% by weight of diatomaceous earth. The evolved phosgene is absorbed into toluene contained in the Dreschel bottle labelled (B). Hydrogen chloride is absorbed in the 20% aqueous sodium hydroxide solution contained in (D), which also serves to remove traces of phosgene escaping from the toluene solution. Bottles (A) and (C) are oriented in such a way to function as suck-back traps.

Phosgene has also been formed from the reaction between the peroxydisulfuryl difluoride, FSO_2OOSO_2F, with an excess of tetrachloromethane at room temperature [1867]:

$$S_2O_6F_2 + CCl_4 \longrightarrow S_2O_5F_2 + COCl_2 + Cl_2$$

5.2.1.2 Hydrolysis

When CCl_4 is heated with a large amount of water in a sealed tube at 250 °C, only CO_2 and HCl are formed. In order to produce phosgene by this procedure, the use of only a small amount of water is essential [649b]. Similarly, the hydrolysis of tetrachloromethane in the gas phase (300–450 °C) proceeds according to the overall reaction [708]:

$$CCl_4 + 2H_2O \longrightarrow CO_2 + 4HCl$$

However, phosgene has been detected in the reaction mixtures in low concentrations, suggesting that the reaction occurs in at least two steps [708]:

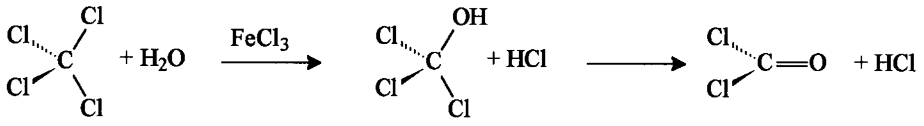
$$\begin{aligned} CCl_4 + H_2O &\longrightarrow COCl_2 + 2HCl \\ COCl_2 + H_2O &\longrightarrow CO_2 + 2HCl \end{aligned} \tag{5.16}$$

The rate of the second step is between 10 and 35 times faster than the first, resulting in only low levels of phosgene being detected.

Even the water contained in 90–96% sulfuric acid may react with CCl_4, in the presence of catalytic amounts of pumice that has been heated to 160 °C, according to Equation (5.16) [1358a]. CCl_4 also reacts with water adsorbed on silica gel to form phosgene and HCl; the reaction proceeds at 110 °C, and is relatively fast at 300 °C, although at higher temperatures further hydrolysis to CO_2 occurs [2015].

Coordinatively-bonded water molecules on the surface of a silicon single crystal were shown to be responsible for the thermal (480–700 K) and photocatalytic (77 K) decomposition of adsorbed CCl_4 to $COCl_2$ [795]. Hydrogen and hydroxyl radicals are considered to be chiefly responsible for the CCl_4 decomposition under the photocatalytic conditions.

Hydrolysis of CCl_4 to $COCl_2$ is catalysed under milder conditions by iron(III) chloride, gallium(III) chloride or antimony(V) chloride [961,1320a]. Indeed, a convenient synthetic method involves the addition of water to a solution of anhydrous $FeCl_3$ in CCl_4 boiling under reflux. This reaction can be carried out using the tetrahydrate of iron(III) chloride (which is dehydrated to $FeCl_3$ *in situ*), but not the hexahydrate. The reaction is considered to proceed by nucleophilic attack of the water upon a reactive trichloromethylmetal chloride complex [961]:



Curiously, neither aluminium(III) chloride nor its hydrates react in a similar way [961]. These methods, particularly those using iron(III) chloride or antimony(V) chloride catalysts, are potentially useful for the small manufacturing scale generation of phosgene. Tetrachloromethane has an ozone-depleting potential similar to the chlorofluorocarbons, which it was largely used to manufacture. As such, it is a regulated substance under the terms of the Montreal Protocol (1987) and its revisions - London (1990) and Copenhagen (1992) (*e.g.* see [111ab]). Tetrachloromethane is therefore scheduled for legislative phase-out by 1996. However, under the terms of the Protocol, controlled substances can still be made for use in subsequent manufacturing processes. This situation may provide an opportunity for manufacturers to convert their spare tetrachloromethane capacity into phosgene.

5.2.1.3 Aerial oxidation

The combustion of CCl_4 in air has been discussed extensively in Section 3.3.1.1, and that coverage complements this current Section.

Tetrachloromethane reacts with an excess of dioxygen, in the gas phase above 300 °C, to form phosgene according to Equation (5.17) [1288b]:

$$2CCl_4 + O_2 \longrightarrow 2COCl_2 + 2Cl_2 \qquad (5.17)$$

Up to about 7 % of the CCl_4 is converted into phosgene, see Fig. 5.7, and the reaction is accompanied by large amounts of carbon dioxide and tetrachloroethene [1088a]. Prolonged heating at 450–480 °C causes further oxydechlorination of the $COCl_2$ to CO_2, according to the overall stoicheiometry indicated in Equation (5.18).

$$COCl_2 + \tfrac{1}{2}O_2 \longrightarrow CO_2 + Cl_2 \qquad (5.18)$$

Further details of the oxidation of phosgene by O_2 will be found in Section 9.7.6.

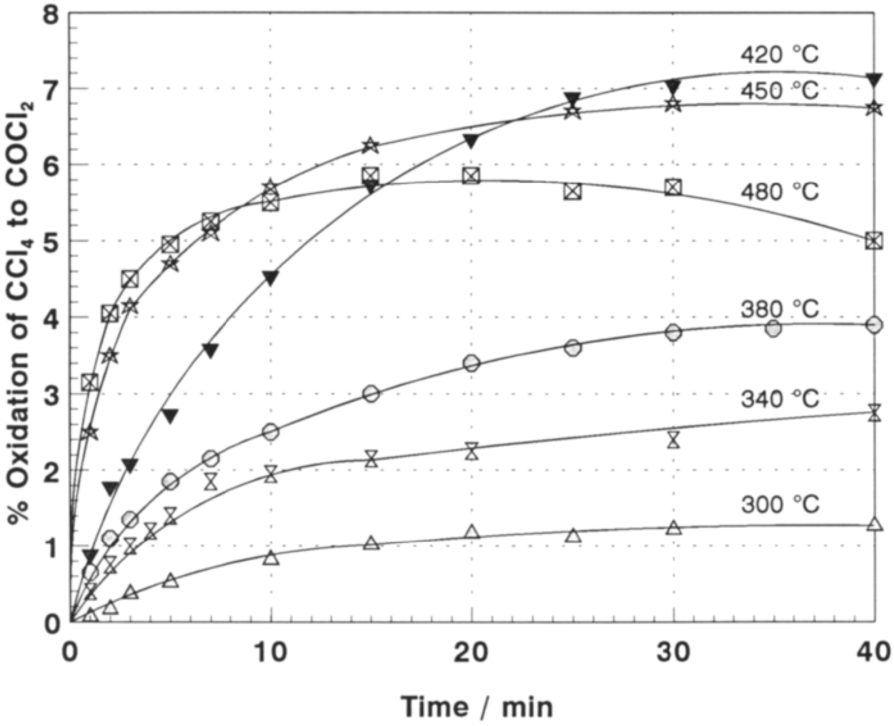


Fig. 5.7 The oxidation of tetrachloromethane to phosgene by O_2 as a function of time [1088a].

The oxidation of CCl_4 to $COCl_2$ is catalysed on a variety of metal surfaces at incipient temperatures above about 100 °C. The reaction is most effectively catalysed by iron, followed by copper, aluminium and then zinc (see Table 5.3) [432,1894].

TABLE 5.3

PHOSGENE FORMATION FROM TETRACHLOROMETHANE/AIR MIXTURES [1894]

	Phosgene/ mg (g of CCl_4)$^{-1}$									
T/°C =	75	100	150	200	250	300	350	400	450	500
Iron	0	1	14	47	82	214	287	176	20	9
Copper	-	0.1	1	6	30	92	216	91	65	-
Zinc	-	-	-	0	0.3	3	12	24	29	23
Aluminium	-	-	0	0.4	8	18	33	24	-	9

At 250 °C, in the presence of $FeCl_3$, tetrachloromethane is oxidised by air to give phosgene in a yield of about 25% [191,1894].

Tetrachloromethane solutions of $[W(CO)_6]$ generate $COCl_2$ and lower oxides of tungsten under an air atmosphere. $[W(CO)_6]$ is considered to combine with dioxygen to form a highly oxidising species, of unknown structure, which is capable of abstracting Cl· from the CCl_4 to generate the $[CCl_3]\cdot$ radical which, in the presence of dioxygen, is a precursor to $COCl_2$ [1880]. The reaction is not accelerated by light, but addition of $[(CO)_5W\{C(OMe)(Ph)\}]$ to the CCl_4 causes spontaneous decomposition to $COCl_2$ and methyl benzoate (see also Section 9.9.2). Radioactive labelling of the carbonyl groups of $[W(CO)_6]$ confirms that the phosgene originates exclusively from the CCl_4 [1880].

The reaction of oxygen atoms with CCl_4 results in the formation of phosgene, in addition to dichlorine, CO and CO_2 [2088a]. The primary reactions in this system are believed to involve the formation of a collision complex:

$$O + CCl_4 \longrightarrow [O.CCl_4] \longrightarrow COCl_2 + Cl_2 \longrightarrow CO + 2Cl_2$$

These reactions are regarded as too slow to consume all of the atoms, and CO_2 is formed by the secondary reaction:

$$COCl_2 + O \longrightarrow CO_2 + Cl_2$$

The oxidation of CCl_4 by O_2 under photochemical and γ-radiolysis conditions is discussed in Section 5.2.5.

5.2.1.4 Reactions with binary oxides

Many oxides react with CCl_4, when heated, to generate phosgene. Indeed, the reaction of metal oxides, in particular, with excess of CCl_4 in a sealed tube at temperatures of around 400 °C has been employed as a general method for the preparation of higher oxidation state anhydrous metal chlorides. Thus, $ReCl_5$, $TcCl_4$, $MoCl_5$, WCl_6 and $TaCl_5$, have been prepared from the corresponding oxides; Re_2O_7, Tc_2O_7, MoO_3, WO_3, and Ta_2O_5 [1130b], and there is some evidence that similar reactions occur with Fe_2O_3, ZrO_2, BeO, V_2O_5, Al_2O_3 (low temperature preparations from the hydrous oxide), and Nb_2O_5 to give $[Fe_2Cl_6]$, $ZrCl_4$, $BeCl_2$, VCl_4, $[Al_2Cl_6]$, and $[Nb_2Cl_{10}]$, respectively [1130b]. In each of these preparations phosgene is expected to be the oxygen carrier for the reaction, although the oxides of cobalt or nickel appear not to react under the above-described conditions [1130b].

5.2.1.4.1 Oxides of Group 14

The special significance of the system:

$$CO_2 + CCl_4 \rightleftharpoons 2COCl_2$$

is described in Sections 5.4 and 8.2.

Silicon(IV) oxide is usually regarded as being inert, but CCl_4 does combine with porous silica (surface area 11 $m^2\ g^{-1}$) at high temperatures (800–950 °C) to give a mixture of tetrachloroethene, phosgene and silicon(IV) chloride [685a]. In contrast, germanium(IV) oxide combines with CCl_4 at 500–865 °C in a stream of dinitrogen according to [475b]:

$$GeO_2 + CCl_4 \longrightarrow GeCl_4 + 2COCl_2$$

5.2.1.4.2 Oxides of Group 15

Phosphorus(V) oxide reacts with a 2–3 molar equivalent of tetrachloromethane in a sealed tube over 48 h at 200–210 °C to furnish a small quantity of $COCl_2$ [850b,850c].

$$P_2O_5 + 2CCl_4 \longrightarrow COCl_2 + CO_2 + 2POCl_3$$

5.2.1.4.3 Oxides of Group 16

The reactions of tetrachloromethane with sulfur(VI) oxide have been discussed in Section 5.2.1.1. Phosgene has been detected in the synthesis of $TeCl_4$ from TeO_2 and CCl_4 [1103a].

5.2.1.4.4 Transition metal oxides

At 300 °C, MoO_3 reacts with CCl_4 in the presence of carbon to form MoO_2Cl_2 and phosgene [1065a].

The reaction of Re_2O_7 with an excess of CCl_4 at 400 °C over a few hours in a sealed tube proceeds according to the following equation [1130b]:

$$Re_2O_7 + 7CCl_4 \longrightarrow 2ReCl_5 + 7COCl_2 + 2Cl_2$$

$GaCl_3$ forms a weak donor–acceptor complex with ReO_3Cl, which then reacts spontaneously with CCl_4 at room temperature to form phosgene according to Equation (5.19) [1266]:

$$ReO_3Cl + CCl_4 \longrightarrow COCl_2 + ReO_2Cl_3 \qquad (5.19)$$

Iron(III) oxide reacts with CCl_4 at 245 °C as shown in Equation (5.20) [649b]:

$$Fe_2O_3 + 3CCl_4 \longrightarrow 2FeCl_3 + 3COCl_2 \qquad (5.20)$$

Zinc(II) oxide is reported to react with CCl_4 at 200 °C to form phosgene and zinc(II) chloride [1824a]. Under conditions in which a deficiency of phosgene prevails, zinc(II) oxide chloride, $ZnO.ZnCl_2$ (*cf.* Section 9.5.7), may be formed [1033]. Carbon dioxide is also formed in this reaction, effectively by the further reaction of phosgene with the oxide [1824a] or oxychloride [1033] (see also Section 9.5.7).

5.2.1.4.5 Actinide metal oxides

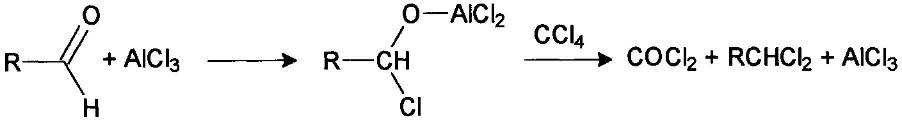
Chlorination of uranium(IV) oxide with CCl_4 at 300 °C results in the co-production of $COCl_2$, according to equation (5.21) [295]:

$$UO_2 + 2CCl_4 \longrightarrow UCl_4 + 2COCl_2 \qquad (5.21)$$

but the chlorination of PuO_2 with CCl_4 results in only a small amount of phosgene being generated [295].

5.2.1.5 Reaction with aldehydes

A novel method for the preparation of phosgene is based on the observation that considerable amounts of $COCl_2$ are evolved when aliphatic aldehydes – CH_3CHO, Me_2CHCHO, or $(CH_2O)_3$ – react with CCl_4 in the presence of aluminium(III) chloride [1005,1006]. The reaction of paraformaldehyde $\{HO(CH_2O)_nH;\ n = 8–100\}$ with CCl_4 in the presence of aluminium(III) chloride at 35–40 °C results in a quantitative yield of $COCl_2$ (based on CH_2O) at the optimal molar ratio of $CCl_4:(CH_2O)_n:AlCl_3 = 1:\frac{1}{2}:\frac{1}{2}$ [1103]. In these reactions, $COCl_2$ is believed to form from an intermediate addition product of the aldehyde with the aluminium(III) chloride [1005,1006]:



At room temperature, even in the absence of a catalyst, CCl_4 was noted to interact with aldehydes, RCHO (R = Me, Pr or Bu) [2089,2090] to form phosgene. In this case, it was considered that the aldehydes absorbed dissolved dioxygen to give the peroxy species, RC(O)OOH. Reaction of this with CCl_4 gave $[CCl_3]\cdot$, which underwent further aerial oxidation to give phosgene [2090]. Although tetrachloromethane, clearly, cannot be recommended as a solvent for aldehydes, it is noted that similar reactions to those described for CCl_4 do not occur in $CHCl_3$ solutions of aldehydes [2089].

5.2.1.6 Oxidations by other species

UV irradiation of CCl_4 in the presence of ethene and NO_2 results in the formation of some phosgene, although no reaction occurs in the absence of the ethene. The mechanisms involved in this reaction are unknown [726].

A report [1800] describing the pyrolysis of tetrachloromethane over degassed charcoal at 1300 °C, postulated to give dichlorocarbene (CCl_4 + C $\longrightarrow$ $2Cl_2C$:), followed by subsequent oxidation ($2Cl_2C$: + O_2 $\longrightarrow$ $2COCl_2$) to give phosgene was noted to be in error [1801]. Cracking of CCl_4 at 1200–1350 °C, occurring on the surface of the activated charcoal in high vacuum, gave a mixture of C, Cl_2, C_2Cl_2, C_2Cl_4, C_2Cl_6, C_4Cl_6 and C_6Cl_6, but not :CCl_2, which was believed to be simulated by a C_2Cl_2–Cl_2 mixture but whose existence could not be confirmed [1801].

Finally, the action of COF_2 on CCl_4 can generate phosgene as a by-product (see Chapter 13) [13].

5.2.2 Trichloromethane

Phosgene is a common impurity in liquid trichloromethane (chloroform) and arises from aerial oxidation, accelerated by exposure to sunlight [134]. Indeed, oxidation occurs neither by air in the absence of sunlight nor by light in the absence of air.

Phosgene is potentially derivable from trichloromethane in contact with a wide variety of oxidising agents, and only selected systems are described in this Section. The early literature concerning this system has been reviewed elsewhere [133,996] and a more recent account has been given [781]. The formation of phosgene from $CHCl_3$ by thermal or photochemical oxidation has been described already in Section 3.3.3, and the photochemical process is developed in Section 5.2.5; the importance in the early use of trichloromethane as an anaesthetic has been alluded to in Section 3.3.4; and the formation of phosgene from trichloromethane, *in vivo*, has been described in Section 2.5.4.

5.2.2.1 Oxidation by chlorosulfonic acid

When heated with trichloromethane, chlorosulfonic acid yields phosgene according to the overall equation [512a]:

$$CHCl_3 + SO_2(OH)Cl \longrightarrow COCl_2 + SO_2 + 2HCl$$

5.2.2.2 Aerial oxidation

$CHCl_3$ is oxidized in an excess of air over strongly chlorinated copper oxide at 450 °C to give phosgene in a yield of about 9% [191]. In the presence of metals, the oxidation of $CHCl_3$ to $COCl_2$ is much less pronounced than for CCl_4, see Table 5.4 [1894].

TABLE 5.4

PHOSGENE FORMATION FROM TRICHLOROMETHANE/AIR MIXTURES [1894]

Catalyst		Phosgene/ mg (g of $CHCl_3$)$^{-1}$						
	T/°C =	275	300	350	375	400	450	500
Iron		0	0.4	4	-	20	115	15
Copper		-	0.1	-	-	29	-	-
Zinc		-	0	0.1	3	6	-	-
Aluminium		-	0	4	-	32	-	-

The aerial oxidation of $CHCl_3$ under photochemical conditions is discussed in Section 5.2.5.

5.2.2.3 Oxidations by other species

$CHCl_3$ is oxidized by trixoygen (ozone) [597b] and by CrO_3 [597a] according to Equations (5.22) and (5.23):

$$CHCl_3 + O_3 \longrightarrow COCl_2 + HCl + O_2 \tag{5.22}$$

$$2CHCl_3 + CrO_3 + O_2 \longrightarrow 2COCl_2 + CrO_2Cl_2 + H_2O \tag{5.23}$$

Photooxidation of $CHCl_3$ with NO_2 (when in the presence of ethene) results in the formation of $COCl_2$ [726] and the reaction between $CHCl_3$ and NO_2 (in the molar ratio,

$CHCl_3$:NO_2 = 0.70:1) is catalysed by activated carbon in a flow system in the temperature range of 393–410 °C to give a mixture of CNCl and $COCl_2$ in yields of 12.2 and 7.8%, respectively [2161].

5.2.3 Other halomethanes and derivatives

5.2.3.1 Bromine derivatives

Bromine compounds are much more expensive than chlorine compounds and, since the atomic weight of bromine is about twice that of chlorine, the halogen cost incurred in the use of bromine compounds as intermediates is likely to be at least an order of magnitude greater than the cost of the corresponding chlorine compound. Not least for this reason, the synthesis of phosgene from bromine-containing compounds is unlikely to be economically practical and are probably not worthy of development on a purely commercial basis. However, C–Br bonds are more readily cleaved than C–Cl bonds, and bromide is readily oxidized back to bromine.

Both CCl_2Br_2 or CCl_3Br react with water in the presence of iron(III) chloride to produce low yields of phosgene [961]. Bromotrichloromethane solutions of $[W(CO)_6]$ generate phosgene in an air atmosphere, the rate of phosgene production being increased relative to CCl_4 solutions, since the $[CCl_3]\cdot$ radical is more easily formed from the former [1880]. Phenyl radicals, produced from the thermal decomposition of PhN(NO)C(O)Me, cause the abstraction of Br· from CCl_3Br to give $[CCl_3]\cdot$, which is scavenged by $[PhN_2O]\cdot$ to give PhN_2OCCl_3. This in turn gives $[PhN_2]^+Cl^-$, PhCl and $COCl_2$: phosgene was only detected in trace amounts, since it reacts further with PhN(NO)C(O)Me to give $[PhN_2]^+Cl^-$, CO_2 and Ac_2O [318].

5.2.3.2 Fluorine derivatives

The regulated chlorofluoromethanes, particularly CCl_2F_2 (CFC-12) and CCl_3F (CFC-11), were (until recently) the largest tonnage fluorochemicals manufactured, and their potential for generation of phosgene has been described in Section 3.3.4.

Dichlorodifluoromethane reacts with WO_2 at 525 °C mainly to give CO, WOF_4 and $WOCl_4$. Small amounts of phosgene and carbonyl difluoride are also formed, but these compounds may arise from the reactions of the CO with the nickel halide films formed on the inside surfaces of the nickel reactor [2159].

5.2.3.3 Nitro derivatives

Trichloronitromethane, CCl_3NO_2, is decomposed by fuming sulfuric acid (containing 20% SO_3) at 100 °C into phosgene (73% yield) and nitrosyl chloride [1825]:

$$CCl_3NO_2 \longrightarrow COCl_2 + NOCl$$

The experimental conditions in this procedure resemble those described for the formation of phosgene from CCl_4. The photochemical decomposition is discussed in Section 5.2.5.

5.2.3.4 Nitrile derivatives

At 500 °C, when passed with air over activated iron surfaces, trichloroethanenitrile, CCl_3CN, decomposes to give a small quantity of phosgene [720,721].

5.2.4 Haloethanes, haloethenes, haloethynes, and derivatives

5.2.4.1 Aerial oxidation

Dichloroethyne is a by-product in the synthesis of some chlorinated hydrocarbons and, particularly, can be formed when trichloroethene is put into contact with strong alkali. In the presence of air, dichloroethyne is spontaneously oxidised to give phosgene as the major product [1697,1698].

Aerial oxidation of trichloroethene in the presence of metals results in the formation of phosgene [597c,1894]. At 450 °C, when passed over zinc, phosgene formation amounted to 69 mg g^{-1} of trichloroethene (corresponding to 8% conversion). Surprisingly, iron gave only 19 mg of phosgene per gram of C_2HCl_3. Tetrachloroethene shows a smaller tendency for phosgene formation under these conditions, the highest concentration of phosgene generated (over iron at 500 °C), however, amounted to only 3 mg per gram of C_2Cl_4 [1894]. Similar concentrations of phosgene were obtained from the oxidation of dichloroethane, pentachloroethane or hexachloroethane, using an excess of air, although higher concentrations were noted from the aerial oxidation of tetrachloroethane (42 mg per gram of $C_2H_2Cl_4$ over iron at 500 °C) [1894].

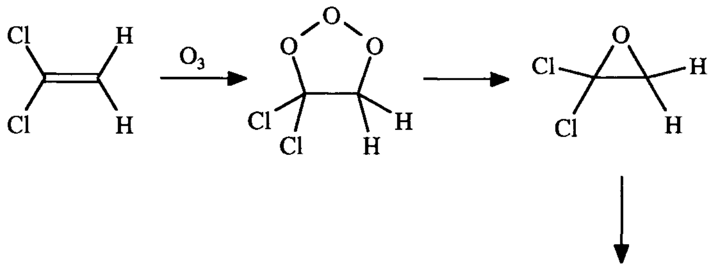
A small amount of $COCl_2$ is formed from the aerial oxidation of 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) at temperatures above 500 °C. At 700, 800, and 900 °C using, 1% of CFC-113 in air, the corresponding quantities of phosgene formed are 200, 750 and 250 p.p.m., respectively [1325]. Under internal arc stress, $C_2Cl_3F_3$ decomposes into over twelve products, including phosgene at 225 p.p.m., and the phosgene levels can increase threefold in the presence of air [606].

5.2.4.2 Oxidation by other species

Phosgene is formed as a major co-product in the vapour-phase reactions of trioxygen (ozone) with tetrachloroethene or 1,1-dichloroethene conducted at 25 °C [103a]. The initial reactions contributing to $COCl_2$ formation are illustrated below:

$$\begin{array}{l} Cl_2C{=}CX_2 + O_3 \longrightarrow X_2C{=}O + Cl_2C\text{-}\dot{O}\text{-}\dot{O} \xrightarrow{O_3} X_2C{=}O + Cl_2C{=}O + 2O_2 \\ (X = Cl \text{ or } H) \end{array}$$

On irradiation of a mixture of 1,1-dichloroethene and nitrogen(IV) oxide in dinitrogen, phosgene is formed as one of the decomposition products, as a result of the formation of ozone (O_3) and the subsequent decomposition of the ozonide [726]:



$COCl_2$, $ClCH_2COCl$, HCl, CO, HCOOH, H_2CO, ...

The formation of phosgene from trichloroethene or tetrachloroethene is explained by an analogous mechanism [726]. No reaction occurs between NO_2 and chloroethene or 1,2-dichloroethene under similar conditions.

Phosgene may be also formed from the fission of longer chain entities formed from the propagation of diradicals with the chloroethene or O_3, for example [103a]:

$$\begin{tikzcd} Cl_2C\text{-}\dot{O}\text{-}\dot{O} + Cl_2C{=}CH_2 \arrow[r] & Cl_2\dot{C}OOCH_2\dot{C}Cl_2 \arrow[r] \arrow[d, "O_3"] & Cl_2C{=}O + ClCH_2C(O)Cl \\ & Cl_2\dot{C}OOCH_2C(Cl_2)OO\dot{O} \arrow[r] & Cl_2C{=}O + Cl_2\dot{C}O\dot{O} + HCOOH \end{tikzcd}$$

Difluorine promotes the reaction of dioxygen with chloro-substituted ethanes and ethenes [1397,1398,1399]; reaction in the vapour or liquid phase giving phosgene, substituted acyl chlorides and chlorinated ketones. Thus, when pentachloroethane was treated with a 49:1 mixture of O_2 and F_2 in a stirred flask at 97–105 °C, fitted with a copper dip pipe and gauze, a small amount of phosgene was produced; the main product was trichloroethanoyl chloride [1398,1400]. When treated similarly, at 70 °C, tetrachloroethane also evolves $COCl_2$ [1398], the main product in this case being dichloroethanoyl chloride. When equal volumes of O_2 and F_2 were saturated with C_2Cl_4, and held at 100 °C for 15 hours in a cylinder packed with copper gauze, $COCl_2$, $CF_2ClCOCl$, $CFCl_2COCl$, and C_2Cl_5F were formed. Similar treatment with $CHCl{=}CCl_2$ at 0 °C gave $CHCl_2COCl$, $CHCl_2COF$, C_2HCl_5, $COCl_2$ and C_4H_2Cl [1397].

The substituted trichloroethane, 1,1,1-trichloro-2,2-bis(chlorophenyl)ethane (DDT), or its component isomers, liberate phosgene when heated with $K_2[Cr_2O_7]$-H_2SO_4 mixtures (see Section 3.3.6) [579].

Thermal decomposition of C_2Cl_6 in the hot detonation gases of nitrocellulose also yields some phosgene [1814].

5.2.4.3 Hydrolysis

Phosgene is one of the products resulting from the hydrolysis of C_2Cl_4. The principal product in the temperature range of 40–120 °C is trichloroethanoyl chloride, from which the phosgene is believed to derive. The hydrolysis reaction is catalysed by metals to give similar products to those obtained in the absence of a metal [1883].

5.2.5 Photochemical by-product formation

Phosgene is, not surprisingly, formed in many photochemical oxidations of chlorocarbons. The current controversy concerning the photochemical reactions of chlorofluorocarbons (CFCs) in the stratosphere (and its popularized focus, the 'ozone hole') [588a] is leading (and will lead) to a significant increase in studies in which phosgene is produced photochemically, but is not the cynosure of the report.

Predating the current fashionable interest by five decades, the photochemical oxidation (λ = 253.7 nm) of liquid tetrachloromethane in the presence of dioxygen was first observed in 1935 [1288b]:

$$2CCl_4 + O_2 \longrightarrow 2COCl_2 + 2Cl_2$$

A quantum yield of unity for the formation of $COCl_2$ from CCl_4 was observed [1288b]. Even earlier, in 1895, Besson [184aa] noted that prolonged exposure of a mixture of C_2Cl_4 and dioxygen to sunlight resulted in the formation of a mixture of $CCl_3C(O)Cl$ and $COCl_2$. In the presence of Cl_2, which acts as a photosensitizer, the major product (87%) is $CCl_3C(O)Cl$ [516b], the minor product (10%) is phosgene [516a].

The detailed studies so far published are summarized in Table 5.5: dichlorine emerges as a very efficient photosensitizer for these reactions. Similar results to the photochemical oxidation of C_2Cl_4 and C_2HCl_3 are produced by the thermal reaction between these chloroalkenes and dioxygen in the presence of difluorine, which acts as a sensitizer [1399]. Surprisingly, no phosgene was detected in the photo-oxidation of CH_3Cl by a mixture of O_2 and Cl_2 [1776c].

A recent patent application [1999a] claims that phosgene can be prepared by irradiation (λ = 200–290 nm) of tetrachloroethene in the presence of dioxygen: C_2Cl_4 is a readily available starting material that is considerably easier and safer to store and transport than phosgene itself.

Equation (5.17) equally applies to the situation in which CCl_4 is exposed to light of wavelength 213.9 nm [1036] or 253.7 nm [1288b] in the presence of dioxygen, and phosgene is formed similarly when CCl_4 is exposed to X-rays or ^{60}Co γ-radiation in the presence of air [1934]. The formation of phosgene on γ-irradiation of CCl_4, in the presence of dioxygen, has been explained by the following reactions [1933], which also partially account for the observation of hexachloroethane:

$$\begin{aligned} CCl_4 &\longrightarrow [CCl_3]\cdot + Cl\cdot \\ Cl\cdot + CCl_4 &\longrightarrow [CCl_3]\cdot + Cl_2 \\ [CCl_3]\cdot + O_2 &\longrightarrow [COCl]\cdot + Cl_2O \\ [COCl]\cdot + CCl_4 &\longrightarrow COCl_2 + [CCl_3]\cdot \\ 2[CCl_3]\cdot &\longrightarrow C_2Cl_6 \end{aligned}$$

The γ-radiolysis of tributylphosphate, $(BuO)_3P{=}O$, in tetrachloromethane produces dibutylphosphate, $(BuO)_2P(O)OH$, as the primary product, along with phosgene and C_2Cl_6, *inter alia* [303].

The oxidation of $CHCl_3$ vapour is accelerated in the presence of dichlorine, particularly when irradiated with light of wavelength 435.8 nm [1824]. The initial reaction stage involves generation of Cl· radicals and formation of $[CCl_3]\cdot$ as indicated below:

$$\begin{aligned} Cl_2 &\xrightarrow{h\nu} 2Cl\cdot \\ Cl\cdot + CHCl_3 &\longrightarrow [CCl_3]\cdot + HCl \end{aligned}$$

The formation of CCl_4 ($[CCl_3]\cdot + Cl_2 \longrightarrow CCl_4 + Cl\cdot$), however, is completely halted in the presence of O_2 (owing to the much more kinetically-favoured reaction ($[CCl_3]\cdot + O_2 \longrightarrow CCl_3O_2$) and the overall reaction occurs principally as follows [1824]:

$$2CHCl_3 + O_2 \longrightarrow 2COCl_2 + 2HCl$$

At $CHCl_3$ and Cl_2 pressures of between about 7 and 20 kPa, and O_2 pressures of between 4 and 13 kPa, the rate of phosgene formation is given by the expression:

$$-d[COCl_2]/dt = kI_{abs}[CHCl_3]^{\frac{1}{2}}$$

in which I_{abs} is the light absorption due to the Cl_2 concentration, relative to the incident light. At 65 °C and with a Cl_2 pressure of 13 kPa, 19 kPa of $CHCl_3$ are converted within 47 min. Between 55 and 75 °C, the reaction rate increases by a factor of 1.23 for each 10 degree temperature rise, corresponding to an activation energy of 18 kJ mol^{-1} [1824].

Ultra-violet irradiation (sunlight) of chloropicrin (CCl_3NO_2) generates significant levels of phosgene [1447]. Indeed, this reaction has resulted in a documented case of phosgene poisoning (a family of three, in October, 1945), as chloropicrin is used for the fumigation of homes against insects [1447], and the reaction is catalysed by absorbing surfaces, including linoleum [1447].

TABLE 5.5

PHOTOCHEMICAL REACTIONS OF CHLOROALKANES WHICH RESULT IN PHOSGENE FORMATION

System	λ/nm	Principal products and comments	Ref.
CCl_4/O_2	213.9	$COCl_2$ ($1<\Phi<2$) and Cl_2 ($\Phi\approx1.3$)	1036
CCl_4/O_2	184.9	$COCl_2$ ($\Phi\approx0.75$) and CO_2[b]	88
CCl_4/O_3	253.7	$COCl_2$ ($\Phi\approx0.87$) and Cl_2; reaction of $O(^1D)$	1036
$CCl_4/O(^1D)$		$COCl_2$ and CO_2[b]	88
$CHCl_3/O_2$	⩾185	$COCl_2$, Cl_2, HOCl and HCl	912
$CHCl_3/O_3$	⩾185	$COCl_2$ and HCl	912
$CHCl_3/O_2$	γ (^{60}Co)	$COCl_2$ and HCl (and Cl_3COOH)	1816
$CHCl_3/O_2/Cl_2$	365.5	$COCl_2$ ($\Phi\epsilon[100,215]$) and HCl	1776a
$CH_2Cl_2/O_2/Cl_2$	365.5	$COCl_2$ ($\Phi\approx4$), HC(O)Cl ($\Phi\approx49$) and HCl	1776c
C_2Cl_4/O_2	-[a]	$COCl_2$ and $Cl_3CC(O)Cl$, *ca.* 1:1	49
C_2Cl_4/O_2	Hg	$COCl_2$ and $Cl_3CC(O)Cl$, *ca.* 3:1	1348
$C_2Cl_4/O_2/O_3$	Hg	$COCl_2$ and $Cl_3CC(O)Cl$, *ca.* <1:1	1348
$C_2Cl_4/O(^3P)$		$COCl_2$ ($\Phi=0.19$) and a polymer	1776b
$C_2Cl_4/O_2/O(^3P)$		$COCl_2$, $CCl_3C(O)Cl$ and CO	1776b
$C_2Cl_4/O_2/Cl_2$	435.8	$COCl_2$ and $CCl_3C(O)Cl$	1000a
$CCl_2{=}CHCl/O_2$	213	$COCl_2$ ($\Phi\approx4$) and $CHCl_2C(O)Cl$ ($\Phi\approx20$)	446b, 1458aa
$CCl_3CHCl_2/O_2/Cl_2$	435.8	$COCl_2$, $CCl_3C(O)Cl$ and HCl	1000a, 1823a
CH_3CCl_3/O_2	-[c]	$COCl_2$ ($\Phi\approx1.3$), HCl, CO, CO_2 and $CH_3C(O)Cl$	387a
$CCl_3CHO/O_2/N_2$	300-400	$COCl_2$, HCl, CO and CO_2	1547

[a] Wavelength not specified. [b] Secondary photoproduct. [c] The full output of a deuterium light was used.

5.3 SYNTHESIS OF PHOSGENE FROM CARBONACEOUS MATERIALS

The chlorination of a powdered coal {analysis: C, 61.5; H, 1.4; N, 1.3; Cl, 2.9%} with liquid dichlorine at 490 °C and 40 atmospheres pressure in a Carius tube (16 h) in the absence of air was found to produce phosgene in a yield (carbon-based) of about 6%. CCl_4 and large amounts of HCl were also formed [ICI103]. The formation of phosgene was also noted during the gaseous chlorination (in the absence of air) of petroleum cokes in the temperature ranges of 500-850 °C [1786] and of 800-1000 °C [717]. A maximum yield of phosgene was recorded at 500 °C, with little formed at temperatures in excess of 700 °C owing to the high degree of phosgene dissociation (see Fig. 5.3) [1856]. The reaction of an activated (birchwood) carbon with a Cl_2–O_2 (40% O_2) mixture resulted in the formation of phosgene at 300 °C, with a maximum concentration (about 16%) occurring at 500 °C; dissociation and oxidation again occurred at higher temperatures [1856a,1864]. However, it is claimed that phosgene is made by passing a mixture of air and dichlorine over coke or other carbonaceous material heated to a temperature of about 1200–1500 °C [1598]:

$$2C + O_2 + 2Cl_2 \longrightarrow 2COCl_2$$

In view of the dissociation of phosgene at such high temperatures this reaction appears to be very unlikely.

An early patent describes the preparation of phosgene and calcium carbide by heating a mixture of calcium oxide, calcium chloride (or NaCl or $MgCl_2$) and carbon in an electric furnace [1289a]. The phosgene is formed from the combination of CO and Cl_2 (in the presence of coke) released by heating the mixture. The overall stoicheiometry corresponds to:

$$2CaO + 2CaCl_2 + 10C \longrightarrow 4CaC_2 + 2COCl_2$$

Passage of the off–gases through a mass of bone–black, coke, or pumice results in the dismutation of the phosgene into tetrachloromethane and carbon dioxide (see Section 8.2).

Phosgene has been formed at the graphite anode during the electrolysis of commercial calcium aluminates (for the production of aluminium–calcium alloys) when the aluminate content of the molten bath became low relative to the chloride–containing melt [233].

5.4 SYNTHESIS OF PHOSGENE FROM CARBON DIOXIDE, CARBONYL SULFIDE OR CARBON DISULFIDE

Various chlorinating agents combine with CO_2, COS, or CS_2 to form phosgene. Carbon dioxide reacts directly with Cl_2 over heated porcelain tubes filled with charcoal to give phosgene [1379]. Also, carbon dioxide is reported to react with $PbCl_2$ at 700 °C, or $NiCl_2$ at 550 °C, to produce small yields of phosgene [168] and the reaction of CO_2 with heated aluminium(III) chloride has been patented [2158] as a process for the production of phosgene, based on the reaction:

$$2AlCl_3 + 3CO_2 \longrightarrow Al_2O_3 + 3COCl_2$$

The equilibrium reaction:

$$CO_2 + CCl_4 \rightleftharpoons 2COCl_2$$

has been discussed in detail in Chapter 8, but it has been known since 1868 that phosgene is produced when carbon dioxide and tetrachloromethane vapour are passed over pumice heated to 350–400 °C [1824a].

Carbonyl sulfide combines with heated copper(II) chloride or with antimony(III) chloride at room temperature to form $COCl_2$, according to Equations (5.24) and (5.25), respectively [1379]:

$$COS + CuCl_2 \longrightarrow COCl_2 + CuS \tag{5.24}$$

$$3COS + 2SbCl_3 \longrightarrow 3COCl_2 + Sb_2S_3 \tag{5.25}$$

Passage of a mixture of COS and Cl_2 through a red-hot porcelain tube was also noted to generate phosgene [589b], according to Equation (5.26):

$$3Cl_2 + 2COS \longrightarrow 2COCl_2 + S_2Cl_2 \tag{5.26}$$

In very early work, Berzelius noted the formation of phosgene from the action of ***aqua regia*** on carbon disulfide [1379]. Similarly, the action of chlorine monoxide, Cl_2O, on carbon disulfide was noted to proceed as follows:

$$3Cl_2O + CS_2 \longrightarrow COCl_2 + 2SOCl_2$$

5.5 SYNTHESIS OF PHOSGENE FROM OTHER CARBONYL HALIDES

$COCl_2$ is co-produced with COF_2 during the comproportionation of COClF over activated charcoal at room temperatures and above, according to the equation [ICI110]:

$$2COClF \rightleftharpoons COCl_2 + COF_2$$

This system is described, appropriately, in more detail in Chapters 13 and 16.

5.6 SYNTHESIS OF PHOSGENE FROM OXYGENATES (OXYGEN-CONTAINING ORGANIC COMPOUNDS)

5.6.1 Chlorination reactions

Tishchenko [2037a] reported that dichlorine reacts, under ambient daylight conditions, with paraformaldehyde to give $COCl_2$ and HCl, stoicheiometrically [2037a]: this was quickly refuted by Brochet [277b,277c]. The thermal, uncatalysed, reaction of Cl_2 with a wide range of other organic compounds (including ethanol, ethanal, propanone, ethyl methanoate and dioxane) at about 600 °C gave a mixture of $COCl_2$ and CCl_4 [1713]. The reactions for MeC(O)OEt and for dioxane are represented below:

$$CH_3C(O)OCH_2CH_3 + 10Cl_2 \longrightarrow 2CCl_4 + 2COCl_2 + 8HCl$$

$$C_4H_8O_2 + 10Cl_2 \longrightarrow 2CCl_4 + 2COCl_2 + 8HCl$$

The reaction of Cl_2 with a number of mixtures {including butan-1-ol and butan-2-ol; cyclohexanol, cyclohexanone, and hexachlorocyclohexane; and phenol, chlorobenzene and dichlorobenzene (isomeric mixture)} proceeded similarly. Many other similar types of mixtures are likely to undergo $COCl_2/CCl_4$ formation under such severe conditions. Indeed, this system can be extended under such forcing conditions (550-660 °C and 80-300 atmospheres) to the reaction of Cl_2 with mixtures of CO, CO_2 or H_2O with benzene, chlorinated benzenes, hexachlorocyclohexanes, trichloroethane, trichloroethene, or tetrachloroethene [1714]. The hydrogen in the system appears as HCl, and some perchlorinated compounds tend to be formed, but the principal carbon-containing products are $COCl_2$ and CCl_4.

Ultra-violet irradiation (both continuous and flash photolysis; $\lambda > 300$ nm) of solutions of α,β-unsaturated ketones {including 4-mentha-6,8-dien-2-one (carvone), verbenone, isophorone, 2-ethylidenecyclohexanone, pulegone and 4-methyl-3-penten-2-one} in oxygenated tetrachloromethane produces phosgene as one of the major photolysis products [1390]: the simple ketones propanone and benzophenone, and the aromatic hydrocarbons naphthalene and anthracene, exhibit parallel behaviour [1390]. Similar photolyses in the dioxygen-free solvent produce no detectable level of phosgene [1390].

Phosgene (along with HCl) has also been produced by heating rice hulls at 190-230 °C in a dichlorine atmosphere [1777b].

5.6.2 Decomposition reactions

5.6.2.1 Thermal or catalytic decompositions

Phosgene has been prepared, or its formation noted, by the thermal or catalytic decomposition of a large number of oxygen-containing organic compounds, and these reactions are summarised in Table 5.6. The thermal decomposition of a series of compounds containing the trichloromethyl group has been reviewed by Melnikov [1379]. Such compounds include: $CCl_3OC(O)Cl$, $CCl_3OC(O)OCCl_3$, $ROC(O)OCl_3$ (R unspecified) trichloromethyl perchlorate, and trichloromethylsulfonyl chloride.

In particular, the decomposition of the so-called materials "diphosgene" {$Cl_3COC(O)Cl$} and "triphosgene" {$Cl_3COC(O)OCCl_3$} (see Chapter 12), as their names may suggest, can be thermally or catalytically induced to generate two or three moles of phosgene per mole of starting material, respectively [781,867,946,947]. Such decompositions are illustrative of the ready fission of the trichloromethoxycarbonyl group:

$$Cl_3COC(O)R \longrightarrow COCl_2 + RC(O)Cl$$

for which relevant examples here include R = alkyl, Cl or $OCCl_3$ [996].

The decomposition of diphosgene is catalysed in the presence of various nitrogen-containing derivatives, such as pyridine, quinoline, or tertiary amines, to give complete

TABLE 5.6

PHOSGENE FORMATION *via* THERMAL OR CATALYTIC DECOMPOSITIONS

Compound	Conditions	Products	Ref.
$Cl_3CC(O)OH$	300-400 °C	$COCl_2 + HCl + CO$	1769
$Cl_3CC(O)ONa$	>170 °C	$Cl_3C(O)Cl$ - major $COCl_2$ - trace	476,943a
$[Cl_3CC(O)O]_2Ca$	>150 °C	$2COCl_2 + 2CO + CaCl_2$	1308
$Cl_3CC(O)OOH$	Gentle heat	$COCl_2 + HCl + CO_2$	649aa
$Cl_3COC(O)Cl$	>100 °C; Pressure Heat under reflux	$2COCl_2$	867,946 947
$Cl_3COC(O)OCl_3$	250-300 °C >78 °C; activated C	$3COCl_2$	781
$Cl_3COC(O)OMe$	*ca.* 165 °C	$COCl_2 + MeOC(O)Cl$	946
$MeO\text{-}2\text{-}C_6H_4OC(O)Cl$	Decomposes during distillation		947
$CCl_3CCl_2OC(O)Cl$	Heat; $AlCl_3$	$CCl_3C(O)Cl + COCl_2$	1458
$(COCl)_2$	>0 °C; $AlCl_3$	$COCl_2 + CO$	1250a,1556, 1936b
$C_6Cl_3(NO_2)_3$[a]	Ignition	$COCl_2$ (15% yield)	1814
$Cl_2C{=}NOH$	20-130 °C	See text	197,654
$CCl_2CCl_2OC(O)O$	NR_3 or $RC(O)NH_2$	$(COCl)_2 + COCl_2$	588,1018a,1377
$CCl_2CCl_2\{OC(O)Cl\}_2$	Boil; py	$(COCl)_2 + 2COCl_2$	588
$Cl_3COC(O)C(O)OCCl_3$	350-400 °C	$3COCl_2 + CO$	323aa

[a] Unspecified isomer

conversion to phosgene [970]. The reaction is also catalysed by passage of the vapours of diphosgene over iron(III) oxide, but is particularly rapidly decomposed, as is triphosgene, over charcoal [781,978a]. However, a continuous stream of phosgene is also emitted when the chloroformate is simply heated under reflux [946]. These compounds may constitute a convenient form by which to transport phosgene, owing to their respective liquid and solid physical states. The application of these "homologues" as reagent substitutes for phosgene is described in Section 12.2.

Phosgene generation can be too rapid to constitute a convenient synthesis. For example, careful heating of the peroxide CCl_3COOOH can result in the formation of phosgene, as indicated in Table 5.6. This reaction, however, can proceed violently and may occur through the formation of trichloromethanol, CCl_3OH, which decomposes instantly to $COCl_2$ and HCl [649aa].

Other materials can generate phosgene by decomposition at room temperature. Thus, $Cl_2C{=}NOH$, commonly known as phosgene oxime, decomposes on standing at room temperature into CCl_3NO_2, $[NH_4]Cl$, NH_2OH, HCl, CO_2, HCl, N_2 and $COCl_2$ [1654]; this reaction is unlikely to constitute a practical method for the synthesis of phosgene. At 128 °C, ClCN, Cl_2O, Cl_2, $[NH_4]Cl$, CO_2, CCl_3NO_2 and $(ClCN)_3$ are formed in addition to phosgene [197].

Catalytic reagents are necessary for phosgene generation in other decomposition reactions. Thus, treatment of tetrachloroethene carbonate with tertiary alkylamines at room temperature, or above, causes a catalytic rearrangement to ethane-1,2-dioyl chloride and phosgene, as indicated in Table 5.6 [588,1377]. This reaction is also catalysed, but less effectively, by activated carbon, PPh_3, $AsPh_3$, dmf, or tetramethylthiuram disulfide [588]. If the carbonate, in the absence of any other added compound, is subjected to prolonged boiling, however, slow decomposition to the stated products does occur [588]. Tetrachloroethene bis(chloroformate) is similarly decomposed by addition of a small quantity of pyridine [588], presumably yielding two moles of phosgene per mole of $(COCl)_2$. The perchlorinated chloroformate, $CCl_3CCl_2O(CO)Cl$, can decompose in two principal ways in the presence of aluminium(III) chloride, to give C_2Cl_6 and CO_2 or to give $Cl_3CC(O)Cl$ and $COCl_2$ [1458].

5.6.2.2 Photochemical or radiochemical decompositions

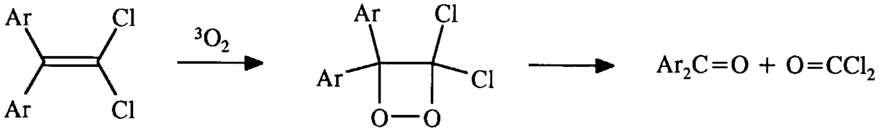
Chloroisocyanate, ClNCO, in the presence of u.v. light, decomposes to give phosgene according to [805a]:

$$2ClNCO \xrightarrow{h\nu} COCl_2 + N_2 + CO$$

and solar irradiation of CCl_3NO_2 in the presence of air resulted in its partial conversion to phosgene [1445]:

$$CCl_3NO_2 \xrightarrow{h\nu} COCl_2 + NOCl$$

On irradiation of 1,1-dichloro-2,2-bis(4-chlorophenyl)ethene at 300 nm in the presence of $^3O_2$, the double bond is cleaved into phosgene and 4,4'-dichlorobenzophenone. The dioxetane is considered to be a likely intermediate in the decomposition [1601a]:



$(Ar = 4\text{-}Cl\text{-}C_6H_4)$

Radiolysis (^{60}Co γ-irradiation) of $CFCl_2CF_2OCCl_3$ results in the formation of phosgene as one of the products, according to the following reaction [2241a]:

$$CFCl_2CF_2OCCl_3 \longrightarrow CFCl_2\dot{C}F_2 + \dot{O}CCl_3$$

$$\dot{O}CCl_3 \longrightarrow COCl_2 + Cl\cdot$$

5.7 SYNTHESIS OF PHOSGENE BY MISCELLANEOUS METHODS

A small quantity of phosgene was obtained when soda (probably a mixture of sodium carbonate and sodium hydrogen carbonate) was heated with phosphorus(V) chloride [850a].

The reaction of hydrogen chloride with *N,N'*-carbonyldiimidazole at −63 °C gave phosgene in a yield of about 50% [1589b].

Ultra-violet irradiation of polychloropinene in moist soil produces CO, CO_2 and HCl, along with some phosgene (a somewhat surprising result, since moist soil catalyses the hydrolysis of phosgene, Section 9.10.3.1) [1862].

5.8 SYNTHESIS OF LABELLED PHOSGENE

Phosgene is a versatile reagent for the isotopic labelling of organic molecules and its use for the preparation of a variety of radiopharmaceuticals is well established (see Section 10.8). Given the vast range of organic compounds which can be prepared from phosgene, there is tremendous scope for the analogous preparation of the corresponding isotopically-enriched or radio-labelled derivatives. In particular, the synthesis of ^{11}C-labelled compounds is possible owing to the frequently rapid reactions involving phosgene, which are essential because of the short lifetime ($t_{\frac{1}{2}}$ = 20.4 min [1730]) of ^{11}C.

Published methods for the preparation of phosgene containing isotopically labelled carbon include the compounds: $^{11}COCl_2$ [275,429,519,1731,1732,1734], $^{13}COCl_2$ [2135], and $^{14}COCl_2$ [178,999,1962–1965]. Despite the commercial availability of phosgene labelled with oxygen-17 or oxygen-18 isotopes, there appear to be no published reports on their synthesis. However, general methods for the preparation of phosgene containing radioactive elements have been described [1883a]. A method suitable for the preparation of phosgene containing radioactive chlorine involves the dissolution of the dichlorine into tetrachloromethane, and its extraction with activated charcoal. Removal of the solvent, and washing of the carbon with dry diethyl ether (ethoxyethane) is followed by passage of carbon monoxide over the charcoal in a heated tube [1883a]. Alternatively, for the preparation of phosgene containing radioactive carbon or oxygen, labelled carbon dioxide and dichlorine are mixed, and passed through a silica tube containing charcoal at between 800 and 1000 °C. Finally the off-gases are passed through activated charcoal held at a lower temperature to produce phosgene [1883a].

The CAS registry numbers for isotopically-labelled phosgene are given in Appendix A3.

5.8.1 $^{11}COCl_2$

^{11}C-Labelled phosgene is a useful material in radiopharmaceutical and nuclear medical applications, since it combines the radiophysical properties of ^{11}C with the extensive reaction chemistry of phosgene to permit the rapid synthesis of a wide range of biologically-active materials with radiochemical labels. Carbon-11 is a short-lived positron-emitting radionucleide, useful for *in vivo* measurements with positron emission tomography (PET) [519]. Because of the short half-life of ^{11}C, it can be administered without excessive radiation damage, but the ability to label with a high specific activity also permits the facility to inject only small amounts of the pharmaceutical [428].

Phosgene containing the short-lived radioactive nuclide ^{11}C has been prepared by zinc reduction of cyclotron-produced ($^{14}N(p,\alpha)^{11}C$)$^{11}CO_2$ to ^{11}CO, followed by chlorination to $^{11}COCl_2$ by passage of the gaseous labelled CO over heated $PtCl_4$ [429,1729,1731], or by u.v. light-induced reaction of the ^{11}CO with Cl_2 [1729,1732,1734]. In the latter method, $^{11}CO_2$ is converted into $^{11}COCl_2$ in a yield of 50% within ten minutes. Modification of this procedure to a completely continuous-flow method permits higher radiochemical yields to be obtained [519].

Alternatively ^{11}CO, obtained directly by the irradiation of N_2 (in the presence of 2% O_2) with 15 MeV protons, was mixed with an equal volume of Cl_2 and the mixture exposed over fifteen minutes to u.v. light. The radiochemical yield was about 75% [275]. Since the total time required to obtain $^{11}COCl_2$ for further synthetic use is about thirty minutes, attempts were made to telescope the synthesis by combining the production of the labelled CO and the radiation-induced reaction with Cl_2 in one step.

The cyclotron irradiation of a mixture of N_2, CO and Cl_2 gave a yield of $^{11}COCl_2$ of 25%, but was of relatively low specific activity owing to the presence of carrier amounts of non-radioactive $COCl_2$ [275].

5.8.2 $^{13}COCl_2$

Phosgene, containing 2-4% by volume of ^{13}C, was obtained by photochemical equilibration (using 253.7 nm mercury line) with isotope-enriched carbon monoxide (see Section 5.1.1) [2135]:

$$^{12}COCl_2 + {}^{13}CO \longrightarrow {}^{13}COCl_2 + {}^{12}CO$$

5.8.3 $^{14}COCl_2$

$^{14}COCl_2$ has been prepared by the photochemical combination of ^{14}CO with an excess of Cl_2 [999]; the excess dichlorine was removed by passage of the gases over antimony. The enrichment of ^{14}C in the photochemical exchange of ^{14}CO with $COCl_2$ was predicted, on the basis of the partition function ratios, Q_{14}/Q_{12}, at 293.16 K, to be about 11.4% [1962]. This value is substantiated by preliminary experiments [1962] (earlier predictions are known to have been calculated in error [1966]).

The experimental and theoretical values of the equilibrium constant for the reaction

$$^{12}COCl_2 + {}^{14}CO \longrightarrow {}^{14}COCl_2 + {}^{12}CO \qquad (5.27)$$

illustrated in Equation (5.27), at between 10 and 500 °C, are recorded in Table 5.7 [1963].

TABLE 5.7

EQUILIBRIUM CONSTANTS FOR THE $^{14}CO/COCl_2$ EXCHANGE OF EQUATION (5.27) [1963]

T/°C	Equilibrium Constant		
	Method (1)[a]	Method (2)[b]	Theoretical
10	1.1051	1.1062	1.1005
20	1.0990	1.0983	1.0940
30	1.0884	1.0888	1.0879
40	1.0830	1.0833	1.0824
50	1.0778	1.0771	1.0773
60	1.0730	1.0723	1.0727
100	1.0555	1.0578	1.0575
200	1.0365	1.0371	1.0375
300	1.0229	1.0215	1.0222
400	1.0119	1.0128	1.0153
450	1.0050	1.0061	1.0134
500	1.0018	1.0021	1.0085

[a] Method (1): from ionization chamber measurements.

[b] Method (2): from Geiger–Müller counter measurements.

The apparent enthalpy of the exchange reaction, from values measured between 30 and 60 °C, is −416 J mol^{-1} (from ionization chamber measurements) and −423 J mol^{-1} (from Geiger–Müller counter measurements), compared to the calculated value of −414 J mol^{-1} [1963]. The kinetics of both the photochemical [1964] and the thermal [1965] reactions have also been measured.

6 THERMODYNAMIC AND PHYSICAL PROPERTIES

Under standard conditions, phosgene is a colourless gas with a density of approximately 3.5 times that of air, in which it is non-flammable. It is easily condensed to a colourless liquid when pure, and in the cylinder it is present as the liquified gas, exerting a vapour pressure of about 157 kPa (1.55 atm) at 20 °C. Its relative molecular mass is 98.9158.

The relative importance of the vapour state of phosgene is reflected in the order of treatment of its thermodynamic, physical and structural properties, and this format is followed where practicable throughout succeeding chapters. The liquid state is considered to be next in importance owing to the ease with which it is attained, and the occasional use of the material as a non-aqueous solvent (Chapter 11). The solid state, although of least importance in the practical sense, is nonetheless an interesting one for $COCl_2$, being capable of existence in three crystalline forms depending upon the conditions of its formation.

6.1 THERMOCHEMICAL PROPERTIES

6.1.1 Gas and vapour phase

Numerous determinations [181a,218,464,1275,1998,2032a] of the standard enthalpy of formation of phosgene have been reported, and the most important of these are summarized in Table 6.1 [464].

Based on the mean of the most recently determined calorimetric [464] and equilibrium [1275] values, the value of $\Delta H^\circ_{f,298}(g)$ is −219.6 ± 0.6 kJ mol^{-1} [464]. From a recent MNDO calculation [514], the value of −221.3 kJ mol^{-1} has been predicted, in good agreement with the experimentally determined quantity. In addition, a value of −223.0 kJ mol^{-1} has been calculated from the determination of elementary rate constants [792a].

The entropy of phosgene in the ideal gas state has been obtained by combining the heat capacity data of the most stable solid form (see Section 6.1.3) with calorimetric measurements on the liquid, and with the enthalpies of fusion and of vaporization [752]. At the boiling point, S° = 280.3 J mol^{-1} K^{-1}; at 298.15 K, S° = 283.7 J mol^{-1} K^{-1}. These values are in almost perfect agreement with those calculated from the energies of the six fundamental vibrational modes, determined by infrared spectroscopy, at 278.5 [1804] or 280.3 [343], and 283.8 J mol^{-1} K^{-1}, respectively [343]. More recently recorded values of the standard entropy are 283.53 [2137b], 283.4 [2137a], 283.7 ± 0.9 [1078d], 283.76 [1973] and 289.1 J mol^{-1} K^{-1} [792a].

TABLE 6.1

STANDARD ENTHALPY OF FORMATION OF PHOSGENE [464]

Year	Experimental Method	$\Delta H^{\circ}_{f,298}$(g)/kJ mol^{-1}	Ref.
1878	Calorimetry[a]	−189	181a
1882	Calorimetry[a]	−228±1	2032a
1882	Calorimetry[b]	−216±2	2032a
1924	Equilibria[c]	−218.9±0.6	218
1967	Calorimetry[d]	−224±1	1998
1970	Equilibria[e]	−219.1±0.6	1275
1972	Calorimetry[a]	−220±1	464

[a] Hydrolysis in alkaline solution. [b] Combustion enthalpy in O_2 and H_2

[c] Synthesis, $CO + Cl_2 \rightleftharpoons COCl_2$. [d] Photochemical synthesis.

[e] Dissociation, $COCl_2 \rightleftharpoons CO + Cl_2$

The enthalpy and entropy values of superheated phosgene vapour have been calculated in the temperature range of 240–600 K for pressures of 5 to 300 kPa, and in the temperature range of 340–600 K at pressures of 0.51 to 15.2 MPa [1843]. The standard free energy of formation for $COCl_2$(g) has been fitted to the equation:

$$\Delta G^{\circ}_f = -220999 + 19.142T\log_{10}(T) - 3.93T \tag{6.1}$$

where T is in K, and ΔG°_f is in kJ mol^{-1} [295]. The value of ΔG°_f at 298.15 K from this equation is −208.05 kJ mol^{-1}, and the value −209.98 kJ mol^{-1} is derived from the following expression at the thermodynamic standard temperature [1948a]:

$$\Delta G^{\circ}_f = -221.67 + 0.0392T$$

The calculated thermodynamic functions for phosgene, C°_p, S°, $-(G^{\circ} - H^{\circ}_{298})/T$, $(H^{\circ} - H^{\circ}_{298})$, ΔH°_f, ΔG°_f and $\log_{10}(K_f)$, are listed in Table 6.2 for the extended temperature range 0–6000 K in the ideal gas state [359aa], and are illustrated over the more normal working temperature range [359aa] in Fig. 6.1. Earlier values for these thermodynamic properties have now been superseded [1360c,1587,1972,1973]. Values for the functions $-(G^{\circ} - H^{\circ}_0)/T$ and $(H^{\circ} - H^{\circ}_0)$/T have been calculated for the range of 15 to 500 K [752] and the heat capacity data of phosgene in the ideal gas state [752] over this temperature

TABLE 6.2

THERMODYNAMIC PROPERTIES OF PHOSGENE IN THE IDEAL GAS STATE [359aa]

T/K	C_p° [a]	S° [a]	$-(G^{\circ}-H^{\circ}_{298})/T$ [a]	$(H^{\circ}-H^{\circ}_{298})$ [b]	ΔH_f° [b]	ΔG_f° [b]	$\log_{10}(K_f)$
0	0.000	0.000	∞	-12.867	-218.372	-218.372	∞
100	36.537	233.747	328.453	-9.471	-219.399	-215.113	112.363
200	48.362	262.618	288.800	-5.236	-219.985	-210.551	54.990
250	53.603	273.992	284.724	-2.683	-220.075	-208.180	43.497
298.15	57.695	283.796	283.796	0.000	-220.078	-205.887	36.071
300	57.835	284.153	283.797	0.107	-220.077	-205.799	35.833
350	61.211	293.332	284.514	3.086	-220.026	-203.423	30.359
400	63.938	301.689	286.147	6.217	-219.945	-201.056	26.255
450	66.184	309.354	288.305	9.472	-219.853	-198.701	23.065
500	68.068	316.427	290.768	12.830	-219.760	-196.356	20.513
600	71.048	329.115	296.127	19.793	-219.587	-191.691	16.688
700	73.282	340.242	301.650	27.014	-219.438	-187.054	13.958
800	74.993	350.144	307.105	34.432	-219.309	-182.437	11.912
900	76.324	359.057	312.390	42.000	-219.198	-177.835	10.321
1000	77.373	367.155	317.468	49.687	-219.102	-173.244	9.049
1100	78.210	374.570	322.327	57.468	-219.020	-168.662	8.009
1200	78.886	381.406	326.969	65.324	-218.952	-164.087	7.143
1300	79.437	387.742	331.403	73.241	-218.898	-159.517	6.409
1400	79.891	393.646	335.641	81.208	-218.859	-154.951	5.781
1500	80.270	399.172	339.694	89.217	-218.836	-150.387	5.237
2000	81.455	422.448	357.605	129.686	-219.018	-127.559	3.331
2500	82.040	440.694	372.464	170.575	-219.846	-104.614	2.186
3000	82.368	455.683	385.122	211.684	-221.515	-81.425	1.418
3500	82.570	468.397	396.133	252.922	-224.076	-57.887	0.864
4000	82.703	479.432	405.871	294.243	-227.366	-33.927	0.443
4500	82.794	489.178	414.596	335.618	-231.079	-9.528	0.111
5000	82.860	497.905	422.498	377.033	-234.905	15.295	-0.160
5500	82.909	505.805	429.718	418.476	-238.620	40.496	-0.385
6000	82.946	513.020	436.364	459.940	-242.119	66.026	-0.575

[a] Units of J mol^{-1} K^{-1}. [b] Units of kJ mol^{-1}.

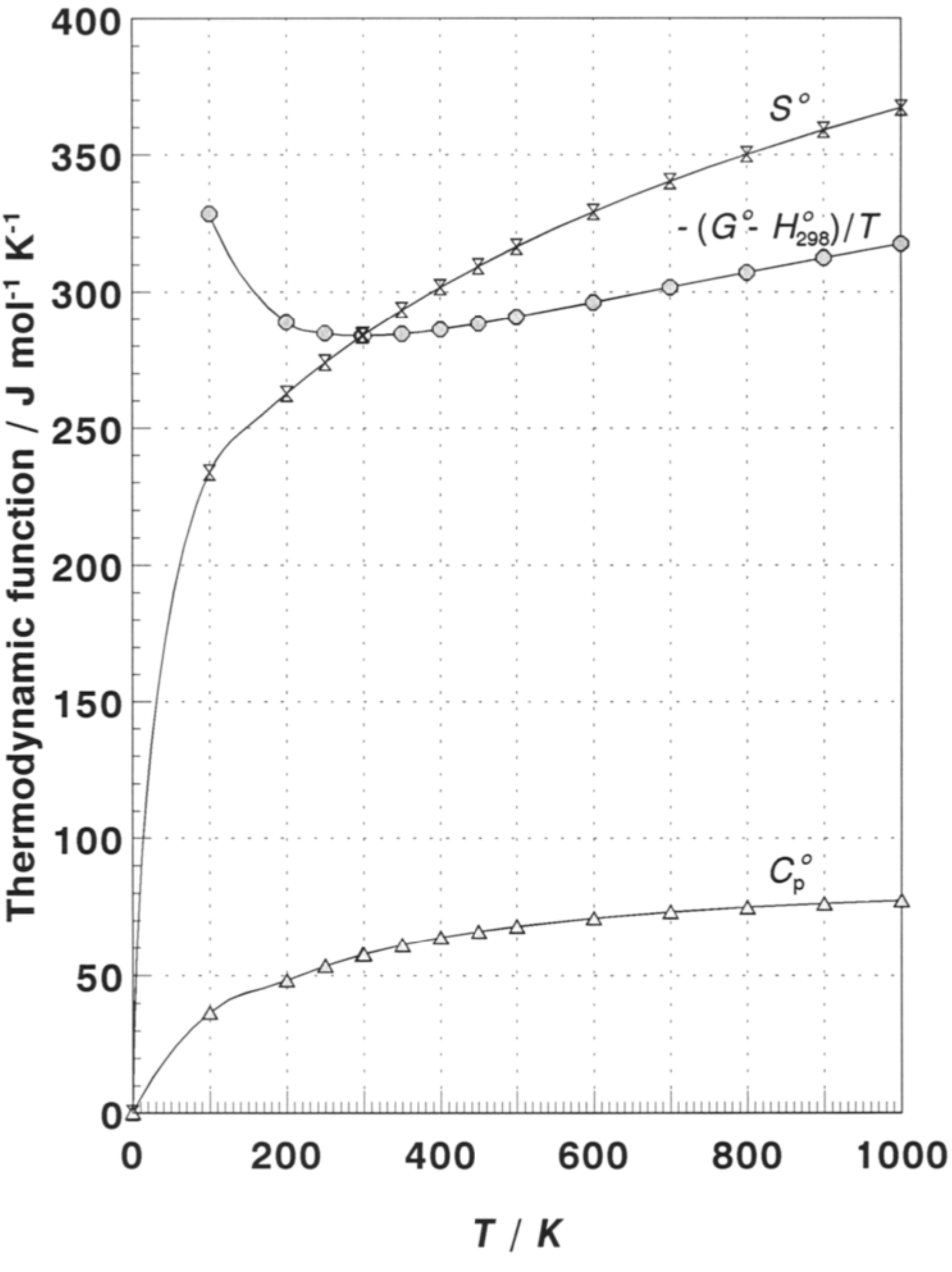
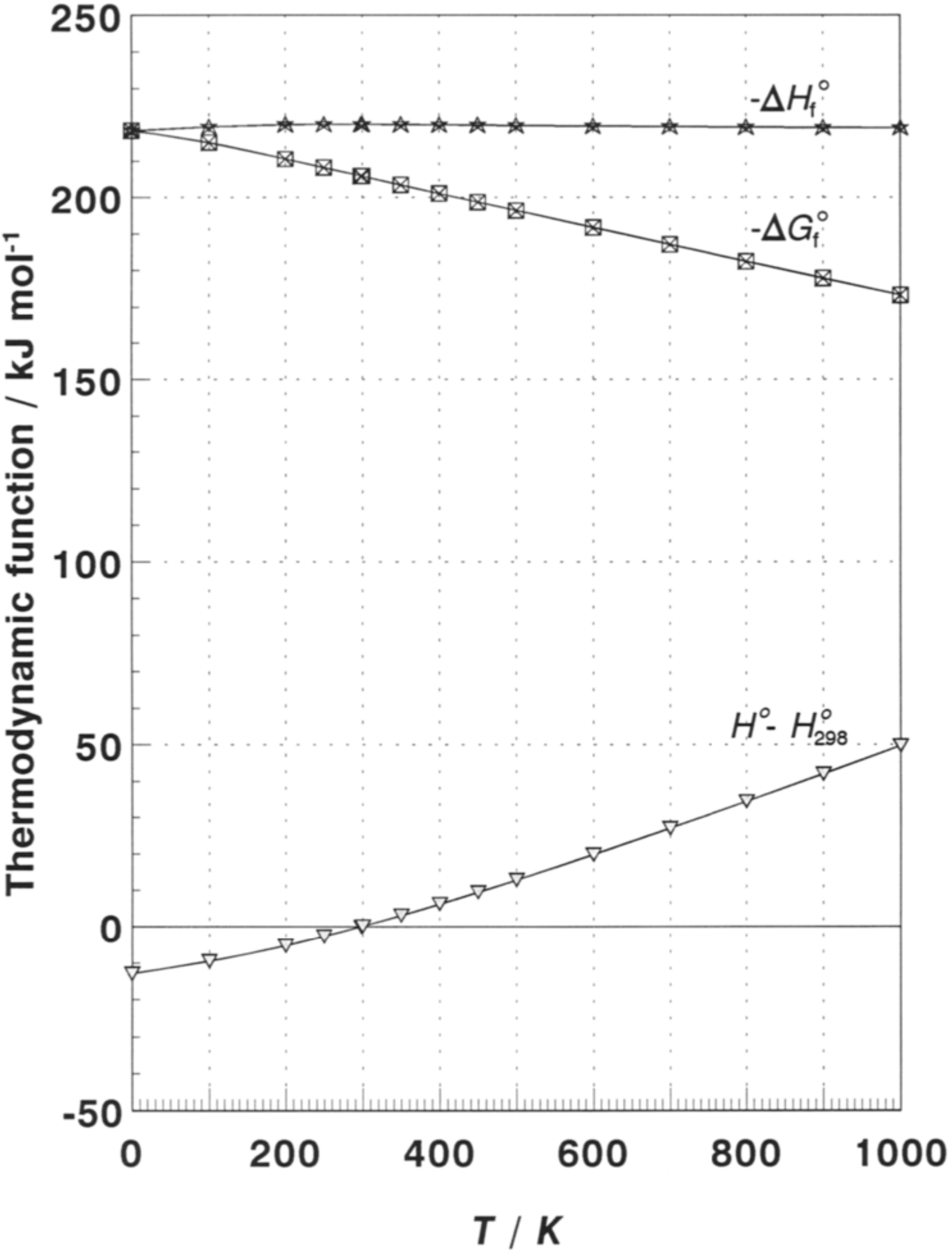


Fig. 6.1 Calculated thermodynamic properties (C_p°, S° and $-(G^\circ - H^\circ_{298})/T$ on this page; $H^\circ - H^\circ_{298}$, $-\Delta H_f^\circ$, and $-\Delta G_f^\circ$ on facing page) of phosgene (ideal gas) in the temperature range of 0–1000 K [359aa].


$-\Delta H_f^\circ$
$-\Delta G_f^\circ$
$H^\circ - H^\circ_{298}$
Thermodynamic function / kJ mol^{-1}
250
200
150
100
50
0
-50
0
200
400
600
800
1000
T / K

range has been fitted by the method of least squares to Equation (6.2) [1843]:

$$C_p = 13.970 + 0.23726T - 3.7147 \times 10^{-4}T^2 + 2.2677 \times 10^{-7}T^3 \qquad (6.2)$$

where T is in units of K and C_p is in J mol^{-1} K^{-1}. Early estimates of ΔG_f° for phosgene are considered to be redundant [1243].

More recently, the data presented by Stull *et al.* have been fitted to a cubic expression, over a wider temperature range (298–1000 K) [1842ac]:

$$C_p = 28.0688 + 0.135971T - 1.37259 \times 10^{-4}T^2 + 0.506546 \times 10^{-7}T^3$$

and (rather less usefully) group contributions to the coefficients have been estimated [1842ab].

Other calculations of thermodynamic functions for phosgene have been made on the basis of using either only five of the six fundamental vibrations [1953–1955] or an incorrectly assigned frequency (230 cm^{-1} instead of 580 cm^{-1}, see Section 7.2) for the sixth fundamental mode, ν_6 [2031]. Calculations of thermodynamic functions based upon those earlier works may also be considered to be obsolete [799,1078c,1134,1135,1927,2179a,2189b].

6.1.2 *Liquid phase*

The enthalpy of vaporization of liquid phosgene measured calorimetrically at the normal boiling temperature has been found to be 24.402 ± 0.003 kJ mol^{-1} [751]. It thus takes about one-ninth as much heat to vaporize phosgene as would be required to vaporize the equivalent quantity of water. The less reliable value of ΔH_{vap} = 24.37 kJ mol^{-1}, estimated from vapour pressure data, is in good agreement with the above direct determination [751]. Using the published vapour pressure data [1971], the enthalpy of vaporization of phosgene has been calculated as a function of temperature [715,1540]. The enthalpies and entropies for the saturated liquid and vapour have been calculated from 230 K up to the critical temperature [1843], and ΔH_{vap} and ΔS_{vap} have also been calculated over this temperature interval [1843], from the Clausius–Clapeyron equation. These data are displayed in Table 6.3 and Fig. 6.2.

The thermodynamic functions, C_p, S°, $-(G-H^{\circ}_0)/T$ and $(H-H^{\circ}_0)/T$, have been calculated for phosgene in the liquid state, see Table 6.4 [752]. The specific heat data (in J g^{-1} K^{-1}) have been fitted to a polynomial [2241]:

$$C_p = 0.80927 + 0.010661T - 1.1332 \times 10^{-4}T^2 + 4.4175 \times 10^{-7}T^3 - 5.8416 \times 10^{-10}T^4$$

6.1.3 *Solid phase*

Solid phosgene exists in three crystalline forms, identified by the following melting temperatures and calorimetrically-determined enthalpies of fusion: solid I, T_m = 145.37 K; ΔH_{fus}° = 5.738 ± 0.004 kJ mol^{-1}; solid II, T_m = 142.09 K; ΔH_{fus}° = 5.587 ± 0.006 kJ mol^{-1}; solid III, T_m = 139.19 K; ΔH_{fus}° = 4.73 ± 0.02 kJ mol^{-1} [752]. Solid III is unstable; it is formed when liquid $COCl_2$ is cooled quickly [2139a] and if permitted to stand a few degrees below the melting point, it converts into one of the other solid forms [752]. Solid II

TABLE 6.3

CALCULATED ENTHALPIES AND ENTROPIES OF VAPORIZATION

T/K	ΔH_{vap}/kJ mol^{-1}	ΔS_{vap}/J mol^{-1} K^{-1}
230	26.85	116.7
240	26.57	110.7
250	26.17	104.7
260	25.77	99.1
270	25.29	93.7
280	25.02	89.4
290	24.64	85.0
300	24.27	80.9
310	23.87	77.0
320	23.44	73.3
330	23.07	69.9
340	22.59	66.4
350	21.97	62.8
360	21.39	59.4
370	20.62	55.7
380	19.89	52.3
390	19.00	48.7
400	17.89	44.7
410	16.52	40.3
420	14.82	35.3
425	13.71	32.3
430	12.61	29.3
435	11.45	26.3
440	10.07	22.9
445	8.41	18.9
450	6.38	14.2
455	1.56	3.43
455.16 (T_c)	0.00	0.00

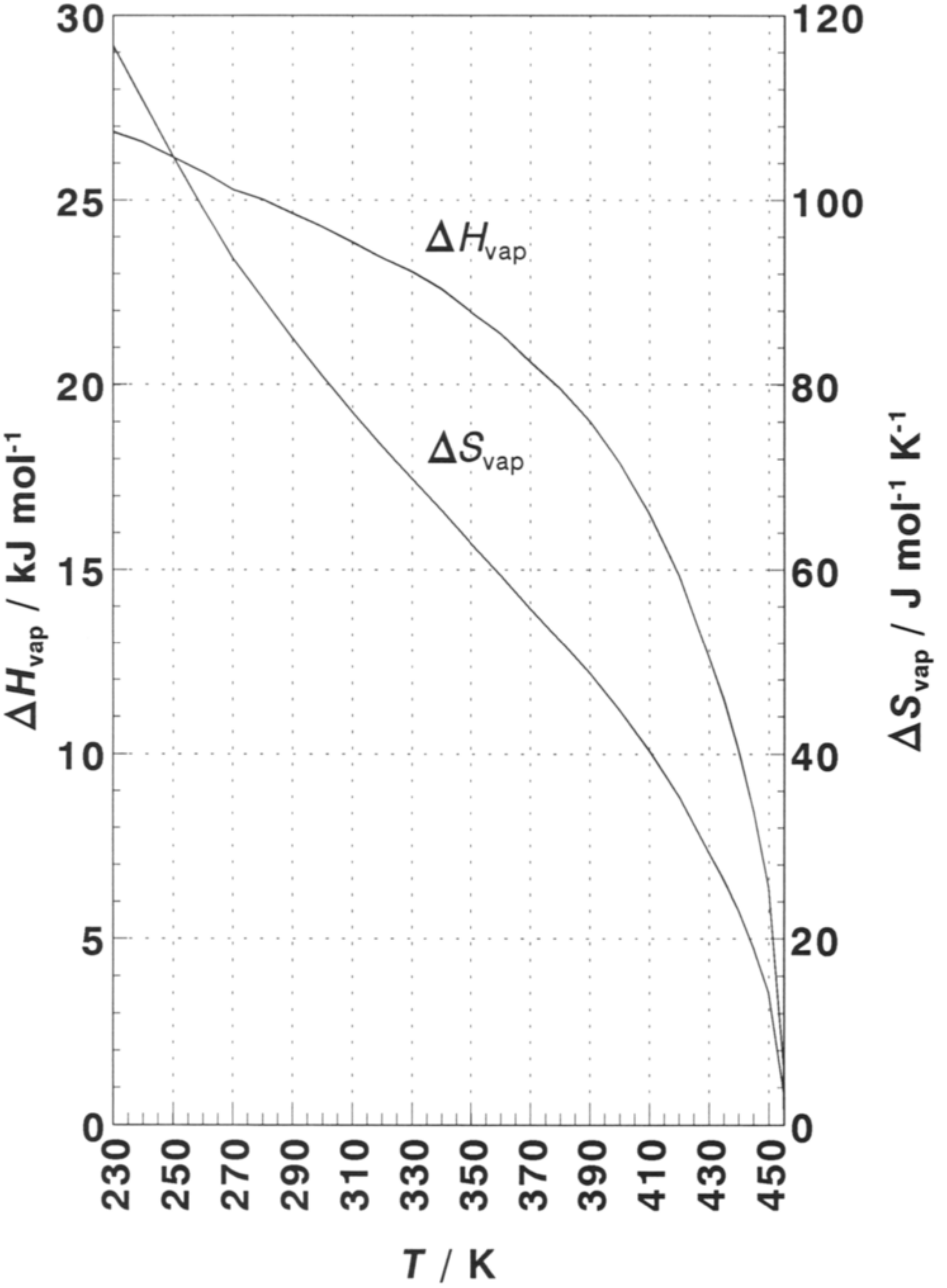


Fig. 6.2 Calculated enthalpies and entropies of vaporization of phosgene as a function of temperature [1843].

TABLE 6.4

THERMODYNAMIC FUNCTIONS OF LIQUID PHOSGENE [752]

T/K	C_p [a]	S° [a]	$-(G-H^\circ_0)/T$ [a]	$(H-H^\circ_0)/T$ [a]
139.19	105.889	121.834	41.187	80.647
140	105.725	122.457	41.664	80.793
142.09	105.366	124.018	42.865	81.185
145.37	104.834	126.415	44.723	81.693
150	104.190	129.696	47.296	82.400
160	102.801	136.373	52.656	83.718
170	101.700	142.570	57.764	84.805
180	100.956	148.365	62.639	85.726
190	100.299	153.808	67.295	86.513
200	99.621	158.933	71.751	87.182
210	99.454	163.787	76.019	87.768
220	99.466	168.414	80.115	88.303
230	99.525	172.837	84.048	88.789
240	99.897	177.084	87.839	89.245
250	100.228	181.167	91.492	89.676
260	100.441	185.100	95.014	90.086
270	100.462	188.895	98.424	90.471
280	100.663	192.548	101.721	90.826
280.71	100.675	192.803	101.952	90.851

[a] Units of J mol^{-1} K^{-1}

was obtained by crystallization from the liquid after supercooling rapidly to 140 K, followed by cooling at a rate of 1 K h^{-1}. This material is stable at the melting point for several days. When solids II or III were allowed to stand, they were eventually converted to solid I, the thermodynamically more stable phase.

The thermodynamic functions of solids I and II are recorded in Table 6.5 [752]. Those of solid III have not been determined, but it is considered that the heat capacity of solid III is similar to the values for solids I and II. The earlier values of C_p [751] for solid II are valid below 118.3 K, and are valid for solid I above 118.3 K.

The entropy of $COCl_2$(s) II at the melting point is greater than that calculated by integrating C_pd(ln$T$) from 0 K to T_m by about 0.84 J mol^{-1} K^{-1}. This discrepancy is attributed to Cl/O exchange disorder in the crystal.

TABLE 6.5

THERMODYNAMIC FUNCTIONS OF SOLID PHOSGENE [752]

T/K	C_p [a]		S° [a]		$-(G-H_0^\circ)/T$ [a]		$(H-H_0^\circ)/T$ [a]	
	I	II[b]	I	II[b]	I	II[b]	I	II[b]
15	8.242	7.004	3.176	2.510	0.833	0.653	2.343	1.858
20	14.531	14.418	6.406	5.602	1.803	1.481	4.602	4.121
25	20.564	20.267	10.297	9.473	3.105	2.686	7.192	6.786
30	25.978	25.351	14.535	13.623	4.657	4.159	9.878	9.464
35	30.518	30.012	18.891	17.891	6.376	5.816	12.514	12.075
40	34.280	33.589	23.217	22.142	8.213	7.590	15.004	14.552
45	37.367	36.476	27.443	26.267	10.117	9.435	17.326	16.832
50	39.894	39.099	31.514	30.246	12.054	11.318	19.560	18.928
55	42.020	41.463	35.418	34.083	14.000	13.213	21.418	20.870
60	43.928	43.455	39.158	37.778	15.941	15.104	23.217	22.677
70	47.304	47.083	46.191	44.760	19.769	18.845	26.422	25.916
80	50.120	50.183	52.697	51.258	23.481	22.493	29.217	28.765
90	52.446	53.116	58.735	57.338	27.070	26.029	31.665	31.309
100	54.097	56.099	64.392	63.086	30.512	29.447	33.869	33.639
110	57.467	58.969	69.743	68.572	33.844	32.757	35.900	35.815
120	59.973	61.630	74.852	73.814	37.049	35.957	37.802	37.857
130	62.484	64.220	79.751	78.852	40.150	39.275	39.602	39.576
139.19[c]	64.756	66.517	84.090	83.303	42.919	41.836	41.171	41.468
140	64.957	66.722	84.475	83.701	43.150	42.078	41.325	41.622
142.09[d]	65.471	67.237	85.437	84.697	43.765	42.689	41.673	42.007
145.37[e]	66.295	-	86.944	-	44.723	-	42.221	-

[a] Units of J mol^{-1} K^{-1}. [b] Values for solid II (theoretical) if thermodynamic equilibrium were obtained. [c] T_m for solid III. [d] T_m for solid II. [e] T_m for solid I.

The transition energies between the solid phases have been estimated [752]. For $COCl_2$(s) I $\longrightarrow$ $COCl_2$(s) III: ΔG = 238.9 J mol^{-1} at 139.19 K; ΔH = 761 J mol^{-1}; ΔS = 3.8 J mol^{-1} K^{-1}; the temperature of transition ($T_{\text{trans}} \approx \Delta H/\Delta S$) is estimated to be 202 K. Since this temperature is above the melting points of the solids, it is clear that solid III is metastable with respect to solid I at normal pressure. For $COCl_2(s)$ II $\longrightarrow$ $COCl_2$ III: ΔH = 741 J mol^{-1}; ΔS = 4.52 J mol^{-1} K^{-1}; T_{trans} (also indicating the absence of a transition) = 164 K. For $COCl_2(s)$ I $\rightarrow$ $COCl_2(s)$ II: ΔG = 128 J mol^{-1}; ΔH = 22.6 J mol^{-1}; ΔS = −0.75 J mol^{-1} K^{-1} [752].

6.1.4 Standard (i.e. at 25 °C) bond dissociation energies

From the difference between the enthalpy of the following reactions:

$$CO(g) + Cl_2(g) \rightarrow COCl_2(g); \qquad \Delta H = -110.4 \text{ kJ mol}^{-1}$$

$$CO(g) + Cl\cdot \rightarrow [COCl]\cdot; \qquad \Delta H = -26.4 \text{ kJ mol}^{-1}$$

the dissociation energy of the C–Cl bond in $COCl_2$ was calculated (using up-to-date enthalpy values) as 323.0 kJ mol^{-1} [308]. Using empirical considerations of the linear relationship between bond length and bond energy, $D(O\text{–}CCl_2)$ and $D(Cl\text{–}CClO)$ were estimated to be 795.0 and 333.9 kJ mol^{-1}, respectively [777]. From modern thermochemical data, the most recent calculations of $D(O\text{–}CCl_2)$ and $D(Cl\text{–}CClO)$ give 660.2 kJ mol^{-1} and 323.4 kJ mol^{-1}, respectively [2105c]. Early calculations of bond energies [580] were based on a similarity principle, assuming that O was bound in phosgene as in CO_2, and that Cl was bound as in CCl_4, no account being taken of delocalisation: this resulted in a gross over-estimation of the C–O bond strength and under-estimation of the C–Cl bond strength.

The energy of atomization for phosgene has been calculated (Hückel) to be 1444 kJ mol^{-1} [1441]; force constant calculations give a range of 1340–1370 kJ mol^{-1} [2034].

6.2 THERMAL PROPERTIES

6.2.1 Vapour pressure and boiling temperature

From the published literature [89,744,860,1514,1591] assembled by Stull [1971], the vapour pressure data of phosgene have been processed [1541] in the form of the Antoine equation, Equation (6.3):

$$\log_{10}(p) = A - \frac{B}{T + C} \tag{6.3}$$

where T is in °C and p is in Pa. The Antoine constants (A, B and C) are detailed in Table 6.6, for the appropriate temperature ranges [1541].

The calculated data are illustrated in Fig. 6.3(A) and 6.3(B) in the form of vapour pressure–temperature curves over the temperature ranges of −93 to 8.3 °C, and 8.3 to 174 °C, respectively. The experimental data according to Giaque and Jones for the more limited temperature range of −57.6 to 8.0 °C (and from which the second set of Antoine

TABLE 6.6

ANTOINE CONSTANTS FOR EQUATION (6.3) [1541]

Temperature range/°C	A	B/°C	C/°C
-92.9 to 8.3 [a]	8.94888	945.332	231.435
-57.6 to 8.0 [b]	9.05103	978.937	234.433
8.3 to 174.0 [a]	9.27105	1072.710	243.295

[a] Derived from the data given in [1971]. [b] Derived from the data given in [751]

constants in Table 6.6 are derived) are presented in Table 6.7, and included as data points in Fig. 6.3(A) [751].

Between *ca.* 100 Pa and standard atmospheric pressure, the vapour pressure of phosgene (based on the data of [1971]) can also be represented (T in K) by Equation (6.4) [2157]:

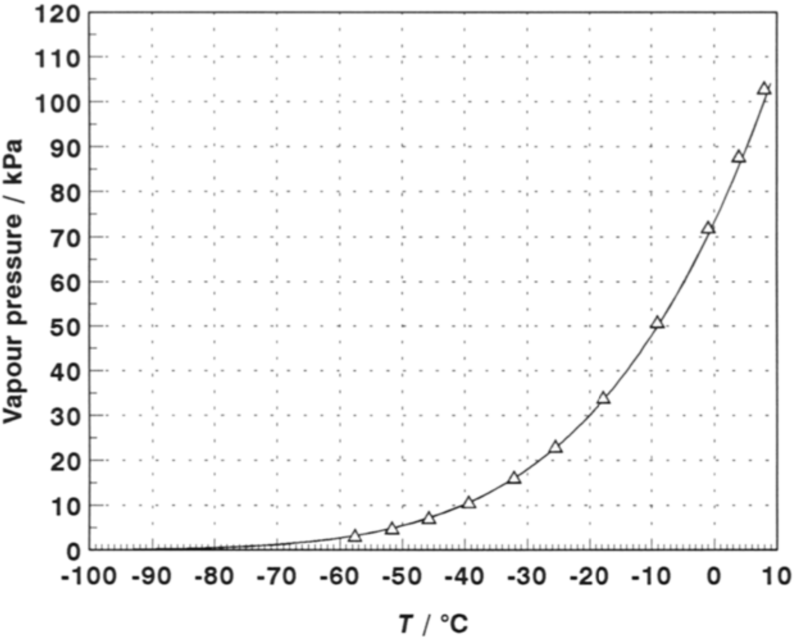
$$\log_{10}(p/\text{Pa}) = -82271\ T^{-1.92} + 3.48583\ \log_{10}(T) - 1.90168 \qquad (6.4)$$

Although this equation fits the data that it was designed to represent, it must be noted that this equation suggests the boiling temperature of 8.3 °C, which is now believed to be inaccurate.

TABLE 6.7

VAPOUR PRESSURE OF PHOSGENE (-57.6 to 8.0 °C) [751]

T/°C	p/kPa	T/°C	p/kPa
-57.62	3.300	-17.78	34.064
-51.65	4.980	-9.09	50.913
-45.78	7.289	-0.95	72.165
-39.36	10.766	3.95	88.002
-32.13	16.281	8.00	103.074
-25.53	23.182		



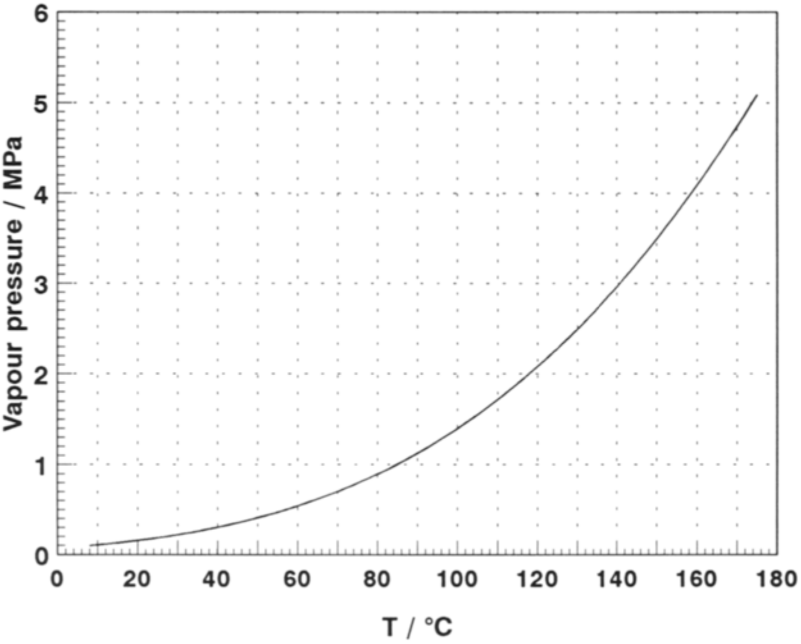


Fig. 6.3 Vapour pressure of phosgene as a function of temperature according to Equation (6.3) [1541]: (A) −93 to 8.3 °C and (B) 8.3 to 174 °C. Experimental data [751] are included in (A).

For the temperature interval 215 to 281 K, the data of Giaque and Jones [751] were represented by Equation (6.5):

$$\log_{10}(p/\mathrm{Pa}) = 10.8051 - 1690.3\,T^{-1} - 7.898 \times 10^{-3}\,T + 5.5847 \times 10^{-6}\,T^{2} \qquad (6.5)$$

Between 0 °C and the critical temperature, the vapour pressure data of phosgene have been summarized by Equation (6.6) (T in K) [744] and, for data above atmospheric pressure, by Equation (6.7) [1843]:

$$\log_{10}(p/\mathrm{Pa}) = 9.4716 - 1207.9\,T^{-1} - 13297\,T^{-2} \qquad (6.6)$$

$$\log_{10}(p/\mathrm{Pa}) = \mathrm{A} + \mathrm{B}T^{-1} + \mathrm{C}\log_{10}(T) + \mathrm{D}T \qquad (6.7)$$

where, A = 8.74064, B = −1290.87, C = 0.413555, D = -5.51349×10^{-4}.

In the most recent work [649], between −20 and +20 °C, the vapour pressure of phosgene has been represented simply by Equation (6.8), T in K.

$$\log_{10}(p/\mathrm{Pa}) = 9.6878 - 1316.0T^{-1} \qquad (6.8)$$

Vapour pressure constants have also been evaluated for a modified expression of the reduced Frost–Kalkwarf equation [1395], but this type of expression is useful only where limited experimental data are available. Unfortunately, a full statistical analysis of all these alternative expansions of $p(T)$ has not been performed.

The normal boiling temperature of phosgene has been determined from the vapour equation of Giaque and Jones [751] as 7.56 ± 0.005 °C. Earlier values, corrected to standard pressure, are 8.3 [151]; 7.69 [1591]; 8.4 [1514,89] and 7.64 °C [744]. The most recent work [649] gives a boiling temperature of 7.92 °C, corresponding very closely to the average of the earlier values.

6.2.2 Critical properties

The critical properties of phosgene have been reviewed elsewhere [1136,1347a,1613, 1614]. The temperature of disappearance of the meniscus was determined to be 181.8 °C; the temperature of reappearance, 181.6 °C [744]. Although the T_c value was rounded off to 182 °C, it is reasonable to assign the value 181.7 °C. The value of 183 °C reported by earlier researchers [860] is considered [1613,1614] to have been derived using a method of inferior accuracy on a sample whose purity was not established.

The observed critical pressure, p_c, of $COCl_2$ was determined to be 5.60 MPa, whereas by extrapolation of the $\log_{10}(p)$ *vs.* $1/T$ plot, the value of 5.63 MPa was estimated [744]. A value of 5.22 MPa had been calculated by earlier co-workers [1591], and the value of 6.01 MPa was calculated from molecular data [174a].

The critical density, derived from the relationship given in Equation (6.9), was found to be 0.52 g cm^{-3} [744], from which the critical molar volume, V_c, was calculated as 190.2 cm^3 mol^{-1}.

$$d_m = 0.715 - 1.07 \times 10^{-3}T \qquad (6.9)$$

The critical compressibility factor, Z_c, calculated from the relation $pV = nZ_cRT_c$, is 0.282. A parameter representing the number of associated molecules of a fluid at the critical composition, and derived from a generalized equation of state, has been described as the cohesive weight [288a]. Under such conditions the cohesive weight of phosgene is said to correspond to the stoicheiometry, $(COCl_2)_{54}$.

6.2.3 *Thermal conductivity*

The thermal conductivity, λ, of phosgene vapour has been calculated at standard pressure. At 15, 50 and 100 °C the thermal conductivities are 9.13×10^{-3}, 1.07×10^{-2}, and 1.29×10^{-2} W m^{-1} K^{-1}, respectively [1198]. Measurement of the thermal conductivity of phosgene vapour at 0 °C, using a calibrated hot wire apparatus, gave the value $(7.61 \pm 0.11) \times 10^{-3}$ W m^{-1} K^{-1} [ICI104], but is not consistent with the data given above when extrapolated to the lower temperature. Estimated values of λ have been extended from 0 to 500 °C corresponding to an increase from 8.0×10^{-3} to 4.6×10^{-2} W m^{-1} K^{-1} [715].

The thermal conductivity of liquid phosgene decreases with increase in temperature [715]. At −80 °C, λ was calculated to be 0.159 W m^{-1} K^{-1}; at 40 °C, the value was calculated as 0.128 W m^{-1} K^{-1}.

6.3 MECHANICAL PROPERTIES

6.3.1 *Density*

The density of phosgene vapour under standard reference conditions was measured to be 4.526 [742] or 4.525 kg m^{-3} [1281]. Using the value of the standard molar volume, $V_{m,0}$, the density of the gas at 0 °C and atmospheric pressure was calculated to be 4.413 kg m^{-3}. Phosgene vapour is thus, unexpectedly, far removed from ideality. An attempt has been made to generalize the Benedict-Wee-Rubin equation of state using three polar parameters as part of a study of a large series of polar substances, which includes $COCl_2$ as one of the examples [1518].

The specific volume ($\nu = 1/\rho$) of phosgene has been calculated over a range of temperatures (240–600 K) and pressures (5–15000 kPa) [1843], and compressibility factors have been tabulated at 15 and 50 °C for the pressure range extending from 20 to 400 kPa [1198].

The densities of the liquid, and of the saturated vapour in equilibrium with the liquid, are shown in Fig. 6.4 and Table 6.8 [739], and a relationship between them has been formulated [983].

TABLE 6.8

ORTHOBARIC DENSITIES OF PHOSGENE ABOVE STANDARD PRESSURE [739]

T/°C	ρ_l/g cm^{-3}	ρ_v/g cm^{-3}
7.95	1.409	0.005
10	1.405	0.005
20	1.381	0.007
30	1.357	0.009
40	1.332	0.012
50	1.306	0.016
60	1.280	0.020
70	1.252	0.024
80	1.224	0.030
90	1.195	0.037
100	1.165	0.046
110	1.134	0.057
120	1.100	0.072
130	1.062	0.090
140	1.017	0.112
150	0.966	0.142
160	0.903	0.182
170	0.826	0.239
180	0.685	0.359
182 (T_c)	0.520	

The density of liquid phosgene, re-determined as a function of temperature in the range −20 to 60 °C [462], is illustrated in Fig. 6.5. The measured values are represented in Equation (6.10), where ρ is in g cm^{-3} and T in °C. This gives a value of 1.402 g cm^{-3} at the normal boiling temperature.

$$\rho = 1.42014 - 2.3120 \times 10^{-3}T - 2.872 \times 10^{-6}T^2 \qquad (6.10)$$

By differentiation of Equation (6.10), the coefficient of volume expansion, τ, was calculated to be 1.563×10^{-3} (−10 °C), 1.696×10^{-3} (10 °C), 1.842×10^{-3} (30 °C), and 2.003×10^{-3} K^{-1} (50 °C) [462].

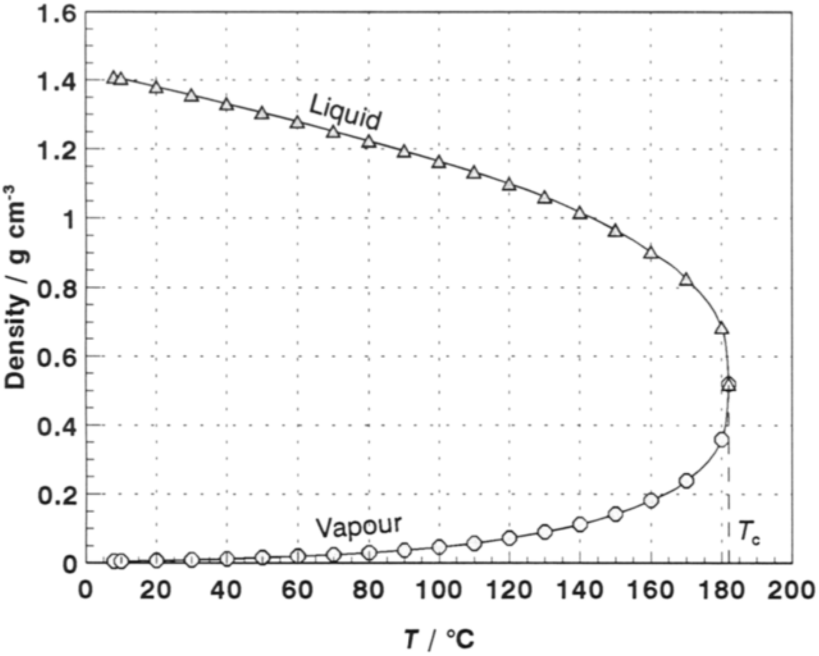


Fig. 6.4 Orthobaric densities of phosgene [739].

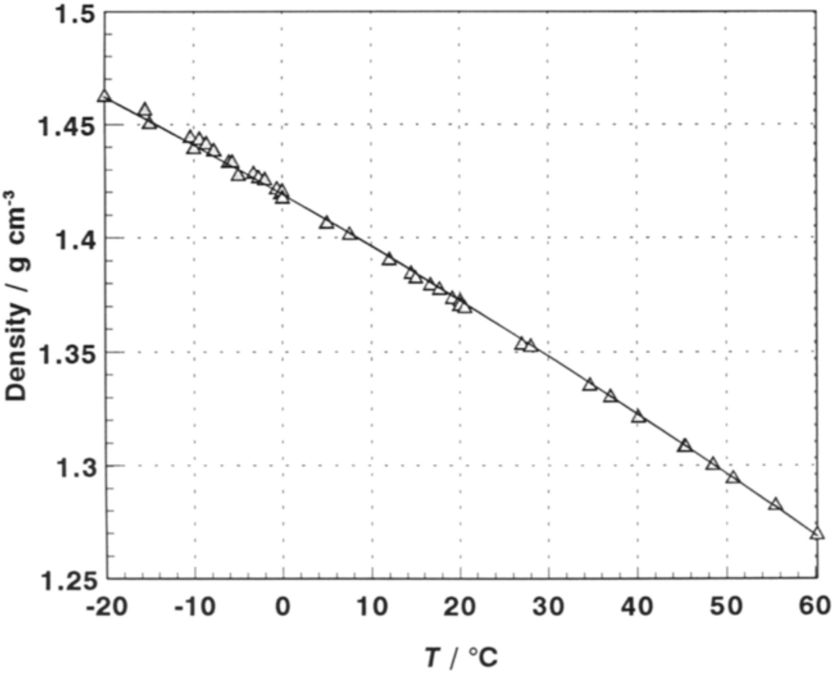


Fig. 6.5 Density of liquid phosgene, −20 to 60 °C [462].

Earlier measurements of densities [89,150,151,739,1591], compared by Davies [462], are believed to be too high, possibly as a result of contamination with higher boiling impurities. Calculations based on molecular data give the density of liquid phosgene (at the normal boiling temperature) as 1.46 g cm^{-3} [174a].

The densities of the saturated liquid and dense phase regions of phosgene have been considered for the temperature range 182–323 K [266]. The high deviation of the calculated density with respect to the experimental values is considered to be a result of the relatively high dipole moment of $COCl_2$.

Based on the most recent density measurements for liquid phosgene [462], the molar volume at 0 °C is calculated to be 69.65 cm^3 mol^{-1}. From the measurement of the density of solid phosgene at −194 °C, and estimation of the coefficient of volume expansion, the molar volume at 0 K was estimated as 50 cm^3 mol^{-1} [195]. The van der Waals volume of phosgene has been estimated (from group increment tables [231a]) as as 34.9 cm^3 mol^{-1}, and the van der Waals area as 5.20×10^9 cm^2 mol^{-1} [985].

6.3.2 *Diffusion coefficients*

The coefficient of diffusion, D, of phosgene into air at 0 °C was measured as 9.5×10^{-6} m^2 s^{-1}. The molecular radius estimated from this value is close to the value calculated from the molar volume of the liquid [1129].

The estimated values of D for $COCl_2$ into water are described in Section 6.6.2 [1315].

6.3.3 *Surface tension*

The surface tension of phosgene (at the liquid–gas interface) at 16.7, 34.5 and 46.1 °C has been measured as 19.51, 17.10 and 15.42 mN m^{-1}, respectively [1591]. These data have been extrapolated, linearly, to the range of −100° to 70 °C [715,1034a], yielding values of 37.15 and 12.2 mN m^{-1}, respectively. The value of 34.6 mN m^{-1} measured at 0 °C [952a] is not consistent with these data, and also appears to be too high on the basis of the prediction (*ca.* 23 mN m^{-1}) using the parachor (an empirical constant for a liquid that relates the surface tension to the molar volume) [1764]. The observed and calculated values of the parachor are given as 151.6 and 145.8 units [475], and the corresponding values of the thermochor are 141.5 and 145.8, respectively [475]. An attempt has been made to relate the parachor to the boiling temperature of $COCl_2$ [193].

A generalized three-parameter equation for surface tension, γ, valid from the triple point to the critical temperature, T_c (where $\gamma = 0$), has been proposed [1922a]:

$$\gamma = AX^{1.25} + BX^{2.25} + CX^{3.25}$$

where X is defined as $(T_c - T)/T_c$, and A, B and C are constants characteristic of a substance. For phosgene, for γ in mN m^{-1}, then A = 76.8219, B = −13.2836, and C = −2.5768 [1922a]. This theoretical line is shown in Fig. 6.6, along with the experimental and predicted data discussed above.

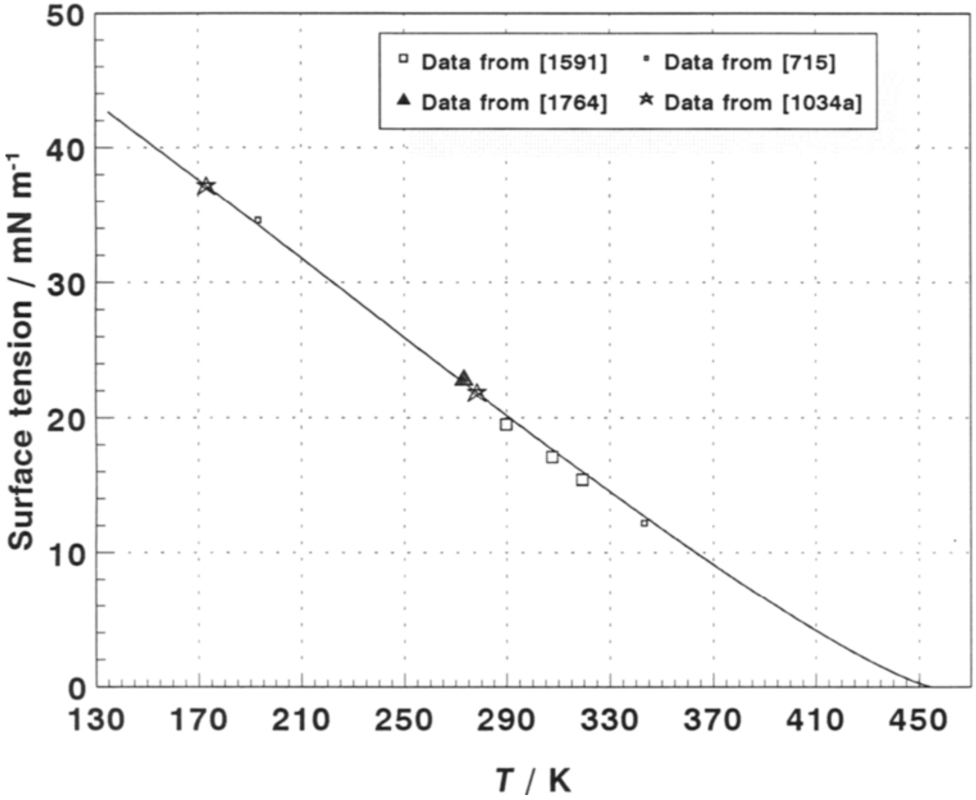


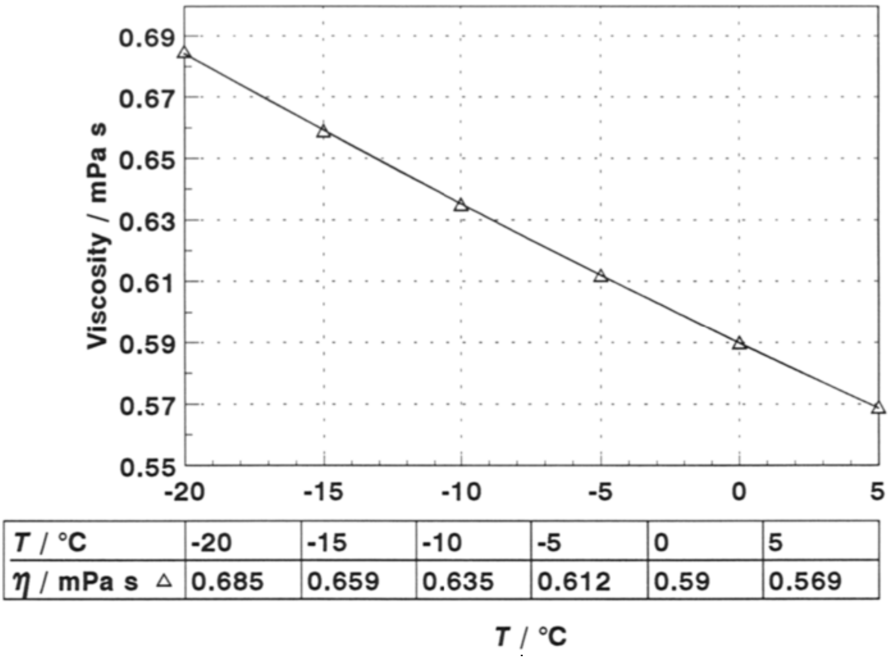
Fig. 6.6 **Theoretical (solid line) surface tension of phosgene [1922a], compared with experimental data or earlier predictions (points).**

6.3.4 Viscosity

No measurements have been recorded for the vapour viscosity of phosgene, but the calculated values in the range 0 to 500 °C have been represented by a linear relationship [715]. At 0 °C, the estimated value of η is 1.095 x 10^{-5} Pa s; at 500 °C, η is estimated as 2.890 x 10^{-5} Pa s. The interpolated values from these data are consistent with other calculations of the viscosity of $COCl_2$ vapour made at standard pressure [1198]; η = 1.44 x 10^{-5} (15 °C), 1.283 x 10^{-5} (50 °C) and 1.478 x 10^{-5} (100 °C) Pa s, respectively.

Liquid viscosities have been measured in the range −20 to 5 °C, and are illustrated in Fig 6.7 [1284]. Calculated values for liquid phosgene have been presented for the temperature range −50 to 40 °C [715], and appear to be about 10% lower than the observed values.

The kinematic viscosity of liquid phosgene at 0 °C was measured to be 2.721 x 10^{-7} m^2 s^{-1}; the value at −5 °C was 2.818 x 10^{-7} m^2 s^{-1} [2243a].



T / °C	-20	-15	-10	-5	0	5
η / mPa s △	0.685	0.659	0.635	0.612	0.59	0.569

Fig. 6.7 Viscosity of liquid phosgene [1284].

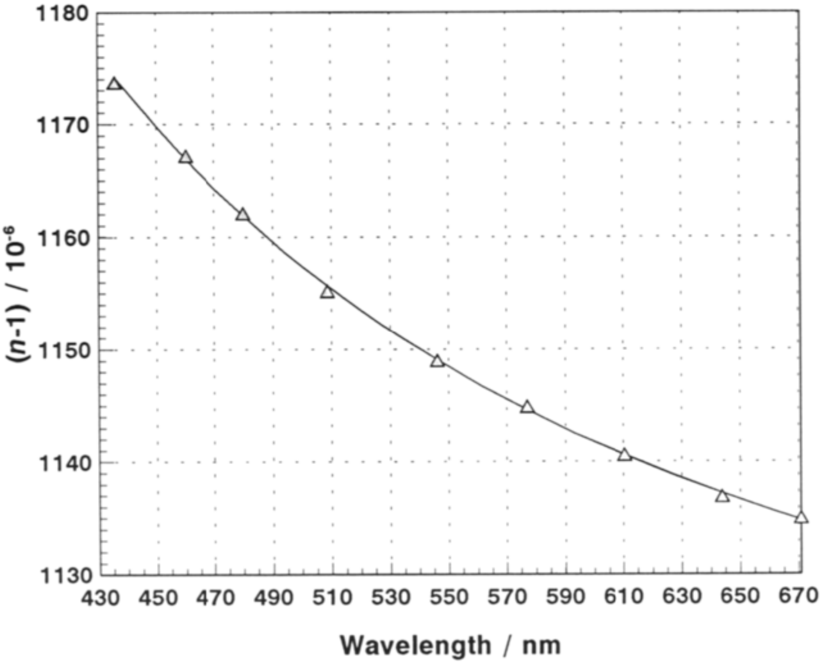


Fig. 6.8 The refractivity of phosgene vapour [1281]: the points represent experimental data, the line represents the theoretical fit (see text).

6.4 OPTICAL PROPERTIES

Values of the observed and calculated refractivity of phosgene vapour at various wavelengths are given in Table 6.9 and illustrated in Fig. 6.8 [1281]. The theoretical values were calculated according to:

$$(n-1) = \frac{9.2574 \times 10^{27}}{(8358 \times 10^{27} - \nu^2)}$$

For white light, the refractivity of the gas, relative to that of air, was recorded by Dulong [565b] to be 3.936, corresponding to a refractive index of 1.001153 at standard reference conditions of 0 °C and atmospheric pressure [565a].

TABLE 6.9

REFRACTIVITY OF PHOSGENE VAPOUR AT VARIOUS WAVELENGTHS [1281]

λ / nm	$(n-1)_{obs}$ / 10^{-6}	$(n-1)_{calc}$ / 10^{-6} a
670.8	1135.0	1134.8
643.8	1136.9	1137.2
610.4	1140.6	1140.6
577.0	1144.9	1144.6
546.1	1149.0	1149.1
508.6	1155.2	1155.7
480.0	1162.1	1161.9
460.2	1167.2	1166.9
435.8	1173.7	1174.2

[a] Calculated from the expression given in the text.

6.5 ELECTRICAL AND MAGNETIC PROPERTIES

6.5.1 Dielectric constant and electric dipole moment

The value of the dielectric constant, ϵ, for phosgene vapour at 15 °C and 101.325 kPa, was measured as 1.0067 [420a]. From dielectric measurements on the vapour, the dipole moment, μ, of phosgene was found to be (3.933 ± 0.050) x 10^{-30} C m (1.179 D) [461]; earlier measurements of ϵ in the vapour phase gave a value for the dipole moment (re-evaluated with modern constants) of (3.97 ± 0.03) x 10^{-30} C m (1.19 D) [1911]. Quantitative Stark effect measurements on $CO^{35}Cl_2$, confined to the rotational $0_{00} \rightarrow 1_{11}$

transition, yielded μ = (3.90 ± 0.03) x 10^{-30} C m (1.17 D) [986], but the calculated values of μ = 1.37 x 10^{-30} (0.41 D) and μ = 1.53 x 10^{-30} C m (0.46 D) obtained by CNDO [292] and MNDO [514] methods are grossly under–estimated; an earlier estimate was much more accurate, at 3.93 x 10^{-30} C m (1.18 D) [168a].

Dipole moment derivatives have been determined both experimentally [981] and theoretically [290,292,1655,1657,2098], although the agreement between these values is poor. These observations are relevant to infrared band intensities (see Section 7.2).

The dielectric constant of liquid phosgene, expressed as a function of absolute temperature, is given by Equation (6.11) in the range of +20 to −132 °C, and is illustrated in Fig. 6.9 [461].

$$\epsilon_0 = -1.013 + 1678.2T^{-1} \qquad (6.11)$$

The value of ϵ at 20 °C, from Equation (6.11), is therefore 4.712. However, the value of ϵ rises considerably with decrease in temperature, reaching *ca.* 10.7 at −130 °C. Previous measurements [1798] of the dielectric constant, made at 0 and 22 °C, are believed to be too low by 8 and 7% respectively [461].

The values of the dipole moment measured for the liquid material are (3.919 ± 0.047) x 10^{-30} C m (1.175 D) at 0 °C; (3.89 ± 0.13) x 10^{-30} C m (1.165 D) at

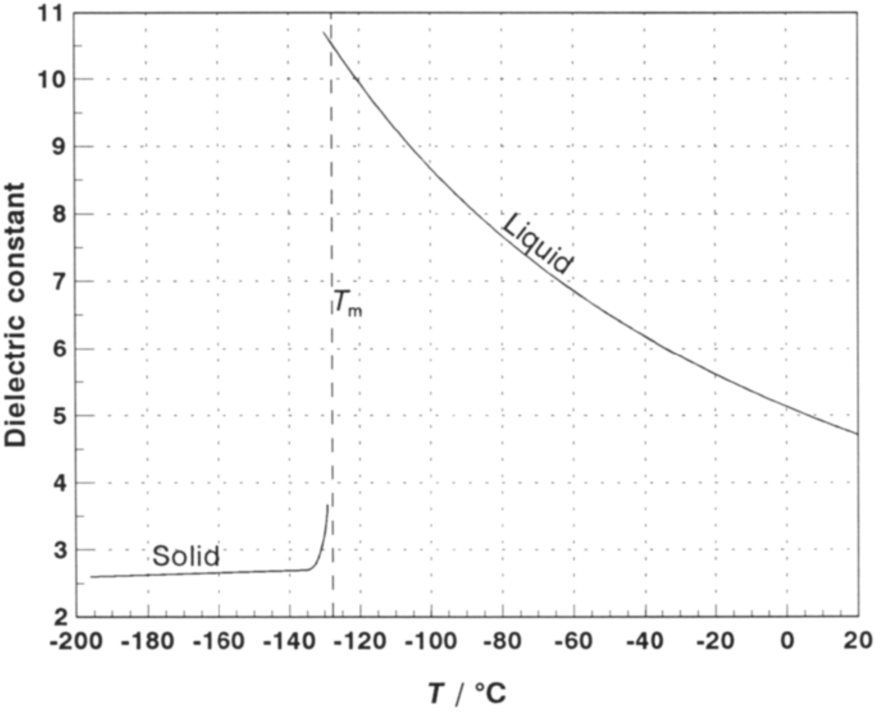


Fig. 6.9 Dielectric constant of solid (10 kHz) and liquid $COCl_2$ [461].

−100 °C [461]. These values are unexceptional considering the structure of the molecule (see Section 7.1), although the values are higher than for the sulfur analogue, $CSCl_2$, or the difluoro-analogue, COF_2 (see Chapter 13). Measurements of the dipole moment made in dilute solution, in non-polar solvents, are generally smaller than those made on the pure liquid: in benzene at 25 °C, $\mu = 3.77 \times 10^{-30}$ C m (1.13 D) [53]; in tetrachloromethane at 0 °C, $\mu = 3.70 \times 10^{-30}$ C m (1.11 D) [53,1218].

At temperatures below the freezing point of phosgene, the value of the dielectric constant was measured as 2.7 ± 0.1, falling by about 0.1 at −196 °C (see Fig. 6.9) [461]. No consistent differences were noted in the dielectric behaviour of samples frozen slowly or rapidly, corresponding to the formation of solids II and III (see Section 6.1.3), respectively.

6.5.2 *Electrical conductivity*

Liquid phosgene is a poor electrical conductor. The specific conductivity of re-distilled technical material (of unspecified purity) was measured as 7×10^{-7} S m^{-1} at 25 °C [736].

6.5.3 *Diamagnetic susceptibility*

The mass diamagnetic susceptibility, represented by χ_m, of phosgene (at 13 °C in a toluene solution) was measured as -0.485×10^{-6} cm^3 g^{-1} (-6.095×10^{-9} m^3 kg^{-1}) [1104]: this corresponds to a molar diamagnetic susceptibility, represented by χ_M, of -48.0×10^{-6} cm^3 mol^{-1} (-6.03×10^{-10} m^3 mol^{-1}). From computation of the mean molecular polarizability (65.72×10^{-25} cm^3), the mass diamagnetic susceptibility, χ_m, was estimated as -0.435×10^{-6} cm^3 g^{-1} (-5.47×10^{-9} m^3 kg^{-1}), the molar diamagnetic susceptibility, χ_M, being -43.1×10^{-6} cm^3 mol^{-1} (-5.41×10^{-10} m^3 mol^{-1}) [374]. The mean molecular polarizability has been measured as 67.8×10^{-25} cm^3 [1281] or 65.78×10^{-25} cm^3 [1258]: calculated values include 59.52×10^{-25} cm^3 [1258] and 67.5×10^{-25} cm^3.

6.6 SOLUBILITY AND VAPOUR-LIQUID EQUILIBRIA

A knowledge of the solubilities of phosgene in liquids is important, not only from the point of view of recognizing suitable media in which to perform reactions, but also to enable the correct choice of solvent for the purposes of extraction.

Owing to its poisonous nature, and for economic reasons, it is desirable to be able to remove phosgene from air. Scrubbing the phosgene-air mixture with liquid absorbent is a useful technique, and quantitative data are required in order to design suitable absorption equipment.

The low solubility of phosgene in water renders this solvent as unsuitable, and organic liquids are usually employed in extractive processes. A common way to treat effluents contaminated with phosgene is to absorb the gas into a suitable solvent (commonly one that is used as the medium for the main reaction); it is then possible to regenerate the phosgene

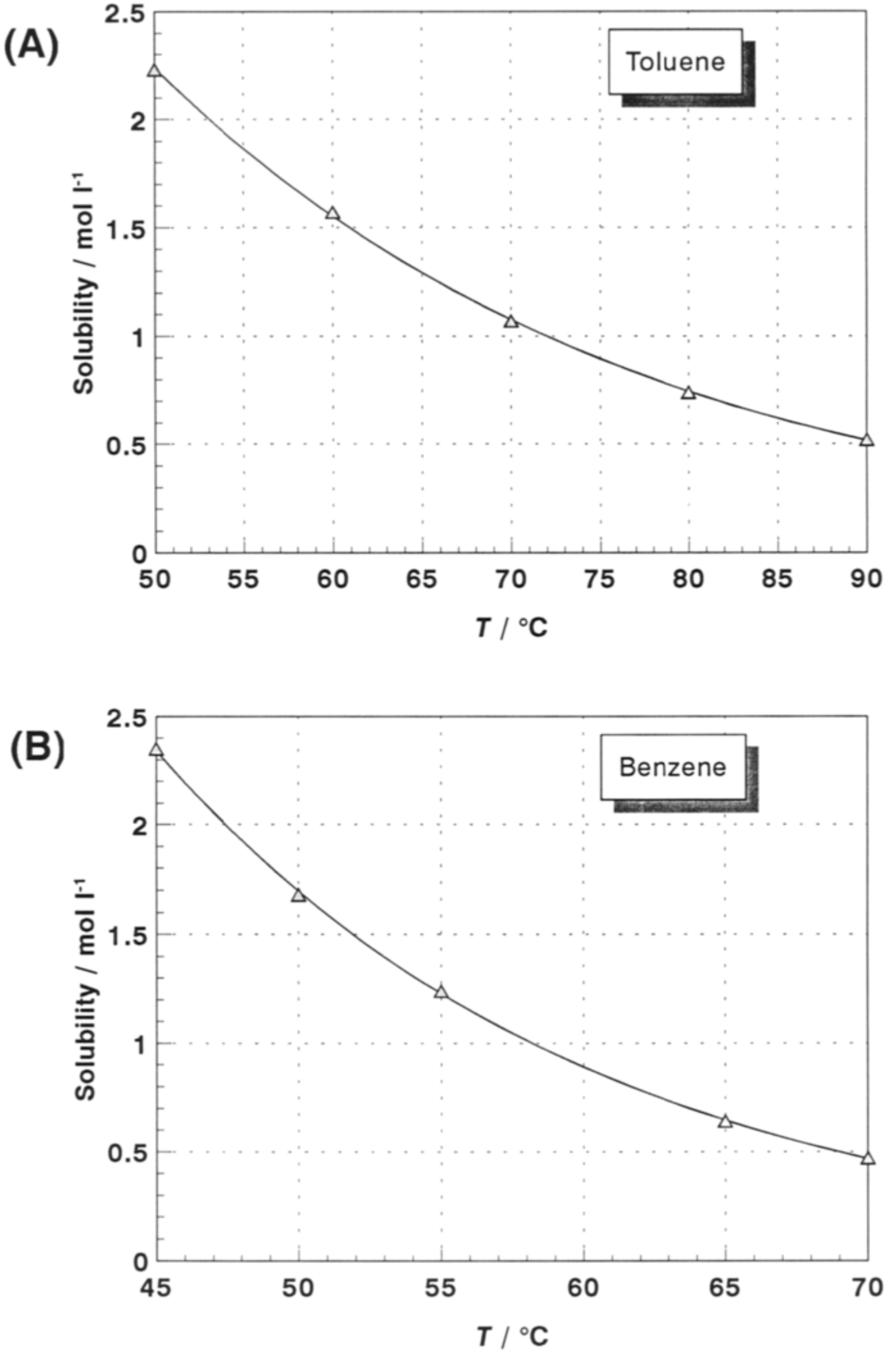
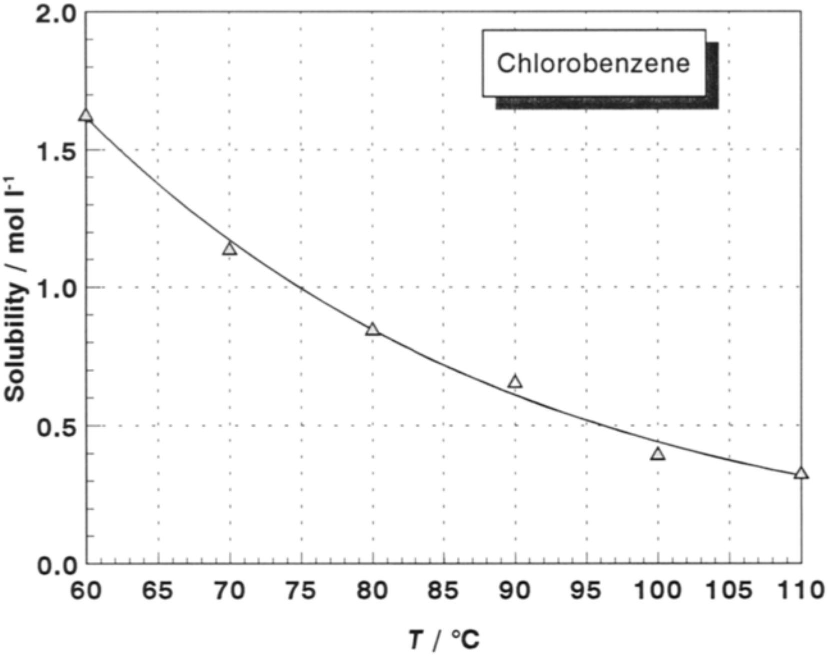


Fig. 6.10 Typical solubility of phosgene in some common aromatic solvents [2060]: (A) toluene, (B) benzene, (C) chlorobenzene (facing page), and (D) 1,2-dichlorobenzene (facing page).


Chlorobenzene
Solubility / mol l⁻¹
2.0
1.5
1.0
0.5
0.0
60
65
70
75
80
85
90
95
100
105
110
T / °C

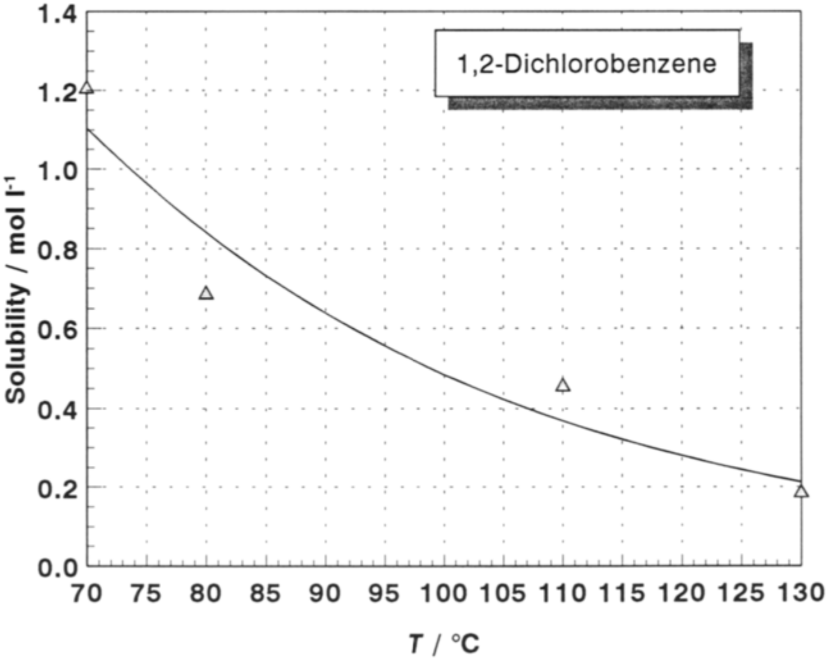

1,2-Dichlorobenzene
Solubility / mol l⁻¹
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
70
75
80
85
90
95
100
105
110
115
120
125
130
T / °C

TABLE 6.10

SOLUBILITY OF PHOSGENE IN ORGANIC LIQUIDS

Solvent	Temp/°C	Solubility[a]	Ref
Toluene	50	25.4	2060
	60	17.9	
	70	12.2	
	80	8.4	
	90	5.9	
Benzene	45	26.6	2060
	50	19.0	
	55	14.0	
	65	7.2	
	70	5.3	
Chlorobenzene	60	14.6	2060
	70	10.2	
	80	7.6	
	90	5.9	
	100	3.6	
	110	2.95	
1,2-Dichlorobenzene	70	9.2	2060
	80	5.2	
	110	3.5	
	130	1.4	
Nitrobenzene	16.8	106.4	89
1-Chloronaphthalene	17.0	104.5	89
Petroleum[b]	12.3	263.8	89
	15.8	163.1	
	16.7	143.4	
	22.4	79.5	
	23.7	71.2	
	29.9	49.2	
	30.0	48.6	

TABLE 6.10 (cont.)

Solvent	Temp/°C	Solubility[a]	Ref
Butyl ethanoate	23.9	82.2	ICI105
	44.0	39.1	
	72.3	14.5	
	91.7	7.5	
	104.6	4.3	
	121.0	1.7	
Xylenes[c]	12.3	457.3	89
	16.4	225.6	
	16.9	217.9	
	23.8	103.4	
	29.8	71.24	
Tetrachloromethane	40	14.6	2060
	50	8.9	
	60	5.2	
	70	3.3	
Tetrachloroethane	16.8	149.7	89
	25.1	89.4	
	29.9	74.9	
Lubricating oil[d]	15.6	79.7	89
	23.5	30.3	
	31.0	24.5	
2-Bromoethanoic acid	60.0 ± 0.5	1.16	1668
Creosote oil[e]	16.2	77.42	89

[a] Solubility given in grams of phosgene per 100 g solvent at ambient pressure. [b] Boiling range 180–280 °C. [c] Coal-tar fraction. [d] Residue of crude petroleum oil; unspecified composition. [e] Unspecified composition, but probably a high boiling fraction of coal tar.

from the solution, and to return it to the principal reaction stage.

The industrial reaction of phosgene with primary amines produces large quantities of by-product hydrogen chloride (see Section 4.7.1) that is contaminated with phosgene. Although most of the $COCl_2$ is removable by cooling, it may be desirable to purify the HCl further to be used in other processes, for example oxychlorination. The production of mono- and di-isocyanates is generally carried out in chlorobenzene, or other chlorinated aromatic material such as 1,2,4-trichlorobenzene, and the separation of phosgene from the solvent, and from the by-product HCl, requires the appropriate data comprising the vapour-liquid equilibria diagrams. This constitutes the basic information for the operation and design of the distillation unit. As far as possible these data are included in the following Sections.

6.6.1 Organic solvents

6.6.1.1 Solubility

The solubilities of phosgene in toluene, benzene, chlorobenzene and 1,2-dichlorobenzene are illustrated in Figs. 6.10(A)-6.10(D), and listed in Table 6.10, as a function of temperature [89,2060,ICI105]. Solutions of phosgene in toluene are available commercially, for example, *ca.* 12.5% (*ex.* Merck, Ltd. in the United Kingdom) and *ca.* 20% (*ex.* Fluka, Switzerland): benzene, chlorobenzene and 1,2-dichlorobenzene are solvents which have been frequently used in the reactions of amines with phosgene. In addition to the data included in Fig. 6.10, the solubility of $COCl_2$ in chlorobenzene was extended to cover the pressure range of 13.3, 26.7 and 53.3 kPa [ICI105] and the partial pressures of phosgene over solutions in 1,2-dichlorobenzene were determined between -10 and 20 °C [ICI106].

The commonly quoted [1378,ICI107,ICI108] values given by Baskerville and Cohen [132] for the solubility of phosgene in toluene, benzene, and tetrachloromethane at room temperature are inconsistent with the data from other sources, both contemporary [89] and modern [2060]. In view of the large discrepancy in these data, the values given for the solubility of $COCl_2$ in the wide range of solvents reported in this paper [132] should be regarded as totally unreliable, and are not quoted here.

$COCl_2$ is considered generally to be soluble in diethyl ether, liquid hydrocarbons, glacial ethanoic acid, ethyl ethanoate and chlorocosane (chlorinated paraffin) [132]; boiling point elevations, determined in liquid phosgene, for ethanoic anhydride and 1,2-dibromobenzene [151] also imply the solubility of phosgene in these solvents. Solubilities of phosgene in other organic solvents at normal atmospheric pressure are presented in Table 6.10.

6.6.1.2 Enthalpies of solution

From thermodynamics, it is known that the mean differential enthalpy of solution, ΔH_{soln}, and the solubilities of a gas, α_g (in mol l^{-1}), as a function of absolute temperature are related by Equation (6.12) [765aa]:

$$\frac{d\{\ln(\alpha_g)\}}{d(1/T)} = \frac{-\Delta H_{\mathrm{soln}}}{R} \qquad (6.12)$$

TABLE 6.11

DIFFERENTIAL ENTHALPIES OF SOLUTION FOR PHOSGENE IN VARIOUS ORGANIC SOLVENTS AT STANDARD PRESSURE

Solvent	$T/^\circ C$	ΔH_{soln} [a]	Ref [b]
Toluene	17–31.5	−32.5 ± 1.1	89
	50–90	−35.7 ± 0.7	2060
Benzene	45–70	−58.5 ± 0.7	2060
Chlorobenzene	12–30	−28.5 ± 2.2	89
	60–110	−34.5 ± 1.8	2060
	25–75	−27.6 ± 0.5	ICI105
1,2–Dichlorobenzene	70–130	−31.4 ± 5.9	2060
	25–75	−25.2 ± 1.0	ICI105
Tetrachloromethane	40–70	−44.8 ± 0.9	2060
Xylenes[c]	12–30	−36.5 ± 1.2	89
1,1,2,2–Tetrachloroethane	17–30	−17.7 ± 1.3	89

[a] Data fitted by linear regression; the values quoted here differ from those in the literature. ΔH_{soln} was calculated from Equation (6.12) in units of kJ (mol $COCl_2$)$^{-1}$. [b] Data on which calculations of ΔH_{soln} are based. [c] Isomeric mixture.

Values of ΔH_{soln} for phosgene in various solvents are recorded in Table 6.11, calculated from Equation (6.12). The mean enthalpy of solution of $COCl_2$ in chlorobenzene has been measured calorimetrically as −24.9 ± 1.1 kJ (mol $COCl_2$)$^{-1}$ at 25 °C [2216]. This integral enthalpy (which approximates to the differential enthalpy, as the experimental value of ΔH does not change with concentration) is close to the enthalpy of vaporization of phosgene (see Section 6.1.2.).

The integral enthalpies of solution, ΔH_{soln}, of phosgene have been determined as a function of $COCl_2$ concentration at 40 °C using a calorimetric method [391]. In benzene, toluene, 1,3–xylene or chlorobenzene, ΔH_{soln} rises sharply to a maximum value of *ca.* 25 kJ mol^{-1} for a solvent:phosgene ratio, *n*, of about 6:1. ΔH_{soln} increases with the number of chlorine atoms in the series C_6H_5Cl < 1,2–$Cl_2C_6H_4$ < 1,2,4–$Cl_3C_6H_3$, the value of *n* also being displaced towards higher values and reaching about 12.5 for 1,2,4–$Cl_3C_6H_3$ (corresponding to a value for ΔH of about 32 kJ mol^{-1}). These results have been taken as indicating the formation of addition compounds between the phosgene and solvent [391]. However, the findings contrast with other calorimetric measurements of phosgene in chlorobenzene in which the individual ΔH_{soln} values remain essentially constant over the solvent:phosgene range of about 2 to 14:1 [2216].

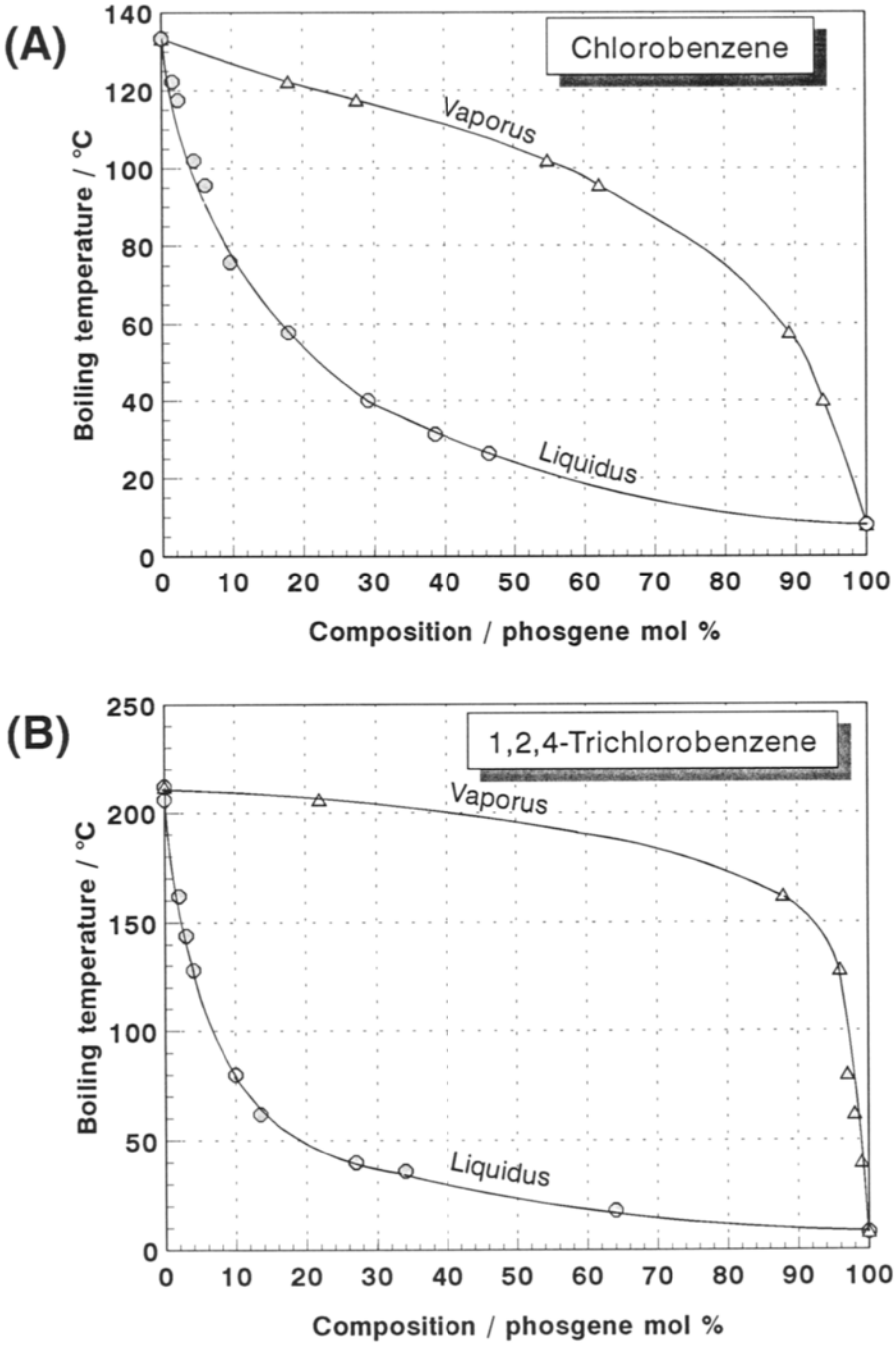
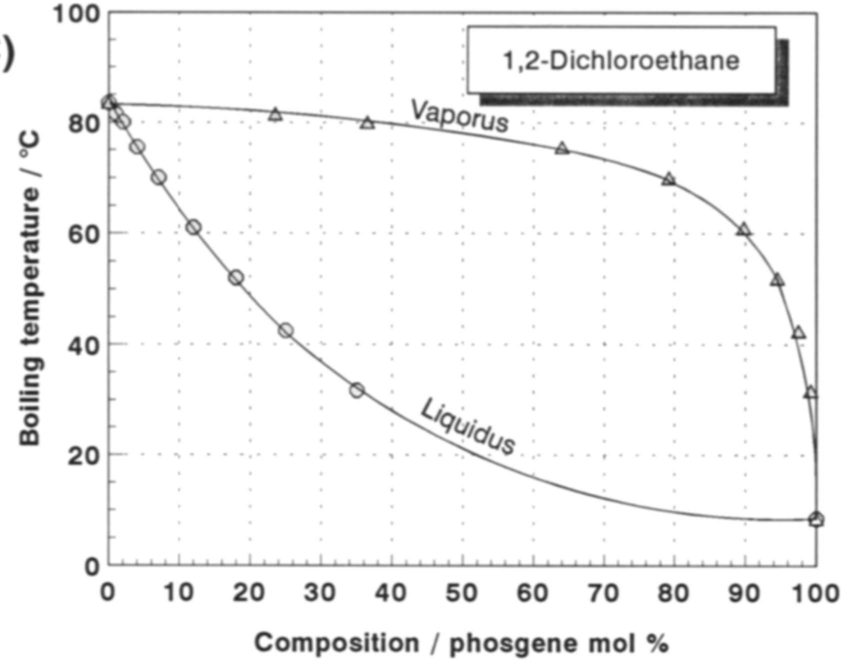
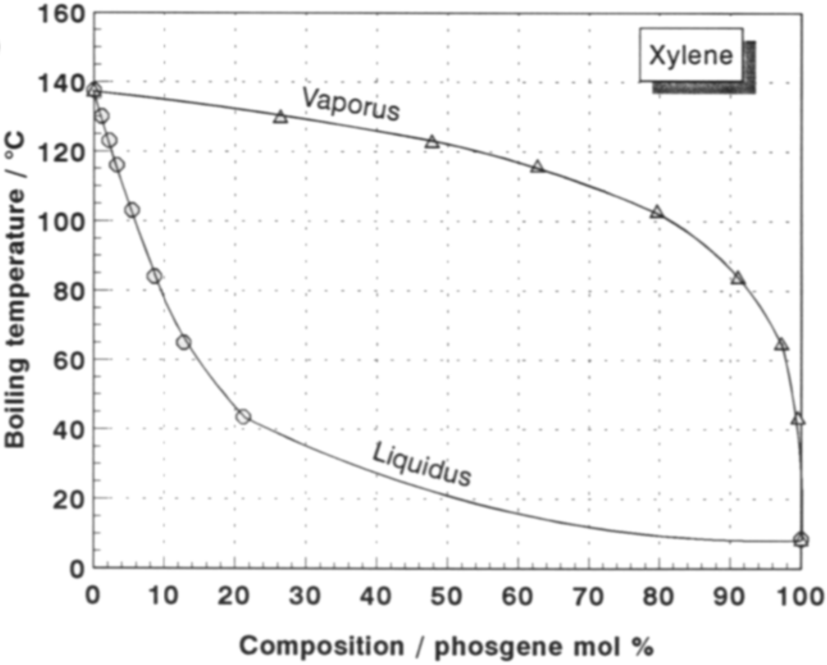


Fig. 6.11 Boiling temperature–composition diagrams for phosgene in (A) chlorobenzene [788], (B) 1,2,4-trichlorobenzene [788], (C) 1,2-dichloroethane (facing page) [1111], and (D) xylene (facing page) [1111].

(C)


1,2-Dichloroethane
Vaporus
Liquidus
Boiling temperature / °C
0
20
40
60
80
100
0
10
20
30
40
50
60
70
80
90
100
Composition / phosgene mol %

(D)


Xylene
Vaporus
Liquidus
Boiling temperature / °C
0
20
40
60
80
100
120
140
160
0
10
20
30
40
50
60
70
80
90
100
Composition / phosgene mol %

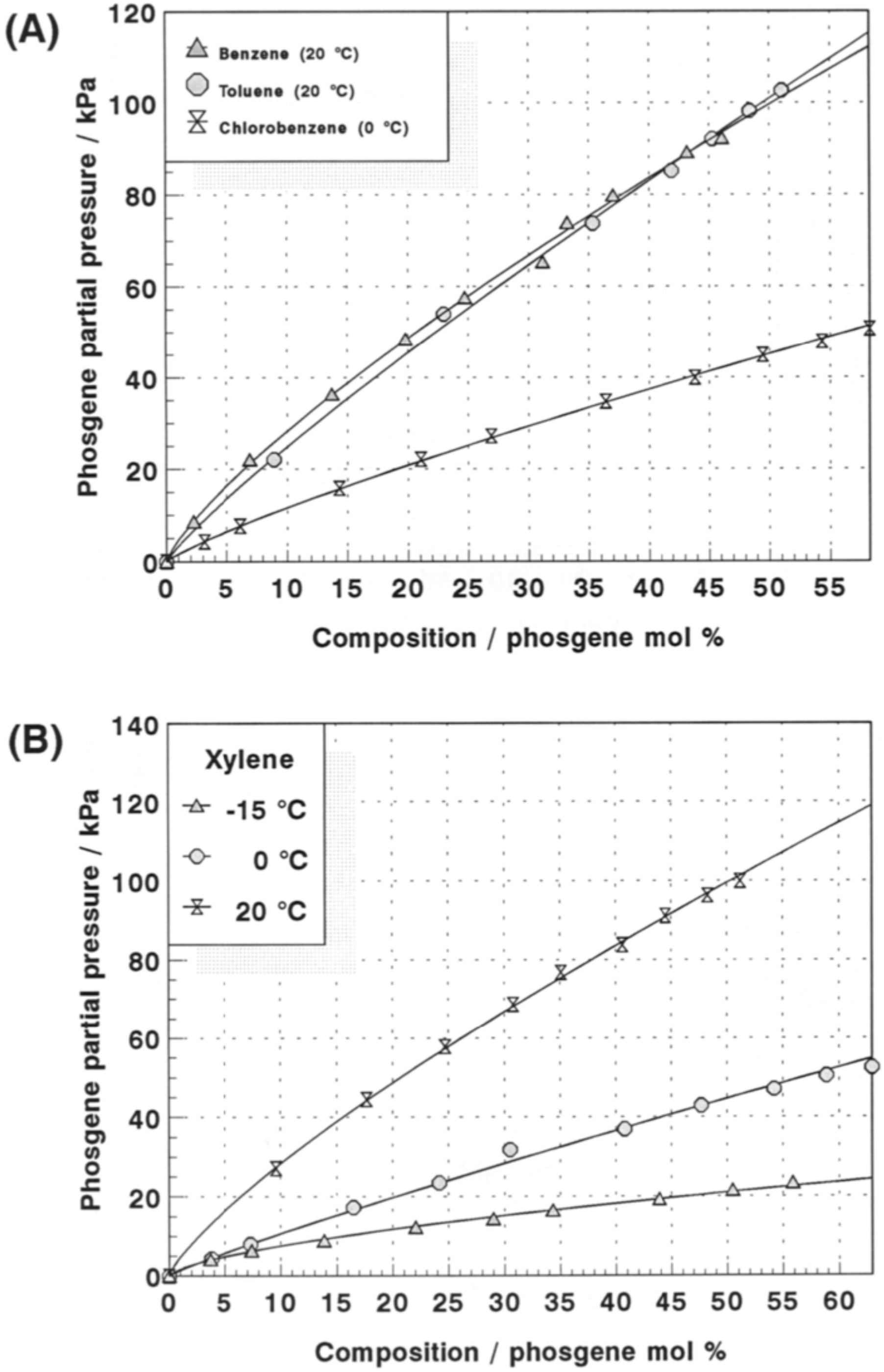
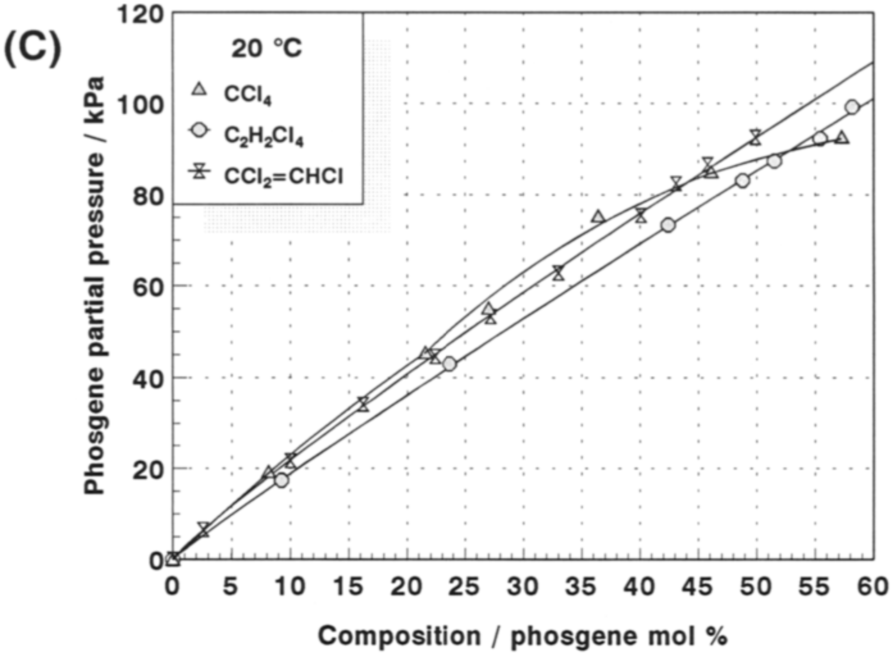
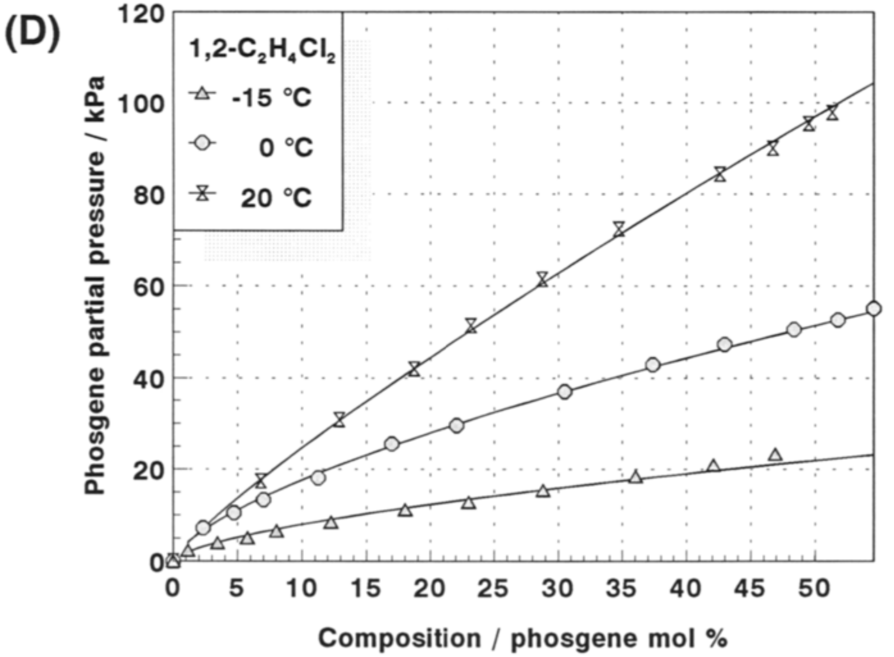


Fig. 6.12 Vapour pressure–composition isotherms for phosgene in organic solvents [1110]: (A) aromatic solvents, (B) xylene, (C) chloroaliphatic solvents (facing page), and (D) 1,2–dichloroethane (facing page).


(C)
20 °C
CCl4
C2H2Cl4
CCl2=CHCl
Phosgene partial pressure / kPa
0
20
40
60
80
100
120
0
5
10
15
20
25
30
35
40
45
50
55
60
Composition / phosgene mol %


(D)
1,2-C2H4Cl2
-15 °C
0 °C
20 °C
Phosgene partial pressure / kPa
0
20
40
60
80
100
120
0
5
10
15
20
25
30
35
40
45
50
Composition / phosgene mol %

6.6.1.3 Vapour-liquid equilibria

6.6.1.3.1 Boiling temperature–composition relationships

Boiling temperature–composition curves for solutions of phosgene in chlorobenzene and 1,2,4-trichlorobenzene [788], and 1,2-dichloroethane and xylene (mixed isomers) [1111] are illustrated in Fig. 6.11(A)–6.11(D) for atmospheric pressure.

6.6.1.3.2 Vapour pressure–composition relationships

The solubility isotherms of phosgene $\{p(COCl_2) < 101.3\ \text{kPa}\}$ have been determined in a variety of solvents at −15.0, 0, or 20 °C, and are illustrated in Fig. 6.12(A)–6.12(D) [1110].

The data [1110] for the phosgene–toluene system at 20 °C have been processed [965] to give a plot of the vapour composition of phosgene, as a function of the liquid composition. The values are listed in Table 6.12. The Wilson parameters and Antoine constants have also been determined for this system [965].

TABLE 6.12

LIQUID–VAPOUR COMPOSITIONS FOR THE PHOSGENE–TOLUENE SYSTEM AT 20 °C [965,1110]

X_{COCl_2} (liquid) [a]	X_{COCl_2} (vapour) [b]
0.0891	0.8966
0.2298	0.9615
0.3532	0.9760
0.4191	0.9812
0.4530	0.9836
0.4838	0.9855
0.5104	0.9868

[a] Liquid composition in mol fraction of phosgene.
[b] Vapour composition in mol fraction of phosgene.

6.6.2 Aqueous solvents

The water–phosgene system is a particularly difficult one to study, since water is a potentially reactive solvent and true equilibrium may not be established between the gas and liquid phases. The hydrolysis reaction of phosgene has been the subject of many conflicting statements and is dealt with in Section 9.10.3.1.

TABLE 6.13

SOLUBILITY OF $COCl_2$ IN WATER [1315]

$T/^\circ C$	Solubility[a]	$D/10^{-10} m^2 s^{-1}$ [b]	k_1/s^{-1}
15	1.079 (0.109)	9.6	3 [c]
25	0.685 (0.069)	12.7	6 [c]
35	0.458 (0.046)	16.1	22
45.5	0.270 (0.027)	20.4	75

[a] Solubility given in g of $COCl_2$ per 100 g of H_2O; values in parentheses are in mol litre^{-1}. [b] Estimated values. [c] Obtained by extrapolation of the values from the two higher temperatures.

For design purposes, the rates of absorption of gaseous phosgene into water have been determined as a function of temperature [1315] and of fluid rates [ICI107] at atmospheric pressure. The dissolution of phosgene into water is represented by Equation (6.13) [1315]:

$$D \frac{d^2[COCl_2]}{dx^2} = \frac{d[COCl_2]}{dt} + k_1[COCl_2] \qquad (6.13)$$

where $[COCl_2]$ is the concentration of dissolved, but unreacted, phosgene and D represents the diffusivity of $COCl_2$ into water. The final term of this equation represents the effect of a *pseudo*-first-order reaction:

$$COCl_2 + H_2O \longrightarrow CO_2 + 2H^+(aq) + 2Cl^-(aq)$$

in which the water is in a large excess. At 15 and 25 °C, the rate-determining factor is the diffusion of phosgene into water; the hydrolysis reaction rate is negligible. At 35 and 45.5 °C, the rate of absorption may be dependent on the hydrolysis of the dissolved $COCl_2$.

The solubility of unreacted phosgene in water is listed as a function of temperature in Table 6.13, along with the values of D and of k_1, used in the calculations. The solubility of phosgene in water at 25 °C and standard pressure is thus calculated to be about 0.69% by weight [1315]. The enthalpy of solution of phosgene in water was estimated to be −28.5 kJ mol^{-1} [1315]. Other estimates of the solubility of phosgene, determined by direct absorption in water using a dynamic method, give a somewhat lower value of 0.3% by weight at 25 °C and standard pressure [ICI17]. This value is similar, in molar terms, to the solubility of carbon dioxide under the same conditions of temperature and pressure.

The solubility of phosgene in 10 *M* aqueous hydrochloric acid at 20 °C was determined by extrapolation of the $[COCl_2]^{-\frac{1}{2}}$ *versus* time plot to $t = 0$ (see Section 9.10.3.1): under ambient conditions the solubility is 0.36% by weight [ICI18]. From analysis of the vapour phase using i.r. spectroscopy, the solubility of $COCl_2$ in 5.6 *M* hydrochloric acid solution was found to be 0.54% by weight. Both the rates of absorption and solubilities of phosgene (25 °C) are reduced in aqueous sodium nitrate solutions (*ca.* 0.5–2.0 *M*) relative to their values in pure solvent [1315]. From the plot of the logarithm of the saturation concentration of phosgene in water (in equilibrium with phosgene gas at standard pressure) against the reciprocal absolute temperature (see Table 6.13), the mean differential enthalpy of solution was calculated to be 28.5 kJ mol^{-1} [1315].

6.6.3 *Other inorganic solvents*

Liquid–vapour equilibria for Cl_2–$COCl_2$ have been calculated on the assumption that the system conforms to ideality [541]. In the region of low dichlorine concentration ($\leqslant$2.5%), the system has been shown, by analysis of the gas and liquid phases, to behave consistently with these calculations. The temperature–composition diagrams are illustrated in Fig. 6.13 at 101.3 and 152.0 kPa [541].

$COCl_2$ is regarded generally as being soluble in CS_2, S_2Cl_2, and some of the liquid metal chlorides, such as $SnCl_4$ and $SbCl_5$ [132]. It is also soluble in both ambient-temperature and high-temperature chloroaluminate ionic liquids (see Section 9.4.3) Boiling point elevations for normal atmospheric pressure in phosgene have been recorded for the following liquids: SCl_2, S_2Cl_2, $AsCl_3$ and $SbCl_5$ [151]. The temperature dependence of the vapour pressure of the $COCl_2$–COSe system has also been investigated [774]. The solvent characteristics of phosgene itself are discussed fully in Chapter 11.

6.6.4 *The phosgene–hydrogen halide system*

The solubility of phosgene, and of its mixtures with hydrogen chloride, in organic solvents is important in relation to the manufacture of phosgene derivatives. In particular, isocyanates (see Section 4.7.1) are frequently prepared from mixtures of phosgene with an amine in a chlorinated aromatic solvent. The co-production of large quantities of hydrogen chloride necessitates the fractionation of the products in order to remove the HCl, and to recover the solvent and any unreacted phosgene for the purpose of recycling. The vapour pressure–composition isotherm of phosgene and of HCl at 20.0–101.3 kPa (Table 6.14) and of mixtures of phosgene and HCl at 101.3 kPa, have been determined in chlorobenzene at 20 °C [2216]. Table 6.14 shows that the two gases have very different solubilities and it has been noted that, when mixed, they lower each other's solubility in chlorobenzene relative to the solubilities of the pure individual components [2216]. The large difference in the solubilities of the two gases is believed to be partly a result of the differences in the entropies of solution [2216].

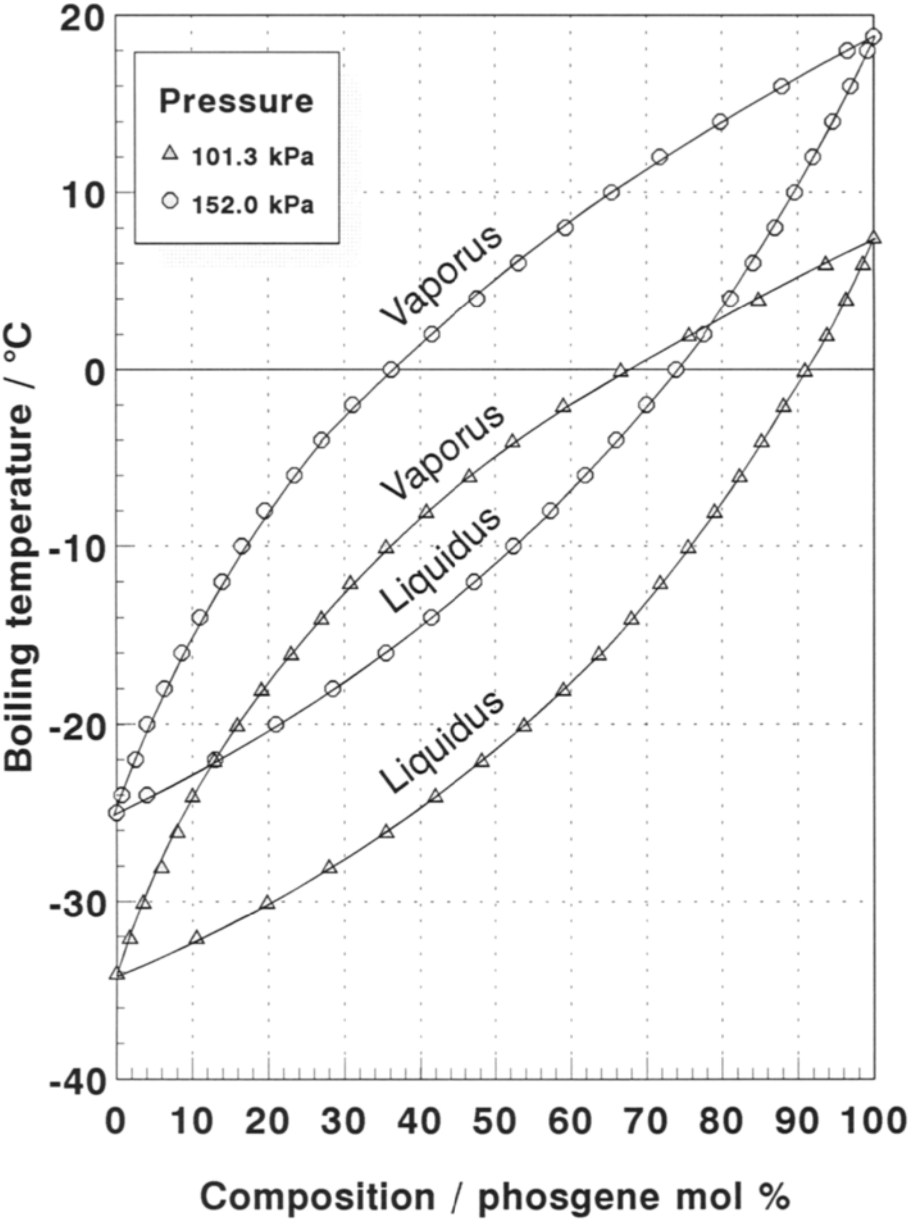


Fig.6.13 Boiling temperature–composition curves for the system phosgene/dichlorine at (a) 101.3 and (b) 152.0 kPa [541].

TABLE 6.14

SOLUBILITY OF PHOSGENE (X_1) AND OF HCl (X_2) IN CHLOROBENZENE AT 20 °C [2216]

p/kPa	20.3	27.2	50.7	66.7	81.1	83.3	101.3
X_1	0.0829	0.1153	0.2438	0.3512	-	0.4805	0.6346
X_2	0.0059	0.0081	0.0151	0.0203	0.0248	-	0.0312

Liquid-vapour equilibria in the phosgene-hydrogen chloride system have also been studied in connection with the problems associated with the separation of these two materials during the production of isocyanates. The system has been examined under atmospheric pressure within the range of the boiling points of the materials, *ca.* 8 to −85 °C. The temperature-composition curve is illustrated in Fig. 6.14 [789]; it shows large deviations from ideality.

Vapour pressure-composition isotherms for the $COCl_2$–HCl system have been investigated between −75 and 0 °C up to a total pressure of about 170 kPa, see Fig. 6.15 [ICI109]. A more detailed study has been published for temperatures of −7.2 (266.2 K) and −79.6 °C (193.6 K) [757a] and these are illustrated for both liquid and vapour phases in Table 6.15 and Figs. 6.16(A) and 6.16(B).

The enthalpies of mixing in the phosgene-hydrogen chloride system have been calculated for the −50 to −75 °C temperature region [ICI109]. For X(HCl) of 0.2, 0.4 and 0.6, the corresponding values of ΔH_{mixing} are −100, −218 and 280 J mol^{-1}, respectively.

During the production of CFC-11 and CFC-12 from the antimony-catalyzed reaction of CCl_4 with HF, the small amount of moisture in the commercial HF is converted into $COCl_2$ by reaction with the tetrachloromethane (see Section 5.2.1.2). The accumulation of phosgene can be reduced by fractional distillation: phosgene forms a constant boiling mixture with HF, containing about 77% (w/w) $COCl_2$ and 23% (w/w) HF at 172 kPa, and boiling at *ca.* 21 °C [174c].

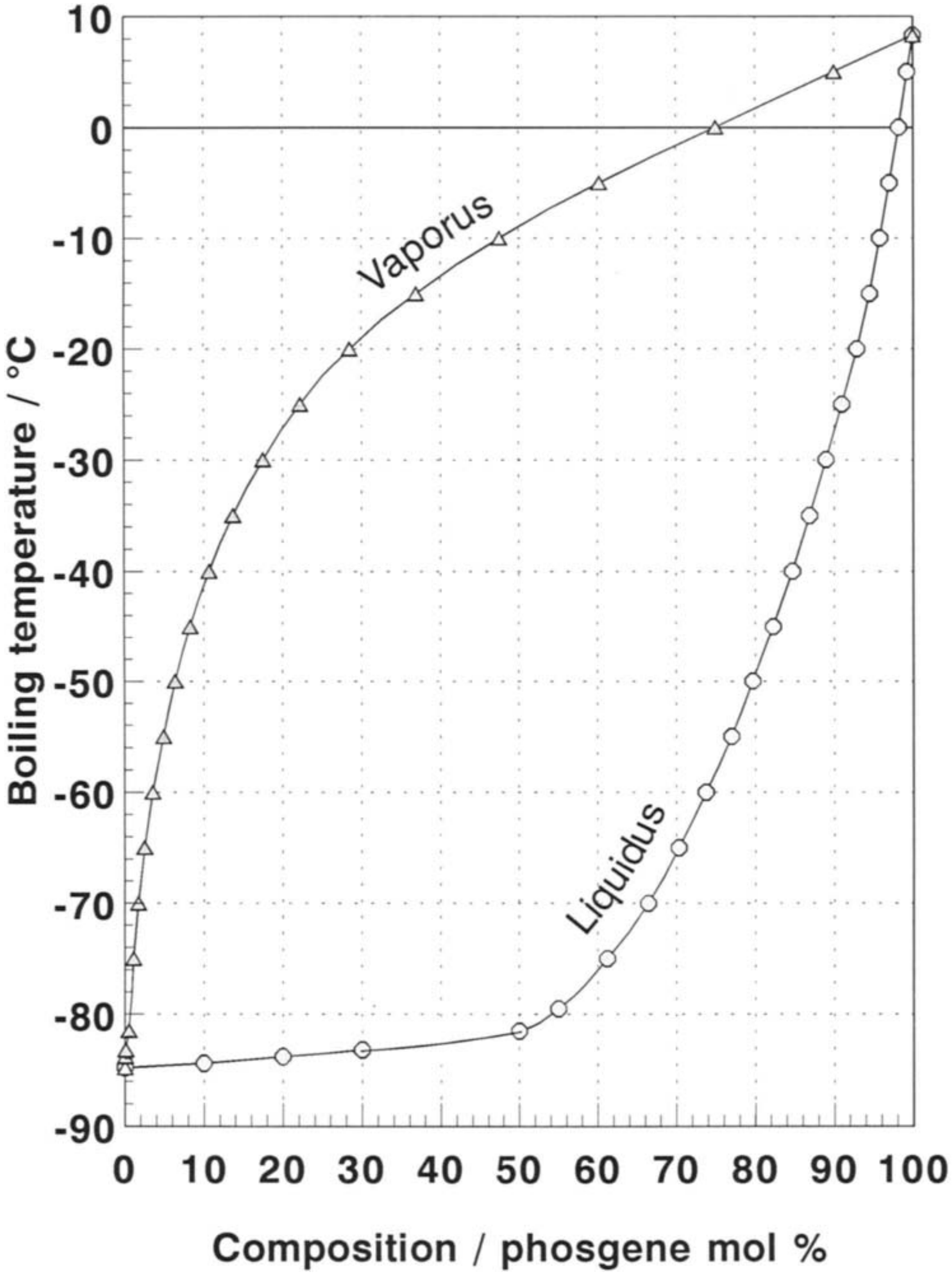


Fig.6.14 Boiling temperature–composition diagram for the system $COCl_2$–HCl at 101.3 kPa [789].

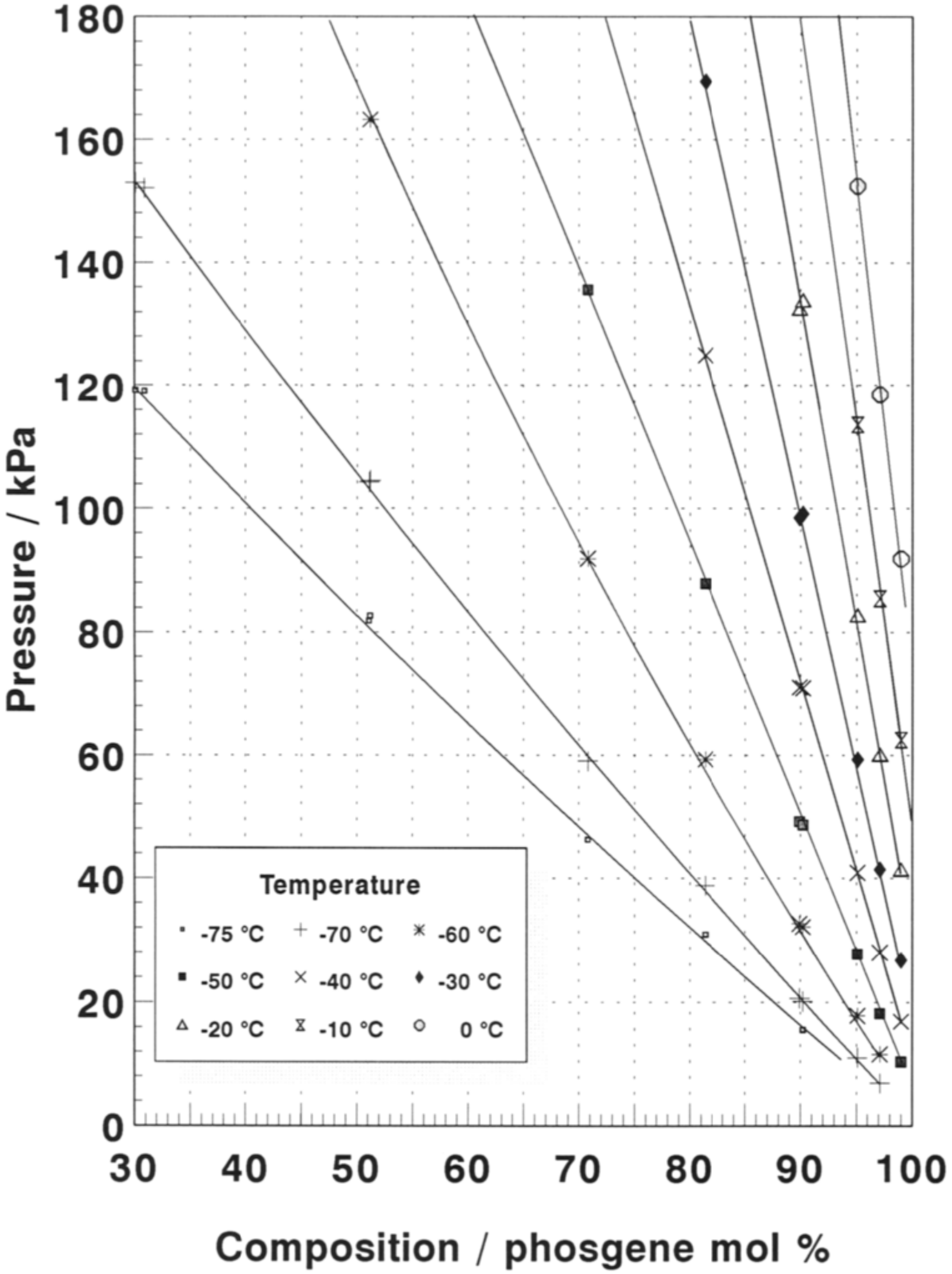


Fig. 6.15 Vapour pressure–composition isotherms for the system $COCl_2$–HCl between –75 and 0 °C [ICI109].

TABLE 6.15

THE VAPOUR PRESSURE OF THE $COCl_2$-HCl SYSTEM AT 266.15 K AND 193.59 K [757a]

266.15 K			193.59 K		
Mol % of $COCl_2$		Pressure/kPa	Mol % of $COCl_2$		Pressure/kPa
Liquid	Vapour		Liquid	Vapour	
0.00	0.00	2162	0.00	0.000	131.0
10.00	0.56	1918	9.84	0.043	119.1
12.13	0.67	1868	11.71	0.052	116.9
14.69	0.82	1809	13.98	0.063	113.2
17.67	0.99	1743	16.70	0.078	109.6
21.14	1.20	1662	19.84	0.095	107.6
25.65	1.47	1565	23.55	0.119	100.5
31.75	1.87	1433	28.79	0.157	93.42
38.93	2.42	1282	35.27	0.214	84.46
48.13	3.27	1091	43.31	0.306	72.88
50.41	3.51	1048	50.07	0.410	63.85
55.54	4.15	943.2	54.90	0.504	56.67
60.59	4.91	839.1	55.16	0.509	56.47
62.34	5.22	799.8	60.01	0.629	50.06
65.74	5.88	735.0	65.14	0.794	42.82
70.99	7.18	629.5	70.22	1.01	35.92
75.90	8.84	532.3	71.76	1.10	33.78
80.81	11.21	435.7	75.19	1.32	30.13
83.72	13.19	378.5	80.11	1.76	23.86
82.23	14.47	351.6	85.07	2.51	17.86
90.65	21.68	244.8	90.16	4.02	11.31
95.41	36.72	154.4	96.45	11.18	4.34
100.0	100.0	54.6	100.0	100.0	0.524

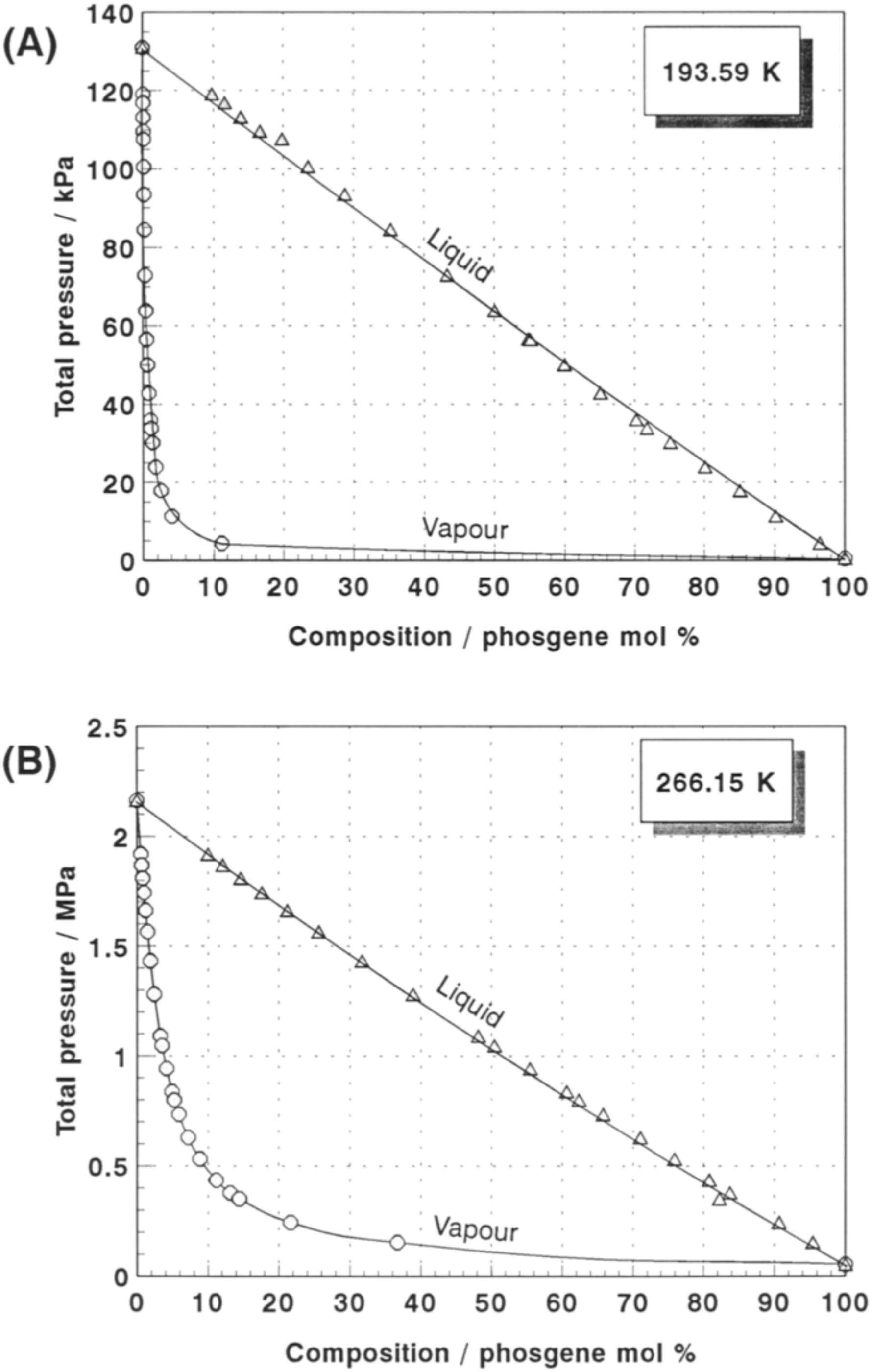


Fig. 6.16 Vapour pressure–composition isotherms for the system $COCl_2$–HCl at (a) −79.6 °C and (b) −7.0 °C [757a].

7 STRUCTURAL AND SPECTROSCOPIC PROPERTIES

The simplicity of the structure of phosgene has precipitated many structural and spectroscopic studies. This Chapter summarizes the results of the studies by electron diffraction, microwave and vibrational spectroscopy, nuclear magnetic resonance and nuclear quadrupole resonance spectroscopy, and mass spectrometry. Studies by electronic absorption and emission spectroscopy, and photoelectron spectroscopy, are discussed in Chapter 17.

7.1 STRUCTURAL DETERMINATIONS

7.1.1 Gas phase structure

The first structural determination of phosgene was an electron diffraction study performed by Dornte [549], which was rapidly refuted and reevaluated by Pauling and coworkers [277e], and then refined by Bauer [141]. It is ironic to note that, in the light of

TABLE 7.1

STRUCTURAL PARAMETERS FOR PHOSGENE[a]

Technique	r(CO)/nm	r(CCl)/nm	$\measuredangle$ClCCl/°	$\measuredangle$ClCO/°	Ref.
e.d.	0.112	0.180	110	125	549
e.d.	0.128	0.168	117	121.5	277e
e.d.	0.1260	0.1674	116.9	121.55	141
e.d.	0.118	0.174	112.5	123.75	30a
e.d.	0.1184	0.1744			1479
m.w.	0.1166	0.1746	111.3	124.35	1724
m.w.	0.11794	0.17401	111.93	124.035	332
e.d./m.w.	**0.11756**	**0.17381**	**111.79**	**124.105**	1475,1476,1479
e.d./m.w.[b]	0.11766	0.17365	111.91	124.045	2224a
x.r.d.[c]	0.115	0.174	111	124.5	2247

[a] Enboldened data are recognized as the best set; all data sets are for the gas phase, unless otherwise stated. [b] Data for the equilibrium structure. [c] Solid state structure.

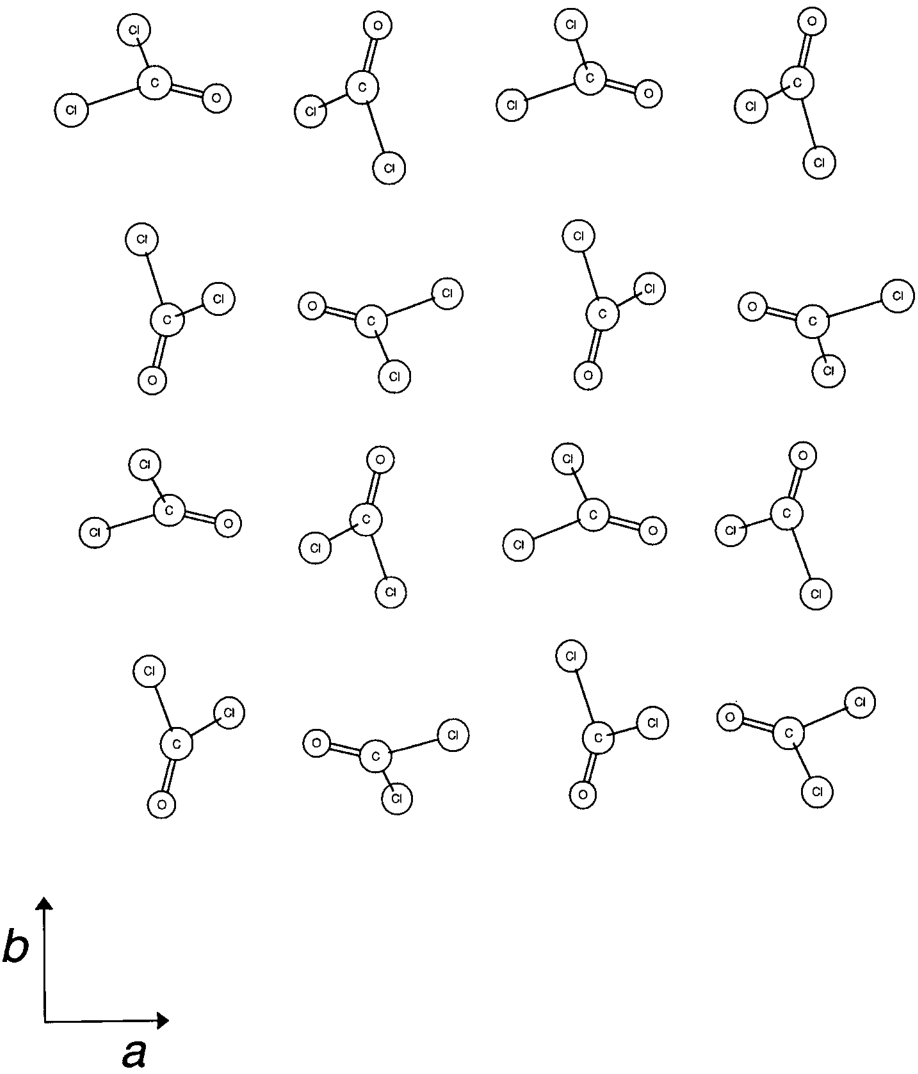


Fig. 7.1 The unit cell of phosgene, viewed down *c* [2247].

recent data (*vide infra*), Dornte's original structure was the most reliable of the early determinations (see Table 7.1).

Phosgene is an ideal molecule for study by microwave spectroscopy, as it possesses eight C_{2v} isotopomers. The first microwave study was reported in 1953, using two of these isotopomers [1724], and these data were improved in a more recent study using three isotopomers [332]: for $^{12}C^{16}O^{35}Cl_2$, A_0 = 7918.794, B_0 = 3474.959, and C_0 = 2412.206 MHz. Centrifugal distortion constants have also been determined [1410]. In the most detailed study to date, all eight isotopomers were studied and the twenty-four ground state rotational constants determined [1475]: for $^{12}C^{16}O^{35}Cl_2$, A_0 = 7918.790, B_0 = 3474.951, and C_0 = 2412.214 MHz. In the most recent paper, the microwave spectra of $CO^{35}Cl_2$ in the vibrationally excited states of all its fundamental vibrational modes (except ν_1) were recorded and analyzed [2225]: these data have been combined with data from vibration-rotation spectra to yield equilibrium rotational constants (see Section 7.2).

In an excellent and lucid article (ideal for teaching purposes), phosgene has been used as a case study for the complementary use of electron diffraction and microwave spectroscopy for precise structure determination [1476]. Full details of this study have also appeared elsewhere [1479,1481], and these data provide the most precise structural details yet determined for phosgene.

From measurements of diffusion coefficients, the effective molecular radius of phosgene in the gas phase was calculated to be 0.242 nm [1129].

7.1.2 Liquid phase structure

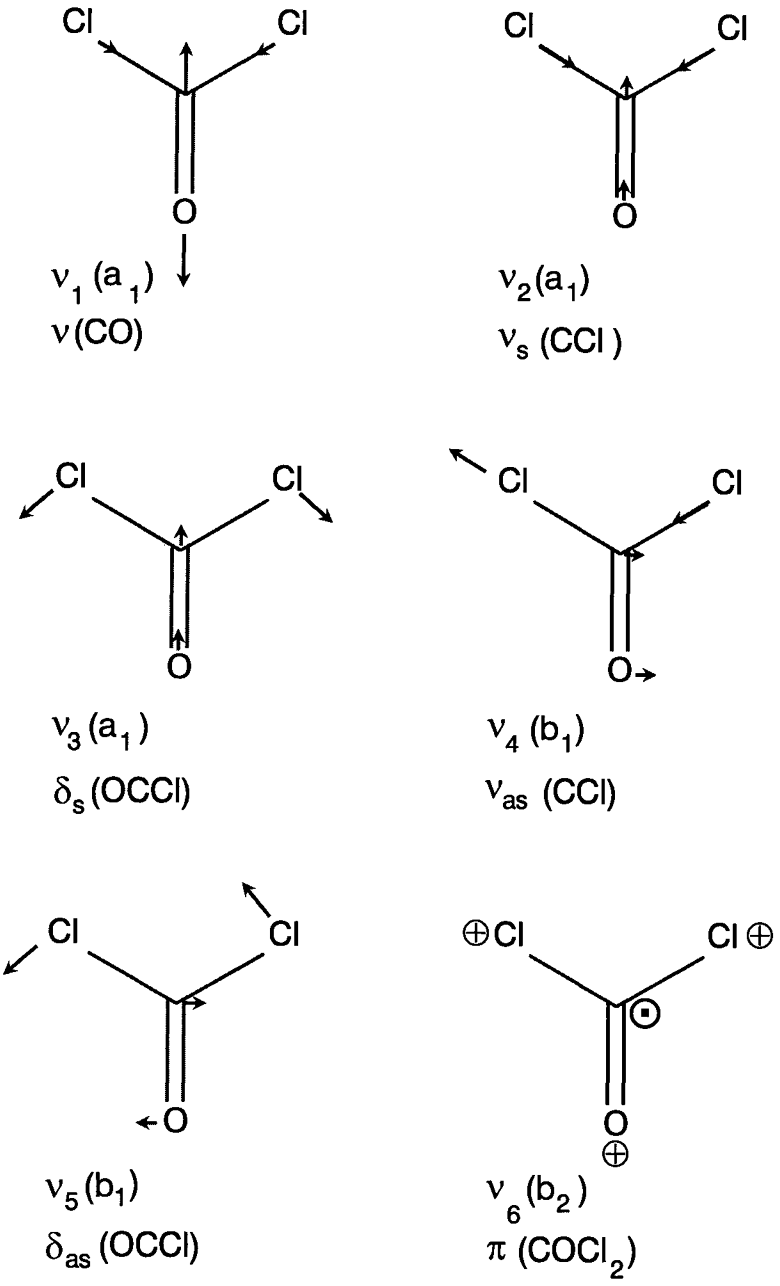
Assuming that phosgene packs as a "cubic molecule" with cube sides equal to its diameter, then (from density data) its effective molecular radius in the liquid state is 0.245 nm [1129].

7.1.3 Solid phase structure

A single crystal of phosgene was grown in a stream of cold dinitrogen, and data was collected at 113 K [2247]: the crystal was tetragonal (a = 1.582, c = 0.572 nm; Z = 16; C^6_{4h} – $I4_1/a$) [2247], and the molecular dimensions of phosgene are summarized in Table 7.1. The unit cell of phosgene is illustrated in Fig. 7.1: no disorder was detected in the crystal {*cf.* the predictions of disorder from entropy calculations (Section 6.1.3)}.

7.2 VIBRATIONAL SPECTROSCOPY

Phosgene has attracted a tremendous amount of attention, both experimental and theoretical, because of its essentially simple structure. Indeed, it has become a classical aid for teaching vibrational analysis and group theory. It possesses C_{2v} symmetry (see Appendix A4), and the fundamental vibrational modes, their symmetry and activity are illustrated in Fig. 7.2.



$\nu_1\,(a_1)$ $\nu(CO)$

$\nu_2(a_1)$ $\nu_s\,(CCl)$

$\nu_3\,(a_1)$ $\delta_s\,(OCCl)$

$\nu_4\,(b_1)$ $\nu_{as}\,(CCl)$

$\nu_5\,(b_1)$ $\delta_{as}\,(OCCl)$

$\nu_6\,(b_2)$ $\pi\,(COCl_2)$

Fig. 7.2 The fundamental vibrations of phosgene.

The results of infrared and Raman studies of phosgene are summarized in Tables 7.2 and 7.3, respectively. In addition, the infrared spectrum of gaseous phosgene has been included in standard catalogues of common molecules [1462a,1463,1615,1859]. Bands originally reported at *ca.* 240 cm^{-1} [1508] have now been shown to be spurious [343,1575]. The *PR* separations of the band envelopes have been studied as part of a larger series of prolate and oblate molecules [1596a], and the near infrared region (2500–10000 cm^{-1}) has also been examined [1338].

TABLE 7.2

INFRARED DATA (UNITS OF CM^{-1}) FOR $COCl_2$[a]

	Medium	$\nu_1(a_1)$ $\nu(CO)$	$\nu_2(a_1)$ $\nu_s(CX)$	$\nu_3(a_1)$ $\delta_s(OCX)$	$\nu_4(b_1)$ $\nu_{as}(CX)$	$\nu_5(b_1)$ $\delta_{as}(OCX)$	$\nu_6(b_2)$ $\pi(COX_2)$	$\nu_2+\nu_5$	Ref.
$COCl_2$	Gas	1827	576		845		444[b]		102,103
$COCl_2$	Gas	1827	575	297	849		440[b]		1508
$COCl_2$	Gas	1827	570	285	849	440	582		146
$COCl_2$	Gas	**1827**	**567**	**285**	**849**	**440**	**580**	**1011**	981,1085
$COCl_2$	Gas	1830	574	303	849	445	586		1806
$COCl_2$	Liquid	1825.5	567		850		583	1013.5	1804
$COCl_2$	Ar;20 K	1803	568		835		582	1006	343
$COCl_2$	Ar;10 K	1817	568		837		581		1806
$^{13}COCl_2$	Gas	1784			821		565		146
$^{13}COCl_2$	Gas	1788			821			1006	1806
$^{13}COCl_2$	Ar;10 K	1775.5	563		809.5		562		1806
$C^{18}OCl_2$	Gas	1788						1014	146
$C^{18}OCl_2$	Gas	1792	564					989.5	1806
$C^{18}OCl_2$	Ar;10 K	1779	558		834		577		1806
$CO^{37}Cl_2$	Ar;10 K		561		835				1806, 1807

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[a] Enboldened data are recognized as the best set. [b] Now recognized to be incorrectly assigned [1575].

The absorption coefficients, α, for phosgene have been measured at three different CO laser frequencies [1805]: at 1834.57 cm^{-1}, α = 44.7 atm^{-1} cm^{-1}; at 1833.51 cm^{-1}, α = 46.5 atm^{-1} cm^{-1}; at 1755.27 cm^{-1}, α = 0.52 atm^{-1} cm^{-1}. These data suggest a lower limit for the detection of phosgene by vibrational spectroscopy, in air at atmospheric pressure, of 96 p.p.b. (see also Section 3.2.6.1.1) [1805].

TABLE 7.3

RAMAN DATA (UNITS OF CM^{-1}) FOR $COCl_2$[a]

	Medium	$\nu_1(a_1)$ $\nu(CO)$	$\nu_2(a_1)$ $\nu_s(CX)$	$\nu_3(a_1)$ $\delta_s(OCX)$	$\nu_4(b_1)$ $\nu_{as}(CX)$	$\nu_5(b_1)$ $\delta_{as}(OCX)$	$\nu_6(b_2)$ $\pi(COX_2)$	$\nu_2+\nu_5$	Ref.
$COCl_2$	Gas		567	290		444			941
$COCl_2$	Gas	1822.7	562.7	296.7	854	441	579		1804
$COCl_2$	**Gas**	**1827**	**567**	**285**	**849**	**440**	**580**		2181
$COCl_2$	Liquid	1810	571	301	834	444			446a[c]
$COCl_2$	Liquid	1809	573	301	835	444	573		1804
$COCl_2$	**Liquid**	**1807**	**573**	**302**	**832**	**442**[b]			1508
$COCl_2$	Liquid	1807	573	302	832	442			45

[a] Enboldened data are recognized as the best set. [b] This band was originally [1508] assigned to 220 cm^{-1}, but has since been corrected [1575]. [c] Also discussed in [1141a].

The vibration–rotation spectra of the ν_1 and ν_4 bands of $CO^{35}Cl_2$ have been measured (using a tunable semiconductor–diode laser), and assigned with the aid of Stark modulation spectra [2224]. The precise values of these bands were determined to be 1828.2012 and 851.0105 cm^{-1}, respectively, and the equilibrium rotational constants for $CO^{35}Cl_2$ were calculated as: A_e = 7950.35, B_e = 3490.22, and C_e = 2425.44 MHz {*cf.* Section 7.1} [2224].

There have been a large number of determinations of molecular force constants, mean amplitudes of vibration, bond asymmetry parameters, Coriolis coupling constants (and inertia defects) and centrifugal distortion constants [146,152,259,271,304,581,840,1221,1222,1278,1312, 1416,1448,1449,1549,1550,1575–1578,1587,1618,1671,1682,1806,1807,1858,1931,1961,1984,2021,2045, 2108,2109–2111,2167a], as well as a determination of the atomic potential energy distribution for ν_1, ν_2 and ν_3 [1674]. Indeed, the relative molecular simplicity of phosgene and the other carbonyl halides seems to present an irresistible attraction to the exponents of the art of force constant calculations.

An empirical rule for calculating $\nu(C{=}O)$ for a range of carbonyl compounds, including phosgene, has been proposed [2223]. Various methods of calculation (including CNDO) have been applied to computation of the carbonyl stretching frequency of $COCl_2$ [1680,1681] and to the determination of dipole moment derivatives [289,292,1473,1657], in order to account for the empirical infrared intensities [981,1279]. More recently, polar tensors and effective charges have been calculated [135,1516], and the sums of the gas phase infrared intensities for the molecules $C(E)X_2$ (E = O or S; X = Cl or F) were shown to be interrelated [135]. CNDO and INDO methods were rather unsuccessful in predicting the relative intensities in the Raman spectrum of gaseous phosgene [2181], and little improvement was achieved using extended Hückel theory [2182]. Similarly, infrared band intensity ratios appear to be poorly suited to the prediction of the $\measuredangle$ClCCl bond angle [1904]. Density of vibrational states, $\rho(E)$, have been calculated [1796].

The force constant (K) for π(COXY), ν_6 for the carbonyl halides, shows a good correlation with a linear expression involving Taft's inductive (σ_I) and resonance (σ_R) parameters for X and Y [604]: $K = 0.233 + 0.199\sum\sigma_I - 0.268\sum\sigma_R$. More remarkable is the linear correlation found, for the same molecules, between $\nu_6/(\mu_X+\mu_Y+\mu_O+9\mu_C)^{\frac{1}{2}}$ and $\{3\chi(C)+\chi(X)+\chi(Y)+\chi(O)\}/\{\frac{1}{2}(r_{CX}+r_{CY})+r_{CO}\}$, where μ_E is the reciprocal of the atomic weight of E, and $\chi(E)$ is the Pauling electronegativity of E [1860]. Unfortunately, the full significance of this fundamentally important observation was not discussed, but similar correlations of K with mean electronegativities are still being pursued [583a,864].

As a rough rule of thumb, the ratio of $\nu(C{=}O)/\nu(C{=}S)$ for a carbonyl compound and its thio analogue is approximately 1.5: it is specifically 1.61 for the pair of molecules phosgene and thiophosgene [1288,1370]. An attempt has been made to correlate the $\nu(C{=}O)$ stretching frequency of carbonyl compounds C(O)XY, including phosgene, with (i) the 'reaction capacity' of the carbonyl bond [71], (ii) the ionization potential [409a], (iii) the $\measuredangle$XCY bond angle [410], (iv) the sum of the electronegativities of X and Y [1060], (v) the $r(C{=}O)$ bond length [1324,1577], (vi) the nett charge carried on C and O [808], and (vii) the bond order, as calculated by HMO [670] or EHMO [1569] theory. As yet there has been no attempt to correlate $\nu(C{=}O)$ with the number of letters in the IUPAC name of the compound. If correlations of this sort really have to be published, the authors should demonstrate that they possess at least a rudimentary understanding of the fundamental principles of statistics.

However, perhaps the last word on preposterous correlations involving the vibrational modes of phosgene lies with Wright and Burgess (from the BP Research Laboratory, Vancouver, Canada), who, in 1971, claimed that the human olfactory threshold correlates well with the lowest fundamental infrared active frequency of a gaseous molecule irrespective of its chemical nature [2213]. Its seems almost churlish to point out that the value selected for phosgene was ν_2, and that both ν_3 and ν_5 occur at lower frequencies – it would be a pity to spoil such a fragrant theory by examining the facts.

7.3 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Phosgene contains three elements, each of which possesses an isotope with a non-zero nuclear spin. Thus, phosgene has been studied by ^{13}C, ^{17}O, and ^{35}Cl nuclear magnetic resonance.

A solution of phosgene in tetrachloromethane exhibits a single ^{13}C resonance (natural abundance) at 142.1 p.p.m. to low field of TMS [2141]. This is 62 p.p.m. to higher field than the carbonyl group in propanone and 30.8 p.p.m. to higher field than the carbonyl group of $(F_3C)_2C{=}O$, indicating the existence of significant π-bonding between the carbon and chlorine atoms (see Chapter 17).

An interesting paper by Gombler [797] compares ^{13}C (and, where relevant, ^{19}F) n.m.r. data for five of the carbonyl halides, and this work has recently been extended [1589b] to include ^{17}O n.m.r. data. These data are summarized in Table 7.4, and the signals

TABLE 7.4

^{13}C, ^{19}F AND ^{17}O N.M.R. SPECTROSCOPIC DATA FOR THE CARBONYL HALIDES[a]

	$\delta(^{13}C)$/p.p.m[b]	$\delta(^{19}F)$/p.p.m[c]	$\delta(^{17}O)$/p.p.m[d]	$^{1}J(CF)$/Hz[e]	$^{2}J(OF)$/Hz[f]	Ref
COF_2	134.2	-23.0		309		797
	134.1	-20.4	259.5	310.3	37.6	1589b
		+21.54[g,h]		308.4[i]		555a
		+23.4[h,j]				1263
		+22.5[h,k]				1263
COClF	140.5	59.7		366		797
	139.9	60.0	375.1	366.4	37.4	1589b
$COCl_2$	141.8[l]					797
	142.1[l,m]					2141
	142.8[n]		483.6[n]			1589b
COBrCl	125.0					797
	127.2[n]		526.5[n]			1589b
COBrF		-83.7[h,m]				1163
	127.6	+84.7	401.9	404.2	41.7	1589b
$COBr_2$	103.4[l]					797
	106.9[n]		549.2[n]			1589b

[a] Dissolved in trichlorofluoromethane, and measured at -50 °C, unless otherwise stated. [b] Measured with respect to TMS. [c] Measured with respect to CCl_3F. [d] Measured with respect to external OH_2 [e] Measured from the C-13 n.m.r. spectra. [f] Measured from the O-17 n.m.r. spectra. [g] Value extrapolated to infinite dilution, temperature not quoted. [h] Presumably measured with a reversed (and unstated) sign convention. [i] Measured in the neat liquid. [j] Measured in diethyl ether. [k] Measured in fluorobenzene. [l] Measured at room temperature. [m] Measured in tetrachloromethane. [n] Measured in dichloromethane.

showing fluorine coupling are illustrated in Fig. 7.3. Plots of the ^{13}C (Fig. 7.4) and ^{17}O (Fig. 7.5) chemical shifts of the carbonyl halides as a function of (A) the sum of the Pauling electronegativity of the halides and (B) the π(CO) bond order (see Section 17.1.2.4) reveal some interesting patterns. As commented on by Gombler [797], the pattern revealed in

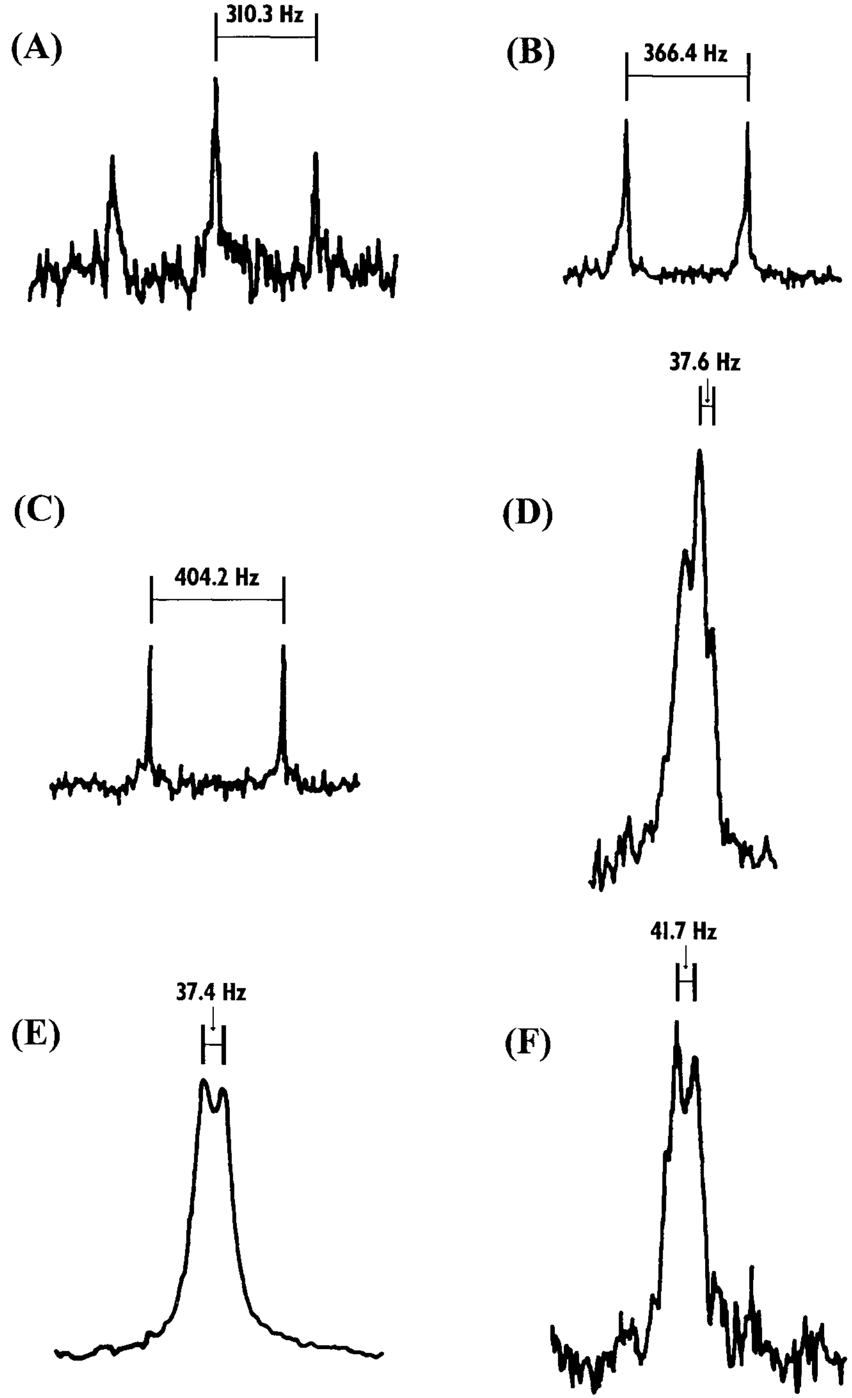

Fig. 7.3 The ^{13}C n.m.r. spectra for (A) COF_2, (B) COClF and (C) COBrF, and the ^{17}O n.m.r. spectra for (D) COF_2, (E) COClF and (F) COBrF [1589b].

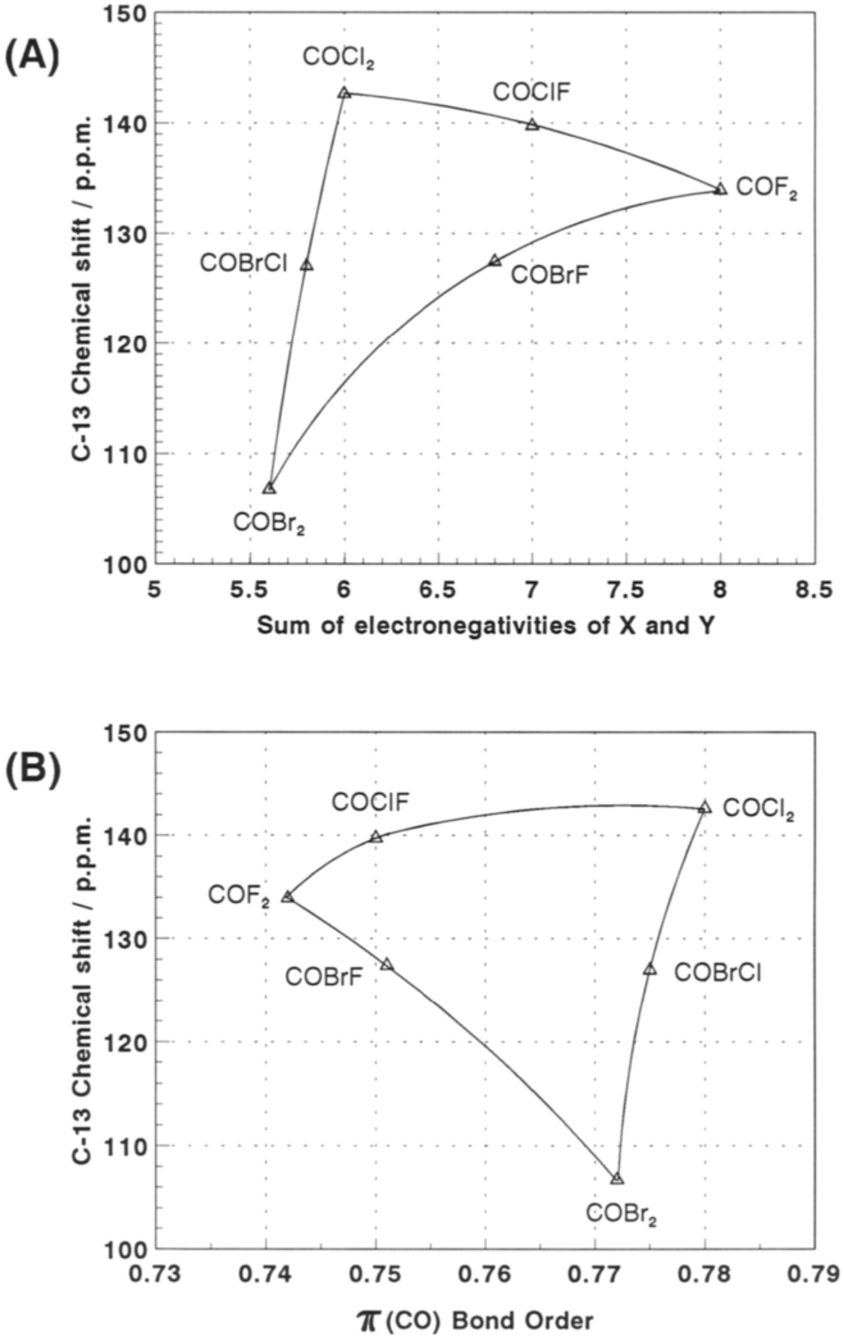

Fig. 7.4 ^{13}C chemical shifts of C(O)XY as a function of (A) the sum of the Pauling electronegativities of X and Y [797,1589b], and (B) the π(CO) bond order [1589b].

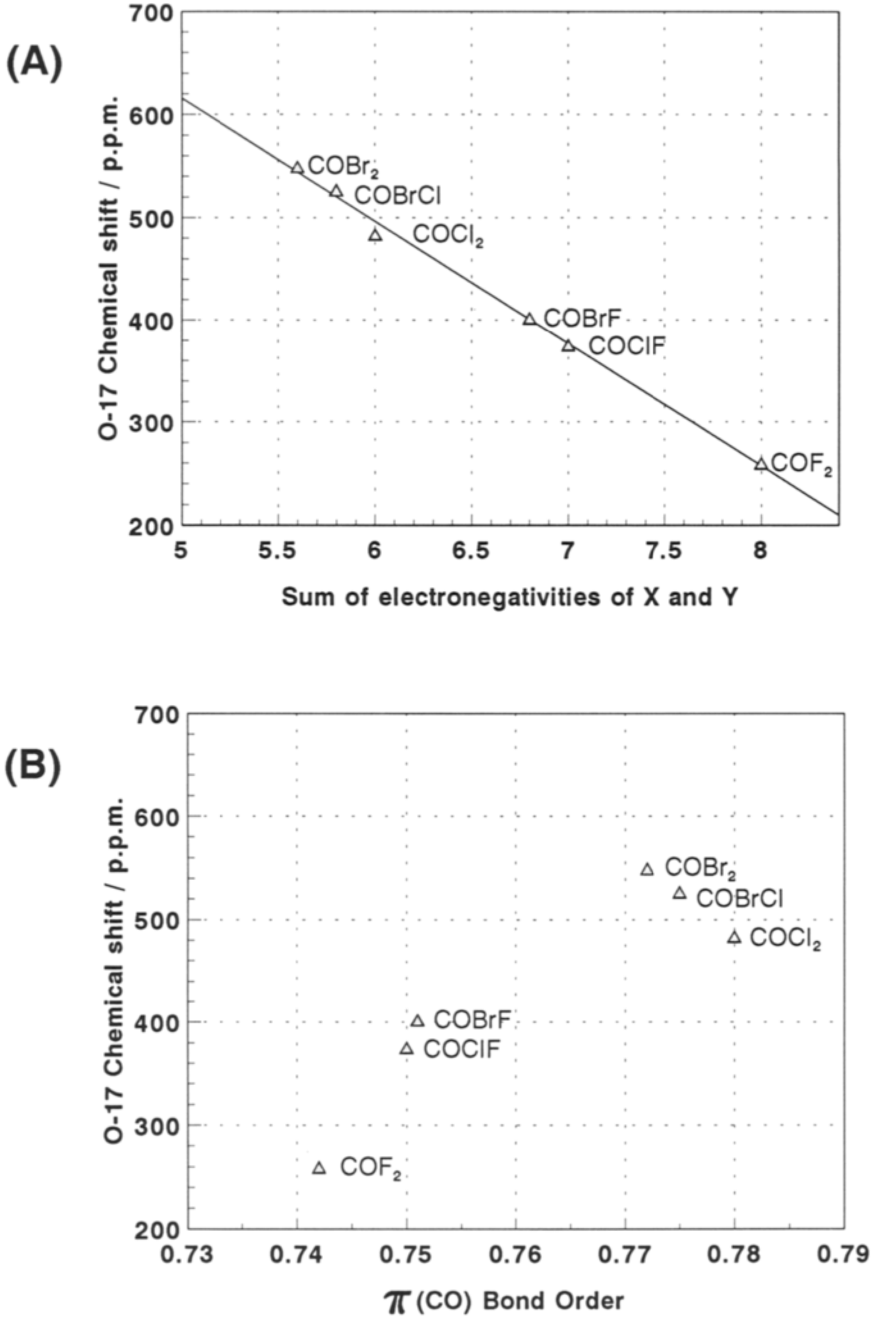

Fig. 7.5 ^{17}O chemical shifts of C(O)XY as a function of (A) the sum of the Pauling electronegativities of X and Y [797,1589b], and (B) the π(CO) bond order [1589b].

Fig. 7.4(A) is indicative of the presence of strong CF π-bonding, and this is supported by the reflection of this pattern in Fig. 7.4(B). The good linear correlation (by conventional linear regression analysis, $r = -0.998$, $n = 6$) between $\delta(^{17}O)$ and $\sum\chi_{X,Y}$, and the lack of significant correlation with the π(CO) bond order, suggest that the inductive effect dominates the determination of terminal oxygen chemical shift {as appears also to be the case with the restricted data set for $\delta(^{19}F)$ [797]} [1589b], whereas the chemical shift of the central carbon atom is determined by a balance of opposing σ and π effects.

Phosgene exhibits a ^{35}Cl chemical shift of 627 p.p.m. relative to aqueous sodium chloride {*cf.* δ 476 p.p.m. for $CH_3C(O)Cl$} [119], again clearly indicative of significant C–Cl π-bonding.

Examination of a solution of phosgene by ^{13}C and ^{17}O n.m.r. spectroscopy is a convenient method of detecting carbon dioxide (δ 125.1 p.p.m. [796]) impurities [1589b].

7.4 NUCLEAR QUADRUPOLE RESONANCE SPECTROSCOPY

The ^{35}Cl n.q.r. spectrum of $COCl_2$ at 77 K has been measured: it shows two lines (at 36.225 and 35.081 MHz) [1262], and an attempt to predict these frequencies by a modified CNDO method led to a 4.63% overestimate [400]. It should be noted that the lower frequency resonance was misquoted as 35.001 MHz by Cohen and Whitehead [400], and

TABLE 7.5

MASS SPECTRAL DATA FOR $COCl_2$ [934a,1071]

m/z	Relative Intensity		Assignment
	[934a]	[1071]	
102,100,98	2	4	M^+
86,84,82	1	1	$[CCl_2]^+$
74,72,70	3		$[Cl_2]^+$
65,63	31,100	100	$[COCl]^+$
49,47	2,5	3	$[CCl]^+$
37,35	11,33	15	Cl^+
28	29	8	$[CO]^+$
12	5		C^+

that suggestions [894] of isomerism in solid phosgene should be regarded as highly speculative {*cf*. Section 7.1.3}. More recently, the complete chlorine nuclear quadrupole coupling tensor has been measured [644], and again (*cf*. Section 7.3) there is a strong indicator of significant π-bonding between the chlorine and carbon atoms (*ca*. 9%).

For a wide range of chlorine-containing compounds, a correlation was found between the ^{35}Cl n.q.r. frequencies and the Taft inductive effects of the other substituents (where known) [199,1611,1838]. Phosgene is the first member (n = 0) of the homologous series, $Cl(CH_2)_nC(O)Cl$, which has also been investigated for regular trends in n.q.r. frequency [648].

7.5 MASS SPECTROMETRY

The mass spectrum (70 eV; E.I.) of phosgene has been recorded (Table 7.5), and is totally unremarkable [1b,934a,1071].

8 DISSOCIATION, DISMUTATION AND PHOTOCHEMISTRY OF PHOSGENE

As seen in Chapter 6, phosgene is thermodynamically stable under standard conditions with respect to its elements, Equation (8.1), and with respect to dissociation, Equation (8.2).

$$C(s) + Cl_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons COCl_2(g) \qquad (8.1)$$

$$COCl_2 \rightleftharpoons CO + Cl_2 \qquad (8.2)$$

$$2COCl_2 \rightleftharpoons CCl_4 + CO_2 \qquad (8.3)$$

It is, however, thermodynamically unstable with respect to dismutation, Equation (8.3). Besson and coworkers [809] have calculated the *equilibrium* composition of the gas phase for an initial phosgene pressure of 13.33 kPa, taking into account the existence of the following species (all gaseous, except carbon): C_1, C_2, C_3, C_4, C_5, O, O_2, Cl, Cl_2, CCl, CCl_2, CCl_3, CCl_4, CO, CO_2, C_2O, C_3O_2, ClO, ClO_2, Cl_2O, C_2Cl_2, C_2Cl_4, C_2Cl_6, COCl, $COCl_2$ and solid carbon. The results of these calculations are illustrated in Fig. 8.1. It is of interest to note that phosgene should have no existence at room temperature, that the dismutation reaction {to form CO_2 and CCl_4, Equation (8.3) and Section 8.2} prevails below 130 °C, that the dissociation reaction {to form CO and Cl_2, Equation (8.2) and Section 8.1} prevails above 830 °C, and that solid carbon is present between 230 and 900 °C. This clearly demonstrates the dominance of kinetic phenomena in the chemistry of phosgene, as phosgene clearly exists, although in a metastable state, and the dismutation reaction cannot be thermally induced. This chapter describes the dissociation and dismutation processes for phosgene in some detail, as well as examining its photochemically induced decomposition.

8.1 DISSOCIATION OF PHOSGENE

8.1.1 Thermal dissociation

The thermal dissociation of phosgene into carbon monoxide and elemental chlorine, Equation (8.2), is the reverse of the reaction used widely, either thermally, catalytically or photochemically promoted, for the synthesis of phosgene (see Section 5.1). Thus, much of the chemistry relevant to this Section has already been covered in Chapters 5 and 6. Much of the early work, both kinetic and thermodynamic, was marred by a lack of appreciation of the importance of high purity, and the fact that the system takes a very long time to come

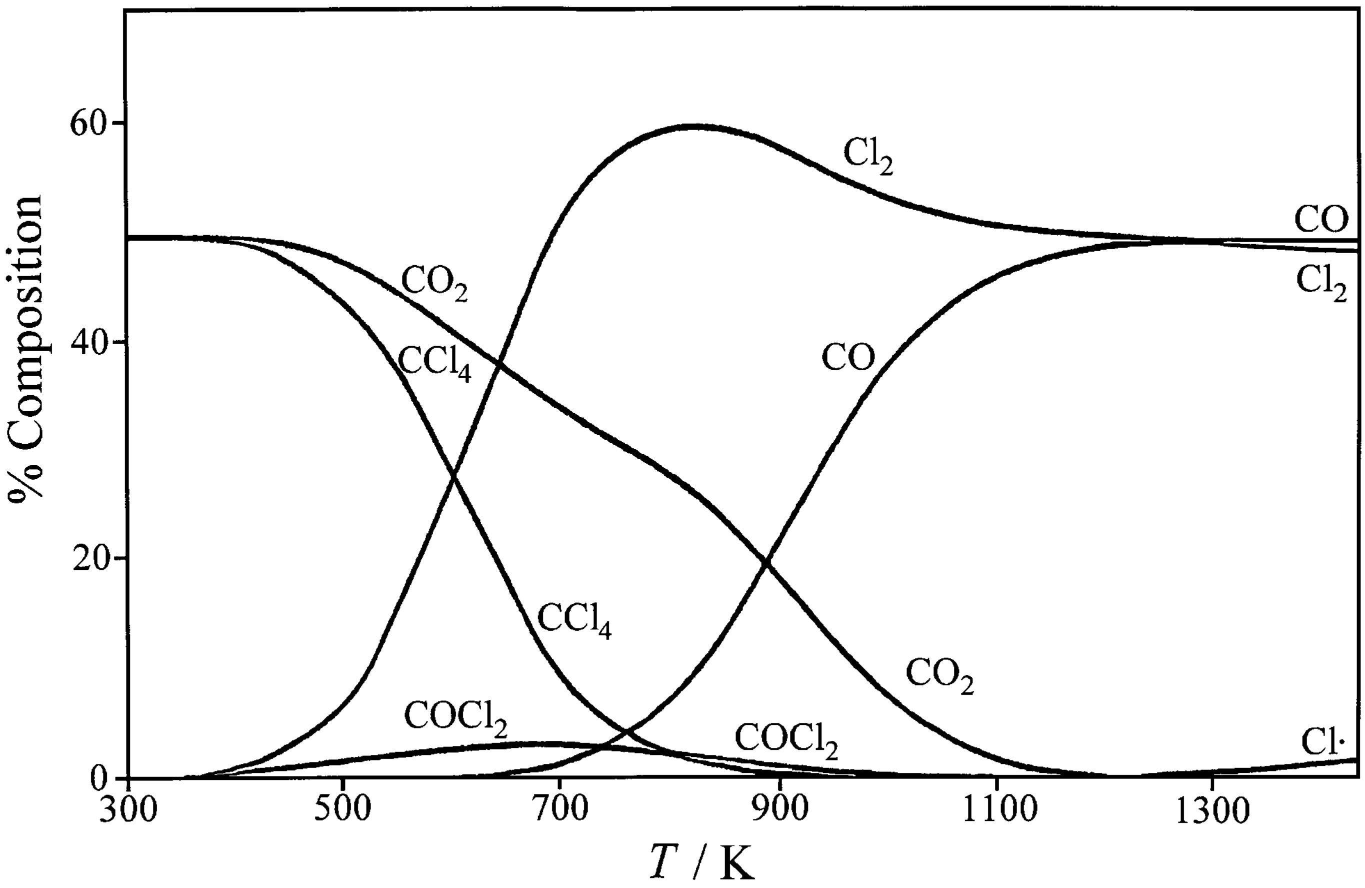

Fig. 8.1 The calculated composition of the gas phase resulting from a sample of phosgene (13.33 kPa) being allowed to achieve its thermodynamic equilibrium [809].

to equilibrium (see, for example, Figs. 5.1 and 5.4). Much of the early work [*e.g.* 216] has been constructively criticized by Dyson [578], and early thermodynamic data assigned to the enthalpy change for reaction (8.2) must be regarded as obsolete [799,2032b]. However, if the best of the early equilibrium data are examined as a function of temperature (see Fig. 8.2(A)), then a reasonable, but high, estimate of the enthalpy of reaction as +(119 ± 6) kJ mol^{-1} is obtained. The degree of dissociation as a function of temperature has been reported in a number of studies [216,223,1375]: $T/{}^\circ C$, $\alpha/\%$; 300, 4.4; 400, 21; 420, 42; 500, 59; 503, 67; 520, 74; 553, 80; 600, 86; 603, 91; 700, 95; 800, 100. These data agree reasonably well with the calculated curves shown in Fig. 5.3.

A modern study of this system by Lord and Pritchard [1275] confirmed that the data of Bodenstein and Plaut [218] were of the highest accuracy: when the data from Bodenstein and Plaut [218] and the modern study [1275] are combined (see Fig. 8.2(B)), a value of ΔH of +(112.5 ± 1.5) kJ mol^{-1} is obtained for reaction (8.2) from the van't Hoff plot [1275]. However, as the slight curvature of the plot betrays, ΔH varies slightly with temperature. The best data treatment yields ΔH°_{298} as +(108.6 ± 0.4) kJ mol^{-1} [1275]. The equilibrium constants for Equation (8.2) are given by [1275]:

$$\ln(K_p/\text{atm}) = -13525.4T^{-1} + 17.15796$$

$$K_c/\text{mol l}^{-1} = (K_p/\text{atm})/(0.08206T)$$

The enthalpy of reaction (8.2) at 25 °C was also determined as +(113.4 ± 1.3) kJ mol^{-1}, directly, by studying the photochemical formation of phosgene from CO and Cl_2 in a microcalorimeter [1998]. The data from Kuznetsov *et al.* [1187] should be disregarded.

The thermodynamic parameters for Reaction (8.2) in the gas phase, as calculated from the JANAF Thermochemical Tables [359aa], are detailed in Table 8.1, and illustrated in Figures 8.3 and 8.4 [1825a]. Further details of this dissociation reaction are given in Sections 5.1.2 and 6.1.4.

Although [COCl]· has been universally recognized as the key intermediate in the thermal dissociation of phosgene, and there is much evidence for its existence in photochemical processes (see Section 5.1.1), no direct empirical evidence for its presence exists. In a recent attempt to observe it, phosgene was heated to between 900 and 1100 °C, and the reaction mixture was then quenched into an argon matrix: although free CO was observed, there was no evidence (perhaps not surprisingly) for the presence of [COCl]· [1311].

The thermal dissociation of phosgene is too slow at temperatures below 500 °C to act as a useful source of [COCl]· radicals [2027]. However, at 1400–2000 K, under shock tube conditions, [COCl]· is the primary decompostion product [1253a]. The bond dissociation energy, *D*(Cl–CClO), has been discussed in Section 6.1.4.

Heating $COCl_2$ in a glass tube, or over aluminium(III) chloride or silicon(IV) oxide, at 400 °C induced 23.6% decomposition into CO and Cl_2, but no traces of CCl_4 were detected [1959]. Under high pressure, however, dismutation is induced (see Section 8.2) [1181,1182].

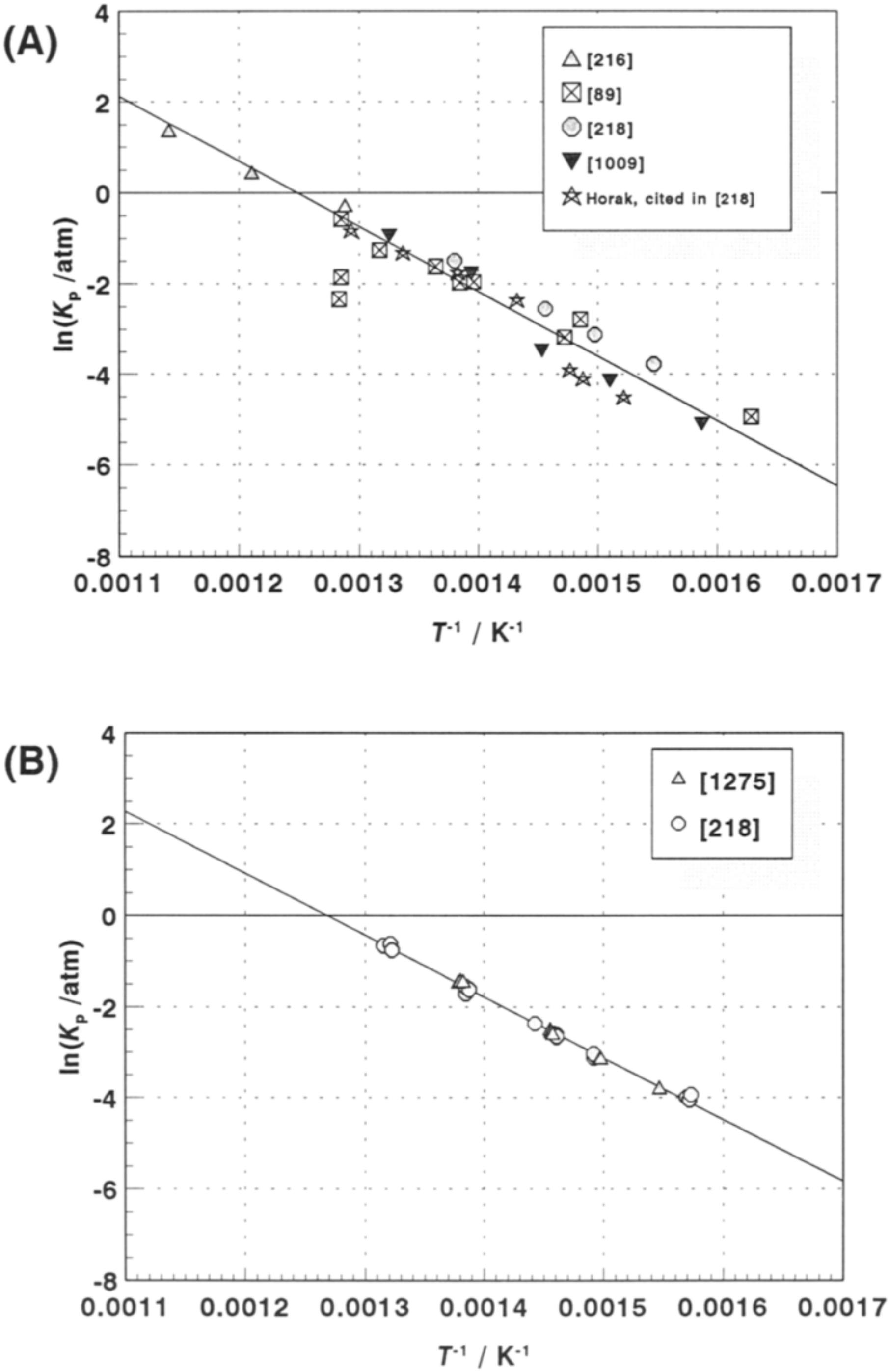

Fig. 8.2 (A) Early measurements of the equilibrium constant for Equation (8.2) as a function of temperature [89,216,218,578,1009], and (B) the best experimental data [218,1275].

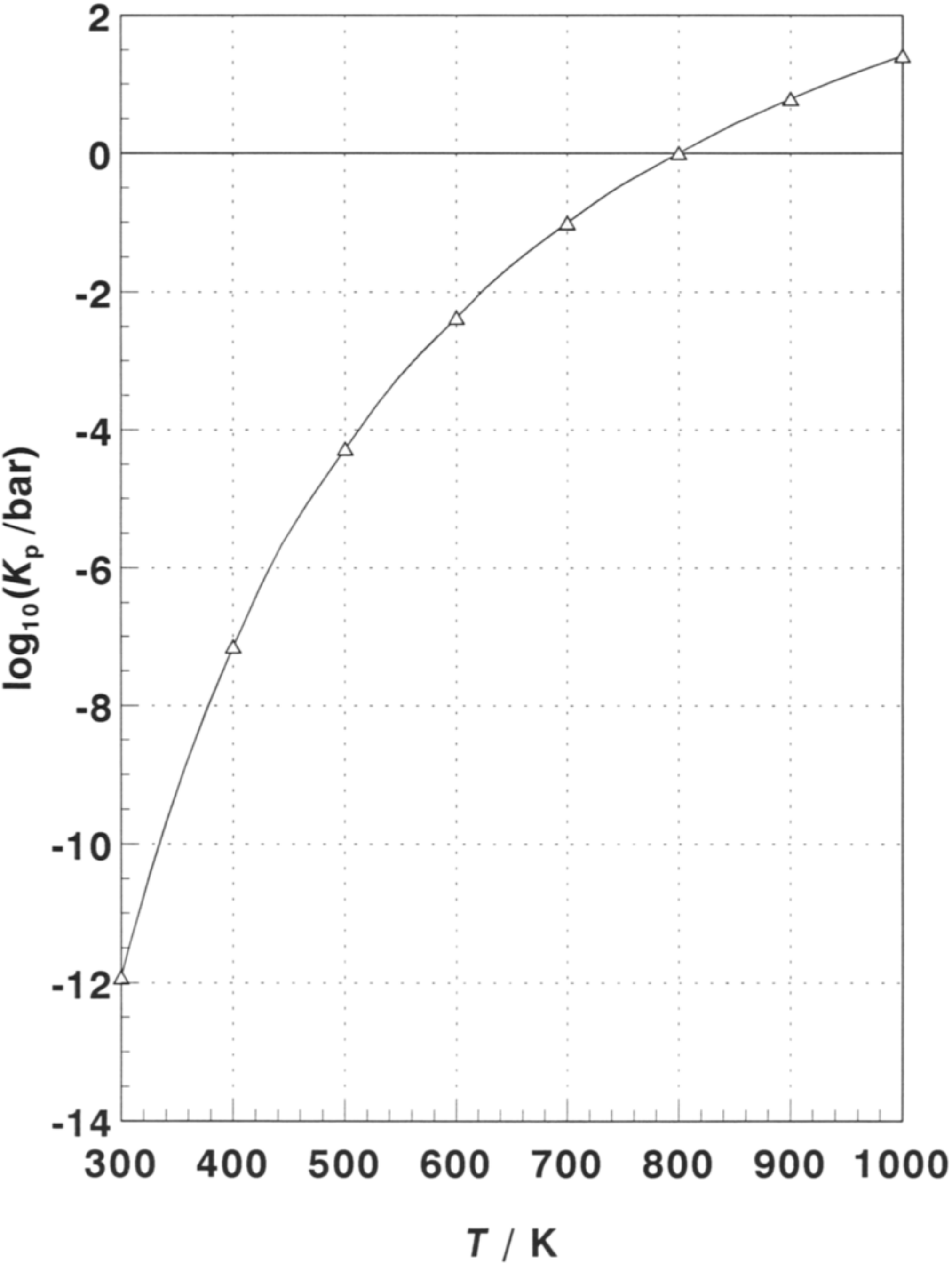

Fig. 8.3 The calculated [1825a] effect of temperature upon $\log_{10}(K_p/\text{bar})$ for the phosgene dissociation reaction, based on data from [359aa].

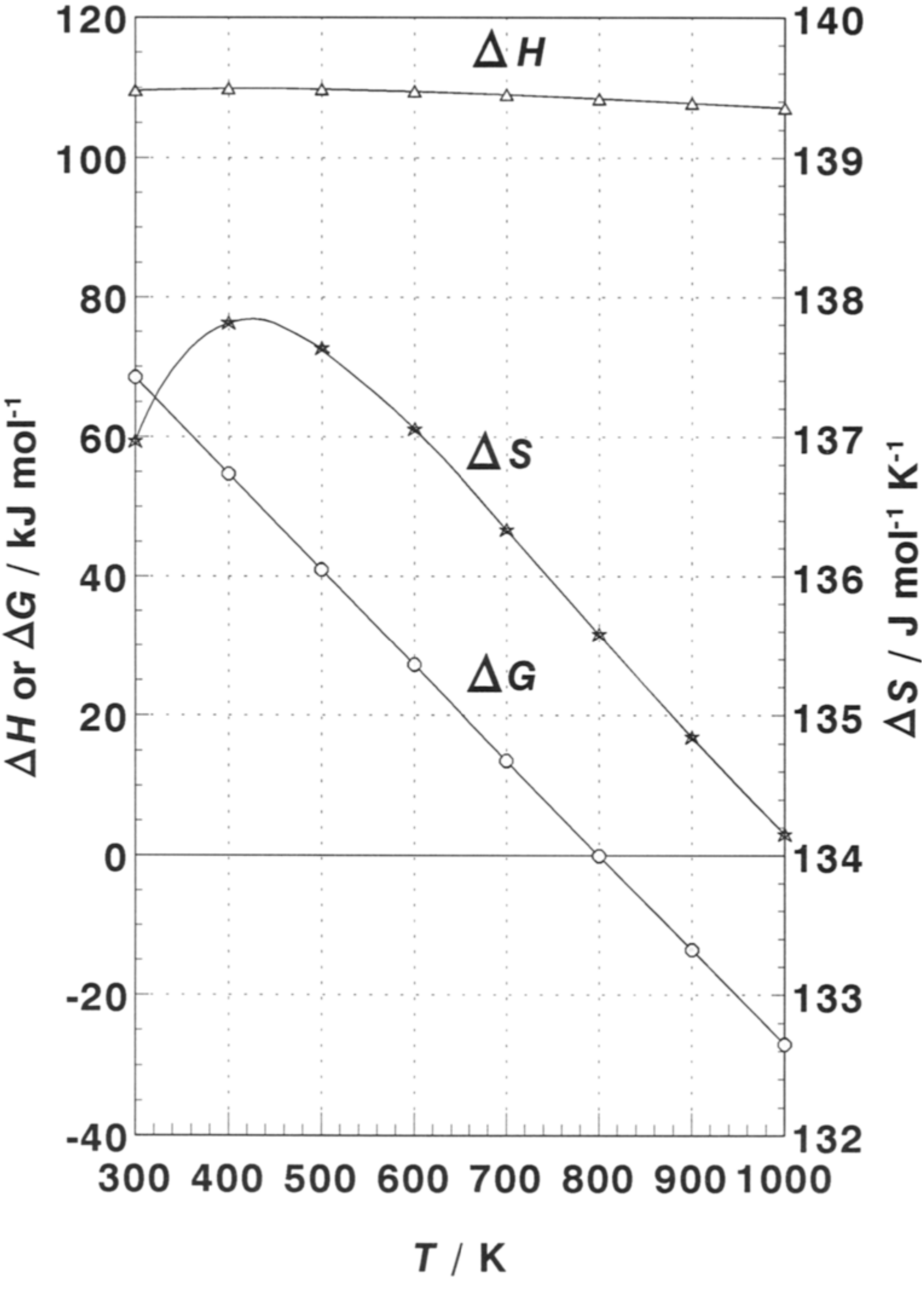

Fig. 8.4 Calculated [1825a] thermodynamic parameters for the phosgene dissociation reaction, based on data from [359aa].

TABLE 8.1

THERMODYNAMICS OF PHOSGENE DISSOCIATION AT 0.1 MPa [1825a]

T/K	ΔS/J mol^{-1} K^{-1}	ΔH/kJ mol^{-1}	ΔG/kJ mol^{-1}	K_p/bar
298.15	136.934	109.551	68.724	9.120×10^{-13}
300	136.967	109.561	68.471	1.198×10^{-12}
400	137.813	109.843	54.718	7.156×10^{-8}
500	137.630	109.757	40.942	5.283×10^{-5}
600	137.053	109.437	27.205	4.282×10^{-3}
700	136.333	108.969	13.536	9.771×10^{-2}
800	135.580	108.404	-0.060	1.009
900	134.846	107.780	-13.581	6.141
1000	134.150	107.119	-27.031	25.82

8.1.2 CO exchange

The exchange between CO and $COCl_2$ has been studied by ^{14}C-labelling of CO (see also Section 5.8.3) [1962,1963]:

$$^{14}CO + COCl_2 \rightleftharpoons CO + {}^{14}COCl_2;\quad K \tag{8.4}$$

The reaction mixture was brought to equilibrium by u.v. irradiation, and the equilibrium constants, K, were measured over a range of temperatures. The measured and calculated (from isotopic partition function ratios†) values of K are compared in Table 5.7: excellent agreement is observed [1962,1963]. From these data, the enthalpy of reaction (8.4) was estimated as −419 J mol^{-1} (*cf.* a calculated value of −414 J mol^{-1}) [1963]. Similar exchange reactions with ^{13}CO were performed, and some wavelength dependence of the achieved equilibrium position (ascribed to a carbon isotope effect) was observed [2135].

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†These values were taken from [1966]; a corrected value for ν_6^{14} was used [1962,1963], but see the footnote to Table 5.7.

8.2 DISMUTATION OF PHOSGENE

The dismutation reaction for phosgene is given in Equation (8.3), and is in competition with the dissociation reaction expressed by Equation (8.2).

The dismutation reaction is potentially of some industrial significance. One of the general methods for the manufacture of tetrachloromethane is the chlorination of methane [2165]:

$$CH_4 + 4Cl_2 \longrightarrow CCl_4 + 4HCl$$

This reaction not only discards half of the chlorine, but generates four moles of waste hydrogen chloride for every mole of product. Moreover, the reaction is not 100% selective. Thus, a preferred method of industrial manufacture uses propene as a feed-stock:

$$CH_3CH{=}CH_2 + 9Cl_2 \longrightarrow 3CCl_4 + 6HCl$$

This reaction, which proceeds at a higher temperature, discards only a third of the chlorine and generates two moles of hydrogen chloride per mole of product. If commercially practical, the dismutation of phosgene would use 100% of the chlorine, have a remarkably high selectivity and generate *no* waste hydrogen chloride. Moreover, the CO_2 co-produced could be reduced to CO in a syn-gas process {the Boudouard equilibrium; Equation (8.5) [2165]}, and used to generate phosgene in the reverse of reaction (8.2).

$$C + CO_2 \rightleftharpoons 2CO \qquad (8.5)$$

The dismutation equilibrium of Equation (8.3) has been examined, by studying the reverse reaction between CCl_4 and CO_2 between 628 and 718 K [1274a]: a value of ΔH of $-(63\pm11)$ kJ mol^{-1} is obtained for reaction (8.3) from the van't Hoff plot (see Fig. 8.5) [1274a]: a fuller data treatment yielded ΔH°_{298} as $-(70.5\pm1.5)$ kJ mol^{-1} [1274a]. However, examination of the scatter of the experimental data (see Fig. 8.5), and comparison of the experimental K_p and ΔH°_{298} values with those calculated from the JANAF tables (*vide infra*) must lead to the conclusion that Lord and Pritchard [1274a] did not reach equilibrium in their study, thus leading to a significant overestimate both of K_p and of ΔH°_{298}. A similar conclusion had been reached by the authors of an earlier equilibrium study [654], who concluded that there were indications of "the existence of an undetermined factor which prevents the reaching of the theoretical equilibrium". Their K_p data (see Fig. 8.5), nevertheless, appear more accurate than those determined in the modern study, as compared with the theoretical values. A new experimental study of this system, perhaps in the presence of a catalyst, is clearly required.

The thermodynamic parameters for Reaction (8.3) in the gas phase, as calculated from the JANAF Thermochemical Tables [359aa], are detailed in Table 8.2, and illustrated in

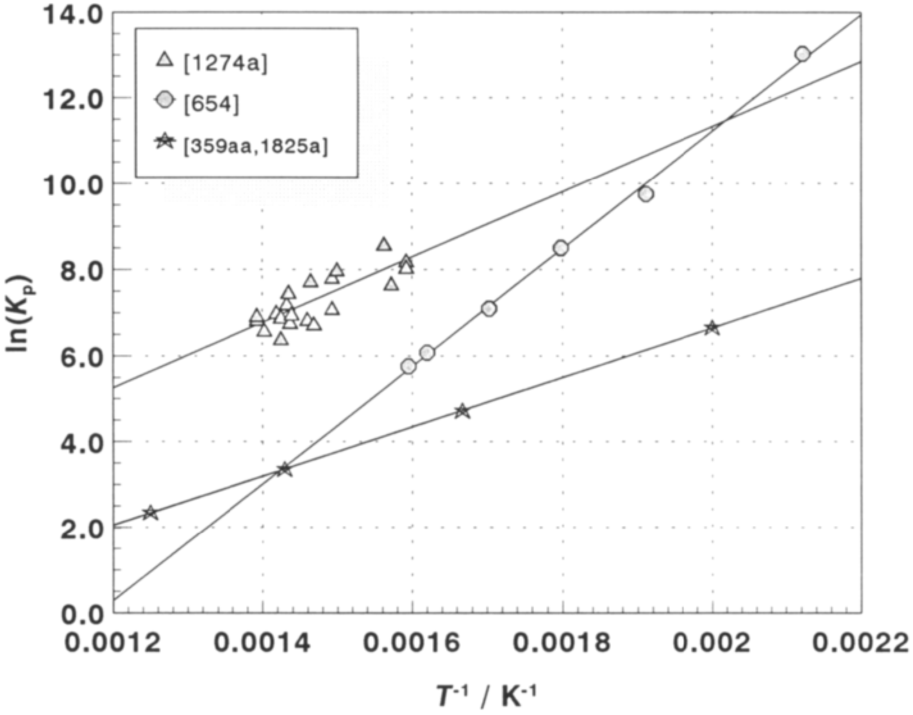


Fig. 8.5 **Empirical measurements of the equilibrium constant for Equation (8.3) [654,1274a] as a function of temperature, compared with calculated values [359aa,1825a].**

Figures 8.6 and 8.7 [1825a]. Taking into account reactions (8.2), (8.3) and (8.6), equilibrium

$$2COCl_2 \rightleftharpoons C + CO_2 + 2Cl_2 \qquad (8.6)$$

yields of CCl_4 from phosgene have been calculated as a function of temperature and pressure [ICI8,ICI9]: these results are summarised in Fig. 8.8. Examination of Figs. 8.6–8.8 shows (a) that dismutation is favoured at low temperature, and (b) that, at low temperatures, little advantage is to be gained by operating at high pressures. Moreover, it is clear that, upon thermodynamic grounds, phosgene dismutation is highly favoured.

Although the reverse of the dismutation reaction (see Section 5.4) was first observed experimentally in 1868 [1824a], when it was observed that phosgene was produced when carbon dioxide and tetrachloromethane vapour were passed over pumice heated to 350–400 °C, the forward reaction has proved more elusive (despite the overwhelmingly favourable thermodynamics). The potential value of the phosgene dismutation was recognised as early as

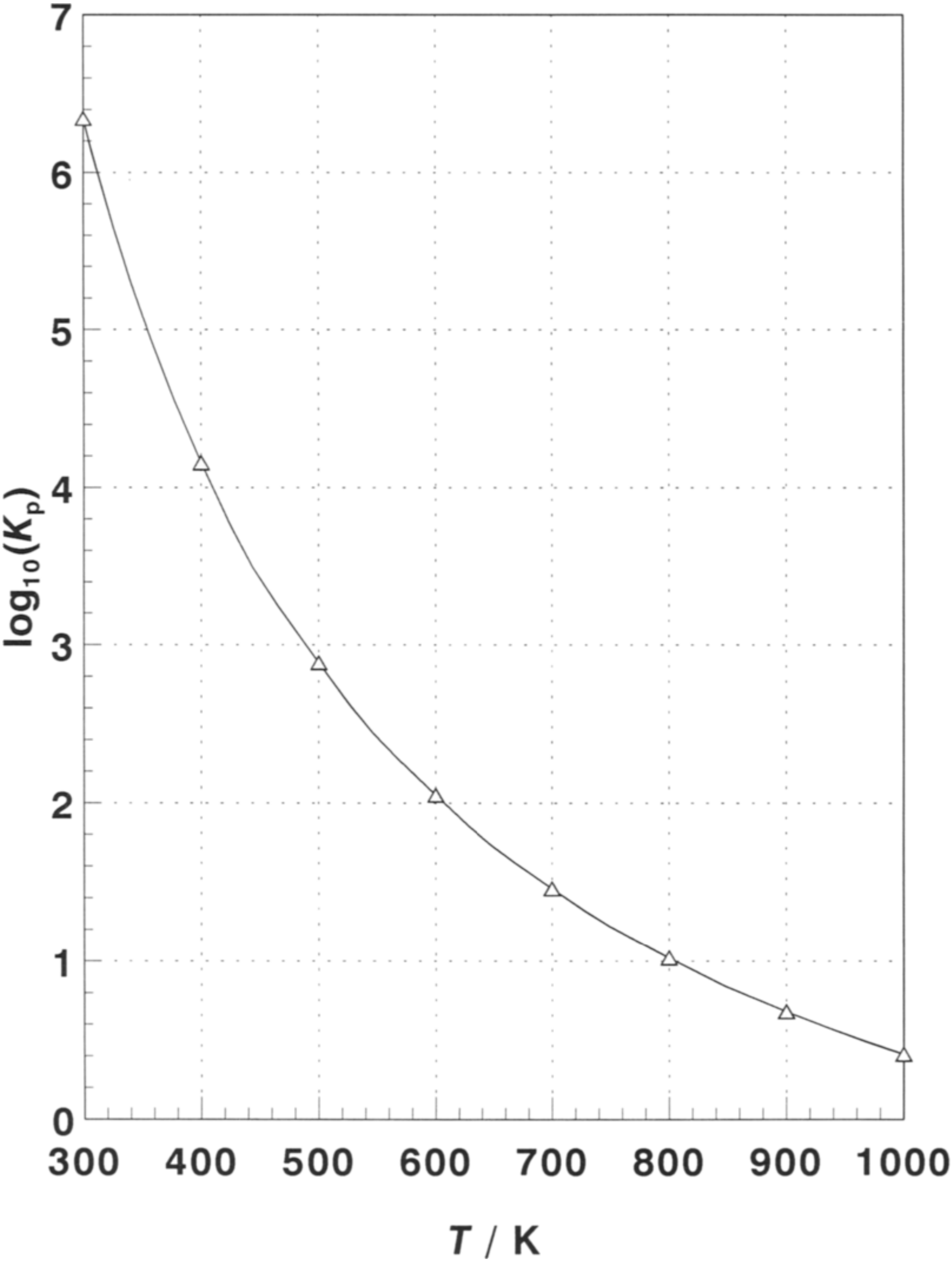


Fig. 8.6 The calculated [1825a] effect of temperature upon $\log_{10}(K_p)$ for the phosgene dismutation reaction, based on data from [359aa].

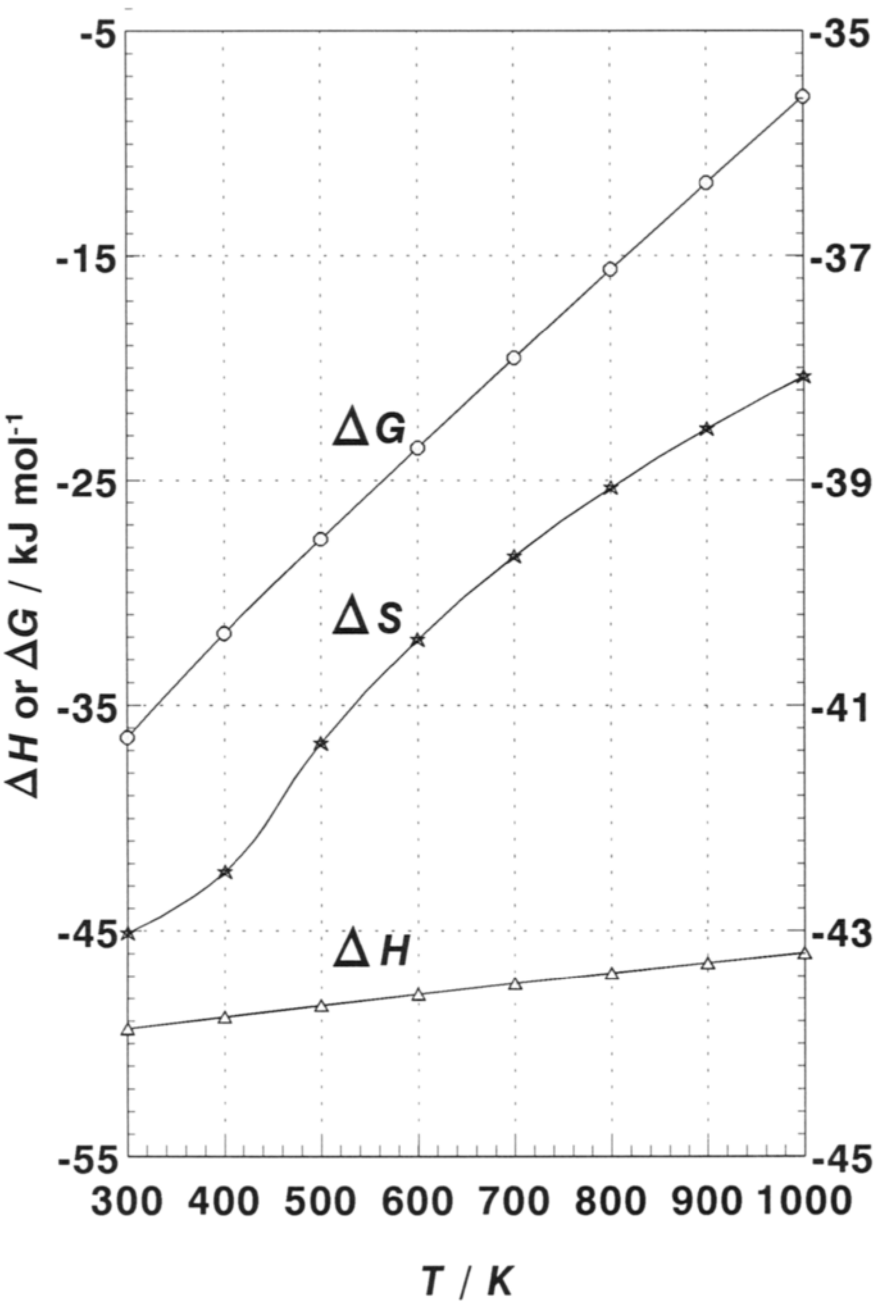


Fig. 8.7 The calculated [1825a] thermodynamic parameters for the phosgene dismutation reaction, based on data from [359aa].

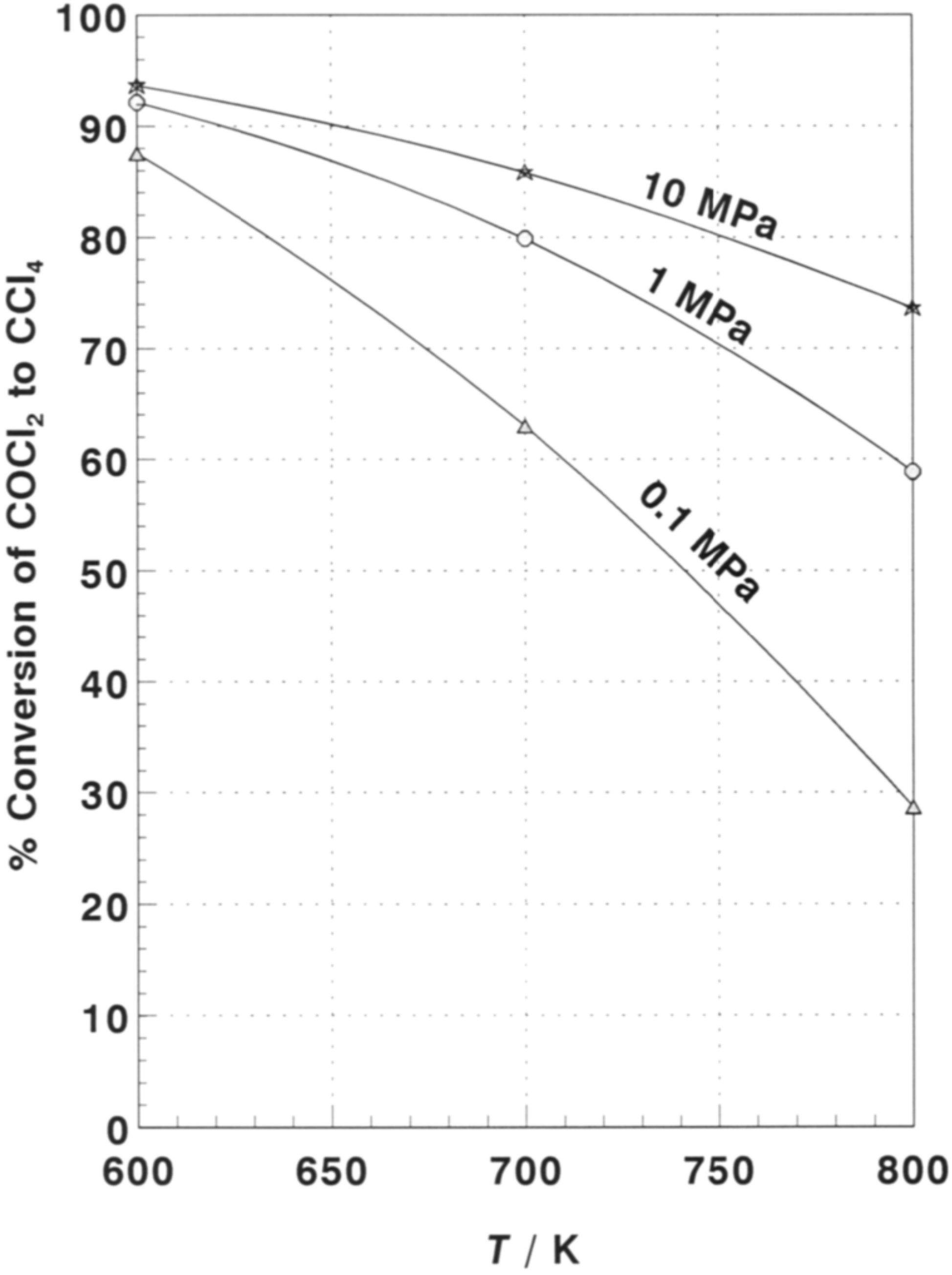


Fig. 8.8 The calculated effect of pressure and temperature upon the equilibrium yield of CCl_4 from the dismutation of phosgene [ICI8,ICI9].

TABLE 8.2

THERMODYNAMICS OF PHOSGENE DISMUTATION [1825a]

T/K	ΔS/J mol^{-1} K^{-1}	ΔH/kJ mol^{-1}	ΔG/kJ mol^{-1}	K_p
298.15	-43.971	-49.347	-36.237	2231000
300	-43.020	-49.337	-36.431	2203600
400	-42.478	-48.824	-31.833	14352
500	-41.338	-48.311	-27.642	772.16
600	-40.423	-47.811	-23.557	112.41
700	-39.681	-47.330	-19.553	28.778
800	-39.068	-46.870	-15.616	10.462
900	-38.542	-46.424	-11.736	4.799
1000	-38.079	-45.985	-7.906	2.588

1905, when a process for preparing tetrachloromethane from phosgene by "passing it through bone-black, coke or pumice" was patented [1289a]. In 1925 [1958], based upon early (somewhat erroneous) thermodynamic data, Stock and Wustrow predicted that reaction (8.3) was thermodynamically favoured at 400 °C. Nevertheless, Stock and coworkers [1957a,1958-1960], and a little later Fink and Bonilla [654], were unable to induce the dismutation thermally (although they claimed to have found traces of CCl_4 upon heating phosgene at 400 °C in the presence of activated charcoal), and concluded that the reaction "cannot take place to any detectable extent" at 400 °C. In 1957, a non-catalytic route from $COCl_2$ to CCl_4 was developed by Haszeldine's group [899-901,903] (see Section 9.1.4.2):

$$COCl_2 + PCl_5 \longrightarrow CCl_4 + POCl_3$$

The first genuine catalytic dismutation process was disclosed by Kung [1181,1182], using the Friedel-Crafts catalysts aluminium(III) chloride or iron(III) chloride. Thus, upon heating phosgene in a Carius tube in the presence of MCl_3 (M = Al, Fe or Bi) at 350-400 °C and 2.5-14.4 MPa, tetrachloromethane was produced in 80-86% yield: no CCl_4 was produced below 1 MPa [1181,1182]. This was rapidly followed by reports that activated charcoal loaded with molybdenum (with dichlorine present in the phosgene feedstock) [620a,ICI7] or with FeX_3 (X = Cl or F) [904], and a range of carbides (B, Si, Ti, Zr, Nb, Ta or V) [769], transition metals, or transition metal halides or oxohalides in the presence of active carbon [773a], also catalysed reaction (8.3), but at pressures approaching atmospheric. Of these, $MoCl_5$ and WCl_6 appeared to be the most effective. Thus, WCl_6/C catalysed the dismutation of phosgene at 500 °C ($COCl_2$ feed rate: 0.93 l h^{-1}) with a 60% conversion to CCl_4 [543,775]: the surface area of the catalyst was also shown to be an important factor [775]. Indeed, in this last process, a CO/Cl_2 mixture may replace phosgene [775]. Features of both these processes have been combined. Thus, heating phosgene (250–350 °C) in an autoclave (0.7–1.4 MPa) with a mixture of MCl_2 (M = Ca, Sr, Ba or Zn), $AlCl_3$ (which combines to give involatile $M[AlCl_4]_2$), and WCl_6 or $MoCl_5$ produces CCl_4 in good yields and high conversion [11,12]. The most convenient, efficient dismutation process to date was reported by Kopsch [1157,IC16], and is achieved by heating phosgene in a Carius tube containing a molten mixture of WCl_6 (or, less effectively, $MoCl_5$) and $FeCl_3$ (or $AlCl_3$) at 275–325 °C to produce CCl_4 with 80–90% conversions: other less propitious conditions for this reaction, including the addition of charcoal, have also been reported [1156a,IC13–IC15]. It should be borne in mind, however, that although the use of charcoal may lower the efficiency of the dismutation catalyst, it does enable the phosgene to be generated *in situ* from CO and Cl_2. The mechanisms by which WCl_6 and $MoCl_5$ catalyse the dismutation of phosgene are discussed in Section 9.2.3.

Although the catalytic dismutation of phosgene undoubtedly represents a valid and efficient process, current costings (when capital plant investment is considered) are unfavourable with respect to established technology. However, the economics of processes of this type are an irregular function of time: if new plant for CCl_4 is ever required (bearing in mind legislative environmental restrictions), a route based on phosgene dismutation will be a serious candidate.

8.3 PHOTOCHEMISTRY OF PHOSGENE

The electronic structure of phosgene has been discussed in some detail in Chapter 17, its photochemical synthesis is described in Section 5.1.1, and its photochemistry has been briefly discussed elsewhere [1551]. However, a brief summary of the pertinent properties would not be inappropriate at this juncture.

Phosgene, in its ground state, is planar and possesses C_{2v} symmetry: the ground electronic state is $\tilde{X}^1A_1$. The first electronic transition (in the near u.v.) is $^1A_1 \longrightarrow {}^1A_2$ ($n \longrightarrow \pi^*$), and has an absorption onset at 33551 cm^{-1}, reaching maximum absorption at 43100 cm^{-1}. The first excited state is pyramidal (C_s symmetry), with a considerably weakened CO bond. There have been six bands identified in the vacuum u.v., the maximum of the lowest energy of these occurring at 64700 cm^{-1}.

The relevant thermodynamic data are:

$$COCl_2 \longrightarrow CO + Cl_2$$

$$\Delta H = 1.09 \pm 0.03 \text{ eV}$$

$$= 105 \pm 3 \text{ kJ mol}^{-1}$$

$$\mathrm{COCl_2} \longrightarrow \mathrm{CO} + 2\mathrm{Cl}\cdot$$

$$\Delta H = 3.56 \pm 0.03 \text{ eV}$$
$$= 343 \pm 3 \text{ kJ mol}^{-1}$$

$$D_0(\mathrm{Cl{-}COCl}) = 3.3 \text{ eV}$$
$$= 318 \text{ kJ mol}^{-1}$$

8.3.1 Photolysis in the near u.v.

The photochemical dissociation of phosgene was first reported by Weigert in 1907 [2162]:

$$\mathrm{COCl_2} \xrightarrow{\lambda\ <\ 260\ \mathrm{nm}} \mathrm{CO} + \mathrm{Cl_2}$$

He noted that, although the decomposition of phosgene was greatly accelerated upon irradiation (between 420 and 510 °C), the position of equilibrium was not displaced, and concluded that the effect of the light was simply catalytic [2162], an observation later confirmed by Bodenstein and Onoda [219]. Less convincing was Weigert's theory of that catalytic action [2163]. The observation of the photodissociation of phosgene into carbon monoxide and dichlorine at room temperature soon followed [398].

In 1930, Henri and Howell [942] incorrectly assumed that the initial step of this reaction involved the formation of CO and 2Cl·. A few years later, Montgomery and Rollefson [1428] studied the kinetics of the photochemical decomposition of phosgene, and derived the rate law:

$$-\mathrm{d}[\mathrm{COCl_2}]/\mathrm{d}t = kI - k'I^{\frac{1}{2}}\,[\mathrm{CO}]^{\frac{1}{2}}\,[\mathrm{Cl_2}]$$

where I = light absorbed

This is consistent with the following simplified mechanism [1428]:

$$\mathrm{COCl_2} + h\nu \longrightarrow [\mathrm{COCl}]\cdot + \mathrm{Cl}\cdot$$
$$[\mathrm{COCl}]\cdot + \mathrm{Cl}\cdot \longrightarrow \mathrm{CO} + \mathrm{Cl_2}$$
$$[\mathrm{COCl}]\cdot + \mathrm{Cl_2} \longrightarrow \mathrm{COCl_2} + \mathrm{Cl}\cdot$$
$$\mathrm{CO} + \mathrm{Cl}\cdot + \mathrm{Cl_2} \longrightarrow [\mathrm{COCl}]\cdot + \mathrm{Cl_2}$$

This is also in reasonable accord with the mechanism of Lenher and Rollefson for the formation of phosgene [1226], and the full mechanism of this process is discussed at length in Section 5.1.1. The quantum yield for the process is essentially unity. This mechanism is believed to apply [1226] even for the small amount of dissociation induced by irradiation in the range 275–305 nm, below the predissociation limit [34,35]. The preliminary photodissociation step has been examined by *ab initio* methods [677a].

Under the conditions of flash photolysis, almost complete dissociation of phosgene into CO and Cl_2 can be induced, although no detectable photochemical reaction is induced between CO and Cl_2 under identical conditions [1523]: this has been ascribed to the very high radical concentrations present, and the high instantaneous temperatures which are generated [1523].

The results of Bradley and Tuffnell [251], who used a combined shock-tube flash-photolysis technique to study phosgene, showed a continuum absorption from 500 to 300 nm, with a molar extinction coefficient of *ca.* 280 l mol^{-1} cm^{-1}: this was ascribed to the presence of an excited state of ethanedioyl chloride [251]:

$$[COCl]\cdot + [COCl]\cdot \longrightarrow \{ClC(O)C(O)Cl\}^*$$

When phosgene is photolyzed in the presence of hydrocarbons, RH (*e.g.* cyclohexane), the chlorine radicals generated in the primary process abstract hydrogen to form HCl [1758]:

$$Cl\cdot + RH \longrightarrow HCl + R\cdot$$

However, R· does not appear to react with phosgene itself, although it will react with Cl_2 to give RCl and regenerate Cl· [1758]. Similar behaviour is observed when phosgene is photolyzed with dichloromethane (in the presence of octafluorocyclobutane, an inert deactivator) [2186]:

$$Cl\cdot + CH_2Cl_2 \longrightarrow HCl + [CHCl_2]\cdot$$

The dichloromethyl radicals combine to give a vibrationally excited state of 1,1,2,2-tetrachloroethane [2186].

Wijnen [2185,2185a] has proposed that the photolysis of phosgene provides an excellent source of chlorine atoms, and has studied the reactions between phosgene and ethene (Section 10.1.2) and phosgene and ethyne (Section 10.1.4) under photochemical conditions. No problems with secondary reactions of phosgene were encountered.

8.3.2 Photolysis in the vacuum u.v.

In contrast to the near u.v. photodissociation of phosgene described above, the photodissociation of phosgene in the vacuum u.v. creates dichlorine in an electronically excited state {which produces emission continua in the 50000–32260 cm^{-1} (200–310 nm) region} as the major primary process [576,1552,2240a]:

$$COCl_2 \xrightarrow{h\nu} CO + \{Cl_2\}^*$$

A two-quantum excitation of phosgene at 193 nm, although giving a total energy above the ionization limit, produces not only neutral Cl_2 in its first excited states, $^3\Pi_g$ and $^1\Sigma_u^+$, but also neutral CO in its v" = 7 $^1\Sigma^+$ ground electronic state [1084a,2194,2195].

8.3.3 γ-Photolysis

Phosgene does not decompose significantly upon γ-irradiation (^{60}Co source) [1204].

8.3.4 Photolysis in the infrared

The i.r. induced photodecomposition of $COCl_2$ with a CO_2 laser is sensitized by boron(III) chloride, and this phenomenon is discussed in detail in Section 9.1.2.2.

The photochemical dissociation of phosgene has been used as the basis of a chemical laser [1386]. When a mixture of $COCl_2$ and H_2/D_2 (which is unreactive in the ground state; see Section 9.7.1) is irradiated with the P_{54} line of a CO_2 laser in a laser cavity, HCl or DCl are produced in excited vibrational states, thus producing a chemical HCl or DCl laser. The P_{54} (1012 cm^{-1}) line of CO_2 is resonant with a phosgene combination band, $\nu_2+\nu_5$ (1011 cm^{-1}; see Table 7.2), causing the phosgene to dissociate, liberating CO and energetic chlorine atoms, which then react with the H_2/D_2 [1386]:

$$\{Cl\cdot\}^* + H_2 \longrightarrow \{HCl\}^* + H\cdot$$

$$\{Cl\cdot\}^* + D_2 \longrightarrow \{DCl\}^* + D\cdot$$

Isotope-selective photodissociation of phosgene has been achieved using the $P_{10}(22)$ transition (1822.0 cm^{-1}) of a tunable uncooled pulsed electroionization CO laser [3a]. By using a mixture of $^{12}C^{16}OCl_2$, $^{13}C^{16}OCl_2$ and $^{12}C^{18}OCl_2$ (in the ratio 10:10:1), a selectivity factor of four for $^{12}C^{16}OCl_2$ over $^{13}C^{16}OCl_2$ was achieved at 67 Pa; the selectivity decreased with increasing phosgene pressure [3a].

9 REACTIONS WITH INORGANIC COMPOUNDS

The reactions of phosgene with inorganic compounds have been the subject of a number of brief, or old, surveys [155,179,578,735,781,996,1378,1379,ICI20], but no comprehensive review has ever been published. By far the majority of the reactions studied are of either halides or oxides with phosgene, the latter reactions often being thermodynamically driven by the formation of carbon dioxide. Both these classes of reaction have important implications for the chemical industry, but perhaps the most interesting and novel chemistry now appearing concerns the reactions of phosgene with hydrides, amides and organometallics. The overall impression that one is left with is that of an iceberg: what is visible is interesting and sometimes fascinating, but what remains hidden is even more tantalizing.

As a codicil to this chapter, a section on phosgenite has been included. This mineral is, in fact, chemically unrelated to phosgene (although its name is eponymous), but its history is so reticulated with that of phosgene that no account of one would be complete without the other. In particular, it demonstrates the emotive force of the name phosgene: not only has this innocuous mineral, $Pb[CO_3].PbCl_2$, been arraigned for the thermal evolution of phosgene, but one crystallographer actually managed to find phosgene in the unit cell of the crystal. *Forsitan et nostrum nomen miscebitur istis* (Ovid).

9.1 MAIN GROUP HALIDES AND OXIDE HALIDES

9.1.1 Reactions of phosgene with Group 1 and Group 2 halides

The reaction between sodium fluoride and phosgene in liquid HCN produces COF_2, along with CO(CN)F (in 14% yield) [2068a,2070]. In contrast, phosgene reacts with a mixture of potassium fluoride and BrCN to give F_3CNCO [2210].

Phosgene reacts with a high temperature ionic liquid, LiF–NaF–KF, at 550 °C to give a mixture of COF_2 (70%), CO_2 (25%), SiF_4 (4–5%) and traces of COClF and unreacted $COCl_2$ [1978, 1979]. However, under far milder conditions, phosgene will react with anhydrous sodium fluoride in a polar solvent ($\epsilon > 20$, *e.g.* ethanenitrile, nitromethane, dimethyl sulfate, ethylene carbonate or tetrahydrothiophene-1,1-dioxide) at 30 °C to give high yields (*ca.* 80%) of pure COF_2 [631]:

$$COCl_2 + 2NaF \longrightarrow COF_2 + 2NaCl$$

In benzene, no COF_2 was formed [631]; with solid NaF and no solvent, small amounts (<20% at 525 °C) of COClF were formed [631,ICI26]. With solid potassium fluoride, the yields of COClF were even lower, but at short reaction times (*i.e.* high effective fluoride ion concentrations), large amounts of COF_2 were initially formed [ICI26].

The reaction of $Na_2[BeF_4]$ with phosgene is described in Section 9.4.2.

In 1956, it was reported that heating equimolar quantities of phosgene and calcium fluoride at 500 °C in a steel bomb gives CF_4 (1%), $CClF_3$ (65%), CCl_2F_2 (30%), CCl_3F (5%), a trace of CCl_4, and some COF_2 and COClF: the formation of the fluoromethanes is promoted by the presence of aluminium(III) fluoride, tin(IV) fluoride, iron(III) fluoride or antimony(V) chloride [1454]:

$$6COCl_2 + 4CaF_2 \longrightarrow 4CaCl_2 + CCl_2F_2 + 2CClF_3 + 3CO_2$$

If the temperature is lowered to below 400 °C, only COClF and COF_2 are formed [1454], and conditions may be optimized to give COClF with a selectivity in excess of 90% [ICI25].

The reaction between phosgene and a mixture of CaF_2 (fluorspar) and KCl at 500 °C and 3.45 MPa gives a mixture containing COF_2, COClF and unreacted $COCl_2$: the solid residue contained $CaCl_2.KCl$, and unreacted KCl and CaF_2, but no $CaF_2.CaCl_2$ (which ties up fluoride in an unreactive form and lowers overall conversions based on fluorspar) [1561]; similar results were obtained in a flow system, but with single-pass yields of COClF only approaching 10% [ICI27,ICI28]. In the presence of iron metal and dichlorine promoters, very high conversions (84%) were achieved [1561].

Phosgene reacts with lithium bromide in propanone to liberate bromine, which slowly reacts with the solvent to give the lachrymator, bromopropanone [1606,1606a].

Phosgene rapidly reacts with a solution of sodium iodide in propanone or ethyl ethanoate, according to [1606] (see also Section 3.2.1.2):

$$2NaI + COCl_2 \longrightarrow 2NaCl + CO + I_2$$

A similar reaction occurs between phosgene gas and solid potassium iodide [1606].

9.1.2 Reactions of phosgene with Group 13 halides

9.1.2.1 Reaction of phosgene with boron(III) fluoride

The two earliest reports of the $COCl_2$–BF_3 system are apparently contradictory: the earlier [738a] claims that phosgene and boron(III) fluoride interact to form compounds (but does not identify these in any way), the later [1329] suggests that phosgene and boron(III) fluoride do not form a complex, even at temperatures as low as −120 °C. However, a more detailed investigation [1329] resolved these anomalies. The phase diagram for the $COCl_2$–BF_3 system is illustrated in Fig. 9.1, and shows clear evidence for complex formation at compositions $BF_3.COCl_2$ (m.pt. −134.3 °C) and $BF_3.2COCl_2$ (m.pt. −137.0 °C) [1329].

Although there is an obvious structure for the 1:1 adduct, proposing a structure for $BF_3.2COCl_2$ is more problematic: the possibility of halide exchange occurring does not appear to have been considered.

9.1.2.2 Reaction of phosgene with boron(III) chloride

Boron(III) chloride is manufactured commercially by passing dichlorine over mixtures of B_2O_3 and carbon at *ca.* 1000–1200 °C, a process which results in the concomitant formation of phosgene. This phosgene impurity, present to a minimum level of 1000 p.p.m. (0.1%) in commercial boron(III) chloride, is unacceptable to the modern electronics industry, which uses boron(III) chloride as a source of boron for doping silicon *p*–type and in the production of fibre optics (to alter the optical and thermal properties of the glass). However, the similarity in vapour pressure, over a wide range of temperatures, between phosgene and boron(III) chloride (see Fig. 9.2) means that physical separation of the components is practically impossible (but see [1845]). Much of the recent research described in this Section is aimed at finding an efficient separation technique.

Phosgene and boron(III) chloride are miscible in all proportions [1329], as predicted earlier [738a] and the phase diagram for the $COCl_2$–BCl_3 system (Fig. 9.3) reveals a eutectic point at −142.3 °C (74.4 mole % $COCl_2$) and no evidence for any complex formation. Moreover, the vapour pressure – composition isotherm (0 °C) for this system (Fig. 9.4) shows a positive deviation from Raoult's law (although Henry's law appears to be well obeyed [649]), indicating the presence of unfavourable interactions between phosgene and boron(III) chloride [376]. Thus, the purification of boron(III) chloride from traces of phosgene will not be complicated by the formation of a thermodynamically stable complex.

Infrared irradiation of gaseous BCl_3, containing a $COCl_2$ impurity, with a 100 W cw CO_2 laser for less than five seconds led to the essentially complete dissociation of the $COCl_2$ (i.r. monitoring) without appreciable loss of BCl_3 [1388,1389]. Even when the phosgene is present in a ten-fold excess over the boron(III) chloride, a 20 s irradiation depletes the phosgene (concomitant carbon monoxide and dichlorine formation is observed). However, irradiation of pure phosgene with the CO_2 laser results in no change in its concentration. It was proposed that the boron(III) chloride acts as an i.r. sensitizer for the removal of the phosgene. The laser radiation (P_{20} line; 944.18 cm^{-1}) is absorbed by the ν_3 fundamental of BCl_3 at 956 cm^{-1} ($COCl_2$ has no fundamental absorptions in this region), and this process is followed by an intramolecular vibrational–vibrational energy transfer (from ν_4 of BCl_3 at 243 cm^{-1} to ν_5 of $COCl_2$ at 240 cm^{-1}), resulting in a sensitized dissociation of $COCl_2$ into CO and Cl_2 [1388,1389]. These results were independently supported [98,1244], and a threshold power of 2.5 W determined. More recently, a third group of workers has suggested that the phosgene dissociation is thermally induced, and does not involve a vibrationally controlled chemical process, as chopping the laser beam (P_{18} line; 946 cm^{-1}; 10 W) considerably reduced the extent of decomposition of the phosgene observed [1715]. Dissociation of phosgene has also been induced by electrical discharge or radio-frequency

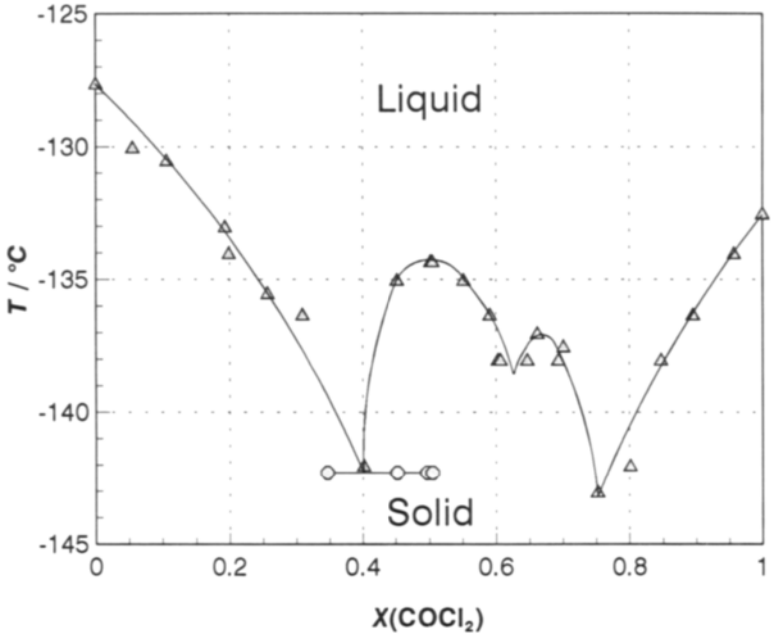


Fig. 9.1 A phase diagram for the $COCl_2$–BF_3 system [1329].

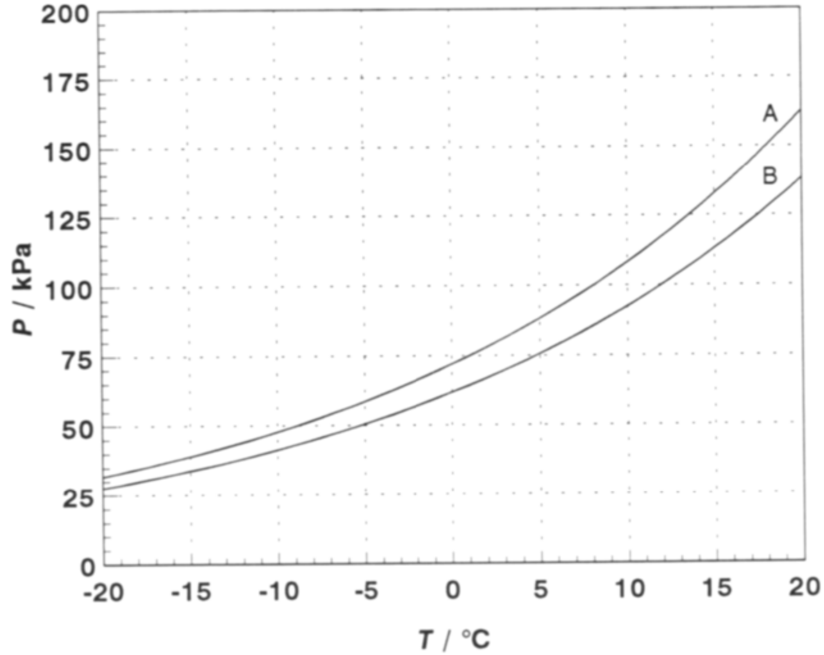


Fig. 9.2 The vapour pressure of (A) phosgene and (B) boron(III) chloride, as a function of temperature (data from [649]).

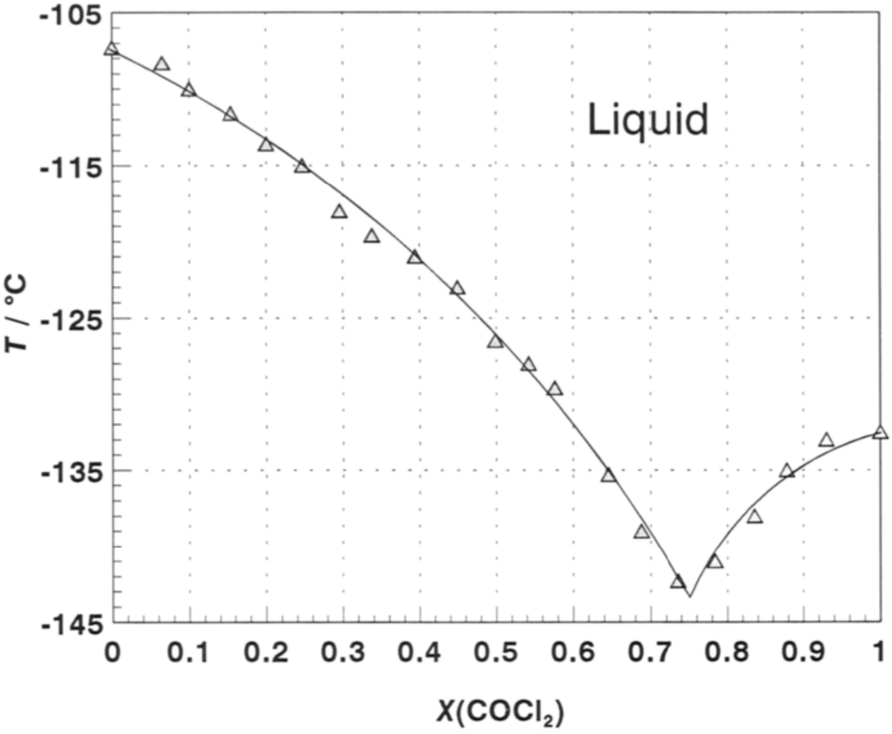


Fig. 9.3 A phase diagram for the $COCl_2$–BCl_3 system [1329].

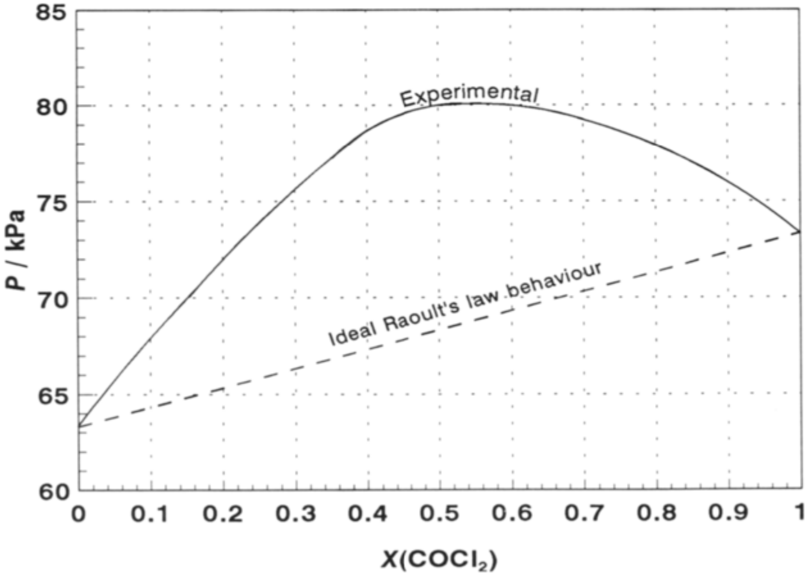


Fig. 9.4 A vapour pressure composition diagram (0 °C) for the $COCl_2$–BCl_3 system [376].

excitation of the gas phase mixture [1391].

An alternative approach to the problem of purifying BCl_3 is to induce photochemical dissociation of the phosgene by irradiation with u.v. radiation from a KrF excimer laser or a more conventional unfiltered mercury arc lamp [685,1001,1002]: boron(III) chloride absorbs at $\lambda < 210$ nm ($\tilde{\nu} > 47619$ cm^{-1}), whereas $COCl_2$ undergoes predissociation at $\lambda < 275$ nm ($\tilde{\nu} > 36364$ cm^{-1}). The experiments were performed both in liquid krypton (−153 °C) and in the gas phase at ambient temperature, and a quantum yield, Φ, of approximately unity was determined for the process (indicating excellent photon utilization and a high selectivity for $COCl_2$ in the presence of BCl_3) [1001,1002]. As found in the i.r. experiments (*vide supra*), commercial BCl_3 can be highly purified in relatively short time periods by u.v. photolysis.

More conventional techniques have also been applied to the problem. Thus, a number of papers have appeared describing gas chromatographic determination of the phosgene impurity levels [14,2071,2250], and a recent report describes the use of Fourier transform mass spectrometry [1692a].

A process for the removal of phosgene by passing the vaporized mixture, with a stoicheiometric quantity of dihydrogen (based upon $COCl_2$), over a carbon catalyst under anhydrous conditions, at 300−700 °C, has been patented [390]. Phosgene has also been removed from boron(III) chloride by passing over copper at 500 °C [1218a], titanium at 350−400 °C [1950a] or boron at 550 °C [1950a], or by passing through zeolites (−80 to +150 °C) [955a]. Finally, new methods of producing boron(III) chloride with lower impurity levels of phosgene are being examined [500,1710a].

9.1.2.3 Reaction of phosgene with boron(III) bromide

In 1895, Besson treated boron(III) bromide with phosgene for 12 h at 150 °C to yield a mixture of $COBr_2$ (b.pt. 63−66 °C) and COClBr (b.pt. 35−37 °C) [184]. However, Von Bartal [2126,2127] and Brochet [2127] both found that they could obtain neither $COBr_2$ nor COClBr from this procedure.

9.1.2.4 Reaction of phosgene with aluminium(III) fluoride

Aluminium(III) fluoride is insoluble in liquid phosgene, and does not appear to react with it, even upon heating under pressure [2128].

9.1.2.5 Reaction of phosgene with aluminium(III) chloride

The interaction between phosgene and aluminium(III) chloride is, perhaps, the most studied Lewis acid−base reaction of phosgene. Nevertheless, the results of these studies are rather inconclusive.

The first report of adduct formation in the $COCl_2$−$AlCl_3$ system was by Baud, and complexes of stoicheiometry $2AlCl_3.5COCl_2$ (m.pt. −2 °C; vapour pressure of 101.325 kPa at 30 °C), $2AlCl_3.3COCl_2$ (m.pt. 9 °C; vapour pressure of 101.325 kPa at 55 °C) and $4AlCl_3.COCl_2$ (solid; decomposes at 150 °C) were claimed [140a]. This work, however, is certainly in error (*vide infra*).

$$COCl_2 \rightleftharpoons [CO]^{2+} + 2Cl^- \tag{9.1}$$

$$COCl_2 \rightleftharpoons [COCl]^+ + Cl^- \tag{9.2}$$

An extensive study of solutions of aluminium(III) chloride in liquid phosgene (in which it is extremely soluble) by Germann and coworkers [735–741,743,745,746] (which is discussed in more detail in Chapter 11) came to the overall conclusion that phosgene exhibits a self-ionization, equation (9.1), and that $2AlCl_3.COCl_2$, say, would best be described as $[CO][Al_2Cl_8]$. These conclusions, even allowing for the more reasonable self-ionization described by equation (9.2) which would imply that $AlCl_3.COCl_2$ might best be described as $[COCl][AlCl_4]$, must now be regarded as erroneous, since the excellent work of Huston [997] showed that such self-ionization is highly improbable. Using labelled aluminium(III) chloride, the following reaction was studied [997,998]:

$$COCl_2 + Al^{36}Cl_3 \rightleftharpoons COCl^{36}Cl + AlCl^{36}Cl_2$$

Although somewhat concentration dependent (owing, in no small part, to the presence of HCl impurities), a typical half-life for this exchange is *ca.* 60 h at 0 °C [997,998]. The exchange is homogeneous, is not photochemical in origin, and the addition of NaCl or MCl_2 (M = Ca, Sr or Ba) does not appear to catalyse it [997,998]. Moreover, the dissolution of $Ca^{36}Cl_2$ in a solution of aluminium(III) chloride in phosgene leads to the formation of $[AlCl_3{}^{36}Cl]^-$, but not to any enhancement of the rate of formation of labelled phosgene [997,998]. Thus,

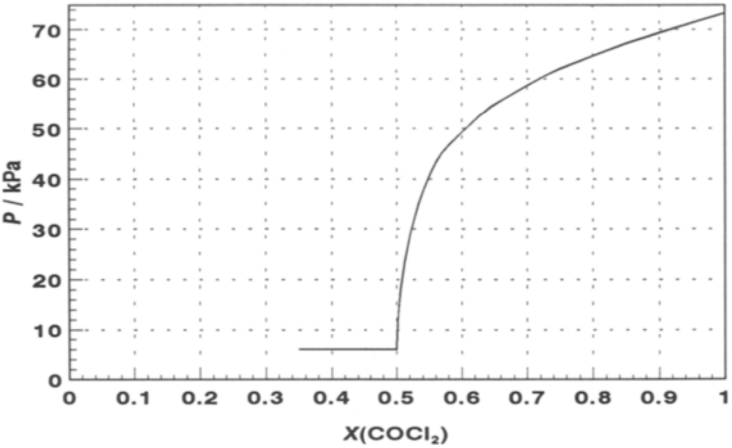


Fig. 9.5 A vapour pressure composition diagram (25 °C) for the $COCl_2$–$AlCl_3$ system [376].

self-ionization can play no part in the formulation of any $AlCl_3$-$COCl_2$ adduct. It should be noted, however, that $[COCl]^+$ has been observed in the presence of the stronger Lewis acid, SbF_5 (see Section 9.1.4.4).

Huston's work [997] also indicated that the reaction between aluminium(III) chloride and $COCl_2$ resulted in the formation of the 1:1 adduct, $AlCl_3.COCl_2$, which readily loses phosgene *in vacuo* at room temperature to yield pure aluminium(III) chloride. This was later confirmed independently by tensimetric titration (see Fig. 9.5) [376], and the i.r. spectrum (see Table 9.1) of the white product (m.pt. 25 °C; dissociation pressures of 4.8 kPa at 0 °C and 58.66 kPa at 25 °C) indicated that the phosgene was *O*-bonded, *viz.* $[Cl_2C{=}O{\longrightarrow}AlCl_3]$, and that no $[AlCl_4]^-$ was present [376]. From the data in this paper, the enthalpy of dissociation of the adduct can be calculated:

$$AlCl_3.COCl_2(s) \rightleftharpoons AlCl_3(s) + COCl_2(g); \qquad \Delta H = +67.8 \text{ kJ mol}^{-1}$$

However, an independent study [1049] of the i.r. spectrum of the product (Table 9.1), whilst reaching the same conclusions concerning the structure of the adduct, contained significantly different vibrational frequencies. To further complicate the situation, a third study [1012] found the 1:1 adduct to be a yellow-brown viscous liquid, which decomposed at room temperature to give $Al_2Cl_6.COCl_2$: the i.r. spectrum of this product (Table 9.1) is different again from the other reports.

TABLE 9.1

I.R. DATA FOR THE $AlCl_3$-$COCl_2$ SYSTEM

Assignment	Free $COCl_2(g)^a$	$AlCl_3.COCl_2^b$	$AlCl_3.COCl_2^c$	$Al_2Cl_6.COCl_2^d$
$\nu(C{=}O)/cm^{-1}$	1827	1635	1715	1620
$\nu_{as}(CCl_2)/cm^{-1}$	849	981		855,840
$\pi(COCl_2)/cm^{-1}$	580			
$\nu_s(CCl_2)/cm^{-1}$	570	690		565
$\delta_{as}(OCCl)/cm^{-1}$	440		396	440
$\delta_s(OCCl)/cm^{-1}$	285		344	
$\nu_{as}(AlCl_3)/cm^{-1}$	-	498	543	535
$\nu_s(AlCl_3)/cm^{-1}$	-		430	480

[a] See Chapter 7. [b] Dry powder [376]. [c] C_2Cl_4 solution in the presence of an excess of $COCl_2$ [1049].
[d] Nujol [1012].

Examination of the i.r. spectra of solutions of aluminium(III) chloride with competing ligands has led to the following series of ligand strengths, with phosgene notably the weakest of those studied [1050]:

$$COCl_2 < MeNO_2 < PhNO_2 < PhCOCl < Me_2O < Ph_2CO < Et_2O < MeCOOH < MeCN < Cl^-$$

The following reaction (ΔG°_{298} = +180 kJ mol^{-1}), not surprisingly, does not proceed at temperatures up to 540 °C [654]:

$$3COCl_2(g) + Al_2Cl_6(g) \longrightarrow 3CCl_4(g) + Al_2O_3(s)$$

It has been reported that passing a mixture of carbon monoxide and dichlorine through a solution of aluminium(III) chloride in trichloromethane at 30–35 °C results in the catalytic formation of phosgene [1628]. Experiments in our own laboratories [1589b] show that there is no observable reaction in the dark, and that, in daylight, the presence of aluminium(III) chloride solution had no detectable effect.

Thus, over a period of eighty years, no single study of the $COCl_2$–$AlCl_3$ system has agreed with any other: clearly, a fresh examination of the problem is required. However, the interaction between aluminium(III) chloride and phosgene has formed the basis of two patents for the purification of aluminium(III) chloride by removal of iron(III) chloride impurities, which apparently are not soluble in the $COCl_2$–$AlCl_3$ system [174b,2199a].

Aluminium(III) chloride is obviously a powerful Friedel–Crafts catalyst in reactions between phosgene and aromatic hydrocarbons: these reactions are discussed in the appropriate sections of Chapter 10.

9.1.2.6 Reaction of phosgene with aluminium(III) bromide

Aluminium(III) bromide is very soluble in liquid phosgene, and the earliest study of the $COCl_2$–$AlBr_3$ system found that either prolonged exposure to sunlight or heating the solutions in a sealed tube at 100–150 °C caused decomposition to CO and Br_2 [184]. Von Bartal [2127], however, found that passing $COCl_2$ through molten aluminium(III) bromide at 100 °C allowed very small quantities of $COBr_2$ to be observed in a distillate which was predominantly free bromine; the residue was found, after vacuum sublimation, to consist largely of aluminium(III) bromide dichloride:

$$AlBr_3 \xrightarrow[100\ ^{\circ}C]{COCl_2} AlCl_2Br + Br_2 + CO\ (+\ COBr_2)$$

The treatment of aluminium(III) bromide with an excess of phosgene at salt–ice temperatures gives an initial 'lively' reaction which, upon warming to 15 °C, proceeds in a vigorous second stage to give COClBr [2127]:

$$AlBr_3 + 3COCl_2 \longrightarrow AlCl_3 + 3COClBr$$

This reaction clearly proceeds *via* an unstable low temperature intermediate, probably $[Cl_2CO \rightarrow AlBr_3]$, which decomposes at 15 °C [2127].

9.1.2.7 Reaction of phosgene with aluminium(III) iodide

Solid aluminium(III) iodide reacts explosively with liquid phosgene, but less violently with a CS_2 solution of $COCl_2$ to give aluminium(III) chloride, iodine, and carbon dioxide [2128]. When phosgene is passed into a solution of AlI_3 in CS_2, the products also include aluminium(III) dichloride iodide [2128]. Passage of phosgene through molten aluminium(III) iodide gave a compound reported as "$Al_2(CO)_2.AlCl_2I$" [2128].

9.1.2.8 Reaction of phosgene with gallium(III) chloride

A preliminary study of the $COCl_2$–$GaCl_3$ system, by tensimetric titration at both 0 °C and −35 °C, indicates the formation of a 2:1 adduct, which dissociates without any evidence for the formation of a 1:1 complex [ICI1]:

$$GaCl_3.2COCl_2(s) \rightleftharpoons GaCl_3(s) + 2COCl_2(g); \qquad \Delta H = +25 \text{ kJ mol}^{-1}$$

9.1.3 Reactions of phosgene with Group 14 halides and oxide halides

9.1.3.1 Reaction of phosgene with carbon halides and oxide halides

The dismutation of phosgene and its related reaction with carbonyl difluoride are discussed in Section 8.2 and Chapter 13. Its reactions with $CO(NCE)_2$ (E = O or S) are described in Section 9.1.7.

Attempts to prepare diphosgene (trichloromethyl chloroformate) or triphosgene (hexachloromethyl carbonate) from phosgene were not successful [973,978a]. In one case, no experimental detail was given [973], whilst in the other case attempts were made to dimerise phosgene by contacting with aluminium(III) oxide or iron(III) oxide, or by exposure to u.v. light whilst cooling to 0 °C [978a]. Curiously, the conversion of thiophosgene, $CSCl_2$, into $Cl_3CSC(S)Cl$, is a simply accomplished transformation, and it is not known why a similar reaction does not occur with $COCl_2$ [978a].

The enthalpy of polymerization of phosgene has been calculated to be −69.5 kJ mol^{-1} under ambient conditions [985a]. Since the free energy of polymerization is always more positive than the corresponding enthalpy by about 40–80 kJ mol^{-1} (owing to the unfavourable entropy considerations), the possibility for phosgene polymerization is just about borderline on thermodynamic grounds [985a]. This contrasts with the ready polymerisation of the isoelectronic 1,1-dichloroethene and the structurally-related methanal (formaldehyde).

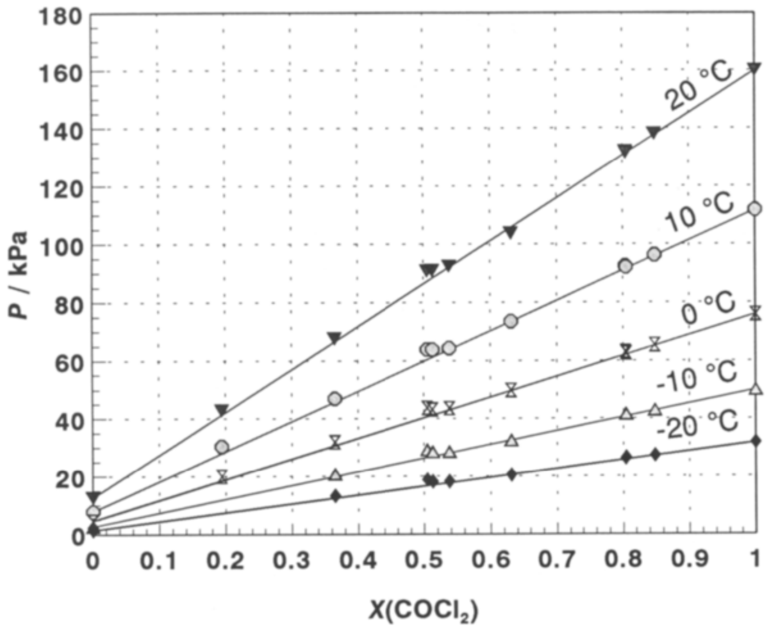


Fig. 9.6 **Vapour pressure – composition isotherms for the $COCl_2$–CCl_4 system [ICI2]. The lines represent the ideal Raoult's law behaviour; most points show a small positive deviation.**

Despite the possibly unfavourable thermodynamics for phosgene polymerization, it may be possible to prepare polyphosgene by alternative routes. Poly(carbonyl fluoride), for example, has been prepared from the reaction of tetrafluoroethene with trioxygen (ozone) (see Chapter 13). Alternatively, the co-polymerisation of phosgene with, for example, alkenes may be worthy of investigation [ICI94].

Tetrachloromethane is an important solvent for phosgene, and vapour pressure – composition isotherms for this system are illustrated in Fig. 9.6 [ICI2]. These curves show, as expected, a slight positive deviation from Raoult's law. Earlier, less reliable, data are discussed in Section 6.6.

The presence of low levels of phosgene has been shown to activate the thermoluminescence of tetrachloromethane [187].

9.1.3.2 Reaction of phosgene with silicon halides

Silicon(IV) fluoride reacts in a quartz tube with phosgene to give carbonyl chloride fluoride with 100% selectivity and 42% conversion, at 420 °C: no COF_2 is formed [377].

An equimolar solution of silicon(IV) chloride and phosgene in tetrachloromethane showed no evidence for complex formation, as monitored by infrared spectroscopy [ICI1]. Indeed, i.r. spectroscopy has been used to determine phosgene levels in commercial $SiCl_4$

[2058], and phosgene impurities have been removed from silicon(IV) chloride by passing over titanium slag or a mixture of zirconium(IV) silicate and coke at 800 °C [1870].

As silicon(IV) oxide is the only common oxide which is not chlorinated by phosgene (see Section 9.4.4) [360], the reaction between phosgene and silicon(IV) chloride was examined both experimentally and theoretically [654]:

$$2COCl_2(g) + SiCl_4(g) \longrightarrow 2CCl_4(g) + SiO_2(s)$$

Heating the reagents in sealed tubes up to 540 °C, in the dark and under a mercury lamp, provided no evidence for this reaction proceeding to any significant extent, not too surprising considering ΔG°_{298} is +50.54 kJ mol^{-1}, a value which will increase with increasing temperature. It was calculated that the reaction might proceed at 25 °C at pressures in excess of 75 MPa [654].

9.1.3.3 Reaction of phosgene with tin halides

The reaction between tin(II) chloride and phosgene has been investigated tensimetrically between 27 and 377 °C: the reaction starts at 262 °C and has an activation energy of 86 kJ mol^{-1} [1187]:

$$SnCl_2 + COCl_2 \longrightarrow SnCl_4 + CO$$

The following reaction (ΔG°_{298} = +235 kJ mol^{-1}) was unsuccessfully attempted [654]:

$$2COCl_2(g) + SnCl_4(g) \longrightarrow 2CCl_4(g) + SnO_2(s)$$

Phosgene is a common impurity found in commercial tin(IV) chloride, and impurity levels have been determined by gas chromatography – mass spectrometry [1515,2257]. Tin(IV) chloride dissolves in phosgene at <−78 °C; removal of the excess of $COCl_2$ at −45 °C led to the isolation of a pale yellow liquid, $[SnCl_4(OCCl_2)_2]$, which decomposes slowly at room temperature back to $SnCl_4$ and $COCl_2$ [1012]. No evidence for a 1:1 complex was found. The 2:1 complex exhibits i.r. bands (Nujol) corresponding to ν(C=O) at 1805 cm^{-1}, $\nu_{as}(CCl_2)$ at 835 cm^{-1}, $\pi(COCl_2)$ at 580 cm^{-1}, $\nu_s(CCl_2)$ at 570 cm^{-1}, δ_s(OCCl) at 300 cm^{-1}, and $\nu(SnCl_4)$ at 359 cm^{-1}, and these bands are only slightly shifted from those of free $COCl_2$ (*cf*. Table 9.1) [1012].

9.1.4 Reactions of phosgene with Group 15 halides

All of the chemistry described in this Section consists of either simple halide exchange reactions (for the formation of other carbonyl halides) or deoxohalogenation reactions (for the formation of perhalomethanes), with the exceptions of the weak adduct formation observed for antimony(V) chloride and dioxide chloride.

9.1.4.1 Reaction of phosgene with nitrogen halides

There are two parallel reactions between phosgene and nitrogen(III) fluoride [771]:

$$3COCl_2 + 2NF_3 \longrightarrow 3COF_2 + 3Cl_2 + N_2$$

$$6COCl_2 + 2NF_3 \longrightarrow 6COClF + 3Cl_2 + N_2$$

At 400 °C in a nickel tube, a 1:1 mixture of $COCl_2$ and NF_3 yields carbonyl difluoride with 100% selectivity, but at 360 °C a mixture of COF_2 (85%) and COClF (15%) is formed. At 310 °C, a 2:1 mixture of $COCl_2$ and NF_3 gives COF_2 (35%) and COClF (65%) [771].

9.1.4.2 Reaction of phosgene with phosphorus halides

Phosgene reacts with phosphorus(V) chloride in an autoclave at 300–400 °C to give tetrachloromethane, with a 60–70% conversion [899-901,903]:

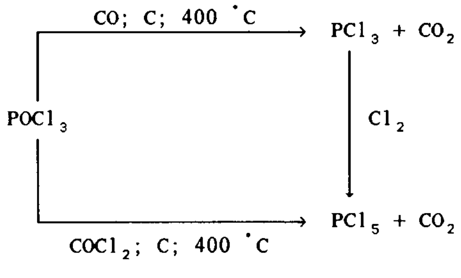
$$COCl_2 + PCl_5 \longrightarrow CCl_4 + POCl_3$$

This reaction has been adapted by pressurizing a mixture of CO and Cl_2 in the presence of a carbon catalyst (impregnated with iron and nickel chlorides) and a less than molar ratio of PCl_3: at 400 °C, it produces CCl_4 in 48% conversion based on carbon monoxide and 96% based on PCl_3 [900,903]. The reaction sequences involved are:

$$CO + Cl_2 \longrightarrow COCl_2$$

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

$$COCl_2 + PCl_5 \longrightarrow CCl_4 + POCl_3$$



The overall reaction is, in effect, the catalysed dismutation of phosgene (see also Chapter 8):

$$2CO + 2Cl_2 \longrightarrow 2COCl_2 \xrightarrow{PCl_3} CCl_4 + CO_2$$

The following related reactions have also been claimed in a patent [903]:

$$COCl_2 + PF_5 \longrightarrow CCl_2F_2 + POF_3$$

$$COCl_2 + PF_3Cl_2 \longrightarrow CCl_4 + POF_3$$

$$COCl_2 + PBr_5 \longrightarrow CCl_2Br_2 + POBr_3$$

$$COCl_2 + PF_3Br_2 \longrightarrow CCl_2Br_2 + POF_3$$

9.1.4.3 Reaction of phosgene with arsenic halides

The reaction of phosgene with arsenic(III) fluoride was reported, in 1920 [1947], to produce COF_2 (albeit in small yields and impure). In 1965, treatment of AsF_3 with an excess of $COCl_2$ (in the presence of catalytic amounts of $SbCl_5$) at 130 °C and 5.5 MPa was shown to produce COClF in 89% yield (with 4% COF_2 and 7% unreacted phosgene) [378]. The reaction between AsF_3 and $COCl_2$, when carried out at 500 °C in an autoclave, produces $CClF_3$ (85%), CCl_2F_2 (10%), along with traces of CF_4 and CCl_4 [1454]. The predominant reaction proceeds according to:

$$2COCl_2 + AsF_3 \longrightarrow CClF_3 + CO_2 + AsCl_3$$

$AsCl_3$ dissolves in liquid phosgene as a monomer [151].

9.1.4.4 Reaction of phosgene with antimony halides and oxide halides

Heating antimony(III) fluoride with a slight stoicheiometric excess of phosgene (in the presence of a catalytic amount of $SbCl_5$) at 135 °C and 3.25 MPa produces COClF (along with a little COF_2) in good yield [589]:

$$3COCl_2 + SbF_3 \longrightarrow 3COClF + SbCl_3$$

Using a slight molar excess of SbF_3 at 15 MPa (rotating autoclave) and 200–280 °C, COF_2 is formed, contaminated with carbon dioxide but free (for the first time) of hydrogen chloride [589]:

$$3COCl_2 + 2SbF_3 \longrightarrow 3COF_2 + 2SbCl_3$$

When a solution of phosgene in SO_2ClF is added to a stirred solution of SbF_5 (five-fold excess) in SO_2ClF at −78 °C, the following reaction is induced [1653c]:

$$COCl_2 + n SbF_5 \longrightarrow [COCl]^+[Sb_nCl_{5n}Cl]^-$$

This is the first reliable observation (*cf.* Section 9.1.2.5) of the chlorocarbonyl cation, $[COCl]^+$, which exhibits $\delta(^{13}C)$ at 133.7 p.p.m. [1653c], shifted about 8 p.p.m. upfield from phosgene itself (see Table 7.4), a remarkably small shift. The same ion can also be generated if the phosgene is replaced by ethanoyl dichloride, $(COCl)_2$, in the above reaction, or by passing CO through a Cl_2/SbF_5 solution [1653c]. As a by-product of these reactions, the known adduct $COClF.SbF_5$ [99] was observed, which decomposed upon warming to give COF_2. Although showing a minimum at $[COCl]^+$ on the potential energy surface, a*b initio* calculations of the atomic charges at the STO-3G level are inadequate to explain the experimental data [1653c].

By analogy, passing CO through an $X_2/SbF_5/SO_2ClF$ (X = Br or I) solution produced $[COBr]^+$ or $[COI]^+$ respectively, exhibiting $\delta(^{13}C)$ at 127.0 p.p.m. {a downfield shift of about 24 p.p.m. from $COBr_2$ itself (see Table 7.4)} and 100.4 p.p.m., respectively (*n.b.* the latter value is paramagnetically shifted by the presence of $[I_2]^+$) [1653c].

Mixtures of $SbCl_5$ and $COCl_2$ are miscible over the entire composition range at 0 °C, and show a very small negative deviation from Raoult's law between 0 and 0.5 mol fraction of phosgene, indicating the possible formation of a weak 1:1 adduct [376]. Dissolution of $SbCl_5$ in phosgene at <-78 °C, followed by removal of the excess of $COCl_2$ at -22 °C, leads to the isolation of a 1:1 adduct, $[Cl_2CO.SbCl_5]$, as a yellow-brown liquid [1012]. The i.r. spectrum (Nujol) of this complex exhibits $\nu(C{=}O)$ at 1820 cm^{-1}, $\nu_{as}(CCl_2)$ at 840 cm^{-1}, $\pi(COCl_2)$ at 582 cm^{-1}, $\nu_s(CCl_2)$ at 570 cm^{-1}, and $\nu(SbCl_5)$ at 400 and 371 cm^{-1}, and these bands are only very slightly shifted from those of free $COCl_2$ (*cf.* Table 9.1) [1012]. This contrasts with an independent report of $\nu(C{=}O)$ at 1667 cm^{-1} for a solution of $SbCl_5$ and $COCl_2$ in tetrachloromethane [477]. Ebullioscopic measurements show that both $SbCl_3$ and $SbCl_5$ dissolve in liquid phosgene as monomers [151].

An antimony(V) oxide chloride, $[Cl_4Sb\{SbO_2Cl\}_3SbCl_4]$, reacts slowly with *pure* tetrachloromethane to yield $SbO_2Cl.\frac{1}{2}COCl_2$, which further decomposes to yield $SbOCl_3$ [477]. The phosgene adduct exhibits i.r. bands (Nujol) corresponding to $\nu(C{=}O)$ at 1633 cm^{-1} and $\nu_{as}(CCl_2)$ at 784 cm^{-1} [477].

9.1.5 Reactions of phosgene with Group 16 halides and oxide halides

Very little chemistry has been performed with the halides and oxide halides of Group 16, and that reported appears to largely parallel that of Group 15. Both S_2Cl_2 and SCl_2 dissolve in phosgene without association [151].

Sulfur(IV) fluoride reacts with phosgene at 250 °C, in the presence of titanium(IV) fluoride, to give CF_4 (90%) and COF_2 (9%) [895].

Although there is no reaction between $S_2O_6F_2$ and phosgene at room temperature in the dark, under u.v. irradiation the following reaction is induced [1867]:

$$COCl_2 + S_2O_6F_2 \longrightarrow CO_2 + S_2O_5F_2 + Cl_2$$

Phosgene will undergo stepwise fluorination by SOF_2 at 300–400 °C [704]:

$$2COCl_2 + SOF_2 \longrightarrow 2COClF + SOCl_2$$

$$COCl_2 + SOF_2 \longrightarrow COF_2 + SOCl_2$$

Thus, treatment of phosgene with an excess of SOF_2 at 400 °C (in the presence of a metal halide catalyst, such as $FeCl_3$, $AlCl_3$, UCl_4, LaF_3, WOF_4 or $SbCl_5$) gives carbonyl difluoride in 96% conversion based upon phosgene [704].

Phosgene is claimed to form a 1:1 adduct, $COCl_2.SOCl_2$, with $SOCl_2$ at ambient temperatures in a mildly exothermic reaction [1782]: the adduct, a colourless liquid, is reported to stabilize liquid sulfur trioxide [1782].

9.1.6 Reactions of phosgene with Group 17 halides

Ebullioscopic measurements indicate that iodine(III) chloride dissolves in liquid phosgene as a monomer [151], but it does not appear to form an adduct [1012].

9.1.7 Reactions of phosgene with pseudohalides and their derivatives

The first reported attempt, in 1871, to prepare $CO(CN)_2$ was by the treatment of mercury cyanide with CO, but this was unsuccessful [338]. In the same paper, however, it was suggested that the reaction of AgCN with liquid phosgene might be more successful [338]. However, a paper published in the same year (by another worker) reported that this reaction was also unsuccessful [761]:

$$AgCN + COCl_2 \longrightarrow AgCl + CO + ClCN$$

One hundred and thirteen years later, it has now been shown that the reaction between solid silver(I) cyanide and gaseous phosgene at 250 °C produces $CO(CN)_2$ in yields in excess of 20% [ICI30]:

$$2AgCN + COCl_2 \longrightarrow 2AgCl + CO(CN)_2$$

With KCN, however, no carbonyl dicyanide was produced [ICI30]:

$$2KCN + COCl_2 \longrightarrow 2KCl + CO + (CN)_2$$

$$KCN + COCl_2 \longrightarrow KCl + CO + ClCN$$

In an early paper, it was discovered that lead(II) thiocyanate reacts with a solution of phosgene in toluene to form (for the first time) carbonyl diisothiocyanate [538]:

$$COCl_2 + Pb(SCN)_2 \longrightarrow CO(NCS)_2 + PbCl_2$$

Moreover, although the author was unable to isolate $CO(NCS)_2$ in a pure form, he did report on many of its reactions with simple organic compounds [538]. This preparation of $CO(NCS)_2$ was optimized by treating a solution of phosgene in toluene with A[NCS] (A = Na or K) in an autoclave at 100 °C [538]. Alternatively, $COCl_2$ reacts with K[NCS] in a LiCl–KCl eutectic mixture at 400 °C to give $CO(NCS)_2$ in 84% yield [1018]:

$$COCl_2 + 2K[NCS] \longrightarrow CO(NCS)_2 + 2KCl$$

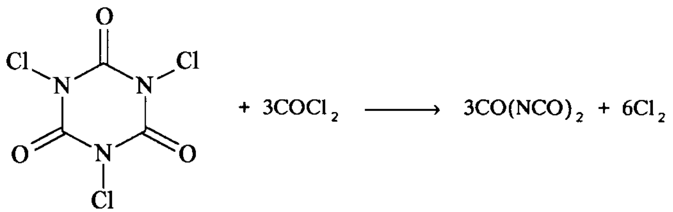
Treatment of a solution of $[NH_4][SCN]$ in thf at 3 °C with phosgene represents a much more convenient synthetic route to $CO(NCS)_2$, in 50–70% yields [299,1041]:

$$COCl_2 + 2[NH_4][SCN] \longrightarrow CO(NCS)_2 + 2[NH_4]Cl$$

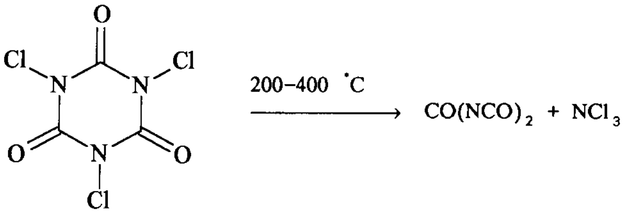
This reaction can also be performed in liquid sulfur(IV) oxide at −22 °C, to give $CO(NCS)_2$ in 75% yield [300]. Attempts to prepare CO(NCS)Cl by the comproportionation reaction between phosgene and $CO(NCS)_2$ were unsuccessful [1018].

Phosgene will react with ClCN at 150 °C and 5.5 MPa, over an active charcoal catalyst, to give $Cl_2C{=}NC(O)Cl$ [860aa,861]: partial hydrolysis of this material by methanesulfonic acid gives carbonyl chloride isocyanate, CO(NCO)Cl, in 90% yield [860a,860b,861]. CO(NCO)Cl can also be prepared (54% yield) by treating $Si(NCO)_4$ with phosgene at 250 °C in an autoclave [1018]. Treatment of CO(NCO)Cl with $[NH_4][NCS]$ in thf at −30 °C gave CO(NCS)(NCO) [1041]. The organic reactions of CO(NCO)Cl have been the subject of an excellent review [861], but are outside the scope of this monograph.

Treatment of trichloroisocyanuric acid (or sodium dichloroisocyanurate) with phosgene at 150–250 °C in 1,3,5-trichlorobenzene or 1,2-dichlorobenzene affords carbonyl diisocyanate, $CO(NCO)_2$, in almost quantitative yield [616]:



This avoids the formation of the explosive by-product NCl_3 in the synthesis of $CO(NCO)_2$ by the thermolysis of trichloroisocyanuric acid [1469a]:



$COCl_2$ reacts with K[NCO] in a LiCl–KCl eutectic mixture at 400 °C to give either $CO(NCO)_2$ or CO(NCO)Cl, according to conditions [1018]:

$$COCl_2 + 2K[NCO] \longrightarrow CO(NCO)_2 + 2KCl$$
$$COCl_2 + K[NCO] \longrightarrow CO(NCO)Cl + KCl$$

A mixture of phosgene and carbonyl diisocyanate will undergo a comproportionation reaction at 180 °C, to give a 56% yield of the mixed product [1018]:

$$COCl_2 + CO(NCO)_2 \longrightarrow 2CO(NCO)Cl$$

The organic chemistry of $CO(NCO)_2$ has been recently explored [22a], but is beyond the scope of this review.

9.2 TRANSITION METAL HALIDES AND OXIDE HALIDES

9.2.1 Reactions of phosgene with Group 4 halides and oxide halides

Perhaps not surprisingly, in view of the results for the $COCl_2$–$AlCl_3$ (Section 9.1.2.5) and $COCl_2$–$SnCl_4$ (Section 9.1.3.3) systems, two independent investigations of the $COCl_2$–$TiCl_4$ system have failed to find any evidence for the formation of specific complex formation [1012,ICI1].

Commercial titanium(IV) chloride is prepared by the chlorination of titanium(IV) oxide:

$$2TiO_2 + 3C + 4Cl_2 \xrightarrow{950\ ^\circ C} 2TiCl_4 + CO_2 + 2CO$$

Phosgene is also formed in the production of $TiCl_4$ by the chlorination of titanium slags [389,1708]. Thus, phosgene {along with HCl, $SiCl_4$, $VOCl_3$, $AlCl_3$, $TiOCl_2$, C_6Cl_6, CO_2, CS_2, COS, SO_2Cl_2, RC(O)Cl (R = CCl_3, $CHCl_2$ or CH_2Cl) and CCl_4 [1589,2059,2248]} is a common, and significant (0.005–2.5% in technical grade $TiCl_4$ [479]), impurity in titanium(IV) chloride. Phosgene is miscible with titanium(IV) chloride in all proportions, and the solubility of phosgene in $TiCl_4$ (see Fig. 9.7) has been determined [478–480,2248], phosgene concentrations being estimated by i.r. spectroscopy [1042,1589,2125] (a technique which has now replaced earlier chemical methods [490]). Using the i.r. band at 1812 cm^{-1}, the detection limit for $COCl_2$ in $TiCl_4$ is 0.0002 wt % [479,2057,2059].

In a recent, and very exciting, publication, it has been shown by Hussey and coworkers [1977a] that phosgene will react *in situ* with a solution of $[TiOCl_4]^{2-}$ in room-temperature halogenoaluminate ionic liquids, such as $AlCl_3$–[emim]Cl ($[emim]^+$ = 1-methyl-3-ethylimidazolium cation), and completely and rapidly convert the oxochloride complex into

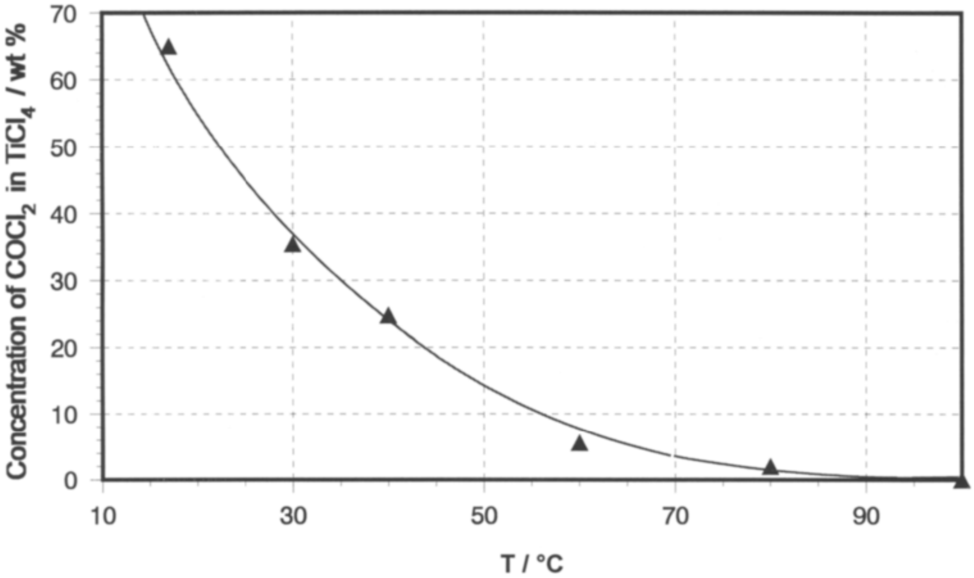


Fig. 9.7 **The solubility of phosgene in titanium(IV) chloride under standard conditions [479,480,2248].**

$[TiCl_6]^{2-}$, according to:

$$[TiOCl_4]^{2-} + COCl_2 \longrightarrow [TiCl_6]^{2-} + CO_2$$

As $[TiCl_6]^{2-}$ had previously been employed as an electrochemical marker for the presence of oxide in these ionic liquids (it reacts with impurities to generate $[TiOCl_4]^{2-}$), the complete conversion of $[TiOCl_4]^{2-}$ to $[TiCl_6]^{2-}$ demonstrates that not only did the phosgene remove all the oxide ion from the titanium(IV) species, it also removed it from the liquid itself {*cf.* Section 9.4.3} [1977a].

9.2.2 Reactions of phosgene with Group 5 halides and oxide halides

Niobium(V) oxide trichloride is a significant impurity in niobium(V) chloride, which is used for the preparation of niobium metal. Indeed oxygen impurities in the 'high-purity' niobium produced in this way originate largely with $NbOCl_3$, and the feasibility of its removal by phosgene treatment has been examined between 380 and 450 °C [223,224]:

$$NbOCl_3(g) + COCl_2(g) \longrightarrow NbCl_5(g) + CO_2(g)$$

This reaction is essentially irreversible and stoicheiometric, and was found to be first-order in both reactants: the Arrhenius frequency factor is 1.33 x 10^6 l mol^{-1} s^{-1} and the activation energy is 91.6 kJ mol^{-1} [223,224]. A later study modified these values to 1.102 x 10^7 l mol^{-1} s^{-1} and 100 kJ mol^{-1} for the elementary reaction, and 1.461 x 10^7 l mol^{-1} s^{-1} and 97.6 kJ mol^{-1} for a four-parameter fit of the data, in which the reaction orders in $NbOCl_3$ and $COCl_2$ were 0.829 and 0.921, respectively [813]. Several patents for the conversion of $NbOCl_3$ to $NbCl_5$ exist [278,568a,568b].

It has now been shown by Hussey and coworkers [1977a,1977b] that phosgene will react *in situ* with a solution of oxochloroniobium(V) complexes in room-temperature halogenoaluminate ionic liquids, such as $AlCl_3$-[emim]Cl ($[emim]^+$ = 1-methyl-3-ethylimidazolium cation), and facilely convert the oxochloride complex into $[NbCl_6]^-$, according to:

$$[NbOCl_5]^{2-} + COCl_2 \longrightarrow [NbCl_6]^- + Cl^- + CO_2$$

The fact that this reaction proceeds rapidly and quantitatively at room temperature demonstrates the tremendous affinity that phosgene has for the oxide ion, even when bound to such a powerful oxide scavenger as niobium(V). Analogous results have been found for the tantalum system, in both room-temperature [120a] and high-temperature ionic liquids [1977c].

9.2.3 *Reactions of phosgene with Group 6 halides and oxide halides*

Molybdenum(V) chloride is reasonably soluble in liquid phosgene at 0 °C, whereas tungsten(VI) chloride is only sparingly soluble. The results of the tensimetric titrations of molybdenum(V) chloride and tungsten(VI) chloride with phosgene at 0 °C are presented in Fig. 9.8 [376]: there is no evidence for complex formation.

Tungsten(VI) oxide tetrachloride is a common impurity in tungsten(VI) chloride. By analogy with niobium(V) oxide trichloride (Section 9.2.2), phosgene might have been expected to convert $WOCl_4$ to WCl_6, according to:

$$WOCl_4 + COCl_2 \longrightarrow WCl_6 + CO_2$$

However, heating phosgene with tungsten(VI) oxide tetrachloride, even up to 900 °C, produces no WCl_6 [934], although this reaction is efficiently catalysed by aluminium(III) chloride, iron(III) chloride and (possibly) chromium(III) chloride [ICI3,ICI6], and reports of the reaction proceeding at lower temperatures exist [ICI6]. Moreover, in the presence of a carbon catalyst, reaction is achieved with an 80% conversion at 400 °C and a 96% conversion at 900 °C, passing through a conversion minimum of 74% at 650 °C [934]. The following reaction was postulated to be important in this process:

$$WOCl_4 + COCl_2 + C \longrightarrow WCl_6 + 2CO$$

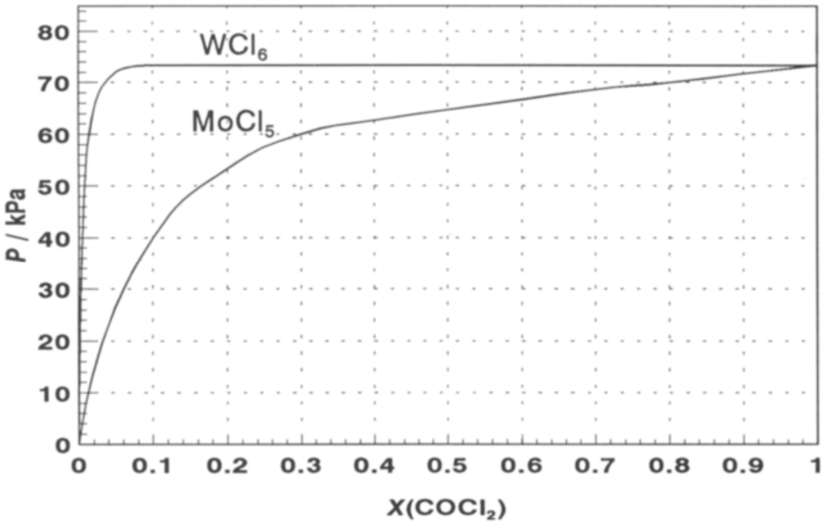


Fig. 9.8 **A vapour pressure – composition diagram (0 °C) for the $COCl_2$–$MoCl_5$ and $COCl_2$–WCl_6 system [376]. As the solubility of the chlorides is unknown, the mol fraction may not represent that present in the homogeneous solution.**

The reason for the lack of reactivity in the absence of the carbon catalyst, and the conversion minimum in its presence, may be attributed to slow reaction kinetics at low temperatures and the following reaction at higher temperatures [934]:

$$WCl_6 + CO_2 \longrightarrow WOCl_4 + COCl_2$$

This reaction is not detectable at 500 °C, but goes to virtual completion at 800 °C [934].

Liquid tungsten(VI) chloride, itself, reacts readily with phosgene according to [ICI3,ICI6]:

$$WCl_6 + COCl_2 \longrightarrow WOCl_4 + CCl_4$$

A build-up of $WOCl_4$ does inhibit the reaction, however [ICI3].

Molybdenum(V) chloride and, especially, tungsten(VI) chloride have been extensively studied as dismutation catalysts for phosgene (*cf*. Chapter 8). The first proposed mechanism for this catalysis involves the self-ionization of phosgene [775]:

$$\begin{aligned} COCl_2 &\rightleftharpoons [COCl]^+ + Cl^- \\ MoCl_5 + Cl^- &\longrightarrow [MoCl_6]^- \\ [COCl]^+ + [MoCl_6]^- &\longrightarrow CCl_4 + MoOCl_3 \\ MoOCl_3 + COCl_2 &\longrightarrow CO_2 + MoCl_5 \end{aligned}$$

The well-documented lack of autoionization phenomena for phosgene would argue against such a mechanism, although it might be enhanced by the presence of charcoal.

A more detailed study of the tungsten system has been performed [ICI6]. The thermodynamics for the $COCl_2/WCl_6$ system at 400 °C are [ICI6]:

$$\begin{aligned}
WCl_6 + COCl_2 &\xrightleftharpoons{K_1} WOCl_4 + CCl_4; && K_1 \mathrel{\hat{=}} 0.05 \\
WOCl_4 + COCl_2 &\xrightleftharpoons{K_2} WCl_6 + CO_2; && K_2 \mathrel{\hat{=}} 1320 \\
2COCl_2 &\xrightleftharpoons{K_3} CCl_4 + CO_2; && K_3 \mathrel{\hat{=}} 66
\end{aligned}$$

The first reaction is endothermic but rapid, whereas the second is exothermic but *extremely* slow. The presence of aluminium(III) chloride or iron(III) chloride catalyses this second step, and allows for the efficient dismutation of phosgene to proceed; this catalysis has been discussed in terms of the following mechanism (M = Al or Fe) [ICI6]:

$$\begin{aligned}
WOCl_4 + MCl_3 &\rightleftharpoons WCl_6 + MOCl \\
MOCl + COCl_2 &\rightleftharpoons MCl_3 + CO_2
\end{aligned}$$

An analogous mechanism, involving $MoOCl_3$, was proposed to account for the efficacy of $MoCl_5$ [ICI6]. The kinetics of phosgene decomposition in the presence of $MoCl_5$ has been studied between 350 and 410 °C: it is initially first-order in phosgene and second-order in $MoCl_5$, but is inhibited by a reaction product ($MoOCl_3$?) [2200]. In the presence of activated carbon, the reaction is first-order in $MoCl_5$ and second-order in phosgene, and some fifteen times faster than the homogeneous system [2200].

9.2.4 Reactions of phosgene with Group 8 halides

Iron(III) chloride is a common impurity in commercial phosgene at the 0.08–0.2% level [1168]. Attempts to isolate an adduct between phosgene and iron(III) chloride were unsuccessful [1012], and a tensimetric titration of ruthenium(III) chloride with phosgene showed no evidence for complex formation [ICI1].

9.2.5 Reactions of phosgene with Group 9 halides

The reaction of phosgene with cobalt(III) fluoride at 500 °C, in an autoclave, produces CF_4 (10%), $CClF_3$ (75%), CCl_2F_2 (15%), and a trace of CCl_3F [1454].

9.2.6 Reactions of phosgene with Group 10 halides

In 1891, Pullinger reported that passing a mixture of dichlorine and carbon monoxide over platinum sponge at 250 °C produced a yellow solid, which was formulated (upon very little evidence) as $PtCl_2(COCl_2)_2$ [1667a]. This is the only claimed isolated phosgene complex of a transition metal, and the report should be considered as incorrect. However, a complex reported as $PtCl_2(CO)_2$ is said to recrystallize from phosgene at 100 °C as large yellow crystals [1667a], and this report may be worthy of further investigation.

Neither platinum(II) chloride [1667a] nor platinum(IV) chloride [1012] show any evidence of complex formation with phosgene. Similarly, treatment of $K[PtCl_3(C_2H_4)]$ with liquid phosgene at 0 °C and atmospheric pressure, or in an autoclave at 100 °C and 1.5 MPa, followed by removal of the phosgene *in vacuo*, gives a residue which shows no evidence for displacement of the coordinated ethene [ICI1].

9.2.7 Reactions of phosgene with Group 11 halides

Neither copper(II) chloride [ICI1] nor gold(III) chloride [1012] show any evidence for adduct formation.

9.2.8 Reactions of phosgene with Group 12 halides

Phosgene reacts with a solution of cadmium(II) iodide in diethyl ether to liberate iodine [1606].

9.3 LANTHANIDE AND ACTINIDE HALIDES AND OXIDE HALIDES

9.3.1 Reactions of phosgene with lanthanide oxide halides

The lanthanum(III) oxide chlorides might all be expected to react similarly with phosgene:

$$LnOCl + COCl_2 \longrightarrow LnCl_3 + CO_2$$

Indeed, the ease of this reaction, as determined by the temperature range of the exothermic d.t.a. peak for heating LnOCl under phosgene, decreases from cerium to gadolinium [306,1087]:

Ce	>	Pr	>	Nd	>	Sm	>	Eu	>	Gd
380-430 °C		370-420 °C		360-400 °C		320-360 °C		290-330 °C		250-305 °C

The most investigated compound is CeOCl, studied both as a pure material and as a compound formed *in situ* in the reaction of CeO_2 with phosgene; it has been suggested (although it seems rather unlikely) that reaction between CeOCl and $COCl_2$ does not actually occur, but that the product derives from equilibrium amounts of carbon monoxide and dichlorine present [307,1087,1088]. The reaction of PrOCl with phosgene has also been the subject of a kinetic study [305].

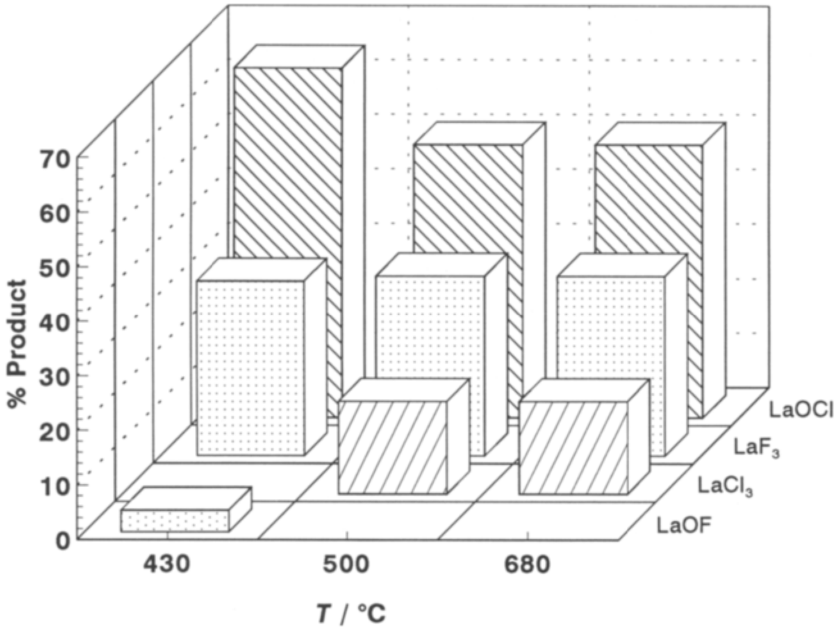


Fig. 9.9 **The product distribution from the reaction of α–LaOF with phosgene as a function of temperature [113].**

The reaction of lanthanum(III) oxide fluoride, α–LaOF, with phosgene has been investigated as a function of time and temperature (430, 500 and 680 °C) by t.g.a., followed by product analysis and characterization by powder X–ray diffraction [113]. This is a much more thorough study than those described above for the lanthanide oxide chlorides, and the results are summarized in Fig. 9.9. All the fluoride ends up as LaF_3 (thus no significant quantities of COClF or COF_2 can be formed), and the major product at each temperature is LaOCl. The product analysis is consistent with the following sequential reactions occurring [113]:

$$3LaOF + COCl_2 \longrightarrow 2LaOCl + LaF_3 + CO_2$$

$$LaOCl + COCl_2 \longrightarrow LaCl_3 + CO_2$$

Clearly, LaOF is significantly more reactive towards phosgene than is LaOCl, but LaF_3 shows no evidence for further reaction once it has been formed.

Very recently, a process for dehydrating hydrated rare earth halides, typically hexahydrates, with phosgene was patented [1612a].

9.3.2 *Reactions of phosgene with actinide halides and oxide halides*

Uranium(VI) fluoride is very soluble in liquid phosgene, dissolving to give a yellow solution, and its solubility has been determined between 158.7 K (0.00502 mol l^{-1}) and 270.8 K (1.73 mol l^{-1}) [1301].

9.4 MAIN GROUP OXIDES AND SULFIDES

An interesting paper qualitatively compared phosgene with a mixture of CO and Cl_2 as a reagent for converting metal oxides into metal chlorides: phosgene was found to be more effective in all eight cases studied [2107a]. In a short review, phosgene has also been compared with a wide range of other chlorinating agents (including Cl_2, CCl_4, S_2Cl_2, NaCl and $CaCl_2$) as a means for extracting main group metals and transition metals from their oxide and sulfide ores [1970]. More recently, the treatment of high-temperature molten salts (*e.g.* a LiCl–KCl eutectic) with phosgene has been proposed as a means of solubilizing intractable metal oxides or sulfides [2049a]:

$$COCl_2(g) + O^{2-} \longrightarrow CO_2(g) + 2Cl^-$$

$$COCl_2(g) + S^{2-} \longrightarrow COS(g) + 2Cl^-$$

The thermodynamic driving force for these reactions (which proceed essentially to completion) is the elimination of CO_2 (or COS), and it is this principle which lies behind all the reactions described in Sections 9.4–9.6.

The reactions of metal sulfides with $COCl_2$ have been proposed as a route to COS [361].

9.4.1 *Reactions of phosgene with Group 1 oxides and sulfides*

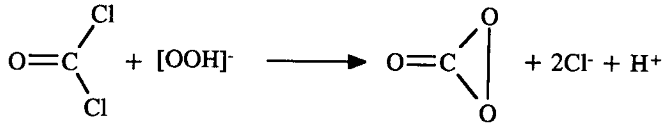
In 1868, Odling reported that phosgene reacted with potassium oxide to give potassium carbonate [1536]:

$$2K_2O + COCl_2 \longrightarrow K_2[CO_3] + 2KCl$$

An early report of the reaction between alkaline hydrogen peroxide and phosgene suggests that methanal is formed [1123]. In a not particularly enlightening study, the reaction between phosgene and sodium peroxide at −10 °C is said to give products of composition $Na_2O_2.NaCl$: in the presence of an excess of phosgene, the products observed were NaCl, CO_2 and O_2 [1341]. These data were used to deduce that $[CO_4]^{2-}$ is incapable of existence!

Phosgene reacts with sodium peroxide, in the presence of suitable sensitizers (for example, rubrene, perylene, 9,10-diphenylanthracene, 9,10-bis(phenylethynyl)anthracene or

3,6-diphenylisobenzofuran) to produce chemiluminescence, *via* a dioxirane mechanism (*cf.* Section 9.7.6) [1946]:



The dioxiranone intermediate, which is formed in small amounts, reacts with the sensitizer to give singlet atomic oxygen and carbon dioxide: the reaction of the singlet oxygen with the sensitizer is responsible for the chemiluminescence [1946].

Treatment of a eutectic mixture of LiCl, KCl and K_2S at 380–400 °C with phosgene generates carbon oxide sulfide in 75% yield [653]:

$$K_2S + COCl_2 \longrightarrow 2KCl + COS$$

9.4.2 Reactions of phosgene with Group 2 oxides and sulfides

Beryllium oxide was first treated with phosgene in the days when beryllium was still being referred to as glucinium (Gl) [360]. Thus, at 450 °C [360]:

$$BeO + COCl_2 \longrightarrow BeCl_2 + CO_2$$

The reaction was reported to be favoured by higher temperatures [1349,1350].

A commercial process for converting the principal ore of beryllium, beryl ($Be_3Al_2Si_6O_{18}$), into beryllium chloride, using phosgene, has been patented [97]:

$$Be_3Al_2Si_6O_{18} \xrightarrow[Na_2[CO_3]]{Na_2[SiF_6]} Na_2[BeF_4] \xrightarrow[500\text{-}800\ ^\circ C]{COCl_2} BeCl_2$$

Magnesium oxide reacts in a similar manner to beryllium oxide at 450 °C [360], the reaction being initiated at temperatures as low as 95 °C [1094]. Calcium oxide, in contrast, only reacts under similar conditions between 280 and 564 °C [1095]. Phosgene is reported to have caused the disintegration of concrete in the basement of an industrial plant: this is ascribed, however, to damage caused by hydrochloric acid liberated by the hydrolysis of phosgene on the surface of the concrete [684]. Phosgene is believed to have no observable action upon dry cement [684].

Calcium oxide in a calcium chloride melt can be converted into calcium chloride by treatment with phosgene {*cf.* purification of room-temperature ionic liquids, Section 9.4.3} [649c]. The melt was being used to produce plutonium metal by reducing its oxide with calcium, and the authors preferred the use of dichlorine or hydrogen chloride to phosgene because of the solubility of the product CO_2 in the melt (which reacts with plutonium to give a carbide) and because of the "toxicity and corrosive nature" of phosgene: as both chlorine and hydrogen chloride are significantly more corrosive than phosgene, and the researchers were working with plutonium, their last reasons for not using phosgene seem a little questionable.

Strontium oxide, in contrast to the other oxides in the Group, gives a mixture of strontium chloride and strontium carbonate at temperatures above 470 °C [1098]:

$$2SrO + COCl_2 \longrightarrow SrCl_2 + Sr[CO_3]$$

Barium oxide, though, is reported to give only $BaCl_2$ and CO_2 at 500 °C [360]. Barium sulfide reacts with phosgene at 400 °C in a manner analogous to its oxide [361]:

$$BaS + COCl_2 \longrightarrow BaCl_2 + COS$$

9.4.3 *Reactions of phosgene with Group 13 oxides and sulfides*

The reaction between boron(III) oxide (or boric acid, borax, kernite or colemanite) and phosgene in a molten salt ($AlCl_3$/NaCl) has been patented as a commercial route to boron(III) chloride [148]:

$$B_2O_3 + 3COCl_2 \xrightarrow{625\ ^\circ C} 2BCl_3 + 3CO_2$$

The practicability of this process must be severely hampered by the problems of purification caused by the separation of mixtures of phosgene and boron(III) chloride, as described in Section 9.1.2.2.

The conversion of aluminium(III) oxide into aluminium(III) chloride is a reaction of increasing current interest, and a recent review [209] has discussed the reasons for this in some detail. Indeed, the reaction between aluminium(III) oxides and phosgene is one of the most studied inorganic reactions of phosgene. It was first observed by Chauvenet in 1911, who reported that reaction occurred at 400 °C [360]:

$$Al_2O_3 + 3COCl_2 \longrightarrow 2AlCl_3 + 3CO_2$$

This reaction, using CO and Cl_2 over a carbon catalyst to form the $COCl_2$ *in situ*, was the basis of a patent for the manufacture of aluminium(III) chloride at between 500 and 800 °C [100]. The kinetics of the reaction between γ-Al_2O_3 and phosgene has been studied between 585 and 1085 K: an apparent order of reaction of 0.75 with respect to $COCl_2$ was determined, with an apparent activation energy of 128–135 kJ mol^{-1} [182,183]. The effect of added charcoal to the kinetics of the reaction were shown to be negligible below 650 °C, but phosgene was found to be superior to a 1:1 CO:Cl_2 mixture [24].

Molten $Na[AlCl_4]$ catalyses the reaction at 600 °C, in a three-phase system with gaseous $COCl_2$ and solid $\gamma-Al_2O_3$, to give very high purity aluminium(III) chloride [962], and this reaction (in the presence of carbon) has formed the basis of a patent for the industrial scale production of aluminium(III) chloride [909]. The chlorination of Al_2O_3 by phosgene has been studied in a LiCl–KCl eutectic melt at 470 °C as a function of pO^{2-}; it is essentially a two-step process [1842]:

$$Al_2O_3(s) + COCl_2(g) + Cl^- \longrightarrow 2[AlOCl_2]^- + CO_2$$

$$[AlOCl_2]^- + COCl_2(g) \longrightarrow [AlCl_4]^- + CO_2(g)$$

The mechanism of this last step must also be more complicated than it appears, since it is second-order in aluminium oxochloride concentration. A dimeric intermediate was postulated [1842]:

$$2[AlOCl_2]^- + COCl_2(g) \longrightarrow [Al_2OCl_5]^- + Cl^- + CO_2(g)$$

$$[Al_2OCl_5]^- + Cl^- \longrightarrow [AlOCl_2]^- + [AlCl_4]^-$$

Treatment of room-temperature halogenoaluminate ionic liquids, such as $AlCl_3$–[emim]Cl ($[emim]^+$ = 1-methyl-3-ethylimidazolium cation), with phosgene results in the rapid and complete removal of oxide impurities (in the form of carbon dioxide) [1a]. As both the product CO_2 and the reactant $COCl_2$ can be removed from the liquid by continuous evacuation [1a], this observation should be invaluable to the pursuance of future work in room-temperature ionic liquids, a field previously handicapped by the ubiquitous presence of the oxide ion. Sulfinyl chloride ($SOCl_2$) has been shown to be an inferior reagent for this purpose [1977a]. In a very recent development, phosgene has also been shown to be effective at removing oxide impurities from high-temperature chloroaluminate ionic liquids, such as $AlCl_3$–NaCl [1977c].

The conversion of aluminium ores into aluminium(III) chloride with phosgene can also be successfully achieved [130,295a], and this conversion is more effective than using either dichlorine or CO/Cl_2 mixtures [1919a,2101a]. Indeed, the literature in this field is burgeoning. Thus, pre-heated bauxite (Al_2O_3, 48.5%; Fe_2O_3, 14.6%; SiO_2, 18.2%; TiO_2, 2.1%) when treated with phosgene at 590–610 °C (a temperature range at a conversion maximum) gives aluminium(III) chloride in 88–90% yield [1996,1996a]: the product is contaminated with iron(III) chloride, but this can be readily removed by selective reduction [2178]. The chlorination of bauxite is catalysed by the presence of carbon [1683a], and the generation of phosgene *in situ* (by irradiating CO/Cl_2 mixtures with light from a high-pressure mercury-vapour lamp) significantly increases the efficiency of the process [1919a]. Phosgene is reported to efficiently chlorinate metakaolin (Al_2O_3, 42.2%; Fe_2O_3, 1.45%; SiO_2, 52.7%; TiO_2, 0.99%) between 500 and 700 °C [208,209,1727a], and also to chlorinate uncalcined kaolin at 500 °C [2160a]. Gibbsite (hydrated alumina), after thermal dehydration, is even more reactive towards phosgene [912a]. Similarly, pre-heated clay can be treated at 600 °C with phosgene in the presence of molten $K[AlCl_4]$ catalyst: ≥89% of the aluminium content of the clay is recovered as aluminium(III) chloride, and the co-produced $SiCl_4$ is recycled as a chlorinating agent [1330-1332]:

$$2Al_2O_3 + 3SiCl_4 \longrightarrow 4AlCl_3 + 3SiO_2$$

A detailed state-of-the-art report of the production of aluminium, *via* aluminium(III) chloride, from clay, and particularly kaolinitic clay, compares the effectiveness of phosgene with other chlorinating agents [1203a]. In a similar manner, fly-ash (typically *ca.* 95% SiO_2-Al_2O_3 in a 5:3 ratio) can be treated with phosgene, and the kinetics of this process between 450 and 800 °C have been investigated [8].

Perhaps the most intriguing use of this reaction is for the dealumination of zeolites with retention of crystallinity. Thus, H-type mordenite chemisorbs phosgene at >100 °C with the release of hydrogen chloride. At higher temperatures (>300 °C), more hydrogen chloride is released, along with carbon dioxide and aluminium(III) chloride [640,641]. A convenient operating temperature for dealumination of a pre-heated sample is 600 °C, with the phosgene diluted with dinitrogen, and a mordenite sample was prepared with 96% dealumination whilst retaining 81% crystallinity [639]. Pre-heated faujasites, such as NaY and $NaNH_4Y$ zeolites, can also be dealuminated with phosgene at 500 °C with crystallinity retention (with concomitant shrinking of the lattice constant), but H-type zeolites are the most reactive [637,638,640a,1112]. Dealuminated NH_4Y zeolites have an enhanced catalytic activity for the conversion of methanol to hydrocarbons [1589d]. Dealuminated mordenite retains its crystallinity up to 800 °C, whereas clinoptilolite loses its crystallinity at 800 °C [879]. Treatment of kaolin with a $COCl_2$-N_2 mixture at 700 °C, followed by conversion with sodium hydroxide solution and hydrothermal crystallization, yields the zeolitic molecular sieve 13X [607a]. This whole field of dealumination of ores and zeolites will clearly attract a good deal of future attention.

Whilst being reactive at high temperatures, zeolite molecular sieves exhibit a high absorption of phosgene at room temperature, a factor which has been utilized in the purification of boron(III) chloride [955a] and trichloromethane [302]. For the purification of trichloromethane, 13X molecular sieves (10 Å pore size) are much more effective than 5A molecular sieves (5 Å pore size), and have the added advantage of removing water and ethanol, too [302].

The reaction between aluminium(III) selenide and phosgene at 219 °C represents a good synthetic route to carbonyl selenide [774]:

$$Al_2Se_3 + 3COCl_2 \longrightarrow Al_2Cl_6 + 3COSe$$

9.4.4 Reactions of phosgene with Group 14 oxides and sulfides

The dissociation of phosgene into carbon monoxide and dichlorine, and CO exchange reactions, are discussed in Section 8.2. However, there is a report that under the right conditions, phosgene will react with carbon monoxide [2184]:

$$COCl_2(g) + CO(g) \longrightarrow (COCl)_2(g)$$

Thus, at 14 MPa and 200–400 °C, ethanedioyl chloride, C(O)ClC(O)Cl, is claimed to be formed from CO and $COCl_2$ (in the presence or absence of a charcoal catalyst) [2184]. A simple consideration of the thermodynamics of this reaction indicates that it is highly improbable. The reaction is endergonic at all accessible temperatures and pressures ($\Delta G^{\bullet}_{298}$ = +28.3 kJ mol^{-1} and $\Delta G^{\bullet}_{1000}$ = +156 kJ mol^{-1}) and, under the conditions of the report, the equilibrium yield of product would be <0.1% [1764].

The solubility of CO_2 in liquid phosgene is discussed in Section 11.3.

Silicon(IV) oxide is, uniquely amongst the common oxides, not chlorinated by phosgene below 650 °C [360]. Indeed, metal silicates at temperatures up to 1500 °C appear to react according to the following simplified equation [120]:

$$MSiO_3 + COCl_2 \longrightarrow MCl_2 + SiO_2 + CO_2$$

Thus, thorite ($ThSiO_4$), gadolinite {$(Y,Ce,La,Dy)_2FeBe_2Si_2O_{10}$}, cerite {$Ce_6(Ca,Fe)_2$-$Si_6O_{23}.3H_2O$} and zircon ($ZrSiO_4$) react with phosgene between 1000 and 1250 °C to give $ThCl_4$, YCl_3, $CeCl_3$ and $ZrCl_4$, respectively: emerald ($Be_3Al_2Si_6O_{18}$) did not react with phosgene up to 1500 °C (*cf.* Section 9.4.2) [120]. The treatment of fly-ash with phosgene is described in Section 9.4.3.

Although bulk silicon(IV) oxide is not chlorinated by phosgene, it does slowly chlorinate the surface [866]. This phenomenon has been used to chlorinate the surfaces of chrysotile asbestos and nonexpanded vermiculite for grafting to polystyrene for use as a filler for polymers and elastomers [1383,1384]. Moreover, in the presence of aluminium(III) chloride, phosgene will convert silica gel into silicon(IV) chloride at between 400 and 700 °C [208a,208b].

The equilibrium constant, *K*, for the reaction between GeO_2 and phosgene (to give $GeCl_4$ and CO_2) has been calculated as a function of temperature: $pK_{373} = -49.12$, $pK_{573} = -34.49$, $pK_{773} = -27.39$, $pK_{973} = -23.17$ and $pK_{1173} = -20.38$ [2105]. The thermodynamics of the following reaction have also been calculated [1191]:

$$GeO + COCl_2 \longrightarrow GeCl_2 + CO_2$$

The reaction between tin(II) oxide and phosgene initiates at 247 °C [1189]:

$$SnO + COCl_2 \longrightarrow SnCl_2 + CO_2$$

The reaction between tin(IV) oxide and phosgene was first observed, at 400 °C, in 1911 [360], and then rediscovered in 1969 [1190]:

$$SnO_2 + 2COCl_2 \longrightarrow SnCl_4 + 2CO_2$$

The treatment of SnO_2 with a CO/Cl_2 mixture has also been reported [26].

Lead(II) chloride has been liberated from the ore pyromorphite with phosgene (see Section 9.4.5) [120]. Similarly, $COCl_2$ reacts with lead(II) sulfide at 350 °C to give $PbCl_2$ and COS [361].

9.4.5 Reactions of phosgene with Group 15 oxides and sulfides

Phosgene has been demonstrated to interfere with the chemiluminescent measurements of NO and NO_2 concentrations using commercial analysers [1056], although no thermal reaction was detected between $COCl_2$ and NO_2 after 1 h at 393 °C [2027].

Calcium phosphate is also readily converted to $POCl_3$ and $CaCl_2$, reacting (in the absence of charcoal) under conditions where a mixture of CO and chlorine does not [296,1708a,1709]:

$$Ca_3[PO_4]_2 + 6COCl_2 \longrightarrow 2POCl_3 + 6CO_2 + 3CaCl_2$$

A process for the commercial production of phosphorus(V) oxide trichloride by treating a pre-heated mixture of wood charcoal with P_2O_5, HPO_3, $H_4P_2O_7$ or H_3PO_4 has been patented [1915].

The action of phosgene upon phosphate minerals was first proposed in 1913, and the generalized reaction is [120]:

$$P_2O_5.xMO + (3+x)COCl_2 \longrightarrow 2POCl_3 + (3+x)CO_2 + xMCl_2$$

As phosphorus(V) oxide trichloride is a volatile liquid, this reaction (like that of the silicates described in Section 9.4.4) represents an interesting method of converting ores into their corresponding metal chlorides. Thus, vivianite ($Fe_3P_2O_8.8H_2O$) is converted to $FeCl_3$, and pyromorphite ($Pb_{10}P_6Cl_2O_{24}$) to $PbCl_2$, between 350 and 500 °C, autunite (or lime uranite; $U_2CaP_2O_{12}.8H_2O$) gives volatile UCl_4 and involatile $CaCl_2$ at 800 °C, and monazite (a mineral composed of phosphates of cerium, lanthanum, thorium and a range of lanthanides) yields volatile $ThCl_4$ [120].

The reaction between phosphorus(V) oxide and phosgene is:

$$P_4O_{10} + 6COCl_2 \longrightarrow 4POCl_3 + 6CO_2$$

Although of little global significance on Earth, this reaction is of tremendous importance on Venus. Oxides of phosphorus have been detected, by the Soviet Vega probes, in the Venusian lower cloud level, and are believed to be products of hypergenesis and, possibly, volcanic activity [50a]. Phosgene is known to be formed in the Venusian clouds by photochemical processes in the upper atmosphere on the daylight side of the planet, and to descend into the clouds containing phosphorus(V) oxide in the lower atmosphere. This catastrophically alters the structure of the phosphoric acid layer, converting the oxide into the volatile $POCl_3$, and depleting the phosphoric acid layer (on the daylight side) to the point of extinction [50a].

Phosgene reacts with arsenic(III) oxide (in the presence of carbon) at temperatures above 175 °C, and almost quantitatively between 200 and 260 °C, to produce arsenic(III) chloride [1402]:

$$As_2O_3 + 3COCl_2 \longrightarrow 3AsCl_3 + 3CO_2$$

John Davy [467] noted in 1812 that Sb_2O_3 reacted with $COCl_2$ to give $SbCl_3$, an "infusible peroxide", and carbon monoxide.

Antimony sulfide and bismuth sulfide both react with phosgene, at 300 and 350 °C respectively, to give their appropriate chlorides [361]:

$$E_2S_3 + 3COCl_2 \longrightarrow 2ECl_3 + 3COS$$

$$(E = As \text{ or } Sb)$$

9.4.6 Reactions of phosgene with Group 16 oxides

Sulfur dioxide reacts with phosgene (see also Section 4.7.5.3) in the liquid phase (autoclave) at between 200 and 400 °C (optimally 250 °C) according to [364a,918a]:

$$SO_2 + COCl_2 \longrightarrow SOCl_2 + CO_2$$

A similar reaction is reported to occur in the gas phase, with an excess of sulfur dioxide in the presence of an activated charcoal catalyst, between 280 and 350 °C [685b]. Reaction in the gas phase, catalysed by charcoal, at 300 °C generates by-product SCl_4 [364a,918a]:

$$SO_2 + 2COCl_2 \longrightarrow SCl_4 + 2CO_2$$

These reactions also produce by-product S_2Cl_2, because SCl_4 breaks down to S_2Cl_2 and Cl_2 [364a,ICI31].

The reaction of SO_2 with phosgene has been operated on an industrial scale to produce $SOCl_2$, by passing a mixture of the two gases (SO_2 in a slight excess) over coconut charcoal at 170–180 °C [ICI10,ICI32]. The yield of $SOCl_2$ based on phosgene is *ca.* 75%, and the predominant impurity is SO_2Cl_2 (*ca.* 12%). At higher temperatures, SCl_2 and S_2Cl_2 grow at the expense of $SOCl_2$, the level of SO_2Cl_2 remaining approximately constant [ICI10].

Phosgene (0.1–1.5 wt.%) is reported to stabilize liquid sulfur trioxide against polymerization [1716].

9.5 TRANSITION METAL OXIDES AND SULFIDES

An interesting paper qualitatively compared phosgene with a mixture of CO and Cl_2 as reagents for converting metal oxides into metal chlorides: phosgene was found to be more effective in all eight cases studied [2107a].

9.5.1 Reactions of phosgene with Group 4 oxides and sulfides

Although the basic reaction of titanium(IV) oxide with phosgene at 400 °C was reported in 1911 to give titanium(IV) chloride [360]:

$$TiO_2 + 2COCl_2 \longrightarrow TiCl_4 + 2CO_2$$

the claim that titanium(VI) dioxide dichloride, TiO_2Cl_2, was also formed [360] can probably be safely ignored! However, titanium(IV) oxide dichloride, $TiOCl_2$, has been more recently detected [1089]. The chlorination of titanium slags (*ca.* 70% TiO_2, 12% FeO, 6% MgO, 6% Al_2O_3, with smaller amounts of Si, V, Cr, Zr and other metal oxides) by phosgene has been patented as a possible commercial route to titanium(IV) chloride [1344a,1784], and phosgene has also been added to the feed in the *preparation* of TiO_2 from $TiCl_4$ and dioxygen, to prevent TiO_2 adhering to the fluidized bed [77].

A careful study of the chlorination of TiO_2 (beneficiated ilmenite) has shown that the reaction proceeds considerably faster with phosgene than with a mixture of CO and Cl_2 [568]. As is common for many of the reactions with metal oxides and phosgene, the reaction rate goes through a maximum at *ca.* 650 °C, drops to a minimum at *ca.* 850 °C, and then starts to rise again (see Fig. 9.10). This is reasonably explained in terms of phosgene dissociation into carbon monoxide and dichlorine (see Chapter 8) becoming appreciable at above 600 °C, with concomitant decrease in the rate of chlorination, followed by an increase as the rate of chlorination by Cl_2 increases with temperature [568]. The same general features were confirmed in a later study, and an activation energy for the chlorination of pure TiO_2 by phosgene was determined as 137 kJ mol^{-1} [1501]. A number of other kinetic studies have also been published [1089,1093]. The presence of potassium ions catalyses the conversion of TiO_2 to $TiCl_4$ by phosgene [1404a].

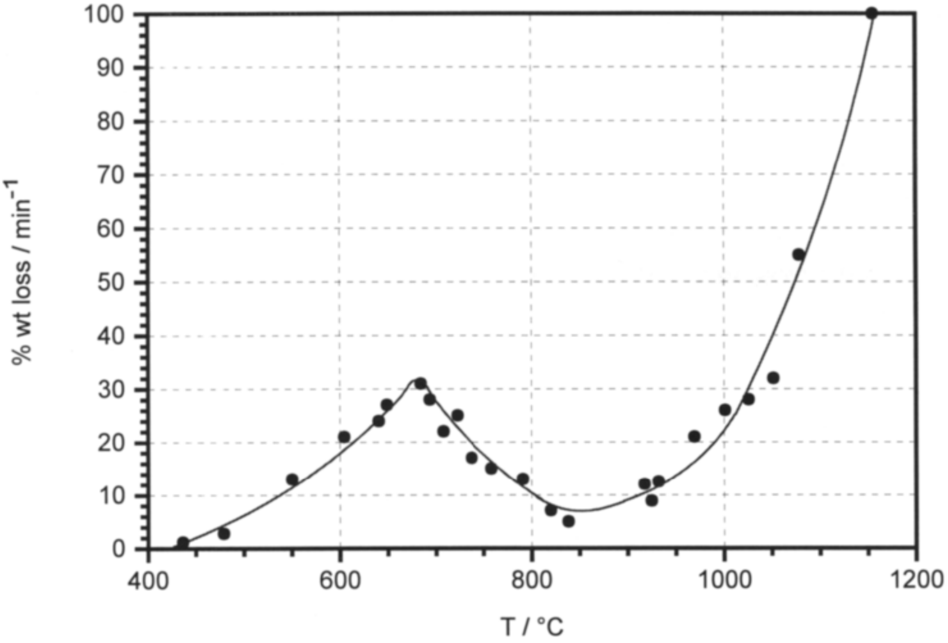


Fig. 9.10 **The rate of chlorination of titanium(IV) oxide by phosgene as a function of temperature [568].**

Zirconium(IV) oxide reacts with phosgene at 400 °C to give zirconium(IV) chloride [360], and zircon ($ZrSiO_4$) reacts with phosgene between 1000 and 1250 °C to give $ZrCl_4$ [120]. Phosgene has been postulated as an intermediate in the chlorination of zircon [1943], anatase or rutile [1767].

9.5.2 Reactions of phosgene with Group 5 oxides and sulfides

Vanadium(V) oxide is reported to react with phosgene at 350 °C to give vanadium(IV) chloride, whereas tantalum(V) oxide reacts with phosgene to give tantalum(V) chloride [360]:

$$V_2O_5 + 5COCl_2 \longrightarrow 2VCl_4 + 5CO_2 + Cl_2$$

$$M_2O_5 + 5COCl_2 \longrightarrow 2MCl_5 + 5CO_2$$
$$(M = Nb \text{ or } Ta)$$

The chlorination of V_2O_5 by CCl_4 has been said to be more effective than that by phosgene, resulting in a build up of phosgene in the products from the CCl_4 reaction [1404b]. However, a very recent isothermal thermogravimetric study has shown that the primary reaction products in these systems (400–570 K) is $VOCl_3$, and not VCl_4 [1586c]:

$$V_2O_5 + 3COCl_2 \longrightarrow 2VOCl_3 + 3CO_2$$

$$2V_2O_5 + 3CCl_4 \longrightarrow 4VOCl_3 + 3CO_2$$

The activation energy for the reaction with phosgene is 48 kJ mol^{-1}, and that for the reaction with CCl_4 is 77 kJ mol^{-1} [1586c].

The kinetics of the reactions of Nb_2O_5 [1089,1090] and Ta_2O_5 [1091] with phosgene have been reported; both reactions show the classic profile (similar to that illustrated in Fig. 9.10) with activation energies in the low temperature regions of 71.5 and 45 kJ mol^{-1}, respectively. The reaction of pyrochlore ore, pre-treated with H_2SO_3, with phosgene has been patented as a method for the extraction of niobium [1232], and phosgene has been postulated as an important intermediate in the chlorination of loparite, pyrochlore and euxenite in the presence of carbon [1943]. The intermediacy of $NbOCl_3$ in the reaction of Nb_2O_5 with $COCl_2$ has also been observed [568a,568b].

One method of separating niobium from tantalum is to pass a gaseous mixture of niobium(V) chloride and tantalum(V) chloride over adjacent beds of calcium oxide and calcium fluoride: the niobium emerges as volatile niobium(V) oxide trichloride whilst the tantalum is trapped in the CaO and CaF_2 beds. The reactions postulated to be responsible for trapping tantalum are [1984b]:

$$[Ta_2Cl_{10}] + 5CaO \longrightarrow Ta_2O_5 + 5CaCl_2$$

$$[Ta_2Cl_{10}] + 2nCaF_2 \longrightarrow 2TaCl_5.nCaF_2$$

$$[Ta_2Cl_{10}] + 2CaF_2 \longrightarrow [Ta_2Cl_6F_4] + 2CaCl_2$$

Tantalum recovery from the CaO and CaF_2 beds can be achieved with phosgene. Over 95% tantalum recovery (as $[Ta_2Cl_{10}]$) can be achieved by treating tantalum(V) oxide with phosgene at 490 °C; similar figures were obtained from the Ta_2O_5–CaO mixtures (although pre-heating of the CaO to 900 °C dramatically reduced the yield to *ca.* 66%) [1984b]. More surprisingly, similar high recoveries (up to 96%) were also achieved by treating the material from the fluoride bed [1984b].

In a rather eccentric process, given the propensity of such systems for halide exchange, the reaction between tantalum(V) oxide and hydrogen fluoride at 90 °C in an autoclave, followed by treatment of the mixture (now a hydrated fluorotantalic acid) with phosgene at 140 °C, has been used for the synthesis of anhydrous tantalum(V) fluoride [1106]:

$$Ta_2O_5 + 10HF + 5COCl_2 \longrightarrow 2Ta_2F_{10} + 5CO_2 + 10HCl$$

9.5.3 Reactions of phosgene with Group 6 oxides and sulfides

Chromium oxide (oxidation state unspecified) reacts with phosgene at 600 °C to give chromium(III) chloride, whereas tungsten(VI) oxide reacts with phosgene to give tungsten(VI) dioxide dichloride [360].

The reaction of a mixture of Cr_2O_3 and ^{14}C-labelled charcoal with phosgene has been studied between 600 and 900 °C, and two parallel reactions are believed to be occurring [282]:

$$Cr_2O_3 + 3COCl_2 \longrightarrow 2CrCl_3 + 3CO_2$$

$$Cr_2O_3 \xrightarrow[COCl_2]{^{14}C} CrCl_3 + {}^{14}CO/CO + {}^{14}CO_2/CO_2 + {}^{14}COCl_2/COCl_2$$

The distribution of ^{14}C-labelled gaseous products is illustrated in Fig. 9.11, and shows clearly that both reactions occur to a significant extent, but that there is a different temperature dependence of each [282].

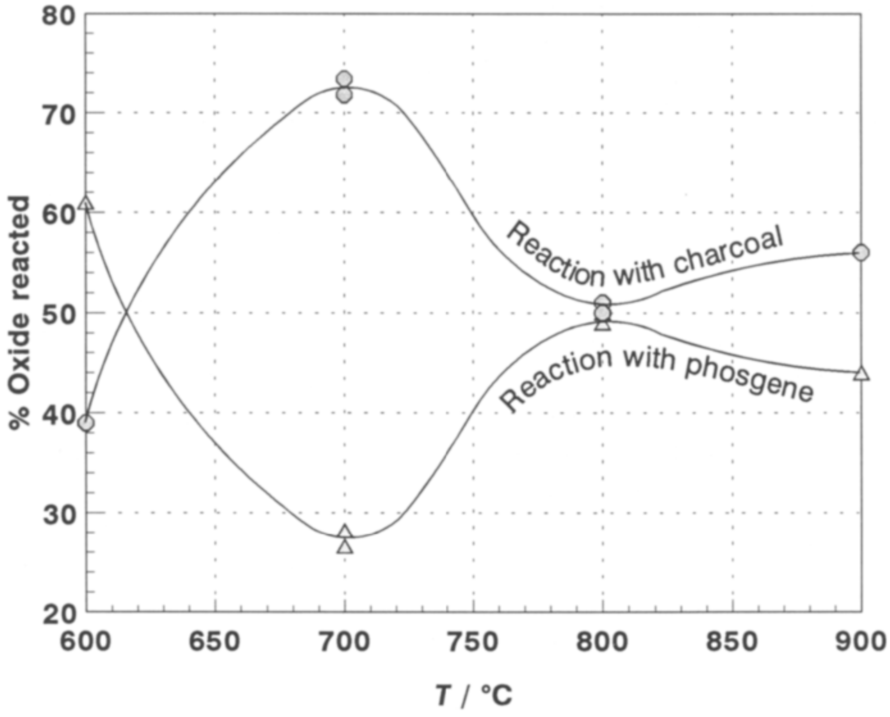


Fig. 9.11 The distribution of ^{14}C-labelled gaseous products compared with non-labelled products for the system $Cr_2O_3/^{14}C/COCl_2$ [282].

The kinetics of the reaction between WO_3 and $COCl_2$ have been studied by thermogravimetric techniques; although the nature of the products was not investigated, they were believed to be a mixture of $WOCl_4$ and WO_2Cl_2 on thermodynamic grounds (also, see Section 9.2.3) [1586d].

9.5.4 *Reactions of phosgene with Groups 7–9 oxides and sulfides*

Manganese(II) oxide reacts with phosgene at 450 °C to give manganese(II) chloride, whereas iron(III) oxide reacts at 350 °C to give iron(III) chloride [360]: iron(II) oxide forms iron(II) chloride [181c]. Liquid phosgene also slowly attacks the iron(III) oxide on the internal surfaces of iron industrial containers to give iron(III) chloride [489]. The reaction between iron(III) oxide and phosgene in the presence of sodium chloride has been proposed as a thermodynamically favourable route to sodium carbonate [ICI35]:

$$2Fe_2O_3 + 3COCl_2 + 6NaCl \longrightarrow 2[Fe_2Cl_6] + 3Na_2[CO_3]$$

The reaction of phosgene with iron ores has been proposed for opening up these minerals [130], and the reactions of FeO, Fe_2O_3, Fe_3O_4, wüstite, hæmatite and magnetite with phosgene have been studied by thermal gravimetric analysis [181c,1586a,1586b].

Procedures for recovering ruthenium [1864d], rhodium [1864f], and iridium [1864e] from waste metal oxide catalysts have been patented. The key step in the procedure is the conversion of the oxides (usually supported on TiO_2 or Al_2O_3) to the chlorides by treating with phosgene in the presence of powdered carbon.

Similarly, both manganese(II) sulfide and iron pyrites, FeS_2, react with phosgene, at 350 and 450 °C respectively, to give manganese(II) chloride and iron(III) chloride [361].

9.5.5 *Reactions of phosgene with Group 10 oxides and sulfides*

Phosgene reacts with nickel(II) oxide at 550 °C [360] or nickel(II) sulfide at 450 °C [361] to give nickel(II) chloride and CO_2 or COS, respectively.

The reaction of phosgene with spent platinum-containing or palladium-containing catalysts {on aluminium(III) oxide, silicon(IV) oxide, or carbon supports} at 140–450 °C has been used as part of a recovery process [20,231,1864a,1864c], and car exhaust oxidation catalysts can be reactivated by heating in phosgene at 260 °C [1251].

9.5.6 *Reactions of phosgene with Group 11 oxides and sulfides*

Phosgene reacts with $CuO.CuCl_2$ according to [ICI13,ICI14]:

$$CuO.CuCl_2 + COCl_2 \longrightarrow 2CuCl_2 + CO_2$$

This reaction was studied between 50 and 450 °C: it has an activation energy of 31 kJ mol^{-1} and a calculated free energy change of $\Delta G^\circ_{573} = -233.8$ kJ mol^{-1}. It can form a part of a catalytic process for ethene oxychlorination to 1,2-dichloroethane (see Chapter 4) [ICI13,ICI14].

A procedure for recovering gold [1864b] from waste metal oxide catalysts has been patented. The key step in the procedure is the conversion of the oxide (supported on Al_2O_3) to the chloride by treating with phosgene in the presence of powdered carbon.

With CuS, phosgene gives the expected $CuCl_2$ at 450 °C [361].

9.5.7 Reactions of phosgene with Group 12 oxides and sulfides

The reaction between zinc oxide and phosgene was first reported in 1812 by Davy in his landmark paper [467], the products being reported as "butter of zinc" and "carbonic acid". One hundred years later, Chauvenet [360] reinvestigated the reaction at 450 °C:

$$ZnO + COCl_2 \longrightarrow ZnCl_2 + CO_2$$

This reaction has also been studied by t.g.a., and initiates at 220 °C [1096]. A d.t.a. study showed a maximum at 277 °C, apparently corresponding to [1033]:

$$3ZnO + COCl_2 \longrightarrow 2ZnO.ZnCl_2 + CO_2$$

The chemisorption of phosgene onto the surface of zinc oxide has been studied by i.r. spectroscopy (37–155 °C) [710] and a pulsed chromatographic technique (25–255 °C) [709]: at temperatures <165 °C, a different mixed phase $ZnO.ZnCl_2$ is formed; at higher temperatures, $ZnCl_2$ forms. With non-stoicheiometric zinc oxide, phosgene reacts more rapidly with samples containing oxygen vacancies than those with interstitial zinc [634,1989,1990].

The reaction of cadmium(II) oxide with phosgene is analogous to that of zinc oxide, and has also been studied by thermal gravimetric analysis: the reaction initiates at 234 °C [1097].

The reaction between phosgene and cadmium(II) sulfide was discovered in 1891 [1529a]:

$$CdS + COCl_2 \longrightarrow CdCl_2 + COS$$

It was later shown that all the Group 12 sulfides react with phosgene in this way, ZnS and CdS at 400 °C, HgS at 350 °C [361].

9.6 LANTHANIDE AND ACTINIDE OXIDES

9.6.1 Reactions of phosgene with lanthanide oxides and Group 3 oxides

The reactions of lanthanide and Group 3 oxides with phosgene at 600 °C were first reported in 1911 [360]:

$$Ln_2O_3 + 3COCl_2 \longrightarrow 2LnCl_3 + 3CO_2$$
$$(Ln = La \text{ or } Y)$$

The reaction with CeO_2 was incorrectly reported as yielding $CeCl_4$ [360]. Cerium(IV) oxide reacts with phosgene to initially form cerium(III) oxide chloride, which can then react with further phosgene (see Section 9.3.1). Thus, the stoicheiometry of the two possible *overall* reactions is [307,1088,2042]:

$$2CeO_2 + 2COCl_2 \longrightarrow 2CeOCl + 2CO_2 + Cl_2$$

$$2CeO_2 + 4COCl_2 \longrightarrow 2CeCl_3 + 4CO_2 + Cl_2$$

The reaction of phosgene with Pr_6O_{11} has been studied by d.t.a., and proceeds by an interesting sequence of reactions [305]. Between 275 and 290 °C, the oxide dissociates according to:

$$Pr_6O_{11} \longrightarrow 3Pr_2O_3 + O_2$$

This is immediately chlorinated (290–310 °C):

$$Pr_2O_3 + COCl_2 \longrightarrow 2PrOCl + CO_2$$

Between 310 and 450 °C, two reactions proceed in parallel:

$$PrOCl + COCl_2 \longrightarrow PrCl_3 + CO_2$$

$$Pr_2O_3 + 3COCl_2 \longrightarrow 2PrCl_3 + 3CO_2$$

The ores gadolinite and cerite react with phosgene between 1000 and 1150 °C to give YCl_3 and $CeCl_3$, respectively (see Section 9.4.4) [120].

9.6.2 *Reactions of phosgene with actinide oxides*

Both uranium(IV) oxide and thorium(IV) oxide react with phosgene, at 450 °C and 650 °C respectively, according to [359a,360]:

$$MO_2 + 2COCl_2 \longrightarrow MCl_4 + 2CO_2$$
$$(M = U \text{ or } Th)$$

For uranium(IV) oxide, the free energy change for this process was calculated as [295]:

$$\Delta G/\text{kJ mol}^{-1} = -300.82 - 0.02443T\log_{10}(T) + 0.0677T$$

This gives values of ΔG of −299 and −303 kJ mol^{-1} at 300 and 800 K, respectively. This reaction is considerably more favoured than the formation of the oxide chloride, for which values of ΔG of −181 and −191 kJ mol^{-1} at 300 and 800 K were derived [295]:

$$UO_2 + COCl_2 \longrightarrow UOCl_2 + CO_2;$$
$$\Delta G/\text{kJ mol}^{-1} = -166.09 + 0.04347T\log_{10}(T) - 0.1575T$$

Indeed, for thorium(IV) oxide, the process has been shown to occur in two steps [1092], and replacement of $COCl_2$ with a CO–Cl_2 mixture results in the process stopping at the oxide chloride stage [1092,1350a]:

$$ThO_2 + COCl_2 \longrightarrow ThOCl_2 + CO_2$$
$$ThOCl_2 + COCl_2 \longrightarrow ThCl_4 + CO_2$$

$ThCl_4$ can be obtained in 91% yield from ThO_2 {prepared by calcining thorium(IV) oxalate} at 600 °C [1610]. For this overall conversion, ΔG° has been calculated as −322 kJ mol^{-1} [1610].

Thus, the ore thorite ($ThSiO_4$) reacts with phosgene between 1000 and 1150 °C to give $ThCl_4$ [120], autunite ($U_2CaP_2O_{12}.8H_2O$) gives volatile UCl_4 and involatile $CaCl_2$ at 800 °C and monazite (a mineral composed of phosphates of cerium, lanthanum, thorium and a range of lanthanides) yields volatile $ThCl_4$ [120]. A process for recovery of uranium from uranium waste products from a nuclear reactor, based upon the generation of UCl_4 by reaction with phosgene, has been patented [90].

Plutonium(IV) oxide (in its normal unreactive form) is reported not to react with phosgene below 700 °C [234,295], but small samples are completely chlorinated at 850 °C [234]:

$$2PuO_2 + 4COCl_2 \longrightarrow 2PuCl_3 + 4CO_2 + Cl_2;$$
$$\Delta H^\circ_{298}(\text{calc}) = -253 \text{ kJ (mol of Pu)}^{-1} \quad [261]$$

Larger samples are only partially chlorinated, since molten $PuCl_3$ prevents the reaction going to completion [234], whereas plutonium(III) oxalate is completely converted into $PuCl_3$ at 600–650 °C, but the product is contaminated with carbon [234]. Plutonium(III) "carbonate", in contrast, is quantitatively converted between 400 and 550 °C [234]. Phosgene has been used in a laboratory study upon the reprocessing (by chlorination) of neutron-irradiated uranium fuels [1491].

In contrast, if plutonium(IV) oxide is prepared in an active form (by thermal decomposition of plutonium(IV) oxalate at 300 °C [1683b,2042], or by calcination of a plutonium nitrate solution [261]), it will react with phosgene at between 350 and 400 °C [2042]. Kinetic studies (between 425 and 525 °C) have shown the reaction to be first order in PuO_2, with an activation energy of 72.0 kJ mol^{-1} [1924]. Moreover, it was demonstrated conclusively that the smaller the PuO_2 particles, the greater the reaction rate [1924], even though the temperatures here were below the melting point of $PuCl_3$. A mechanically-stirred fluidized bed process for converting active PuO_2 into $PuCl_3$ with phosgene at 455 °C has been developed: 95% conversion at a rate of 150 (g of Pu) h^{-1} was achieved [261]. A process for the production of plutonium metal from plutonium oxide, *via* the chloride, and explicitly using phosgene as the chlorinating agent, has been described [1683b].

9.7 MAIN GROUP ELEMENTS

It is remarkable how poorly documented, on the whole, are the reactions of phosgene with the main group elements. There are very few classical studies of the reactivity of the elements with phosgene at low temperature, although the number of purely physical investigations are increasing.

9.7.1 Reactions of phosgene with Group 1 elements

Dihydrogen does not react with phosgene thermally, even when subjected to an electric spark [467]. However, a mixture of H_2, O_2 and $COCl_2$ (in the ratios 2:1:2) ignites explosively, according to [467]:

$$2H_2 + O_2 + 2COCl_2 \longrightarrow 4HCl + 2CO_2$$

At atmospheric pressure and ambient temperature, irradiation (mercury lamp) of a mixture of phosgene and dihydrogen induces reaction according to [269]:

$$COCl_2 + H_2 \longrightarrow CO + 2HCl$$

The initial quantum yield for this process was determined as *ca.* 3.8 [1427]. At 10 °C, slight traces of methanal, H_2CO, were detected, but there is little evidence to sustain the claim [269] of its intermediacy in the gas phase reaction.

The derived rate law for the photochemical reduction of phosgene is [1427]:

$$\frac{d[CO]}{dt} = kI_0[COCl_2]\left\{1 + \frac{k_2[H_2]}{[CO][M]}\right\}$$

This rate law was accounted for by a simple mechanism (which has been queried [1074]) [1427]:

$$\begin{aligned} COCl_2 + h\nu &\longrightarrow COCl\cdot + Cl\cdot \\ Cl\cdot + H_2 &\longrightarrow HCl + Cl\cdot \\ COCl_2 + H\cdot &\longrightarrow CO + HCl + Cl\cdot \\ CO + Cl\cdot + M &\longrightarrow COCl\cdot + M \\ 2COCl\cdot &\longrightarrow COCl_2 + CO \end{aligned}$$

Phosgene has been investigated as a possible extinguisher for the dihydrogen–dioxygen system, and the explosion limits were plotted; the explosions followed a normal course [2092]. The addition of small amounts of phosgene (2.71%) to a dihydrogen–air flame will, however, reduce the flame speed [1396].

Sodium vapour reacts rapidly ($k = 8.56 \times 10^{10}$ l mol^{-1} s^{-1} at 270 °C) with gaseous phosgene, the reaction being chemiluminescent (Na D-line) [933]. The following mechanism was proposed:

$$\begin{aligned} \text{Na} + \text{COCl}_2 &\longrightarrow [\text{NaCl}] + [\text{COCl}]\cdot \\ \text{Na} + [\text{COCl}]\cdot &\longrightarrow [\text{NaCl}]^* + \text{CO} \\ [\text{NaCl}]^* + \text{Na} &\longrightarrow [\text{NaCl}] + \text{Na} + h\nu \end{aligned}$$

Phosgene is also recorded to react at room temperature with Na–K and Na–Ca alloys and with sodium or lithium amalgam [857,858,1711]:

$$2\text{K} + \text{COCl}_2 \longrightarrow 2\text{KCl} + \text{CO}$$

Indeed, Davy (in 1812) noted that "The action even of potassium heated in the gas was not violent. But from the great absorption of gas, and from the precipitation of carbon indicated by the blackness produced, not only the new gas [phosgene], but likewise the carbonic oxide [CO], appeared to be decomposed" [467]:

i.e.

$$4\text{K} + \text{COCl}_2 \longrightarrow 2\text{KCl} + \text{K}_2\text{O} + \text{C}$$

However, a sublimed sample of potassium is recorded not to react with liquid phosgene in a sealed tube at room temperature, even upon standing for twelve months in the dark [735].

9.7.2 Reactions of phosgene with Group 2 elements

Phosgene does not react with metallic magnesium at room temperature [735], but does react with magnesium amalgam dispersed in diethyl ether according to [1606]:

$$\text{Mg}_{\text{Hg}} + \text{COCl}_2 \longrightarrow \text{MgCl}_2 + \text{CO}$$

It is also reported to react with Na–Ca alloy at room temperature (see Section 9.7.1) [857].

9.7.3 Reactions of phosgene with Group 13 elements

Boron is reported to react with phosgene between 500 and 600 °C (in the presence of an excess of sodium chloride) according to [1950a]:

$$3B + 3COCl_2 \longrightarrow 2BCl_3 + 3CO$$

Although aluminium foil does not react with liquid phosgene in the dark, upon amalgamation or exposure to bright sunlight, a vigorous reaction occurs, accompanied by the liberation of carbon monoxide [735].

9.7.4 Reactions of phosgene with Group 14 elements

The thermodynamics of the following reaction have been calculated [1191]:

$$Ge + 2COCl_2 \longrightarrow GeCl_4 + 2CO$$

John Davy himself reported that phosgene reacts with molten tin to give tin(IV) chloride ("the liquor of Libavius") and carbon monoxide [467]. The activation energy for the reaction between tin and phosgene is 67 kJ mol^{-1} [1188].

9.7.5 Reactions of phosgene with Group 15 elements

The reaction between phosgene and active nitrogen (in an unheated reaction vessel) has been studied in some detail [106], the sole reaction products being equimolar quantities of CO and Cl_2. The reaction (which emits a pink light) appears to be initiated by an energy transfer process from an electronically excited N_2 species, $A^3\Sigma_u^+$, to a phosgene molecule, which becomes vibrationally excited. Subsequent collision with nitrogen atoms produces electronically excited phosgene, which then dissociates into carbon monoxide and dichlorine [106].

Davy reported that elemental arsenic and antimony both react with phosgene, upon heating, to produce their respective chlorides and carbon monoxide [467]. Phosphorus, however, can be sublimed in an atmosphere of phosgene without any reaction occurring [467].

9.7.6 Reactions of phosgene with Group 16 elements

The solubility of O_2 in liquid phosgene is described in Section 11.3.

Phosgene is oxidized by dioxygen, in the gas phase, between 150 and 500 °C according to [707,1088a]:

$$COCl_2 + \tfrac{1}{2}O_2 \longrightarrow CO_2 + Cl_2$$

The equilibrium constant for this reaction has been calculated [236] over a wide temperature range: $\log_{10}(K)$ (T/K); 29.21 (298), 21.0 (500), 11.75 (1000), 8.64 (1500), 7.10 (2000). The activation energy was determined as 56 kJ mol^{-1} [707]: no CO was detected in the product mixture, indicating to the authors that the oxidation occurred *via* a mechanism involving [COCl]· radicals [707]. Reaction conditions for the complete decomposition of phosgene by combustion have been calculated [955].

The first report of the photochemical oxidation of $COCl_2$ by O_2 was in 1933, and the overall rate law determined (for irradiation by a mercury quartz lamp) was [1738]:

$$\frac{\mathrm{d}[CO_2]}{\mathrm{d}t} = \frac{kI_0[COCl_2][O_2]}{\{[O_2] + k'[Cl_2]\}}$$

This rate law was accounted for by a simple mechanism [1738]:

$$\begin{aligned}
COCl_2 + h\nu &\longrightarrow COCl\cdot + Cl\cdot \\
COCl\cdot + O_2 &\longrightarrow CO_2 + ClO\cdot \\
COCl_2 + ClO\cdot &\longrightarrow CO_2 + Cl_2 + Cl\cdot \\
COCl\cdot + Cl_2 &\longrightarrow COCl_2 + Cl\cdot \\
Cl\cdot + M &\longrightarrow \tfrac{1}{2}Cl_2 + M \\
Cl\cdot + Cl\cdot &\longrightarrow Cl_2
\end{aligned}$$

The overall quantum yield for the photochemical oxidation of phosgene was determined as *ca.* 1.8 [1427].

As the primary photogenerated products are $COCl\cdot$ and $Cl\cdot$, phosgene acts as a photosensitizer for the oxidation of carbon monoxide (to carbon dioxide). Indeed, the photosensitized oxidation of CO is so much faster than the photochemical oxidation of phosgene itself that the oxidation of the phosgene could be neglected until the CO was largely depleted (>80% reaction) [1739]. At low dioxygen pressures, the rate law is given by [1739]:

$$\frac{\mathrm{d}[CO_2]}{\mathrm{d}t} = kI_0^{\frac{1}{2}}[COCl_2]^{\frac{1}{2}}[CO]^{\frac{1}{2}}[O_2]^{\frac{1}{2}}$$

At higher dioxygen pressures, the rate law becomes [1739]:

$$\frac{\mathrm{d}[CO_2]}{\mathrm{d}t} = kI_0^{\frac{1}{2}}[COCl_2]^{\frac{1}{2}}[CO]^{\frac{1}{2}}$$

The mechanism (which has been queried [1074]) proposed to account for these results is [1739]:

$$\begin{aligned}
COCl_2 + h\nu &\longrightarrow COCl\cdot + Cl\cdot \\
CO + Cl\cdot + M &\longrightarrow COCl\cdot + M \\
COCl\cdot + O_2 &\longrightarrow CO_3Cl\cdot \\
CO_3Cl\cdot + CO &\longrightarrow 2CO_2 + Cl\cdot \\
CO_3Cl\cdot + COCl\cdot &\longrightarrow 2CO_2 + Cl_2
\end{aligned}$$

The quantum yield for this process was found to be in the range of 87–110 [1427].

The reaction between phosgene and ozone (trioxygen) at 200 °C is faintly chemiluminescent, and readily explosive [2049]. The u.v. irradiation of a mixture of phosgene, ozone or dioxygen, and toxic hydrocarbons in air resulted in the oxidative decomposition of the hydrocarbons [1061].

Upon irradiation of an aqueous solution of phosgene (buffered at pH 2.2) with X-rays, the amount of hydrogen peroxide formed was found to decrease with increasing phosgene concentration: the activated oxygen formed during the irradiation appears to oxidize phosgene to carbon dioxide in preference to forming hydrogen peroxide [1267].

The photolysis of $N^{18}O_2$ (at 366 nm) produces atomic ^{18}O: this reacts with phosgene according to [1025a]:

$$COCl_2 + {}^{18}O \rightleftharpoons C^{18}OCl_2 + O$$

At 298 K, this reaction proceeds with a second-order rate constant of 1.9×10^6 l mol s^{-1}; the activation energy for the process was estimated as 12.5 kJ mol^{-1} [1025a].

Electronically excited oxygen atoms $O(2^1D_2)$, generated by photolysing ozone, are quenched by phosgene with an absolute second-order rate constant (at 300 K) of 7.1×10^{-10} cm^3 $molecule^{-1}$ s^{-1} [660]. Rates relative to COF_2 and COClF have also been measured [660,1038] and critically evaluated [1808]; phosgene is the most efficient quencher of the three gases studied, and quenching is accompanied by chemical decomposition of the phosgene, CO having been detected [1038].

The lack of reactivity of sulfur towards phosgene is evidenced by the observation that it can be sublimed in an atmosphere of phosgene without reaction [467].

9.7.7 Reactions of phosgene with Group 17 elements

There was no reaction when difluorine was bubbled through liquid phosgene at 6 °C, but the vapour over the reaction mixture was explosive [992]. However, when a mixture of difluorine and phosgene were passed over calcium fluoride, a reaction (frequently explosive) occurred to yield a liquid which boiled at −42 °C [992]. Although then thought to be a mixture of COF_2 and dichlorine, it is likely that this reaction produced the first samples of carbonyl chloride fluoride (*cf*. Section 9.1.1), thirty-seven years before this material was first identified.

The reaction of phosgene with F_2 at −78 °C, in the presence of CsF, produces equal amounts of CF_3OF and Cl_2 [1287a,1754b]:

$$COCl_2 + 2F_2 \longrightarrow CF_3OF + Cl_2$$

The phase diagram for the solid-liquid equilibria of the $COCl_2$–Cl_2 system has been determined (but not published in detail), and apparently indicates compound formation at $xCOCl_2.Cl_2$ (x = 1, 8 or 16), $3COCl_2.5Cl_2$ and $COCl_2.xCl_2$ (x = 3 or 10) [742]. The solutions are nearly ideal, and their liquid–vapour equilibria are described in Chapter 6. Good evidence for the existence of $COCl_2.Cl_2$ and $COCl_2.Br_2$ has been obtained from a recent i.r matrix isolation (Ar; 12 K) study [1aa]. I.r. spectroscopy has also been used to detect phosgene impurities in liquid chlorine [1664].

Data from the study of the photochemical formation of phosgene [308] has enabled kinetic and thermodynamic data for the following reactions to be determined [791,792]:

$$COCl_2 + Cl\cdot \longrightarrow [COCl]\cdot + Cl_2 \qquad (9.3)$$

$$[COCl]\cdot + Cl\cdot \longrightarrow CO + Cl_2 \qquad (9.4)$$

For reaction (9.3), the activation energy is 83 kJ mol^{-1}, the Arrhenius frequency factor is 2.51×10^{11} l mol^{-1} s^{-1}, the activation entropy is 70 J mol^{-1} K^{-1}, and the bond dissociation energy, D(CCl), is 313 kJ mol^{-1}; for reaction (9.4), the activation energy is 3.3 kJ mol^{-1}, the Arrhenius frequency factor is 3.98×10^{11} l mol^{-1} s^{-1}, the activation entropy is 65.7 J mol^{-1} K^{-1}, and D(CCl) is 29 kJ mol^{-1}.

The following ion–molecule reaction has been studied by quantitative ion cyclotron resonance (i.c.r.) and ion cyclotron double-resonance (i.c.d.r.) techniques [550,551]:

$$COCl_2 + [Cl_2]^- \longrightarrow [COCl_3]^- + Cl\cdot$$

The reaction proceeds by a simple ion transfer mechanism [550].

Ebullioscopic measurements indicate that iodine dissolves in phosgene as I_2 [151].

9.7.8 *Reactions of phosgene with Group 18 elements*

The quenching of $Ar(^3P_{0,2})$ metastable atoms by phosgene has been used to generate the first excited triplet metastable state of carbon monoxide, $CO(a\,^3\Pi)$, in a high state of vibrational excitation, according to [2012a]:

$$Ar(^3P_{0,2}) + COCl_2 \longrightarrow Ar(^1S_0) + CO(a\,^3\Pi) + Cl_2 \text{ (or } 2Cl\cdot)$$

The quenching rates for $Ar(^3P_2)$, $Ar(^3P_0)$ and $Kr(^3P_2)$ by phosgene have been measured as 47×10^{-11}, 42×10^{-11} and 52×10^{-11} cm^3 $molecule^{-1}$ s^{-1} with corresponding cross-sections of 100, 89 and 140 $Å^2$, respectively [2107]. $Kr(^3P_1)$ reacts with phosgene to generate KrCl(B,C) [263].

The quenching of $Xe(6s,^3P_2)$ metastable atoms by phosgene has been studied [1146,1844], and the vibrational energy transfer monitored [2004]. The reaction of excited xenon atoms ($^3P_2$ or $^3P_1$) with phosgene generates XeCl(B,C), the emission from which, XeCl(B–X) and XeCl(C–A), has enabled vibrational relaxation and transfer between the B and C states to be studied in some detail [263,558].

9.8 TRANSITION ELEMENTS AND ACTINIDES

There is a lacuna of serious chemical studies upon the reactions of phosgene with the transition metals, even extending to a shortage of published data concerning the rate of attack of phosgene upon the metals most commonly used in its storage, transfer, reactions and transport.

9.8.1 Reactions of phosgene with Group 4, Group 5 and Group 6 elements

Phosgene is reported to react with titanium sponge between 300 and 450 °C according to:

$$Ti + 2COCl_2 \longrightarrow TiCl_4 + 2CO$$

Treatment of pure molybdenum powder with phosgene produces $[Mo_2Cl_{10}]$ below 600 °C, $MoCl_3$ at 600 °C, and molybdenum(II) chloride at 700–800 °C [1255a,1255b]: with powdered tungsten, phosgene yields $[W_2Cl_{10}]$, WCl_6, and (predominantly) $WOCl_4$ [1255b], and with tantalum powder, the only metal-containing product was tantalum(V) chloride [1255b]. This system is long overdue for reinvestigation.

9.8.2 Reactions of phosgene with Group 8 elements

Pure iron is not attacked by phosgene, even in the presence of dichlorine, but impure iron rapidly forms iron(III) chloride [1168].

The interaction of phosgene with the (001) surface of metallic ruthenium has been studied by high-resolution electron energy loss spectroscopy (HREELS), temperature programmed desorption and Auger electron spectroscopy [934a]: the first monolayer of $COCl_2$ desorbs at 138 K, only 16 K above its multilayer desorption temperature. Only 5% of the first monolayer is dissociated into CO and Cl·, presumably due to absorption at defect sites. The HREELS results are consistent with an η^1–Cl bonding mode for the phosgene {see Fig. 9.12(A)} [934a].

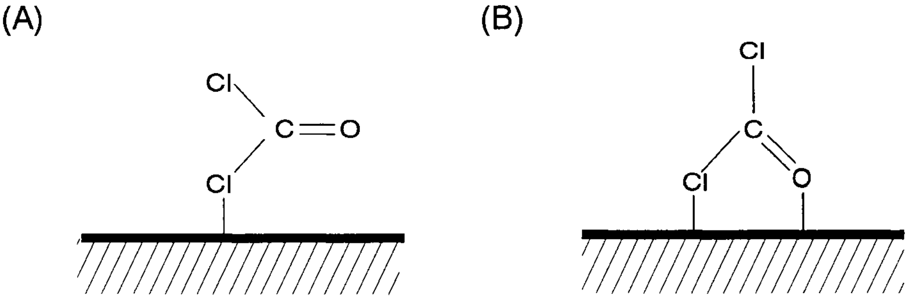


Fig. 9.12 (A) The η^1–Cl bonding mode, and (B) the η^2–Cl,O bonding mode, for phosgene on a metal surface [934a,2252d].

9.8.3 Reactions of phosgene with Group 9 elements

The presence of carbon monoxide catalyses the direct chlorination of metallic iridium to iridium(III) chloride under conditions of u.v. irradiation: it has been postulated that this is due to the intermediate formation of phosgene [1950].

9.8.4 Reactions of phosgene with Group 10 elements

Nickel, even after prolonged exposure at 400 °C, shows no significant signs of reaction with phosgene [ICI15,ICI16]. ™Inconel (Ni, 80%; Cr, 14%; Fe, 6%) is similarly unreactive [ICI16]. However, at temperatures between 400 and 550 °C, nickel is slowly attacked according to [810]:

$$\mathrm{Ni + COCl_2 \longrightarrow NiCl_2 + CO}$$

The activation energy for this reaction was found to be 73 kJ mol^{-1} [810].

Phosgene will absorb on the Pt(111) face of metallic platinum at 110 K; HREELS results are consistent with an η^2–Cl,O bonding mode for the phosgene {see Fig. 9.12(B)} [2252d], although an η^1–Cl bonding mode could not be eliminated as a possibility {see Fig. 9.12(A)} [2252d]. Upon u.v. irradiation, the adsorbed phosgene dissociates to give adsorbed chlorine atoms and some desorbed CO: in the 254–290 nm region, direct excitation of the adsorbate–substrate complex, along with some substrate excitation, occurs; at >290 nm, substrate excitation dominates [2252d]. Analogous studies, with similar findings, have been reported for $COCl_2$ on Pd(111) [660a,2252c].

9.8.5 Reactions of phosgene with Group 11 elements

The reaction of phosgene with copper has been used to purify boron(III) chloride (see Section 9.1.2.2) [1218a]. Copper does not react with phosgene at room temperature [735], but does react between 260 and 400 °C, with an activation energy of 100 kJ mol^{-1}, to give copper(I) chloride [809]:

$$\mathrm{2Cu + COCl_2 \longrightarrow 2CuCl + CO}$$

At high temperatures and long reaction times, some copper(II) chloride may be formed.

However, in the $BuNH_2$–O_2–CCl_4 and py–O_2–CCl_4 systems, phosgene is said to be responsible for the oxidation of copper to copper(II) chloride [1237]. Similarly, phosgene is claimed as an intermediate in the dissolution of copper in a dmso–CCl_4 mixture [2018a]:

$$\mathrm{Cu + COCl_2 + 2OSMe_2 \longrightarrow [CuCl_2(OSMe_2)_2] + CO}$$

However, the facile reaction between dimethyl sulfoxide and phosgene (see Section 10.6.5.1) makes this a questionable postulate.

Phosgene will absorb on the Ag(111) face of metallic silver [2252a,2252b]. Upon u.v. irradiation, the adsorbed phosgene dissociates to give adsorbed chlorine atoms and gas phase CO, at photon energies above 2.6 eV [2252a,2252b].

9.8.6 Reactions of phosgene with Group 12 elements

Zinc reacts with phosgene, upon heating, to give zinc(II) chloride and carbon monoxide [467], although reaction is reported at room temperature [735].

Bubbling pure phosgene through mercury has no visible effect [1275]: rapid discoloration of the mercury indicates the presence of free Cl_2 in the phosgene (which can be removed by passage of the gas through wash bottles containing "cottonseed oil") [620b].

Phosgene will quench metastable mercury atoms according to [2251a]:

$$Hg(^3P_2) + COCl_2 \longrightarrow HgCl(B) + [COCl]\cdot$$

Study of this reaction led to an experimental value of D(CCl) for phosgene of 334 kJ mol^{-1} (*cf*. Chapter 6 and Section 9.7.7) [2251a].

9.8.7 Reactions of phosgene with the actinides

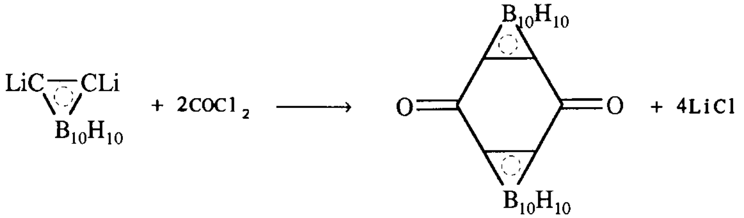
Phosgene can be removed as an impurity from Group 18 gases by passage over uranium metal at 500–1000 °C; the reaction products were not investigated [1505].

9.9 ORGANOMETALLICS

9.9.1 Reactions of phosgene with main group organometallics

Phosgene reacts with butyllithium in diethyl ether to give principally 5-butylnon-4-ene, along with some Bu_3COH and a trace of Bu_2CHOH: the dehydration of the tertiary alcohol to the alkene is favoured by excess of phosgene [763]. With phenyllithium, phosgene reacts to give good yields of Ph_3COH [763].

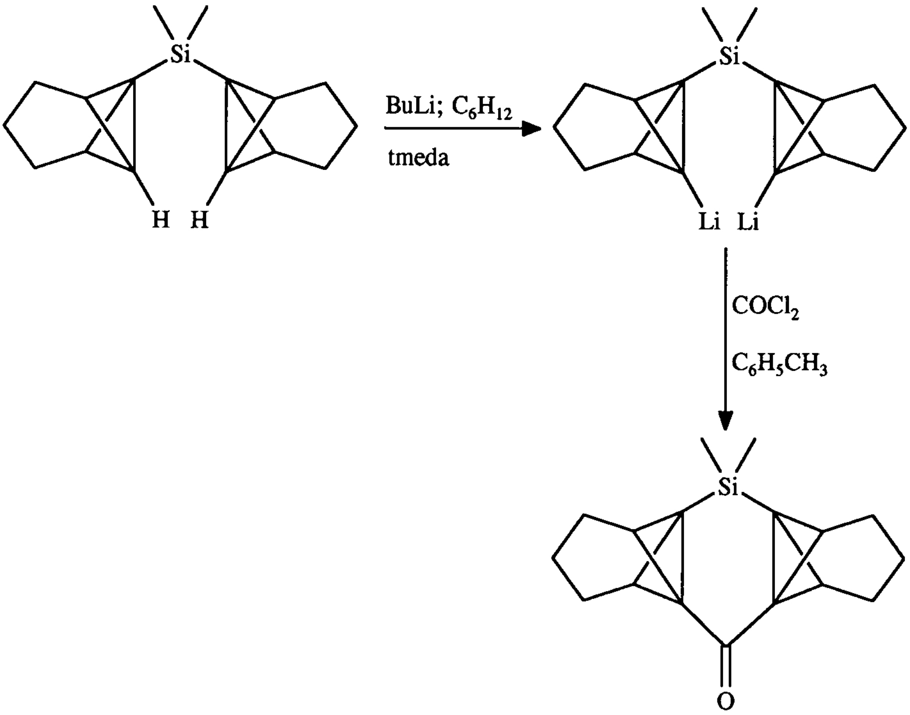
Treatment of the dilithium salts of 1,2-dicarba*closo*dodecaborane, $Li_2[1,2\text{-}C_2B_{10}H_{10}]$, with phosgene generates an interesting dimeric compound in 50% yield [1701]:



In contrast, the salt of the 1,7- isomer, $Li_2[1,7\text{-}C_2B_{10}H_{10}]$, simply results in the derivitization of the skeletal carbon atoms to give low yields of the di(acid chloride),

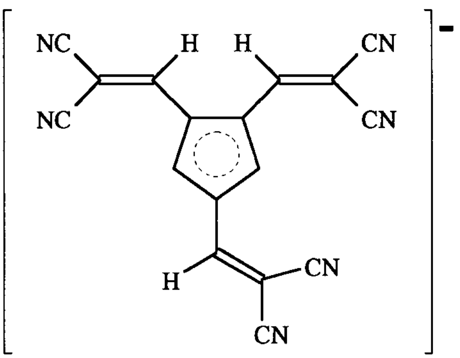
$1,7\text{-}(COCl)_2\text{-}1,7\text{-}C_2B_{10}H_{10}$, along with two discrete and isolable oligomers, $ClC(O){-}[{-}CB_{10}H_{10}CC(O){-}]_x{-}Cl$ (x = 3 or 5) [1701].

In a somewhat related reaction, a doubly lithiated tricyclo[4.1.0.0^{2,7}]heptylsilane has been cyclized to yield a [4.1.1]propellane derivative [311b]:



The sodium salts of alkynes are reactive towards phosgene. Thus, treatment of Na[C≡CCMe$_3$] with phosgene in diethyl ether at 0 °C yields $Me_3CC{\equiv}CC(O)Cl$, along with some $(Me_3CC{\equiv}C)_2CO$ [1017]. Performing the reaction with less phosgene, and then hydrolysing the resultant mixture, results in the isolation of $(Me_3CC{\equiv}C)_3COH$ [1017].

Treatment of the potassium salt of the cyclopentadienyl species illustrated below with $COCl_2$ gave unstable orange crystals of molecular formula $C_{19}H_4Cl_2N_6O_2$, of uncertain structure [1352].



It is appropriate that the first report of the reaction of phosgene with Grignard reagents was published by Grignard himself [828a]. Thus, with a 2:1 or 3:1 molar excess of Grignard reagent over phosgene in toluene solution, the overall theoretical reactions (after work-up) are [828a]:

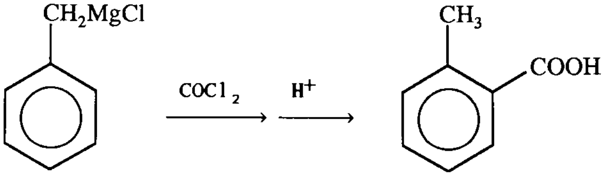
$$\mathrm{2RMgX + COCl_2 \longrightarrow R_2C{=}O + 2MgXCl}$$

$$\mathrm{2RMgX + COCl_2 \xrightarrow{H_2O} R_2CH(OH) + MgXCl + Mg(OH)X}$$

$$\mathrm{3RMgX + COCl_2 \xrightarrow{H_2O} R_3COH + 2MgXCl + Mg(OH)X}$$

However, when R is larger than Me or Et, the reactions are often more complex than this, leading to the formation of hydrocarbon by-products. For example, $\mathrm{Me_2CHCH_2CH_2MgBr}$ in a two molar excess over phosgene yields some $\mathrm{C_{16}H_{32}}$ in addition to $\mathrm{(Me_2CHCH_2CH_2)_2CH(OH)}$, and in a three molar excess yields a mixture of $\mathrm{(Me_2CHCH_2CH_2)_2CH(OH)}$ and $\mathrm{(Me_2CHCH_2CH_2)_3COH}$ [828a].

The reaction of phosgene with a range of substituted benzylmagnesium chlorides (*i.e.* $\mathrm{ArCH_2MgCl}$) in diethyl ether has been studied between −10 and −20 °C [1020]. The parent compound, $\mathrm{PhCH_2MgCl}$, reacts to give the 2-substituted carboxylic acid (following the normal work-up procedure) [1020]:



Similar reactions are given by the 4-methyl- and 2,4-dimethyl- derivatives, and by PhCH(Et)MgCl, producing (after work-up) the corresponding 6-carboxylic acid [1020]. However, for the 2-methyl-, 3-methyl-, and 2,3-dimethyl- derivatives, unidentified by-products were also formed [1020].

In an unusual reaction, phosgene reacts with Mg(C≡CCN)Br in diethyl ether at −30 °C to yield BrC≡CCN [1351].

Treatment of $\mathrm{Me_3SiCN}$ with phosgene results in its cleavage to form tricyano(trimethylsiloxy)methane, $\mathrm{Me_3SiOC(CN)_3}$, in excellent yield [1250]: the intermediacy of $\mathrm{CO(CN)_2}$ was postulated (see also Section 10.4.1):

$$\mathrm{COCl_2 + 2Me_3SiCN \longrightarrow CO(CN)_2 + 2Me_3SiCl}$$

$$\mathrm{CO(CN)_2 + Me_3SiCN \longrightarrow Me_3SiOC(CN)_3}$$

This seems a reasonable mechanism, as the reaction of $Me_3Si(NCS)$ with phosgene gives $CO(NCS)_2$ [45a] and the reaction of tributyltin(IV) isocyanate with phosgene has been utilized for the synthesis of carbonyl diisocyanate [22a]:

$$COCl_2 + 2Me_3SiNCS \xrightarrow{120\ ^\circ C} CO(NCS)_2 + 2Me_3SiCl$$

$$COCl_2 + 2Bu_3SnNCO \xrightarrow{160\ ^\circ C} CO(NCO)_2 + 2Bu_3SnCl$$

The analogous treatment of Me_3SiNCO with $COCl_2$, however, gave no reaction below 200 °C [22a].

The reactions of a wide range of silyl ethers, Me_3SiOR (R = Me, Et, Pr, $CHMe_2$, allyl, $CH_2C{\equiv}CH$, Bu, CH_2CHMe_2, CH(Me)Et, CMe_3, Ph, C_6H_{11}, $CH_2CH{=}CHPh$, CH_2SiMe_3 or $SiMe_3$), and a couple of silyl esters, $Me_3SiOC(O)R'$ (R' = Me or CF_3), with phosgene in toluene at 22 °C have been studied kinetically (see also Section 10.4.3.2) [1852]:

$$Me_3SiOR + COCl_2 \longrightarrow Me_3SiCl + ROC(O)Cl$$

The reaction rates decreased with increasing length, degree of branching or degree of unsaturation of R, and the esters were much less reactive than the ethers [1852]. Both $Me_3SiOCMe_3$ and $Me_3SiOSiMe_3$ were unreactive towards phosgene, and the reaction with Me_3SiOPh was extremely slow. The reactivity of some germanium {Et_3GeOMe and $Et_3GeOC(O)Me$} and tin {Bu_3SnOMe and $Bu_3SnOC(O)Me$} derivatives was also evaluated, and the order of reactivity was found to be [1852]:

$$Sn > Ge >> Si$$

Indeed, Et_3GeOMe and Bu_3SnOMe were reported to react with phosgene "almost immeasurably fast" [1852]. Oxasilacycloalkanes also undergo facile cleavage of the silicon–oxygen bond, the reaction becoming slower as the ring size increases [1852]:

$$Me_2\overline{Si(CH_2)_nO} + COCl_2 \longrightarrow ClSiMe_2(CH_2)_nOC(O)Cl$$
$$(n = 3 \text{ or } 4)$$

The reaction of the bifunctional compound $Bu_3Sn(CH_2)_3NHSiMe_3$ with phosgene in toluene at 3 °C results in the cleavage of the Si–N bond [507]:

$$Bu_3Sn(CH_2)_3NHSiMe_3 + COCl_2 \longrightarrow Bu_3Sn(CH_2)_3NCO$$

The product, tributyl(3-isocyanatopropyl)tin(IV), can also be prepared by treating

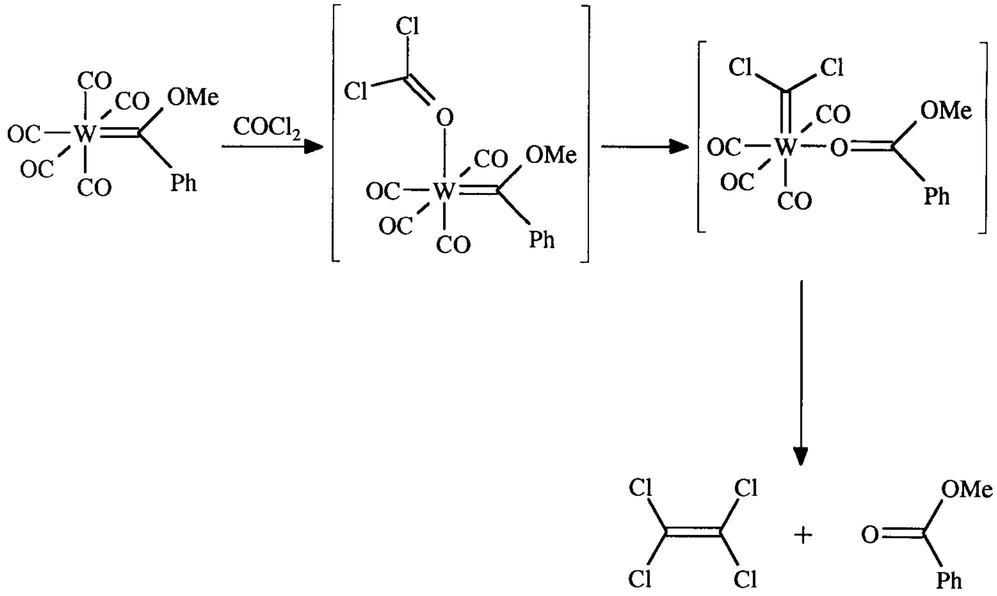
$Bu_3Sn(CH_2)_3NH_2$ with phosgene (*cf.* Section 10.4.1) [507].

Phosgene reacts with 2-hydroxyethyldichloroarsine, $AsCl_2(CH_2CH_2OH)$, to produce a poorly characterized oil which could be decomposed to eventually yield $AsCl_2(CH_2CH_2Cl)$ [1857]. The reaction between $AsHPh_2$ and phosgene yields only $AsPh_2Cl$ [1948].

9.9.2 Reactions of phosgene with transition metal organometallics

Treatment of a hexane solution of $[Cr(CO)_5\{PH[N(CHMe_2)_2]_2\}]$ with phosgene, both at room temperature and under reflux, resulted (rather surprisingly) in the chromium(0) complex being recovered unchanged [1107ac].

In a recent fascinating publication, pentacarbonyl(methoxyphenylcarbene)tungsten(0), $[W(CO)_5\{C(OMe)Ph\}]$, was treated with phosgene in octane in a sealed tube at 70 °C: this reaction produced a mixture of methyl benzoate, PhC(O)OMe, and tetrachloroethene [1143]. The proposed mechanism, although tentative, is of some interest, as it involves initial coordination of the phosgene, and then oxygen loss to form a dichlorocarbene ligand [1143]:



Organomanganese(II) halides react with phosgene in diethyl ether (−40 − +20 °C) in a predictable manner [323]:

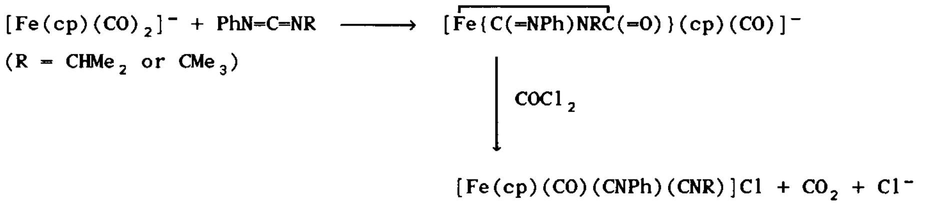
$$RMnI + COCl_2 \longrightarrow RC(O)R + R_2$$

Thus, $(C_7H_{15})MnI$ reacts with phosgene to give $(C_7H_{15})_2CO$ (55%) and $C_{14}H_{30}$ [323].

Metal carbamoyl complexes can readily be converted into isonitrile complexes with phosgene (in the presence of NEt_3), a procedure which can be utilized to prepare complexes of isonitriles which do not exist in the free state [635]:

$$[L_nM{-}C(O)NHR] + COCl_2 + NEt_3 \longrightarrow [L_nM{-}C{\equiv}NR]Cl + CO_2 + [NHEt_3]Cl$$

Using this method, the complex $[Fe(cp)(CO)_2\{C(O)NHMe\}]$ has been converted into $[Fe(cp)(CO)_2(CNMe)]Cl$, and *cis*-$[Pt(PPh_3)_2\{C(O)NHMe\}Cl]$ has been used to prepare *cis*-$[Pt(PPh_3)(CNMe)Cl_2]$ [635]. In an interesting variation on this procedure, the reaction of phosgene with unsymmetrical carbodiimide adducts of iron has been used to prepare iron(II) complexes containing two different isonitrile ligands at a now chiral centre [636]:



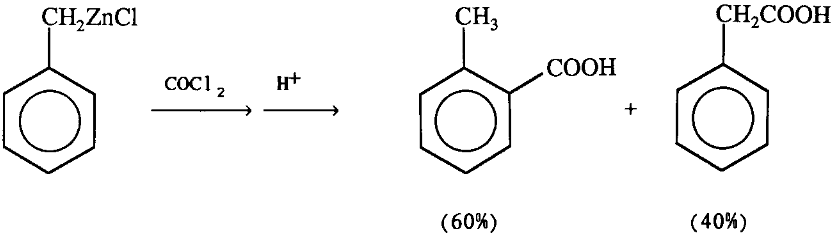
$$[Fe(cp)(CO)_2]^- + PhN{=}C{=}NR \longrightarrow [Fe\{C({=}NPh)NRC({=}O)\}(cp)(CO)]^-$$

$(R = CHMe_2 \text{ or } CMe_3)$

$$\xrightarrow{COCl_2} [Fe(cp)(CO)(CNPh)(CNR)]Cl + CO_2 + Cl^-$$

In a series of early reports, dimethylzinc(II) is shown to react with phosgene to give a white crystalline solid, described as $Zn(CH_3)_2.C_2H_3OCl$ [313a–313f]. This solid reacts with water to give 2-methylpropan-2-ol, Me_3COH (and not ethanoic acid, as frequently misquoted, *e.g.* [578]) [313a–313f], and the overall reaction should be compared with that of the Grignard reagent (see Section 9.9.1). This is a system long overdue for reinvestigation.

Unlike the analogous Grignard reagent, benzylzinc(II) chloride reacts with phosgene to give two products, one ring substituted, the other side-chain substituted [1020]:



Diphenylcadmium(II) reacts with two equivalents of phosgene in toluene to yield PhC(O)Ph as the main product, but no PhC(O)Cl [601]. Indeed, the reaction of CdR_2 with phosgene appears to be a general route to the symmetrical ketones, $R_2C{=}O$ [2010a].

$Hg(CH_2Ph)Cl$ does not appear to react with phosgene at temperatures below which it decomposes to give $PhCH_2CH_2Ph$ [1020]. In contrast, treatment of $Hg\{CH_2C(O)H\}_2$ with phosgene in thf yielded divinyl carbonate, $\{CH_2{=}C(H)O\}_2C{=}O$ [1461a]. Similarly, treatment of either $Hg\{CH_2C(O)R\}Cl$ (R = H or Me) or $Hg\{CH_2C(O)R\}_2$ with phosgene in a polar solvent (*e.g.* nitrobenzene, CH_2Cl_2 or MeCN) at 20–60 °C affords $CH_2{=}C(R)OC(O)Cl$ (*i.e.* vinyl or isopropenyl chloroformates; for a review of their properties, see [61]) in excellent yields (>75%) [1622]. The work was extended to include R = Ph, CMe_3 or C_3H_5, and the synthesis of 1-cyclohexenyl chloroformate from mercury biscyclohexanone [1558].

9.10 HYDRIDE DERIVATIVES

9.10.1 Reactions of phosgene with Group 13 and Group 14 hydrides

In a remarkable and surprising (but undoubtedly correct) report, it was found that all attempts to bring about a reaction between diborane and phosgene met with failure [280a].

Phosgene is reduced by Li[AlH_4] in bis(2–ethoxyethyl) ether to produce low yields (22%) of methanol [583].

The silicon–hydrogen bond in silanes is remarkably resistant to the action of phosgene (*cf.* B_2H_6): $SiCl_4$ is formed on treating $HSiCl_3$ with phosgene, but only under very severe conditions (*ca.* 500 °C) [1409].

9.10.2 Reactions of phosgene with Group 15 hydrides

9.10.2.1 Reactions of phosgene with ammonia and hydrazine

The reaction between ammonia and phosgene (in a 4:1 stoicheiometry) was first reported in 1812, in the paper in which John Davy reported the discovery of phosgene [467]. The white product was claimed by Regnault in 1838 [1696a] to be a mixture of ammonium chloride and an "isomeric carbamide of urea", but Hofmann [972a] and Natanson [1483aa] later correctly demonstrated that it was a mixture of ammonium chloride and urea itself. The overall reaction between phosgene and ammonia in benzene is thus deceptively simple [2168]:

$$COCl_2 + 4NH_3 \longrightarrow CO(NH_2)_2 + 2[NH_4]Cl$$

and has been patented as a route to artificial manure [1875a].

As early as 1869, Bouchardat [240,686] had identified guanidine {$C(=NH)(NH_2)_2$}, 1,3,5–triazine–2,4,6–triol (cyanuric acid), and "melanuric acid" {probably cyamelide, a polymeric form of cyanic acid, $(CNOH)_n$} as by–products of the reaction. Fenton [641a] suggested, in 1879, that the urea may not be a primary product, but formed by secondary reactions. Further, in 1905, Hantzsch and Stuer [880aa,1970a] detected the formation of cyamelide when the reaction was performed at 0 °C in light petroleum. The reaction was investigated in some detail by Werner in 1918, and in addition to urea, the following by–products were also found: $H_2NC(O)NHC(O)NH_2$ (biuret), 1,3,5–triazine–2,4,6–triol (cyanuric acid), ammelide (6–amino–1,3,5–triazine–2,4–diol), and cyamelide: no evidence for the formation of guanidine was found. The triazine derivatives probably arise from the trimerization of cyanic acid, HOCN, which is generated from the decomposition of the intermediate carbamoyl chloride [2168]:

$$COCl_2 + 2NH_3 \longrightarrow CO(NH_2)Cl + [NH_4]Cl$$
$$CO(NH_2)Cl \longrightarrow HOCN + HCl$$

HOCN will also react with ammonia (Wöhler's synthesis) to give urea, and with biuret to give ammelide [2168]. The intermediacy of HOCN was confirmed in 1936, when the salts $K_2[Co(NCO)_4]$ and AgNCO were isolated from the system [671]. At 500 °C, carbamoyl chloride, $CO(NH_2)Cl$, can be isolated in almost quantitative yield [1898]: it can be converted into cyanuric acid by heating at 180 °C [1898]. Initial results of an i.r. study of the kinetics of the gas-phase reaction between NH_3 and $COCl_2$ have recently been reported: ammonium chloride, ammonium isocyanate, isocyanic acid (HNCO) and urea were detected [625a].

An early study [443a] reports that phosgene reacts with hydrazine hydrate to give $[N_2H_5]Cl$, carbon dioxide and water.

The reaction between hydrazine and phosgene, *in vacuo*, yields a mixture of $[N_2H_6]Cl_2$ (53 mol %), $(H_2NNH)_2CO$ (40 mol %), and $H_2NNHC(O)NHNHC(O)NHNH_2$ (7 mol %), along with a trace of NH_2NHCO_2H [776]. The primary reaction product was thought to be $NH_2NHCOCl$, which could then react with either hydrazine, to form $(H_2NNH)_2CO$, or with phosgene, to form $ClC(O)NHNHC(O)Cl$. This last product could then react with further hydrazine to give $H_2NNHC(O)NHNHC(O)NHNH_2$ [776].

9.10.2.2 Reactions of phosgene with phosphine derivatives

No reaction was observed between PH_3 and phosgene [184a]. However, phosphonium bromide reacts very slowly with phosgene at 0 °C, and reacts rapidly at 50 °C, purportedly according to [184a]:

$$6[PH_4]Br + 5COCl_2 \longrightarrow 10HCl + 6HBr + 2PH_3 + P_4H_2$$

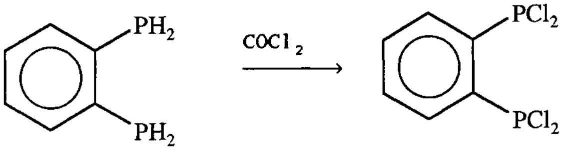
Phosphonium iodide also reacts with phosgene between 0 and 10 °C, in a reaction formulated as [184a]:

$$4[PH_4]I + 8COCl_2 \longrightarrow 16HCl + 8CO + 2P + P_2I_4$$

More useful is the reaction of phenylphosphine with phosgene, reported in 1879 [1392aa]:

$$PPhH_2 + 2COCl_2 \longrightarrow PPhCl_2 + 2CO + 2HCl$$

This reaction has now been generalized, and PRH_2 (R = Me_2CHCH_2, $CNCH_2CH_2$, cych or C_8H_{17}) or PR_2H (R = Bu) have been converted (in yields of 70% or better) to $PRCl_2$ or PR_2Cl, respectively, by treatment with phosgene at low temperature [935a]. Similarly, the reaction between 1,2-bis(phosphino)benzene and phosgene in dichloromethane at −78 °C generates the attractive synthetic reagent, 1,2-bis(dichlorophosphino)benzene, in *ca.* 50% yield [1196b]:



Attempts to prepare this compound with phosgene substitutes, such as ethanedioyl dichloride or sulfinyl chloride, gave much poorer yields [1196b]. The tetrachloro derivative was used to prepare a wide range of interesting symmetrical or unsymmetrical bidentate phosphine ligands in good yields [1196b], and is a very promising new reagent.

9.10.3 Reactions of phosgene with Group 16 hydrides

9.10.3.1 Reactions of phosgene with water

The reaction between water and phosgene is, arguably, the most important inorganic reaction of phosgene. However, there has been remarkably little attention paid to this reaction in the open literature. It is poorly understood, to the extent that the folklore (based only on selective qualitative observation and the values of the *pseudo*-first-order rate constants for hydrolysis of homogeneous solutions) states that hydrolysis is rapid – a potentially lethal piece of misinformation. The facts are that the total process of hydrolysis (which includes dissolution, a slow process, and must allow for the low solubility of phosgene in water, which is less than 1 wt % at 20 °C, see Section 6.6.2) is very slow, and that it is perfectly possible to study the chemistry and solubility of phosgene in aqueous solution (see Section 6.6.2). Moreover, the hydrolysis products (carbon dioxide and hydrogen chloride) themselves retard the hydrolytic process [1778]. As recently as 1971, a paper (from Porton Down) opens with the sentence "There is little quantitative information on the interaction of phosgene with water or aqueous solutions" [1483].

John Davy in 1812 [467], and Odling in 1868 [1536], reported that phosgene reacts with water to give hydrochloric acid and carbonic acid. Davy also reported that it did not appear to be hydrolysed by aqueous ethanol ("common spirits of wine") [467], and could pass through water without apparent reaction ("had not its intolerable smell convinced me that the gas was unaltered, I should not have conceived that it could pass through water undecomposed") [467]. The importance of Davy's astute observations was not, however, generally realized! In 1920, it was reported that although atmospheric moisture decomposes phosgene very slowly [1778], phosgene in contact with moist earth hydrolyses rapidly [488]: in a separate report, 1 g of phosgene was said to be hydrolysed completely by 100 cm^3 of water in 20 s [1591]. The poisoning of water supplies by phosgene was not considered a problem because $COCl_2$ is "quickly decomposed by water" [2019].

In 1937, the reaction between phosgene and water was reported to be completely irreversible [110]:

$$COCl_2 + H_2O \longrightarrow CO_2 + 2HCl$$

although there was "a good deal of unofficial evidence during the World War that phosgene could be kept indefinitely in contact with a sufficiently concentrated hydrochloric acid solution" [110].

The first report of the kinetics of phosgene hydrolysis in solution was for toluene solutions, in 1941 [2106]: the results of this study are, however, not very reliable. In aqueous propanone at −20 °C, the *pseudo*-first-order rate constant was determined as 1.2 s^{-1} [2080]. Böhme [226] suggested that the hydrolysis in aqueous 1,4-dioxane was first-order, but later work showed that the reaction followed the expected second-order kinetics [ICI17]. In water itself, the *pseudo*-first-order rate constants for the hydrolysis of phosgene were determined as 2.8 s^{-1} at 13 °C ($t_{\frac{1}{2}}$ = 0.25 s) [ICI17], 5.3 s^{-1} at 20 °C [1389a], 22 s^{-1} at 35 °C [1315], and 75 s^{-1} at 45.5 °C [1315]: values of 3 s^{-1} at 15 °C, and 6 s^{-1} at 25 °C were extrapolated from these data [1315]. The activation energy for this process was calculated as 77 kJ mol^{-1} [1483] or, more reliably, 53 kJ mol^{-1} [1389a].

The enthalpy of hydrolysis for phosgene has been determined [464]:

$$COCl_2(g) + H_2O(l) \longrightarrow CO_2(g) + 2HCl(g);$$
$$\Delta H^{\circ} = -(72.2 \pm 0.9)\ \text{kJ mol}^{-1}$$

This should be compared with the enthalpy of solution of phosgene in water, which was estimated to be −28.5 kJ mol^{-1} [1315]. The equilibrium constant for the reaction has been calculated [236] for a wide temperature range: $\log_{10}(K)$ (T/K); 22.4 (298), 18.42 (500), 11.24 (1000), 10.14 (1500), 9.12 (2000).

Phosgene dissolves very slowly in water (see Section 6.6.2), but rapidly in 1 *M* aqueous sodium hydroxide solution, in which the overall reaction is [464]:

$$COCl_2 + 4NaOH \longrightarrow Na_2[CO_3] + 2NaCl + 2H_2O$$

The second-order rate constant for this reaction is 1.6 x 10^4 l mol^{-1} s^{-1} in 1 *M* sodium hydroxide solution at 25 °C [1315], which is 9.14 x 10^6 times larger than the equivalent rate constant in water [1315]. The temperature dependence of this reaction has also been studied [2183a].

The *pseudo*-first-order rate constant for the hydrolysis of phosgene in 10 *M* hydrochloric acid is approximately 1.2 x 10^{-2} s^{-1} ($t_{\frac{1}{2}}$ = 0.96 min) at 20 °C [ICI18].

Charcoal (and, indeed, moist earth, *vide supra*) is an active catalyst for the hydrolysis of phosgene (see Section 4.4.2), and passage of phosgene through a continuously irrigated column of activated charcoal is the method of choice for its hydrolytic decomposition in a normal laboratory situation. Ironically, trace amounts of phosgene (40–80 p.p.m.) have been used to dry commercial dichlorine in the presence of activated charcoal [2014].

Although it has long been known that the hydrolysis of phosgene in moist air is slow [1778], a detailed study of the hydrolysis of phosgene in the gas phase (between 220 and 420 °C) did not occur until 1969 [708]. The reaction proceeded according to:

$$COCl_2 + H_2O \longrightarrow CO_2 + 2HCl$$

The reaction is second order ($k_2 \simeq$ 10.1 l mol^{-1} min^{-1} at 300 °C) with an activation energy of 50.3 kJ mol^{-1} [708]. It is an indication of how slowly phosgene hydrolyses that it is hydrolysed only thirty-five times faster than tetrachloromethane at 350 °C, and ten times faster at 450 °C [708]. This point was emphasized in a study published a decade later, in which this reaction was studied in the range 260 to 346 °C [313]. The activation energy was redetermined as 59.4 ± 8.8 kJ mol^{-1}, with a pre-exponential factor of 9192 l mol^{-1} s^{-1} [313]. These data, when extrapolated to atmospheric conditions in the atmosphere at sea level (water vapour pressure of 10 torr, phosgene concentration of 1 p.p.b., 298 K), give an effective half-life for phosgene hydrolysis of 113 years. Despite the dangers of extrapolating experimental data beyond the temperature régime under which they were measured, this figure clearly disperses the myth that "phosgene is rapidly hydrolysed in air" [*e.g.* 1019], and that its use as a war gas was discontinued because "it could not be used in misty or rainy weather [1019]". However, it should be remembered that moist earth acts as a heterogeneous catalyst for this process [488], and may lower the half-life to the order of minutes [1078a].

Strangely, and unfortunately, the authors of a paper published in 1989 were unaware of both of these previous studies, and derived an independent value for the upper limit of the rate constant, $k_2 \leqslant 0.4336$ l mol^{-1} min^{-1} at 296 K [908a], some four orders of magnitude larger than the value extrapolated from the previous data [313]. A limited study was also published in 1991 [625a].

The gentle reaction of phosgene with water has been utilized to convert hydrated metal chlorides into anhydrous metal chlorides, at temperatures between 100 and 200 °C. The following hydrated salts were successfully dehydrated: $MCl_2.6H_2O$ (M = Mg, Sr, Co, Cr or Ni), $M'Cl_2.2H_2O$ (M' = Ba, Sn or Cu), $SnCl_4.5H_2O$, $FeCl_2.4H_2O$, $FeCl_3.6H_2O$ and $TlCl_3.xH_2O$ [918]; attempts to dehydrate $BeCl_2.4H_2O$ were unsuccessful [918]. New patents for dehydrating hydrated rare earth halides, typically hexahydrates [1612a], and for removing water from HF (in the syntheses of niobium(V) and tantalum(V) fluorides) [1481a], with phosgene have been granted.

9.10.3.2 Reactions of phosgene with hydrogen sulfide and hydrogen selenide

Hydrogen sulfide does not react with phosgene in the cold [184a]. However, upon heating in a sealed tube, carbonyl sulfide, COS, was formed [184a]. In contrast, at 230 °C, phosgene reacts with H_2Se to give carbon monoxide and Se_2Cl_2 [184a].

9.10.4 Reactions of phosgene with hydrogen halides and hydrogen cyanide

The reaction between phosgene and hydrogen fluoride in a copper bomb at 80 °C and 1.93 MPa results in the formation of carbonyl chloride fluoride, COClF, as well as hydrogen chloride and some by-product COF_2 [1885]: at 7 °C and atmospheric pressure, only a small degree of reaction was detected [1470]. A mixture of phosgene and anhydrous hydrogen fluoride, when passed over activated charcoal at 775–850 °C in a graphite tube, gives tetrafluoromethane in 20% yield, along with smaller amounts of CF_3Cl, COF_2 and COClF [399]; at temperatures below 600 °C, COF_2 is the principal product [399,2069]. In the presence of iron(III) chloride at 425 °C, $CClF_3$ was obtained in 54% yield (along with CCl_2F_2, 14%, and CF_4, 4%), whereas at 350 °C, CCl_2F_2 was the major product (47%)

[900]. Indeed, the reaction between hydrogen fluoride and phosgene has been examined under a wide variety of conditions as a synthetic route to COF_2, and is discussed in more detail in Chapter 13 [2069].

Electrochemical fluorination of phosgene bubbled through anhydrous liquid hydrogen fluoride at 12–13 °C produces COF_2 (82%), CF_3OF (10%) and CF_4 (8%), along with dichlorine and traces of ClF_3 and OF_2 [1470]. However, a similar process performed at 0 °C in a static system is reported to produce COClF (90.7%), $COCl_2$ (5.7%) and COF_2 (3.6%) [2132]: addition of NaF has the advantages of reducing the cell voltage and raising the boiling point of the solvent [2132].

There is a very early report that phosgene reacts with hydrogen bromide above 200 °C to produce trace amounts of $COBr_2$ [184a]. Hydrogen iodide reacts with phosgene vigorously to liberate iodine and carbon monoxide [184a].

The infrared spectra of phosgene in the presence of HX (X = Cl or Br) or DX (X = Cl or Br) have been recorded in liquid argon, krypton and xenon: the shifts (to lower frequency) in ν(HX) and ν(DX) indicate the presence of weak hydrogen bonding [1461]. Moreover, the presence of phosgene broadens the rotational lines in the vibrational spectrum of HF [1905].

Hydrogen cyanide – air mixtures have a wide flammability range (7.8–42.4 vol % of HCN), but addition of phosgene lowers these limits, and at a ratio of $COCl_2$: HCN of 0.86, the mixture never becomes flammable [1361].

9.11 AMIDES

Lithium amide derivatives react with phosgene to give an interesting variety of isocyanates. Phosgene reacts with either of the hydrazides $LiN_2(SiMe_3)_3$ or $Li_2N_2(SiMe_3)_2$ to yield the dimer $[\{OCNN(SiMe_3)_2\}_2]$ [2177]. The lithium reagent $LiN{=}C(CF_3)_2$ reacts with phosgene to give the unexpected product $(CF_3)_2C{=}NC(CF_3)_2NCO$, along with traces of $(CF_3)_2C(Cl)NCO$ [1985,1986]. In contrast, $LiN{=}S(CF_3)_2$ reacts with $COCl_2$ to give $O{=}C\{N{=}S(CF_3)_2\}_2$ [1440].

Sodium amide reacts slowly at room temperature with a toluene solution of phosgene to give sodium isocyanate, according to [1605,1606]:

$$3Na[NH_2] + COCl_2 \longrightarrow Na[NCO] + 2NaCl + 2NH_3$$

By-products, including urea, are generated by reaction of the generated ammonia with unreacted phosgene. In contrast, gaseous phosgene reacts with solid sodium amide at 250 °C to form sodium cyanamide [1605]:

$$5Na[NH_2] + COCl_2 \longrightarrow Na_2[NCN] + 2NaCl + Na[OH] + 3NH_3$$

At 500 °C, the reaction between sodium amide and phosgene becomes 'very lively' and catches fire: the products include sodium melanurates and their chloro derivatives [1605].

Hexamethylphosphoramide, $(Me_2N)_3P{=}O$, reacts with phosgene to give an interesting chlorophosphonium salt, in a manner similar to the formation of chloroiminium salts (Vilsmeier reagents) {*cf*. Sections 10.2.2.3 and 10.2.7} [1638]:

$$(Me_2N)_3P{=}O + COCl_2 \longrightarrow [(Me_2N)_3PCl]Cl + CO_2$$

The silver salt of trifluoromethanesulfonamide, $CF_3SO_2NAg_2$, reacts with phosgene in a sealed tube at 80 °C to give the pseudohalide CF_3SO_2NCO and silver(I) chloride [154].

Treatment of $Hg(NSOF_2)_2$ with phosgene in an autoclave at 120 °C gave $CO(NSOF_2)_2$ in 68% yield [984].

9.12 MISCELLANEOUS REACTIONS

9.12.1 Reactions with ions in the gas phase

9.12.1.1 "*Gedanken*" experiments

The protonation of $COCl_2$ has been studied by *ab initio* techniques, using a 4-31G basis set [1073a,1950b]: the species $[Cl_2C{=}O\cdots H]^+$ is predicted to have a longer C=O bond, but shorter C–Cl bonds, than the neutral phosgene molecule.

9.12.1.2 Electron and ion cyclotron resonance studies

Ion cyclotron resonance (i.c.r.) spectrometry is a specialised technique of growing importance. It enables the detailed study of ion-molecule reactions (and their mechanisms) in the gas phase, giving both absolute and relative thermochemical quantities and rate constants.

The rate constant for the capture of low energy (thermal; <1 eV) electrons by $COCl_2$ has been measured by electron cyclotron resonance (e.c.r.) as 5×10^{-8} cm^3 s^{-1} [1817]. Thus, phosgene is a much more effective electron scavenger than dichlorine or chloroalkanes. The process of electron capture is believed to be [1817]:

$$COCl_2 + e^- \longrightarrow [Cl_2]^- + CO; \qquad \Delta H = -134 \text{ kJ mol}^{-1}$$

At 30–70 eV, three primary ions are formed by electron impact [1071,1720]:

$$COCl_2 + e^- \longrightarrow Cl^- + COCl\cdot$$

$$COCl_2 + e^- \longrightarrow [Cl_2]^- + CO$$

$$COCl_2 + e^- \longrightarrow [COCl]^- + Cl\cdot$$

The relative abundance of these ions is shown in Fig. 9.13. The most abundant ion is

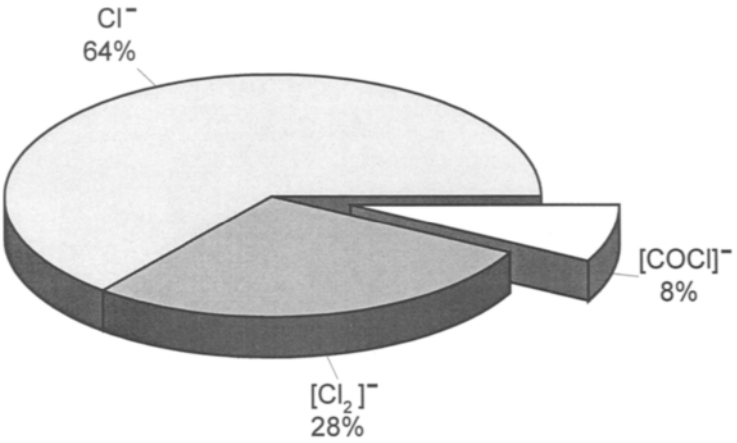


Fig. 9.13 **Relative abundance of the negative ions formed by electron impact (70 eV) with phosgene at 10^{-6} torr (13.33 mPa) [1071].**

chloride, followed by $[Cl_2]^-$ and $[COCl]^-$, formed here, too, by the impact of thermal electrons [1071]. Phosgene has thus been used as a source of both thermal $[Cl_2]^-$ and $[COCl]^-$, which were used as chloride transfer reagents to a wide range of carbonyl compounds [1073] and other neutral organic molecules [1557].

The secondary negative ion, $[COCl_3]^-$, is formed in two parallel processes, the former being eight times faster than the latter [1071]:

$$COCl_2 + [COCl]^- \longrightarrow [COCl_3]^- + CO$$

$$COCl_2 + [Cl_2]^- \longrightarrow [COCl_3]^- + Cl\cdot$$

The i.c.r. experiments suggest upper limits on the enthalpy of formation for $[COCl]^-$ of -356 kJ mol^{-1} and for $[COCl_3]^-$ of -464 kJ mol^{-1} [1071].

Protonation of phosgene has been observed in phosgene-formaldehyde mixtures [1072]:

$$COCl_2 + [H_2CO]^+ \longrightarrow [Cl_2COH]^+ + HCO$$

$$COCl_2 + [HCO]^+ \longrightarrow [Cl_2COH]^+ + CO$$

The data yield a calculated upper limit for the enthalpy of formation for $[Cl_2COH]^+$ of $+724$ kJ mol^{-1} [1072].

9.12.2 Salmagundi

The reactions between phosgene and Group 1 alkoxides, A[OR], have been discussed along with those of the corresponding alcohols in Section 10.3.1.1. In general, the reactions of the alkoxides are faster and more specific than those of the alcohols, hence the prevalence of base catalysis.

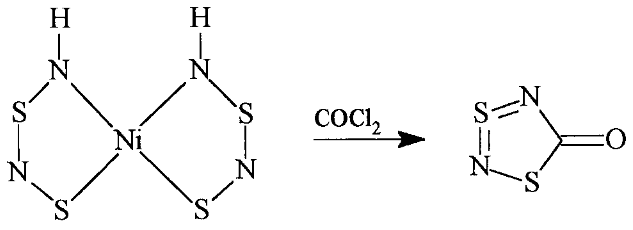
Phosgene reacts with $Ph_3COMgBr$ to give only Ph_3CCl, but with PhOMgBr it gives $(PhO)_2CO$ in good yield [242a]. Phosgene reacts with Mg(SH)Br in benzene solution; following the usual work-up procedures, the products isolated included COS, urea and thiourea [1403].

Phosgene is briefly reported to react with trimethyl borate, $B(OMe)_3$, to produce $B(OMe)_2Cl$ [1601].

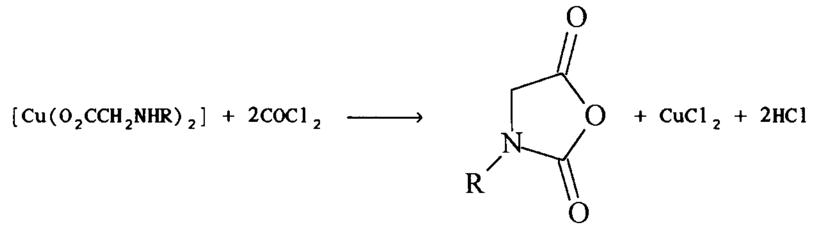
Phosgene was found to be a suitable reagent for the plasma etching of the semiconductor GaAs, but it reacted more slowly than dichlorine [1910]. It has also been used, mixed with CO_2, as an etchant gas for refractory metals and, particularly, their silicides [701a].

Phosgene reacts with $Cs[S_3N_3]$ in MeCN at −78 °C to give good quality $(SN)_x$ in 22% yield, along with S_4N_4 (56% yield) [371].

In an unusual reaction, $[Ni(S_2N_2H)_2]$ reacts with phosgene in thf at room temperature to give a heterocyclic ketone, S_2N_2CO, along with $NiCl_2$ and S_4N_4 [931]:

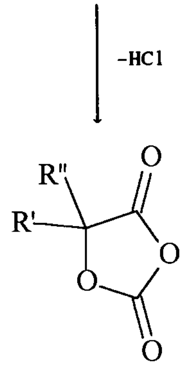


N-Carboxy-2-amino acid anhydrides are important precursors for polypeptides, and can be conveniently prepared (*cf*. Section 10.3.4.5) by treating a tetrahydrofuran suspension of copper(II) complexes of 2-amino acids {*e.g.* $[Cu(O_2CCH_2NHR)_2]$ (R = H or Me) or $[Cu(O_2CCH(Me)NH_2)_2]$} with phosgene [876]:



In a similar manner, the copper(II) complexes of 2-hydroxycarboxylates, $[Cu\{O_2CC(OH)R'R''\}_2]$ (R',R" = Ph or C_6F_5) react with phosgene according to [1907]:

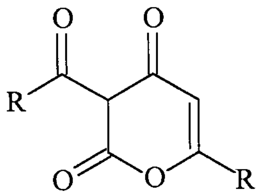
$$[Cu\{O_2CC(OH)R'R''\}_2] + 2COCl_2 \xrightarrow{Et_2O} R'R''C(OH)C(O)C(O)Cl + CuCl_2$$



The presence of pyridine catalyses the cyclization step [1907], and the reaction is to be preferred, as a route to substituted 1,3-dioxolan-2,4-diones, to the reaction of phosgene with the free 2-hydroxycarboxylic acids (see Section 10.3.4.1), as there is no formation of R'R''C(Cl)C(O)Cl as by-product [1907].

Treatment of a benzene suspension of the copper(II) complex of heptane-2,4,6-trione (htH_2) with phosgene gives a cyclic organic product [193a]: the analogous copper(II) complexes of nonane-3,5,7-trione (ntH_2) and undecane-4,6,8-trione ($udtH_2$) give a similar product [1298]:

$$[Cu(L)] + COCl_2 \longrightarrow$$



(L = ht, R = Me;
L = nt, R = Et;
L = udt, R = Pr)

Finally, phosgene reacts with $[Hg\{ON(CF_3)_2\}_2]$ at 20 °C to give $\{(CF_3)_2NO\}_2C{=}O$, with some $C(O)\{(CF_3)_2NO\}Cl$ [588c].

9.13 PHOSGENITE

Phosgenite is a white or yellow-brown lead ore, $Pb[CO_3].PbCl_2$, named for phosgene in 1820, because it contains the elements carbon, oxygen and chlorine [367a]. It has also been known as horn-lead (Hornblei), salzsaures Bleierze, corneous lead, phosgene spar, Phosgen-spath, cerasine, kerasite, galenoceratite, or cromfordite [367a,718c,1378a]. Its history and early mineralogy has been the subject of a number of early reviews [1378a,1728,2140]. It was first discovered in Bage Mine, Bole Hill (near Wirksworth, Derbyshire, England) {*n.b.* this location is often incorrectly referred to as "Cromford" or "Matlock" [1107a]}, in 1801. Phosgenite has also been found in deposits in Wheal Rose, Sithney (Cornwall,England) [1760a]; Penberthy Croft Mine, St. Hilary (Cornwall, England) [1107a]; Caldbeck (Cumberland, England) [1107a]; Elgin (Scotland) [1378a]; Gibbas and Montevecchio (Sardinia) [1378a]; Terrible Mine, Ilse, Custer County (Colorado, U.S.A.) [2140,2151a]; Monteponi (Sardinia) [645,1137,1728]; Christian Levin (Essen-Borbeck, Germany) [1676,1677,1826]; Bobrek (Upper Silesia, Poland) [1378a]; Zyryanovsky (W. Altai, Russia) [1617]; Broken Hills (New South Wales) and Dundas (Tasmania) [2140]; Laurion (Greece) [11340]; Zarban and Kali-Kafi (Iran) [118]; Mibladen (Morocco) [722]; and Salar del Plomo (Catamarca, Argentina) [51]. Phosgenite was also discovered growing upon anchors in the Mediterranean Sea [798], in ancient metallic artifacts immersed in sea water off Mahdia (Tunis) [1197b], in lead pipes exposed to a hot spring at Bourbonne-les-Bains (France) [1393] and in an ancient lead pot in Wookey Hole (England) [1393]. The existence of a paper entitled "Phosgenite from the Terrible mine near Ilse, Custer County, Colorado" [2140] summons up pictures of Gothic horror - a sinister mine of mysterious death, traced to the presence of a mineral which evolves phosgene. As will be seen in the following paragraphs, the connection between phosgenite and phosgene has remained on this level - instinctive, lacking in solid foundation, but nevertheless reported.

Phosgenite is readily synthesized in the laboratory under mild conditions. The first report of synthetic phosgenite was from Döbereiner, who boiled a mixture of lead(II) chloride and lead(II) carbonate in water [540a]. It was later prepared by Friedel and Sarasin [686a] by heating a mixture of lead(II) chloride, lead(II) carbonate and water in a sealed tube at 180 °C, and then by de Schulten [510] by passing carbon dioxide over a filtered aqueous solution of lead(II) chloride. An alternative preparation, appropriate albeit unattractive, involves treating anhydrous lead(II) hydroxide with phosgene under pressure in a sealed tube at 175 °C [878]. A bromide analogue of phosgenite, $Pb_2Br_2CO_3$, has also been prepared [510]. Most recently, phosgenite has been prepared by passing carbon dioxide through an equimolar aqueous solution of lead(II) chloride and sodium hydroxide until the pH is between 3 and 4.5 [1482], an improvement upon an earlier method [503] which involved treating aqueous lead(II) chloride with sodium carbonate, while following the reaction conductimetrically.

There have been many crystallographic studies upon phosgenite [1137,1455,1499,1718, 1728,1829,1830], and those reporting the unit cell dimensions are summarized in Table 9.2. Remarkably, the first report of the full structure of phosgenite to be published [1570] found no evidence for the presence of carbonate ions (despite all the chemical indications to the contrary), and formulated the structure as $2PbO.CCl_2O$ (thus reinforcing the association between phosgenite and phosgene). This error was corrected, ten years later, by the work of two independent groups [1538,1877,1878], almost simultaneously (the publication of the work of one group [1878] having been delayed by the air raids on Leipzig in 1943). These reports

TABLE 9.2

CRYSTALLOGRAPHIC PARAMETERS FOR TETRAGONAL PHOSGENITE (Z = 4)

Year	a/nm	c/nm	c/a	Ref.
1887			1.0876	1140
1927			1.0889	1760a
1934	0.812	0.88[a]	1.084	1570
1944	0.8125	0.8860	1.091	1538
1944	0.8139	0.8856	1.088	1877,1878
1958	0.8112	0.8814	1.086	1393
1962	0.815	0.8867	1.088	1482
1974	0.8160	0.8883	1.089	761a

[a] Reported as 0.44 based upon $Z = 2$ in [1570].

unambiguously confirmed the structure of the double salt as $PbCl_2.Pb[CO_3]$, showing the error in the original work to have arisen from the use of a *pseudo* cell ($Z = 2$), the real unit cell being twice the size (see Table 9.2). The structure has been recently reexamined [761a], and shown to contain {(Pb,Cl) Cl (Cl,Pb)} sheets connected by planes of perpendicular carbonate ions (Fig. 9.14): an individual (Pb,Cl) plane is shown in Fig. 9.15. The lead atoms have nine close neighbours, four oxygen atoms and five chlorine atoms in a deformed monocapped square antiprism (see Fig. 9.16), with $\bar{r}$(PbO) at 0.2598 nm and $\bar{r}$(PbCl) at 0.3160 nm suggestive of an essentially ionic structure [761a]. Furthermore, a detailed i.r. and Raman study has unambiguously identified the internal vibrations of the carbonate ion [1757]. Some optical properties of phosgenite have also been reported [126,143], and the $^{12}C/^{13}C$ ratio determined [2179]. A solubility product for phosgenite ($pK^{\bullet}_{sp} = 9.91$) has also been measured [1482].

Dyson [578] reported, without citing his source, that phosgene may be formed by heating the lead ore phosgenite, which decomposes to some extent according to the reaction:

$$Pb_2Cl_2CO_3 \longrightarrow 2PbO + COCl_2$$

Phosgenite, both natural and synthetic, has since been studied by thermal gravimetric analysis [1482] and differential thermal analysis [147]. These early studies both agree that

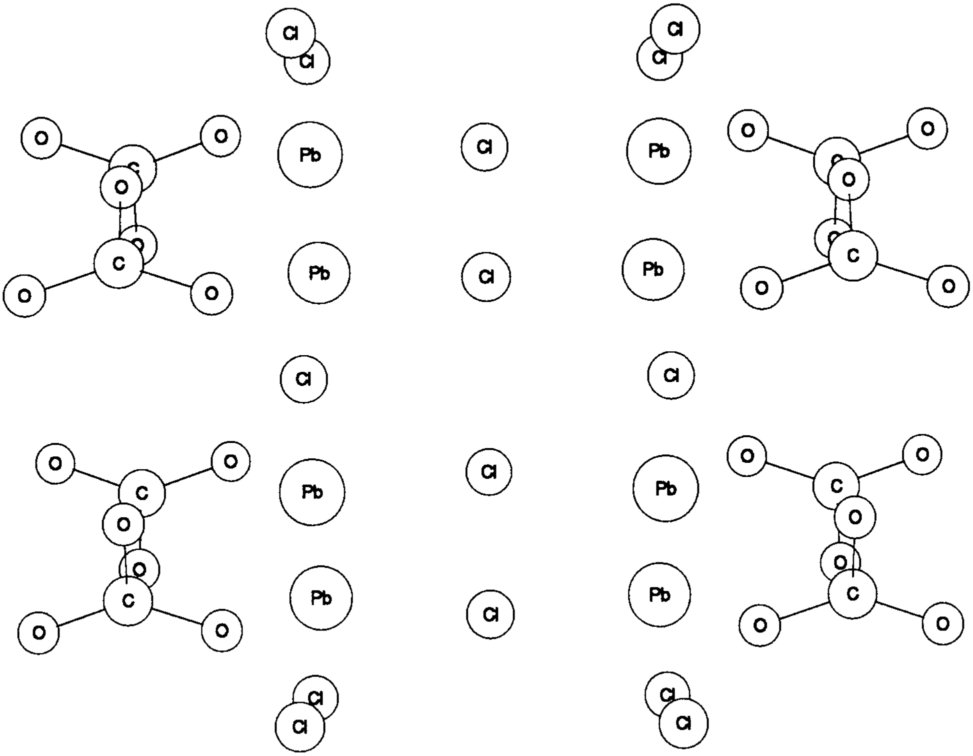


Fig. 9.14 The crystal structure of phosgenite viewed down the *b* axis [761a].

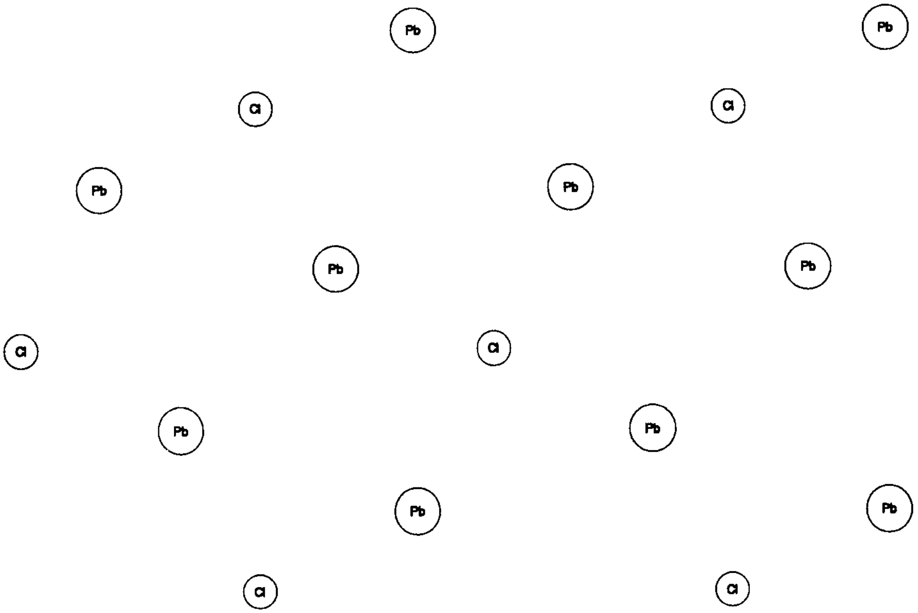


Fig. 9.15 A (Pb,Cl) plane of phosgenite, viewed down the *c* axis [761a].

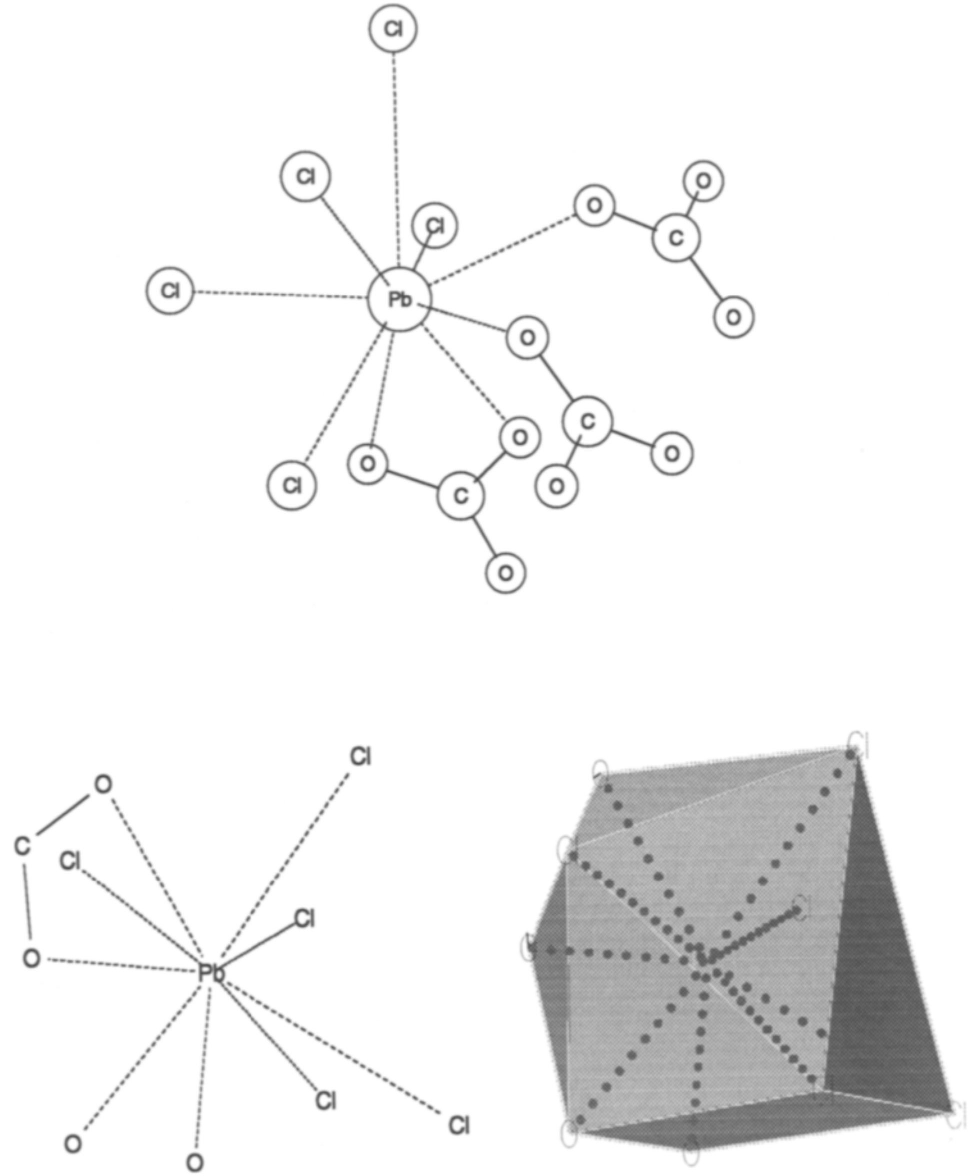


Fig. 9.16 Three different perspectives of the nine-coordinate deformed monocapped square antiprismatic arrangement of near-neighbours around the lead atoms in phosgenite [761a].

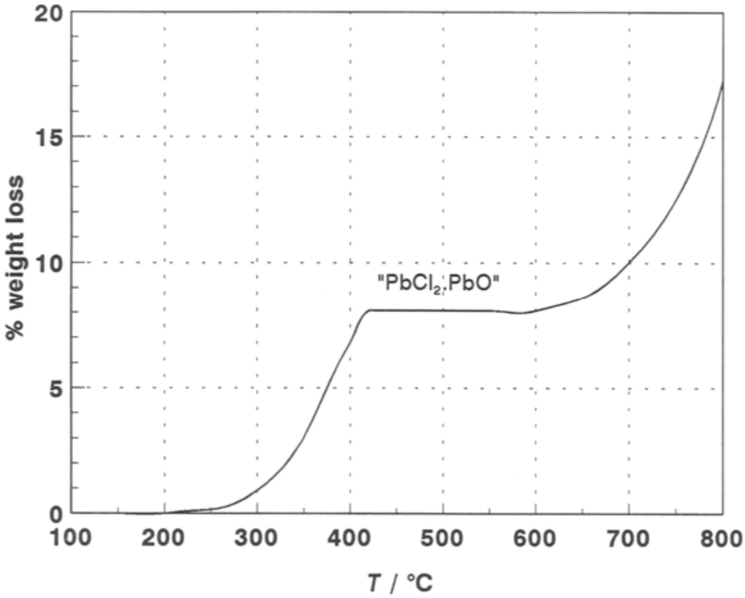


Fig. 9.17 **A thermogram for synthetic phosgenite [1482]**

phosgenite starts to lose CO_2 at *ca.* 250 °C, the process being complete by *ca.* 450 °C:

$$Pb_2Cl_2CO_3 \longrightarrow PbCl_2.PbO + CO_2$$

The thermogram [1482] is illustrated in Fig. 9.17, and shows a plateau for *ca.* 200 °C above the formation of $PbCl_2$.PbO phase: the d.t.a. study detected the melting of this phase at *ca.* 550 °C [147], and commented that the x.r.d. patterns of this phase (both before and after melting) did not resemble PbO, $PbCl_2$ *or* $PbCl_2$.PbO. More recently, a detailed study [109] of the thermal decomposition of synthetic phosgenite between 292 and 342 °C, whilst concurring with the stoicheiometry of the above decomposition, identified the product as a mixture of two other known oxide chlorides:

$$4Pb_2Cl_2CO_3 \longrightarrow 3PbCl_2.2PbO + PbCl_2.2PbO + 4CO_2$$

The enthalpy of decomposition of phosgenite, measured under a flow of dinitrogen, was found to be +69 kJ mol^{-1}, and from this value $\Delta H^{\circ}_{f,600}$ for phosgenite was estimated as −62.4 kJ mol^{-1} [109]. In none of these reports was there any mention of phosgene evolution, but the identity of the evolved gas was not established by any method other than percentage weight loss. Thus, although unlikely, a minor decomposition route, possibly involving reaction between lead(II) chloride and carbon dioxide (see Chapter 5) can not yet be totally excluded.

10 REACTIONS WITH ORGANIC COMPOUNDS

Although there can be no sharp boundary between inorganic and organic chemistry, phosgene is normally regarded as an inorganic compound. Its reactions with organic compounds, however, are multifarious. Indeed, phosgene is regarded by most organic chemists as a laboratory reagent, used for the purpose of preparing and examining other substances, whilst most industrial chemists regard the material as a synthesis intermediate - especially for the production of isocyanates, organic carbonates and chloroformates, carbamates, and polyurethane and polycarbonate resins. Indeed, the only wide-scale use of phosgene as an end-product of itself has been as a war gas (Chapter 1). Because phosgene is considered as a reagent, or intermediate, it is frequently not cited in journal indices, appearing often only in experimental notes as a material for affecting the chlorination, carbonylation or dehydration of some organic compound. For these reasons, no single literature review of reasonable length could be expected to be totally comprehensive; omissions are to be expected. Notwithstanding these remarks, it is hoped that at least one example of each organic reaction type has been included in this Chapter.

Fortunately, many excellent reviews and compilations concerning the organic chemistry of phosgene have appeared [96,155-157,162,164a,179,426,578,781,996,1019,2215]. The most recent review, by Babad and Zeiler [96] provides a summary of the literature between 1933 and 1970. The very early literature of phosgene is covered by Dyson [578] in a monograph published in 1927. Although the nomenclature used in this last review is occasionally cumbersome, and some of the interpretations of the chemistry are doubtful, it is nonetheless a useful adjunct to any modern description of the organic chemistry of phosgene. In addition, there exists a particularly useful early bibliography (covering the period 1812-1919) on phosgene and its derivatives [179], in which reactions of phosgene with particular classes of compounds are listed alphabetically.

The nomenclature employed in this Chapter is not strictly systematic. Where ambiguity has arisen, the recommendations of the IUPAC's Nomenclature of Organic Chemistry [1011] have been followed, although (because of the ubiquitous use of phosgene in industry) many trivial names (*e.g.* formaldehyde for methanal) have been retained. Meaningless or ambiguous terms such as phosgenation, as elsewhere in this book, have been avoided. Instead, where necessary, reactions have been described strictly according to the reaction type.

A recurring theme of this Chapter is the ability of phosgene to form cyclic derivatives with bifunctional compounds, where the functionalities are close to each other: its applications to liquid chromatography have been recently reviewed [856b]. The reactions of phosgene with heterocyclic compounds have not been treated separately, since these reactions are frequently sufficiently similar to those of the parent functional group. The voluminous quantity of literature concerning the condensation polymerization reactions of phosgene have been deliberately excluded, but examples have been cited here, and elsewhere in this book, to provide an adequate description of the principles of this type of chemistry.

10.1 REACTIONS WITH HYDROCARBONS

10.1.1 Alkanes

The reactions of phosgene with alkanes have been surprisingly little studied. In some early work, phosgene is reported to react with methane on exposure to sunlight to give some ethanoyl chloride [313a,888]. No thermal reaction was observed by Berthelot between phosgene and methane or ethane [181b], but when passed over charcoal at 400 °C, methane and phosgene combine according to [968a,968b]:

$$CH_4 + COCl_2 \longrightarrow CH_3Cl + CO + HCl$$

Phosgene has been shown to have an effect on the flammability limits of hexane in air [1362]. At room temperature and atmospheric pressure, the upper and lower limits of flammability of hexane in air are 7.7 and 1.5% v/v. Addition of phosgene to the hexane brings the upper and lower limits together until they meet at 3.4% v/v hexane and 19.1% v/v phosgene [1362].

The reaction of phosgene with cyclohexane has been investigated by several workers [280,836,1100,1630,1918]. Under u.v. irradiation (Hg-vapour lamp), a mixture of cyclohexane and $COCl_2$ gave a *ca.* 10% yield of $C_6H_{11}COCl$ [1918], whereas Kharasch and Brown report [1100], without giving much experimental detail, that the yield of this reaction appears to be quantitative. A similar reaction was induced by γ-irradiation from a ^{60}Co source [836]:

$$C_6H_{12} + COCl_2 \xrightarrow{h\nu \text{ or } \gamma} C_6H_{11}COCl + HCl$$

The mechanism of substitution of the COCl group into the cyclohexane ring was considered to occur according to the following scheme [280]:

$$\begin{aligned} COCl_2 &\longrightarrow [COCl]\cdot + Cl\cdot \\ C_6H_{12} + Cl\cdot &\longrightarrow [C_6H_{11}]\cdot + HCl \\ [C_6H_{11}]\cdot + COCl_2 &\longrightarrow C_6H_{11}COCl + Cl\cdot \end{aligned}$$

In contrast, Runge [1758] found that large amounts of chlorocyclohexane were formed in addition to the carboxylic acid chloride when phosgene was combined, under u.v radiation, with cyclohexane. It was thought to be derived from the reaction of $C_6H_{11}\cdot$ with dichlorine, generated from phosgene photochemically.

The effect of phosgene upon a variety of alkanes (*e.g.* pentane, 2-methylbutane or hexane) or cycloalkanes (*e.g.* cyclohexane or methylcyclohexane) in the presence of aluminium(III) chloride is to give symmetrical ketones; no carboxylic acid chlorides were isolated from this reaction:

$$2RH + COCl_2 \xrightarrow{AlCl_3} R_2CO + 2HCl$$

The reaction of polyethene with $COCl_2$ (from the photolytic oxidation of tetrachloroethene) results in an increased amount of oxygen-containing groups in the polymer [1667].

10.1.2 Alkenes

Phosgene combines with alkenes only when the reactions are suitably catalysed, or induced by radiation.

The reaction of phosgene with ethene has been investigated by several workers [1119-1121,1579,2103]. Pace [1579] claimed that, in the presence of an aluminium(III) chloride catalyst in toluene solution, an acid chloride $ClCH_2CH_2COCl$ was produced. However, this work could not be independently confirmed [1120,2103], and no conditions were found under which the acid chloride was formed. In toluene, only products derived from reactions with the solvent were isolated [1120,1121,2103]. $ClCH_2CH_2COCl$, however, is considered to be formed *in situ* when CS_2 is used as the solvent in the presence of aluminium(III) chloride: although the acid chloride could not be isolated, the corresponding methyl or ethyl ester was formed by treatment of the reaction product with methanol [1119] or ethanol [1120,1121]. Reports of the aluminium(III) chloride catalysed reactions of phosgene with $Me_2CHCH{=}CH_2$ or with $PhCH{=}CH_2$ [1579] to give $Me_2CHCHClCH_2COCl$ or $PhCHClCH_2COCl$, respectively, should be similarly treated with suspicion.

In a flow system, at 200-250 °C, phosgene combines with ethene over activated charcoal to give 1,2-dichloroethane, with an activation energy calculated to be 29.6 kJ mol^{-1} [ICI88,ICI89,ICI90]. A small quantity of chloroethene is formed at temperatures as low as 100 °C from the simultaneous decarbonylation and dehydrochlorination of the intermediate acid chloride [ICI90]:

$$C_2H_4 + COCl_2 \longrightarrow (ClCH_2CH_2COCl) \longrightarrow \begin{cases} \longrightarrow ClCH_2CH_2Cl + CO \\ \longrightarrow CH_2{=}CHCl + CO + HCl \end{cases}$$

No reaction occurs in the gas phase, in the absence of a catalyst, except at very high temperatures (>335 °C), and whilst the reaction is catalysed by pure graphite (E_a = 73.2 kJ mol^{-1}), only small yields of $ClCH_2CH_2Cl$ are obtained. Boron nitride (isostructural with graphite) also catalyses the reaction, but is even less effective than is graphite [ICI89]. The reaction of phosgene with ethene has also been examined over a $CuCl_2$-intercalated graphite catalyst [ICI88]. The reaction proceeds according to:

$$C_2H_4 + 2CuCl_2 \longrightarrow C_2H_4Cl_2 + 2CuCl$$
$$2CuCl + COCl_2 \longrightarrow 2CuCl_2 + CO$$

The activation energy for the nett reaction was calculated to be 64.0 kJ mol^{-1} in the range 60–180 °C. Above about 180 °C, the reaction becomes diffusion controlled, owing to the lack of any effective pore-structure in the catalyst.

The photolysis of phosgene in the presence of ethene gives results which are quite different from those obtained by the photochlorination of ethene with molecular chlorine, in which the main reaction product is 1,2-dichloroethane. The proposed mechanism for the phosgene reaction is given below [2185]:

$$\begin{aligned}
COCl_2 &\xrightarrow{h\nu} [COCl]\cdot + Cl\cdot \\
[COCl]\cdot &\xrightarrow{fast} CO + Cl\cdot \\
C_2H_4 + Cl\cdot &\longrightarrow [C_2H_4Cl]\cdot \\
2[C_2H_4Cl]\cdot &\longrightarrow Cl(C_2H_4)_2Cl \\
C_2H_4 + [C_2H_4Cl]\cdot &\longrightarrow [C_4H_8Cl]\cdot \\
[C_4H_8Cl]\cdot + [(C_2H_4)_xCl]\cdot &\longrightarrow C_4H_9Cl + CH_2{=}CH(C_2H_4)_{x-1}Cl
\end{aligned}$$

Since chlorine atoms, alkyl radicals and chloroalkyl radicals do not attack phosgene, no regeneration of chlorine atoms occurs by secondary reactions. Hence, the principal reaction products, 1-chlorobutane and 1,4-dichlorobutane, are formed from the reactions of the $C_2H_4Cl\cdot$ radical with C_2H_4 and by combination of $C_2H_4Cl\cdot$ radicals [2185]. The yield of CO is directly proportional to the absorbed light intensity, and is thus an internal standard for the quantity of chlorine atoms generated. The absence of $(COCl)_2$ or $ClCH_2CH_2COCl$ as reaction products indicates that the $COCl\cdot$ radical is too short-lived, under the experimental conditions, to take part in radical-radical reactions. Other photochemical products detected and identified included C_2H_2, CO_2, 1-C_6H_{12}, C_2H_5Cl, 1-$C_6H_{13}Cl$, 1,2-$C_2H_4Cl_2$, 1,3-$C_4H_8Cl_2$ and 1,6-$C_6H_{12}Cl_2$ [922].

In the γ-ray induced reaction of $COCl_2$ with ethene, the following products were obtained: carbon monoxide, 1-chlorobutane, 1-chlorohexane, 1-chlorooctane, 1-chlorodecane, 1-chlorododecane, 1,2-dichloroethane, 1,4-dichlorobutane, 1,6-dichlorohexane and 1,8-dichlorooctane. Various acids, such as $ClCH_2CH_2COOH$ and $Cl(CH_2)_4COOH$, were also produced. The mean degree of polymerization and the ratio of mono- to di-chlorinated products increase with increasing reaction pressure [2002].

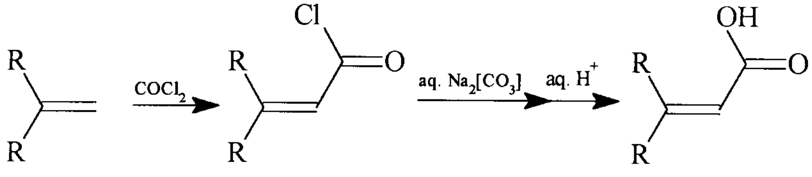
A novel scheme for the manufacture of methyl 2-methylpropenoate (methyl methacrylate) has been devised, based upon the reaction of phosgene with propene in the presence of aluminium(III) chloride, followed by treatment with methanol and dehydrochlorination of the resulting ester [1699]:

$$CH_3CH{=}CH_2 + COCl_2 \longrightarrow (ClCH_2CH(Me)COCl) \xrightarrow{MeOH} ClCH_2CH(Me)CO_2Me$$

$$ClCH_2CH(Me)CO_2Me \longrightarrow CH_2{=}C(Me)CO_2Me + HCl$$

Other esters of 2-methylpropenoic acid (methacrylic acid) are said to be similarly prepared [1699].

Unusually, substitution by the -C(O)Cl group occurs in the following reactions [177a]:



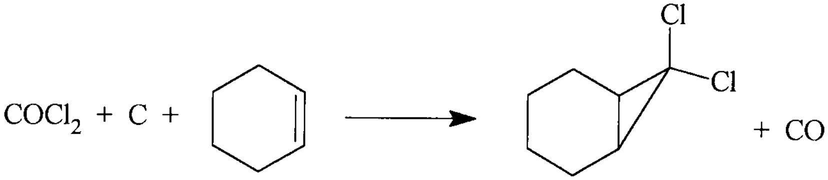
(R = 4-MeOC$_6$H$_4$)

in which the acid chloride was hydrolysed to the corresponding propenoic (acrylic) acid [177a].

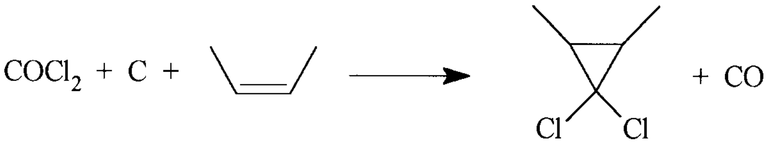
The addition of phosgene to a mixture of caesium fluoride and $(CF_3)_2C{=}CF_2$ in diglyme gave the acid fluoride $(CF_3)_3CCOF$ [1132].

The reaction between 1-butene and phosgene induced by γ-radiation results in the formation of 1-chlorobutane, 2-chlorobutane, 1,2-dichlorobutane, octenes and monochlorooctanes. The rate of the reaction was found to be proportional to the 0.93 power of the dose rate [2001]. Amongst the gaseous by-products, dihydrogen, ethene and hydrogen chloride were detected [2000].

Co-deposition of a gas-phase mixture of phosgene and cyclohexene at 77 K with carbon vapour from a 16 V AC arc results in the formation of 7,7-dichloronorcarane (25% yield):

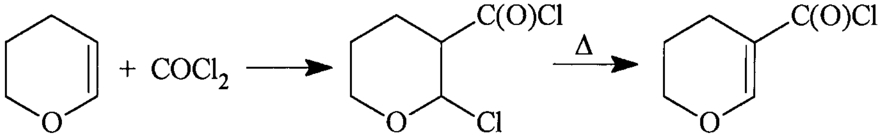


This reaction proceeds *via* the deoxygenation of phosgene by atomic carbon to give the dichlorocarbene intermediate. When a gas-phase mixture of $COCl_2$ and *cis*-2-butene was used as the reactive matrix:

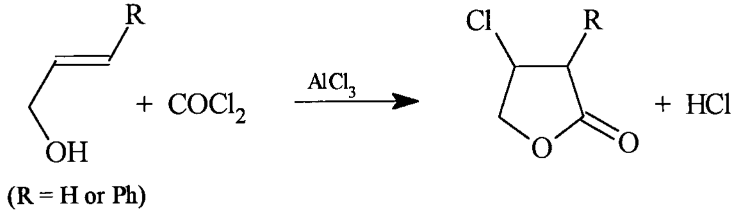


the reaction proceeded to give the *cis*-isomer of the cyclic product. *Trans*-2-butene gave the corresponding *trans*-isomers. These results indicate that the $:CCl_2$ species formed by the deoxygenation of phosgene is of a singlet multiplicity [1895].

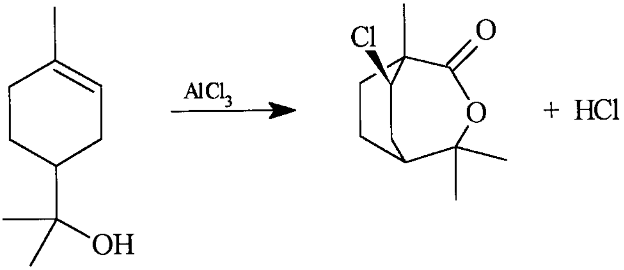
Phosgene was noted not to have any action upon pinene [719], but it was found to add to the double bond of 2,3-dihydro-4*H*-pyran to give 2-chlorotetrahydropyran-3-carbonyl chloride. This product, when heated under reduced pressure, readily eliminates HCl [914]:



Unsaturated alcohols, in the presence of aluminium(III) chloride, give chlorolactones on reaction with phosgene [1579]:



Similarly, terpineol combines with $COCl_2$ to form an unusual cyclic ester [1579]:



10.1.3 Dienes

The so-called "ene" reaction has not been observed with phosgene, although it occurs readily with the related carbonyl pseudohalide, $CO(CN)_2$ [972]. Moreover, no Diels-Alder product is obtained when 1,3-cyclohexadiene is reacted with phosgene. Acyl chlorides are formed at 80 °C and very high pressures, but no reaction occurs between 1,3-cyclohexadiene and $COCl_2$ at atmospheric pressure [1185].

The cumulated diene, tetraethoxyallene (1,1,3,3-tetraethoxypropadiene) reacts with $COCl_2$ to eliminate two molar equivalents of chloroethane and form a ketene [1766].

$$\begin{tikzcd}
(EtO)_2C{=}C{=}C(OEt)_2 + COCl_2 \arrow[r, "-EtCl"] & ClC(O)C(CO_2Et){=}C(OEt)_2 \arrow[d, "-EtCl"] \\
 & O{=}C{=}C(CO_2Et)_2
\end{tikzcd}$$

10.1.4 Alkynes

The reaction of phosgene with ethyne is not straightforward: a compound of undefined constitution is produced from the passage of ethyne into liquid phosgene at −5 °C; the resulting brown liquid is converted, at *ca.* 100 °C, into a plastic solid [79]. Similar poorly characterized reaction products were also generated by the treatment of ethyne with phosgene in an autoclave at 100 °C [79,1672].

The reaction between ethyne and phosgene has also been studied under photochemical conditions (>220 nm) [2185a]. As in the analogous reaction with ethene (see Section 10.1.2), the phosgene merely acts as a convenient source of chlorine radicals: the principal products were CO, $CH_2{=}CHCl$, 1-chloro-1,3-butadiene, benzene and polymer; trace amounts of $HC{\equiv}CCl$ and C_6H_5Cl were also detected [2185a].

Treatment of a mixture of C_2H_2 and CO with phosgene, under pressure, and in the presence of a palladium catalyst (*e.g.* $[PdCl_2(PPh_3)_2]$) gave good yields of *trans*-Cl(O)CCH=CHC(O)Cl and *trans,trans*-Cl(O)CCH=CHCH=CHC(O)Cl [2129]. The photolysis of a mixture of $COCl_2$ and $PhC{\equiv}CH$ in the presence of NO gave PhCN, CO and HCl; $MeC{\equiv}CH$, similarly gave MeCN [849].

Alkynes can, however, undergo addition reactions with phosgene. $COCl_2$ adds to 1-alkynyl ethers, $RC{\equiv}COR'$ (R = H or alkyl; R' = alkyl), according to [2094]:

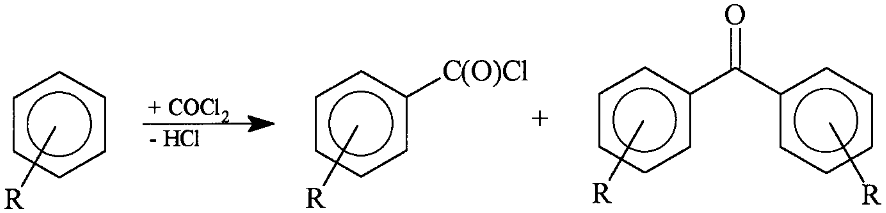
$$R{-}C{\equiv}C{-}OR' + COCl_2 \longrightarrow RC(COCl){=}C(OR')Cl$$

A similar, but slower, addition occurs with 1-alkynyl thioethers to give the sulfur analogues [2094], and ethynes, $Me_2NC{\equiv}CC(O)R$ (R = H, Me, OMe or NMe_2), having both electron-donating and electron-accepting groups attached directly to the alkyne group, undergo addition reactions with $COCl_2$ to form the highly reactive materials $Me_2NC(Cl){=}C\{C(O)R\}(COCl)$ [706].

10.1.5 Aromatic hydrocarbons

10.1.5.1 Reactions in the presence of Lewis acids

Phosgene can react with arenes, when in the presence of a Friedel-Crafts catalyst such as aluminium(III) chloride [1556,2026], to give predominantly benzoyl chlorides or benzophenones, depending on the reaction conditions [2196]:



This system has been cited frequently (*e.g.* [96]) as a method for the production of aromatic acids. Hence, benzoic acid is formed from the hydrolysis of benzoyl chloride, prepared from benzene and an excess of liquid phosgene in the presence of dissolved aluminium(III) chloride [1754]. Toluene or chlorobenzene react similarly to give 4–chloro– or 4–methylbenzoic acids *via* the corresponding acid chlorides.

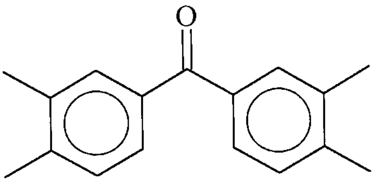
The acid chlorides C_6H_5COCl [915,1753] and 4–ClC_6H_4COCl [915] were also produced from C_6H_6 and C_6H_5Cl, respectively, by using an excess of $COCl_2$ in the presence of aluminium(III) chloride at low temperatures, and by using CS_2 as a solvent. In early work [888], benzene is reported to react with $COCl_2$ in the presence of sunlight to give an unspecified amount of C_6H_5COCl.

Upon protracted contact with aluminium(III) chloride at higher temperatures, and especially if the aromatic hydrocarbon is itself used as the solvent, the product of the reaction between phosgene and aromatic hydrocarbons is usually the corresponding benzophenone [2026]. Friedel and Crafts [686aa] found that $COCl_2$ reacts with benzene in the presence of a stoicheiometric amount of aluminium(III) chloride to give benzophenone:

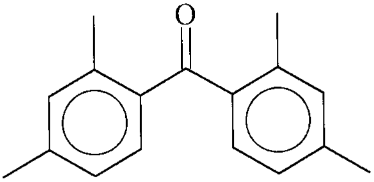
$$C_6H_6 + COCl_2 \xrightarrow{AlCl_3} C_6H_5COCl + HCl$$

$$C_6H_5COCl + C_6H_6 \xrightarrow{AlCl_3} C_6H_5COC_6H_5 + HCl$$

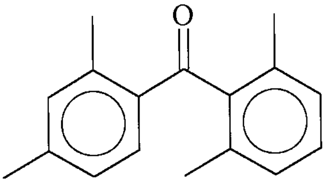
The effect of a variety of experimental conditions upon the yield or course of the reaction has been recorded. The reaction was monitored as a function of time, temperature, mixing method, varying reactant proportions, catalyst type and CS_2 dilution [2196]. The reaction of $COCl_2$ with benzene in the presence of aluminium(III) chloride was also examined at 80 °C using a 10:1 molar ratio of C_6H_6:$COCl_2$ and a 0.5:1.0 molar equivalent of aluminium(III) chloride. The reaction was found to be stoicheiometric rather than catalytic, due to adduct formation between the product ketone and the aluminium(III) chloride [312]. Similar results were obtained with 1,3– or 1,4–dimethylbenzenes at 140 °C. Aluminium(III) bromide and gallium(III) chloride gave similar results to aluminium(III) chloride, but antimony(V) chloride and iron(III) chloride produced even less hydrogen chloride. Neither $SbCl_3$, $ZnCl_2$, $SnCl_4$ nor CF_3SO_3H promote the reaction of $COCl_2$ with benzene or 1,3–dimethylbenzene [312]. The reaction of chlorobenzene with phosgene using aluminium(III) chloride as a catalyst gave a mixture of almost equal amounts of 2,4'– and 4,4'–dichlorobenzophenones, and the optimum conditions for the reaction were determined [367]. 1,2–Dimethylbenzene, $COCl_2$ and aluminium(III) chloride (molar ratios 6:1:1) combine at 60 °C within 2 h to give predominantly the expected ketone [620]:



Some of the 2,3,3',4'-isomer was found as a minor product. Similarly, the products formed from the reaction of phosgene with 1,3-dimethylbenzene in the presence of aluminium(III) chloride were:



(major)



(minor)

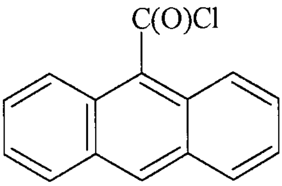
The treatment of a mixture of an essentially aromatic hydrocarbon fraction (dimethylbenzenes, alkylbenzenes, $PhCHMe_2$, 1,3,5-$Me_3C_6H_3$, C_{10} aromatics, *etc*; boiling range 150–200 °C) with phosgene in the presence of aluminium(III) chloride gave a mixture of polyalkylated benzophenones, having an average of nineteen carbon atoms per molecule [1043].

Fluorobenzene reacts with HF and $COCl_2$, when pressurized to 6 bar with BF_3 for 3 h at 80 °C, to give $(4\text{-}FC_6H_4)_2CO$ and some $2\text{-}FC_6H_4COC_6H_4F\text{-}4$ [509a,509b].

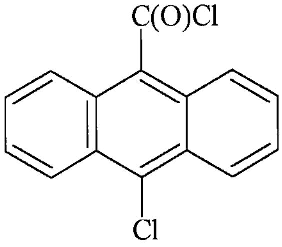
Biphenyl and phosgene react in the presence of aluminium(III) chloride to give 4,4'-diphenylbenzophenone [4c]:

$$COCl_2 + C_6H_5C_6H_5 \longrightarrow (C_6H_5C_6H_4)_2CO + 2HCl$$

Anthracene, at 180–200 °C, gave some anthracene-9-carboxylic acid chloride (**10.1**) on reaction with $COCl_2$ in the presence of aluminium(III) chloride [811a], whilst at 240–250 °C, 10-chloroanthracene-9-carboxylic acid chloride (**10.2**) was formed [153b].



(10.1)

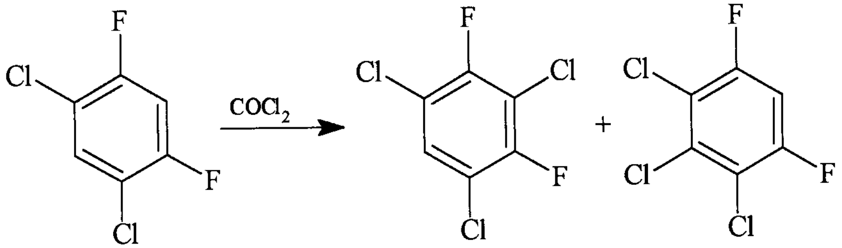


(10.2)

10.1.5.2 Reactions in the absence of Lewis acids

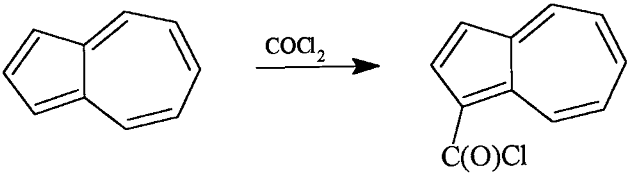
The direct chlorination of benzene usually results in the formation of high proportions of tetra- and hexa-chlorobenzenes. In contrast, pentachlorobenzene can be formed from the chlorination of tetrachlorobenzene with phosgene: 1,2,4,5-tetrachlorobenzene and phosgene were heated for an hour at 300 °C and then for 2 h at 350 °C to give C_6HCl_5 (with C_6Cl_6 and 2,3,5,6-tetrachlorobenzoyl chloride as by-products). Pentahalobenzenes were similarly forced by treatment of dichlorodifluorobenzene with phosgene [1662]:

e.g.

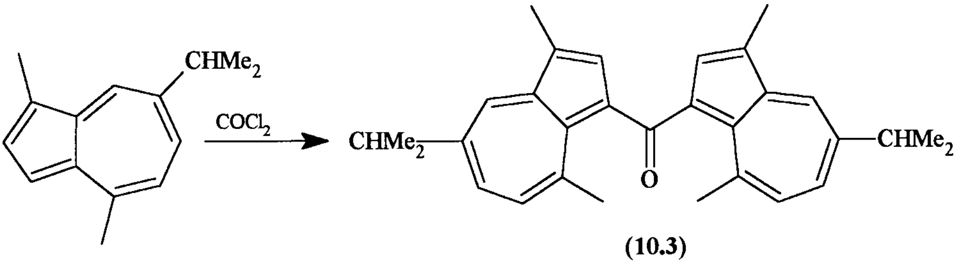


Although phosgene is commercially available in toluene solution, this is not an inert solvent under photochemical conditions. Thus, irradiation of a solution of $COCl_2$ in toluene with light from a mercury lamp produced $PhCH_2Cl$ in 82.1% yield [1150].

Phosgene in toluene reacts with azulene at room temperature in the absence of a Friedel-Crafts catalyst according to [2052a]:



The azulene derivative, guaiazulene (1,4-dimethyl-7-isopropylazulene), also reacts with $COCl_2$ to give the expected ketone, (10.3) [1698a]:



(10.3)

The product, **(10.3)**, decomposes back to regenerate guaiazulene upon treatment with acid [1698a].

10.2 REACTIONS WITH NITROGEN COMPOUNDS

10.2.1 Amines and related compounds

No other organic functional group possesses as much variety in its reactions with phosgene as does the amine system, and the significance of the reaction of phosgene with this class of compounds is reflected in the observation that more papers have been published on this subject than on any other single aspect of the use of phosgene as a reagent for organic synthesis.

The largest single industrial use of phosgene is in the manufacture of isocyanates (Section 4.7.1), which are prepared from the reactions of phosgene with primary amines. Ironically, many of the product isocyanates are many times more toxic than phosgene itself (see Section 4.7.1.1), and it is a curious fact that much of the literature on preparative routes to the isocyanates is concerned with phosgene-free methods. Not only do phosgene and its reactions with amines now play an important rôle in the modern organic chemical industry, but it was also instrumental in the early dyestuffs industry (see Sections 4.7.4).

A multitude of products are available from the reactions of phosgene with amines depending upon the reaction conditions, but the initial interaction is invariably the result of nucleophilic attack of the nitrogen lone pair at the phosgene carbon centre. This intermediate, depending upon the nature and class of amine, may then eliminate hydrogen chloride to form a carbamoyl chloride, or it may rearrange to form an ionic derivative. Secondary reactions may then follow in which isocyanates or urea derivatives are produced. The differing reactivity of a mixture of primary, secondary, and tertiary aromatic amines has been used for their separation [748].

Many of the tertiary amines have been used either as acid acceptors, or as catalysts in the preparation of chloroformates. The catalytic mode of action is probably the result of the formation of the inherently unstable salt-like intermediate $[R_3NCOCl]Cl$, which is itself a reactive acylating agent.

The importance of this class of reactions is reflected in the number of reviews devoted to the subject [79a,96,578,1782b,2036a]. The following Section has been written with due deference to these useful sources.

10.2.1.1 Simple primary amines

The reaction of phosgene with a primary aliphatic or aromatic amine {Equation (10.1)} is generally rapid, and takes place initially according to a 1:1 stoicheiometry, even at temperatures as low as −15 °C [1861]:

$$RNH_2 + COCl_2 \longrightarrow RNHCOCl + HCl \qquad (10.1)$$

The hydrogen chloride produced in this reaction reacts further with the amine to generate an ammonium salt, $[RNH_3]Cl$, which itself can react with further $COCl_2$ {Equation (10.2)} [619,988,1154]:

$$[RNH_3]Cl + COCl_2 \longrightarrow RNHCOCl + 2HCl \qquad (10.2)$$

This reaction proceeds at a much slower rate than the former reaction, and a variety of materials have been reported to catalyse it.

The final product of the reaction of $COCl_2$ with a primary amine depends very much on the reaction conditions. If an excess of the amine is used at low temperatures then substituted ureas may form {Equation (10.3)}:

$$4RNH_2 + COCl_2 \longrightarrow (RNH)_2CO + 2[RNH_3]Cl \qquad (10.3)$$

These are the products of the reaction when phosgene is bubbled into a solution of the amine in an inert solvent. Indeed, the reaction of phosgene with aniline constitutes a method for the quantitative determination of $COCl_2$ (see Section 3.2.2) [*e.g.* 1168]:

$$4C_6H_5NH_2 + COCl_2 \longrightarrow (C_6H_5NH)_2CO + 2[C_6H_5NH_3]Cl$$

In the presence of an excess of phosgene, phenyl isocyanate slowly appears.

If, on the other hand, an excess of $COCl_2$ is employed or if the hydrogen chloride formed as a result of Equation (10.1) is removed as it is produced (for example, by the use of a strong base, such as a tertiary amine), then the final product will be the carbamoyl chloride, RNHCOCl, of Equation (10.1). Performing the reaction at high temperatures in the presence of an excess of phosgene results in the formation of RNCO and HCl, consistent with the overall stoicheiometry of Equation (10.4) [2086], since the carbamoyl chlorides are easily dehydrochlorinated to the corresponding isocyanate by heating, Equation (10.5). Processes for the manufacture of isocyanates usually involve both a cold stage {Equation (10.1)} and a hot stage {Equations (10.2) and (10.5)}. Methods for preparing isocyanates by continuous processes have been described [1749,1896].

$$RNH_2 + COCl_2 \longrightarrow RNCO + 2HCl \qquad (10.4)$$

$$RNHCOCl \longrightarrow RNCO + HCl \qquad (10.5)$$

The kinetics of the formation of carbamoyl chlorides from primary aromatic amines and $COCl_2$ have been studied by a quench-flow technique [200,436], which indicated second-order kinetics, and an S_N2 mechanism.

Kinetic measurements on reactions of an excess of phosgene with primary aromatic amines were carried out in toluene at −5, +5 and +25 °C [436]. The results are summarized in Table 10.1, and the mechanism of the bimolecular nucleophilic substitution reaction is:

$$ArNH_2 + COCl_2 \longrightarrow [ArH_2N^{+}\text{—} CCl_2O^{-}] \xrightarrow{ArNH_2} ArNHCOCl + [ArNH_3]Cl$$

TABLE 10.1

SECOND ORDER RATE CONSTANTS, ACTIVATION ENTHALPIES AND ACTIVATION ENTROPIES FOR THE REACTIONS OF PHOSGENE WITH SOME PRIMARY AROMATIC AMINES [436]

Amine	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$			$\Delta H^{\ddagger}/\mathrm{kJ\ mol^{-1}}$	$\Delta S^{\ddagger}/\mathrm{J\ mol^{-1}\ K^{-1}}$
	$T/^{\circ}\mathrm{C}$				
	-5	5	25		
Aniline	116	183	359	22.85	-119.2
4-Chloroaniline	56.7	87.5	157	27.53	-110.9
4-Aminotoluene	315	438	708	16.40	-115.5
2-Aminotoluene	85.2	123	288	26.94	-106.7
2,4-Diaminotoluene	39.0	58.3	113	22.59	-115.1
2,6-Diaminotoluene	18.8	27.6	57.2	24.52	-115.9

Moreover, kinetic data have also been measured for the equilibrium [435]:

$$\mathrm{PhNHCOCl} \rightleftharpoons \mathrm{PhNCO + HCl}$$

Although reactions are usually carried out in organic solvents, phosgene reacts with a wide range of aliphatic or aromatic primary amines in the vapour phase:

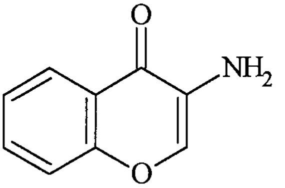
$$\mathrm{RNH_2 + COCl_2 \longrightarrow RNHC(O)Cl + HCl}$$

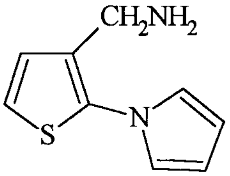
$$\mathrm{RNHC(O)Cl \rightleftharpoons RNCO + HCl}$$

The hydrogen chloride generated in the first step ensures that the carbamoyl chloride is normally the primary reaction product. However, if the hydrogen chloride is removed before the reaction products are cooled, then isocyanates are prepared directly [1897,1898]. The vapour phase preparations are especially suitable for the lower aliphatic carbamoyl chlorides, RNHCOCl {R = Me, Et, Pr, $\mathrm{CH_2{=}CHCH_2}$, Bu or $\mathrm{CH_3(CH_2)_4}$} [1897].

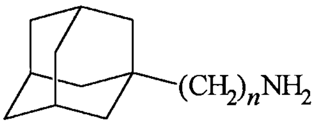
The equilibrium yields in reaction (10.4) have been calculated for R = Me (500–900 K) [167] and R = Ph (298–1000 K) [1159]. At normal pressures, the results show that the reactions are favourable over the entire temperature ranges examined.

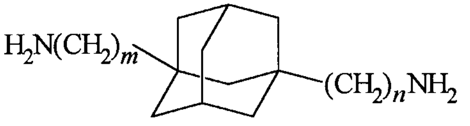
One of the most efficient methods for producing an isocyanate is to heat the dry, powdered alkylammonium chloride in a stream of phosgene {Equation (10.2)}, the carbamoyl chloride then decomposing *in situ* {Equation (10.5)} [619]. This method constitutes one of the earliest for the preparation of isocyanates, RNCO, having been studied for phenyl isocyanate by Hentschel in 1884 [945a] and for methyl and ethyl isocyanate by Gattermann and Schmidt in 1887 [721a]. These solid–gas reactions have now been largely superseded by reactions in organic solvents, and a large assortment of isocyanates have been prepared by the direct reaction of phosgene with aliphatic or aromatic primary amines, RNH_2, which include R = $C_nF_{2n+1}CH_2$ (n = 1–9) [1405], I-4-C_6H_4 [2005], NO_2-4-C_6H_4 [1867a], $CH_3(CH_2)_n$-4-C_6H_4, $CH_3(CH_2)_n$-E-4-C_6H_4 ($n \geqslant 6$, E = O, S or –C(O)O–) [823], $Me_3Si(CH_2)_3$ [1406a] and $Bu_3Sn(CH_2)_3$ [507]. Heterocyclic derivatives such as those illustrated below also readily give the expected isocyanates upon treatment with phosgene [1687,1993].





Similarly, mono– and di– aminoadamantyl derivatives (n,m = 0, 1 or 2) were converted into their corresponding isocyanates by reaction with phosgene [1101].





The reactions of phosgene with diamino compounds are amongst the most important of its industrially–related reactions. Indeed, especial note is made of the 2,4– and 2,6–diaminotoluenes, and of 4,4'–diaminodiphenylmethane and other commercially important materials (see Section 4.7.1.1). Phosgene was also noted to react with 1,4-$C_6H_4(NH_2)_2$ as a slurry in 1,2–dichlorobenzene [613], and with 3,3'–diaminodiphenylmethane at 125 °C in chlorobenzene [2062], to give the corresponding diisocyanates.

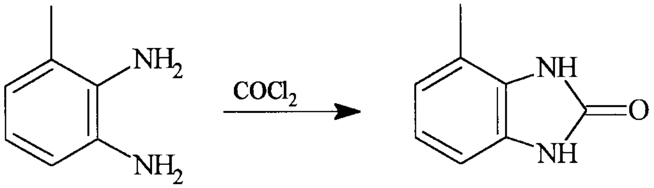
The reactions of the dihydrochloride salts of 2,4– and 2,6–diaminotoluene with phosgene in toluene or 1,2–dichlorobenzene solutions have been examined at 25–90 °C [1923]. With the 2,4–isomer, acylation occurs initially at the 2–position, followed by a slower acylation at the 4–position: direct acylation of both NH_2 groups occurs at equal rates in the 2,6–isomer. The rate constants and activation parameters have also been determined for the reactions of the hydrochloride salts of aniline and 4-chloroaniline with phosgene in toluene solution [2061]:

$$[R\text{-}4\text{-}C_6H_4NH_3]Cl + COCl_2 \longrightarrow R\text{-}4\text{-}C_6H_4NCO + 3HCl$$
$$(R = H \text{ or } Cl)$$

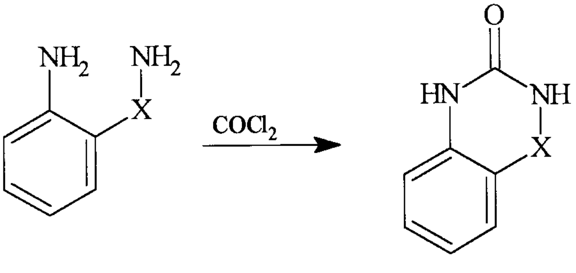
Reaction of $COCl_2$ with $[NH_3(CH_2)_6NH_3]Cl_2$ gives $OCN(CH_2)_6NCO$ [620b], and polyamines, or their salts with primary or secondary alcohols, were similarly converted into polyisocyanates [1684].

10.2.1.2 Cyclization involving primary amines

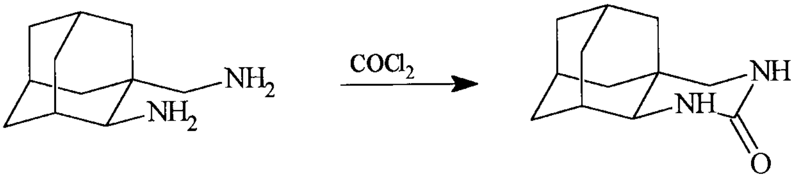
Cyclizations can occur when two amino groups are adjacent on a benzene ring. For example, reaction of phosgene with 2,3-diaminotoluene in chlorobenzene gave a precipitate containing a five-membered ring, considered to be a cyclic urea [1154]:



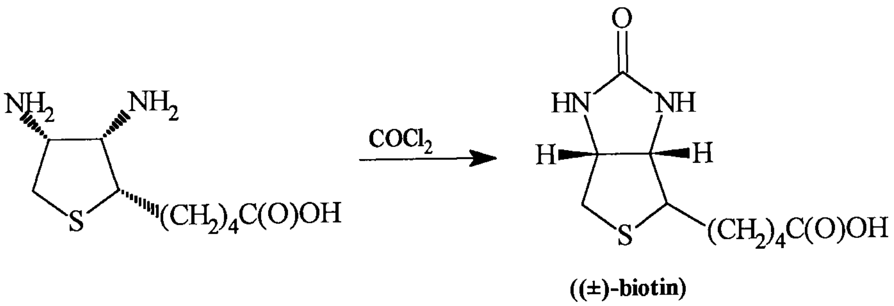
The compounds $2\text{-}H_2NC_6H_4XNH_2$ (X = CH_2, CHMe, $(CH_2)_2CHMe$, $CH_2CHMe(CH_2)_3$, $CH_2CHMeCHMe$ or CH_2CH_2CHPh) were cyclized similarly to give six-, seven- or eight-membered heterocyclic rings [1081]:



Alicyclic compounds behave analogously. Thus, diaminoadamantyl derivatives can be cyclized [78]:

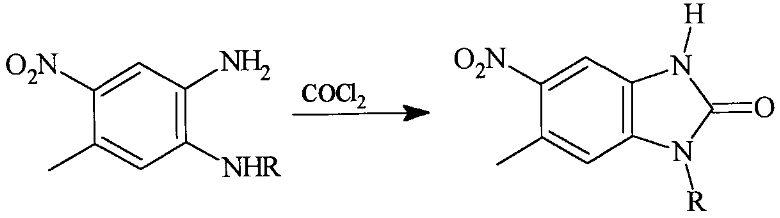


and an all-*cis* tetrahydrothiophene derivative will give (±)-biotin [1340]:

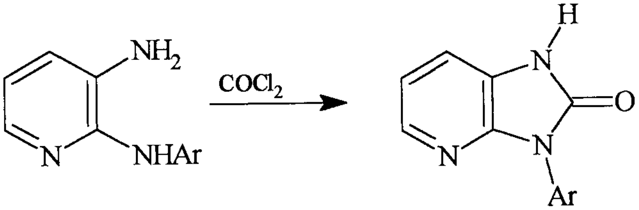


((±)-biotin)

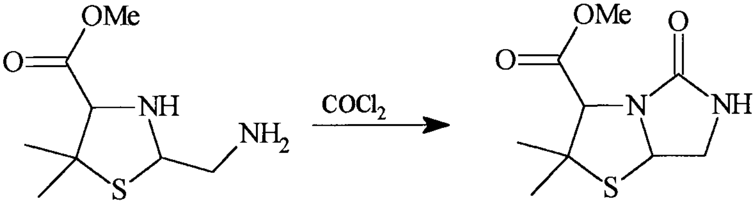
Cyclization can also occur between primary and secondary amine functions that are adjacent on a ring. Thus, the following reaction has been used to prepare a bactericide [2]:



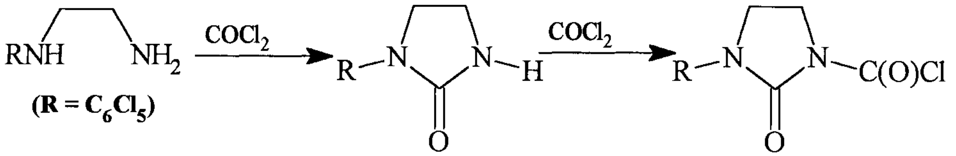
and an anilinopyridine was cyclized to imidazopyridin-2-one [393]:



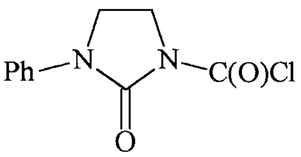
Similarly, a thiazolidine, in the presence of $Na[HCO_3]$, gave a fused-ring product [409]:



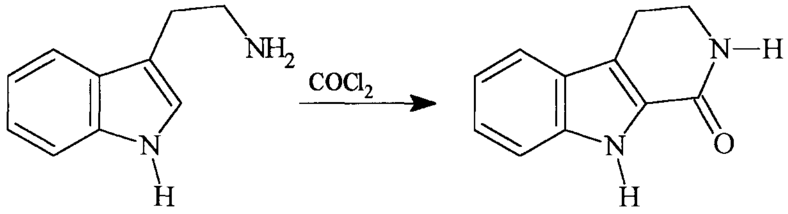
The reaction of phosgene with $RNHCH_2CH_2NH_2$ ($R = C_6Cl_5$) gave a cyclic urea [1130a]:



Treatment of $Ph_2NCH_2CH_2NH_2$ (containing both primary and tertiary amine functions) with $COCl_2$ affords an imidazolidine, with concomitant formation of PhCl [1290]:

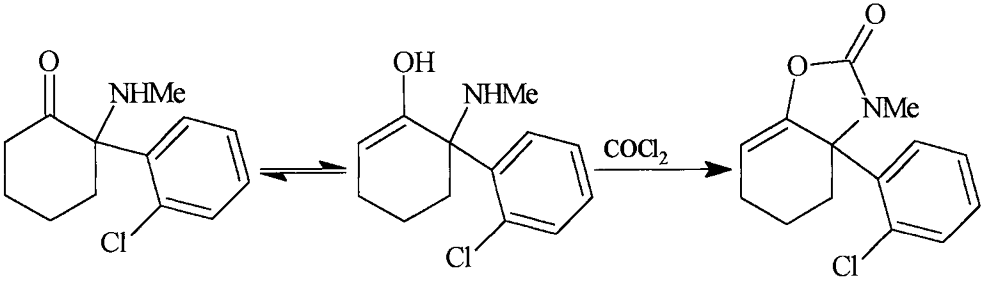


Tryptamine undergoes a straightforward cyclization reaction with phosgene [856a]:



(tryptamine)

whereas ketamine (an anæsthetic) reacts *via* its enol form [856a]:



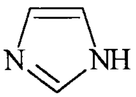
(ketamine)

10.2.1.3 Secondary amines

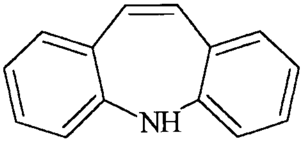
The effect of phosgene on a secondary amine R_2NH (R_2 = Me_2 [1392e], Et_2 [1286a] or MePh [1392f]) is generally to form the corresponding carbamoyl chloride, according to Equation (10.6):

$$R_2NH + COCl_2 \longrightarrow R_2NCOCl + HCl \qquad (10.6)$$

The heterocyclic materials illustrated below behave similarly, the N-H functionality being converted to N-C(O)Cl [1891,2144]:



(imidazole)



(iminostilbene)

The hydrochloride salt formed as a by-product from the combination of R_2NH with $COCl_2$

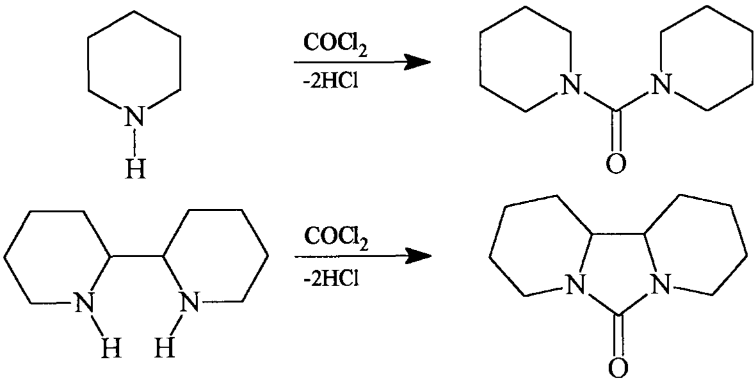
may also react further with phosgene at elevated temperatures, according to Equation (10.7) [721a]:

$$[R_2NH_2]Cl + COCl_2 \longrightarrow R_2NCOCl + 2HCl \qquad (10.7)$$

As was found for the primary amines, the final product of the reaction depends largely upon the reaction conditions, not least because R_2NCOCl (R = Me, Et or Ph) is a very reactive compound, and can combine with an excess of the amine to form the tetrasubstituted urea [1392a,1392b]:

$$R_2NCOCl + R_2NH \longrightarrow (R_2N)_2CO + HCl \qquad (10.8)$$
$$(R = Me,\ Et\ or\ Ph)$$

These products may also be prepared from the reaction of $COCl_2$ with the hydrochloride salt of the secondary amine [1451]. In some cases, ureas are formed immediately, for example, in the reactions of piperidine [1652] or 2,2'-bipiperidine [668] with phosgene [1652]:



Reactions are normally carried out in the liquid phase in well-cooled solutions of the secondary amine, R_2NH, in an inert organic solvent, using an excess of phosgene to produce the carbamoyl chloride, largely irrespective of the nature of R [9,516,766,1200,2036a]. However, reactions may also be conducted in the vapour phase, and, at 275 °C, $COCl_2$ was found to react with R_2NH {R = Me, Bu or $CH_3(CH_2)_4$} according to Equation (10.6) [1897,1898]. At normal pressures, in the temperature range 100–700 °C, the equilibrium yield for the reaction between dimethylamine and phosgene to give methyl isocyanate was calculated to be virtually 100% [167]:

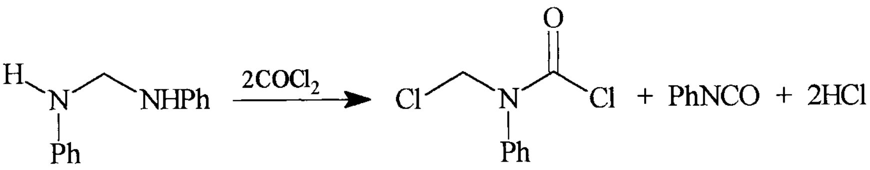
$$Me_2NH + COCl_2 \longrightarrow MeNCO + MeCl + HCl$$

However, there is no recorded example of such a reaction ever having been observed.

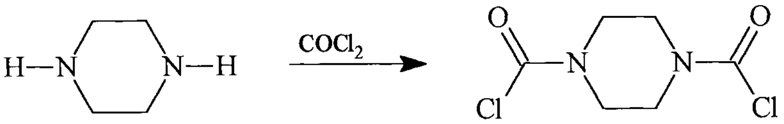
Mixed carbamoyl chloride–isocyanate compounds can be prepared by reaction of phosgene with a material possessing both a primary and a secondary amine function:

$4\text{-}NH_2C_6H_4CH_2NHPh$ gives the expected product, $4\text{-}OCNC_6H_4CH_2N(COCl)Ph$, under mild conditions [2086].

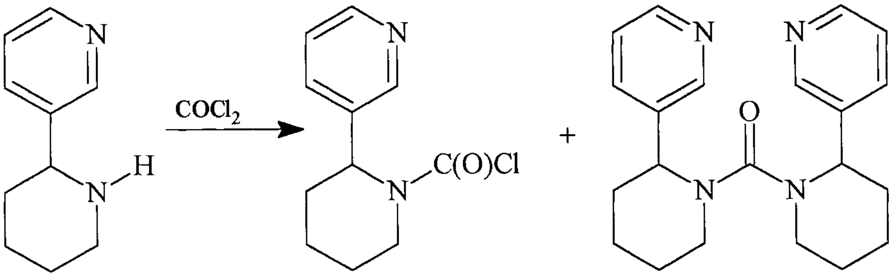
In a surprising reaction, *N*,*N'*–diphenylmethylene diamine (a possible intermediate formed in the commercial production of TDI, see Section 4.7.1.1) reacts with phosgene by cleavage of a carbon–nitrogen bond to give a mixture of products [2086]:



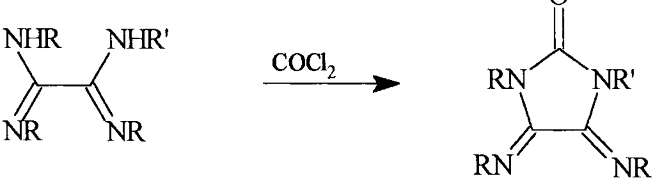
The initial attack of $COCl_2$ at a nitrogen atom causes the release of HCl, which is believed to facilitate the cleavage of the other, rather weak, C–N bond. Piperazine, in contrast, reacts in the expected manner [186,1437]:



and the naturally occurring alkaloid insecticide, anabasine, $C_{10}H_{14}N_2$, reacts with phosgene to produce three main products [667]. At low temperatures, the adduct "$C_{10}H_{14}N_2.COCl_2$" is formed, whereas under normal conditions the carbamoyl chloride and urea derivatives are isolated [667]:

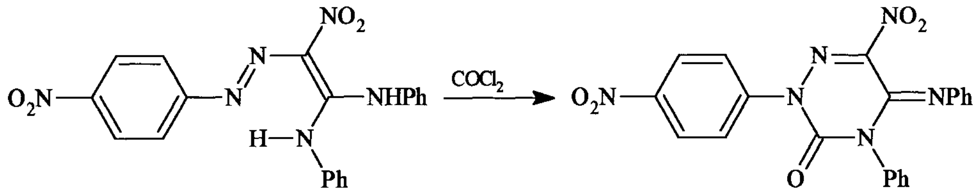


Imidazolidones have also been prepared from di–secondary amines [149,666]:

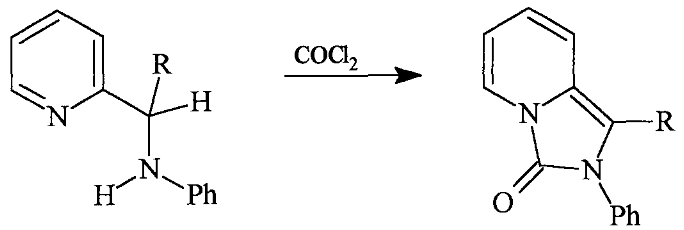


(R = Ph, $4\text{-}MeC_6H_4$ or $4\text{-}MeOC_6H_4$;
R' = Me, $CH_2{=}CHCH_2$, $4\text{-}PhN{=}NC_6H_4$
or $2\text{-}NO_2C_6H_4$)

An unusual cyclization reaction, involving an interesting rearrangement, has been used to prepare a triazine derivative [1791]:



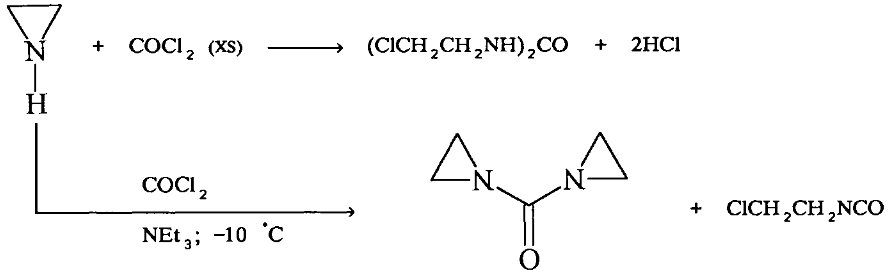
In a similar rearrangement, imidazo[1,5-a]pyridin-3(2H)-ones were prepared by condensing aminomethylpyridines with phosgene [1583]:



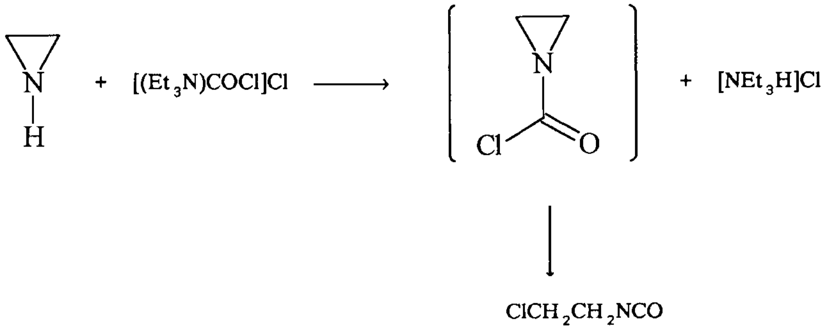
(R = CO_2R' or $CONH_2$;
R' = Me, Et or CH_2Ph)

The amine ester $MeC(O)ONHCMe_3$ reacts with $COCl_2$ to form the corresponding carbamoyl chloride, $MeC(O)ON(COCl)CMe_3$ [29].

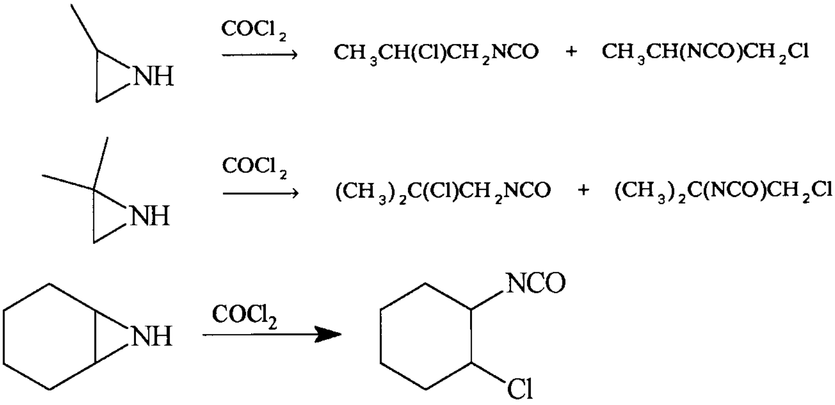
Attempts to prepare a carbamoyl chloride from aziridine, CH_2NHCH_2, and phosgene have resulted only in the formation of ureas [186,2042b]:



The addition of aziridine to $[(Et_3N)COCl]Cl$ also results in the formation of $ClCH_2CH_2NCO$, suggesting that the carbamoyl chloride may be a reaction intermediate [1042a]:



The reactions of phosgene with other aziridines are illustrated below [1042a]:



10.2.1.4 Tertiary amines

Tertiary amines, NR_3, form 1:1 and 1:2 ionic derivatives with phosgene (reaction (10.9) {R_3 = Me_3 [807, 1750], Et_3, Pr_3, $Et_2(PhCH_2)$ [1968a] or $(PhCH_2)_3$ [1969]} and reaction (10.10) {R_3 = Et_3, Pr_3, $Et_2(PhCH_2)$, $CH_3(CH_2)_5$ or $CH_3(CH_2)_7$ [1968a]}, respectively), which are stable generally only at low temperatures (*ca.* −20 to −80 °C):

$$R_3N + COCl_2 \longrightarrow [R_3NCOCl]Cl \qquad (10.9)$$

$$2R_3N + COCl_2 \longrightarrow [(R_3N)_2CO]Cl_2 \qquad (10.10)$$

$[Me_3NCOCl]Cl$ [807] and $[Et_3NCOCl]Cl$ [1969] decompose between −10 °C and room temperature to give the alkyl chloride, RCl, and a molar equivalent of R_2NCOCl. Thus, on reaction in toluene at 60−70 °C, NMe_3 and $COCl_2$ react directly to give Me_2NCOCl and MeCl. The latter recombines with an excess of NMe_3 to give $[NMe_4]Cl$ [1750].

Equilibrium yields have been calculated for the hypothetical production of methyl isocyanate from the reaction of Me_3N and $COCl_2$ [167]:

$$NMe_3 + COCl_2 \longrightarrow MeNCO + 2MeCl$$

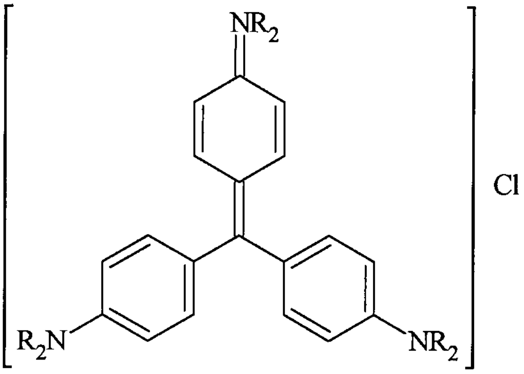
Although the reaction is calculated to be highly favourable between 100 and 700 °C, no reaction of this type appears ever to have been reported.

The kinetics of the reactions of phosgene with tertiary amines (NEt_3, NPr_3, $NPhEt_2$ or NEt_2CH_2Ph) have been examined at between 6 and 40 °C [1968]. The rate of 1:1 salt formation is much greater than the rate of its ensuing decomposition. The rate-determining step of the reaction is thus that of the decomposition of the ionic intermediate:

$$R_3N + COCl_2 \xrightleftharpoons{\text{fast}} [R_3NCOCl]Cl \xrightarrow{\text{slow}} R_2NCOCl + RCl$$

The activation energies were calculated to be 72.0 (NEt_3), 43.9 (NPr_3), 26.6 (NEt_2CH_2Ph) and 104.6 (NEt_2Ph) kJ mol^{-1}, respectively.

With *N*,*N'*-dimethylaniline and an excess of $COCl_2$ between 0 and 50 °C, $Me_2N{-}4{-}C_6H_4COCl$ is formed [1392c,1721], whilst reaction of one mole of $COCl_2$ with two molar equivalents of NMe_2Ph gives the product $Me_2NC_6H_4C(O)C_6H_4NMe_2$, known as "Michler's Ketone" [1392d]. In the presence of zinc or of aluminium(III) chloride, "crystal violet" is the main product of the reaction [972b], a material of considerable importance in the early dyestuffs industry (see Section 4.7.4).



(crystal violet; R = Me)

Reaction of NEt_2Ph with phosgene, whilst producing $[PhNEt_2COCl]Cl$ at low temperature, proceeds at room temperature according to [1969]:

$$2NEt_2Ph + COCl_2 \longrightarrow (Et_2NC_6H_4)_2CO + 2HCl$$

$$(Et_2NC_6H_4)_2CO + NEt_2Ph \longrightarrow \text{"crystal violet" } (R = Et)$$

Decomposition of $[(R_3N)_2CO]Cl_2$ (R = Et or $PhCH_2$) at room temperature proceeds according to [2042b]:

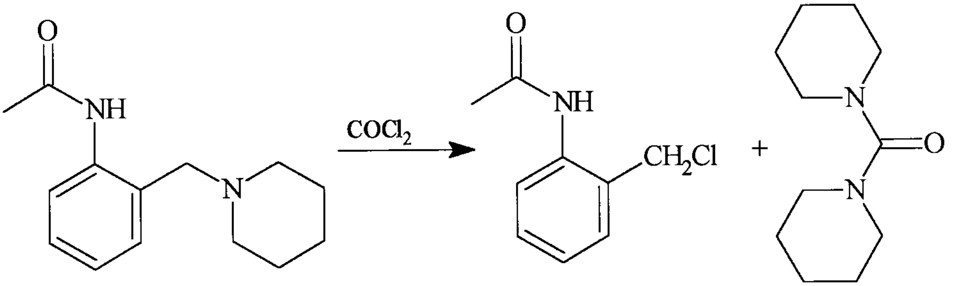
$$[(R_3N)_2CO]Cl_2 \longrightarrow R_2NCOCl + RCl + NR_3$$

The salt $[(py)_2CO]Cl_2$ decomposes in a similar manner [2042b]. The reaction of phosgene with an excess of NR_2Ph (R = Me, Et or Bu) at the respective boiling temperatures of the amines results in the formation of the tetrasubstituted ureas [1213,2139]:

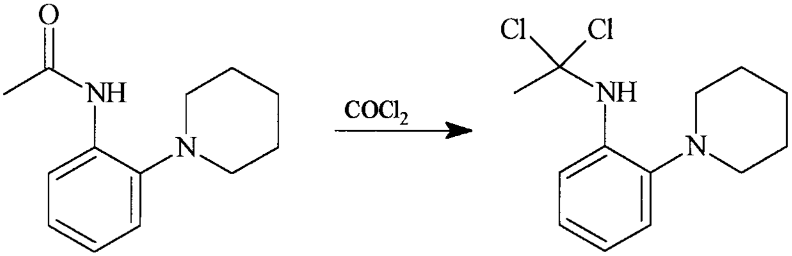
$$2C_6H_5NR_2 + COCl_2 \longrightarrow (C_6H_5NR)_2CO + 2RCl$$

Me-2-$C_6H_4NMe_2$ (which is considered to be inert to the preceding treatment) reacts with $COCl_2$ in the presence of aluminium(III) chloride for an extended period at high temperature to give the corresponding *N,N'*-dimethyl-*N,N'*-ditolylurea [1685]. However, the mixed urea $(PhEtN)_2CO$ was prepared simply by mixing NEt_2Ph and the secondary amine NHEtPh in xylene and aqueous NaOH and adding $COCl_2$ [573].

Phosgene reacts with amidobenzyl piperidines (substituted at the 2-, 3-, or 4- aromatic ring positions) at room temperature to give the corresponding amidobenzyl chlorides, and a substituted urea. The reaction is typified by that shown for the 2-isomer [1179a]:

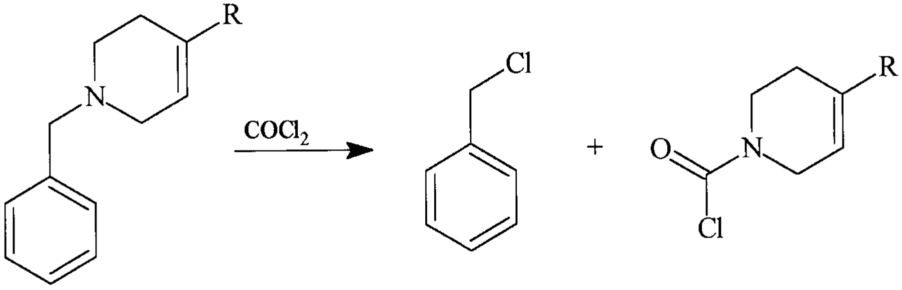


In contrast, when the basicity of the amine is reduced by direct conjugation to the aromatic ring, a chloro-substituted product is formed without cleaving the *N*-piperidyl - carbon bond [1179a]:



Triphenylamine, NPh_3, when condensed with $COCl_2$ in the presence of aluminium(III) chloride, resulted in the formation of a polymer, along with a small quantity of Ph_2N-4-$C_6H_4COC_6H_4$-4-NPh_2 [675].

Treatment of a 1-benzyl-1,2,5,6-tetrahydropyridine with phosgene at 100 °C over 12 h results in the cleavage of the benzyl carbon-nitrogen bond [1537]:



(R = CO_2Et)

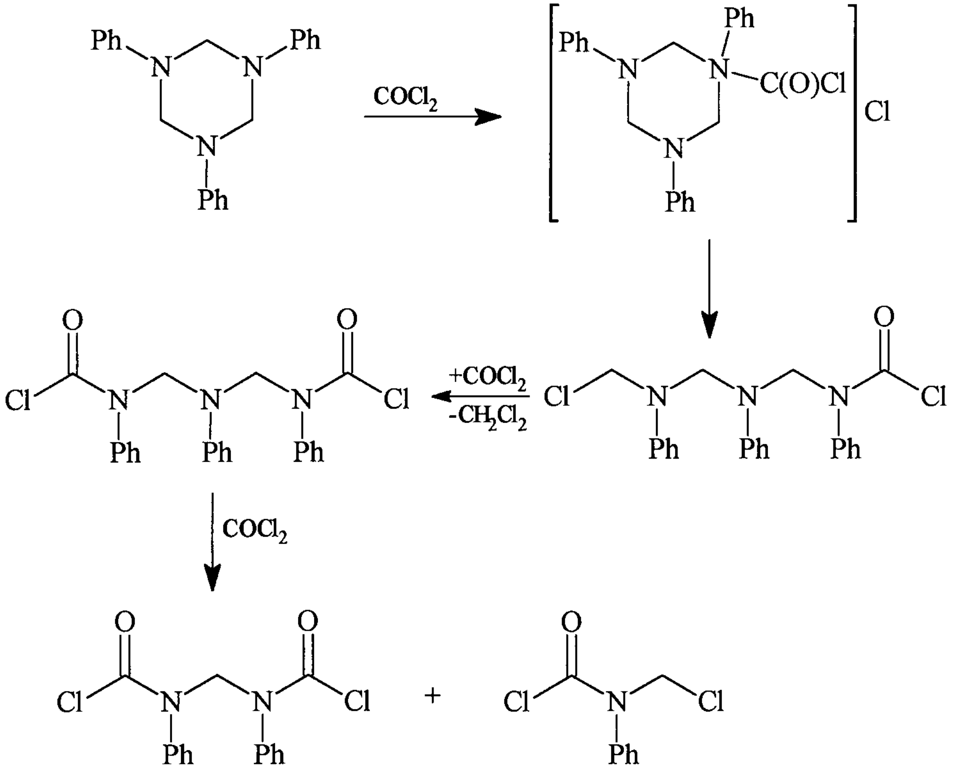
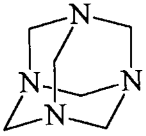


Fig. 10.1 Reaction of phosgene with 1,3,5-triphenylhexahydro-1,3,5-triazine [2086].

Similarly, reaction of a substituted triazine with $COCl_2$ also involves C–N bond cleavage, and this is illustrated in Fig. 10.1 [2086].

10.2.1.5 Hexamethylenetetramine

Although several workers have studied the reaction of hexamethylenetetramine (hmt; 1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane) with phosgene, the product has never been fully characterized, despite its alleged importance as a prophylactic agent in phosgene poisoning (Section 2.6).



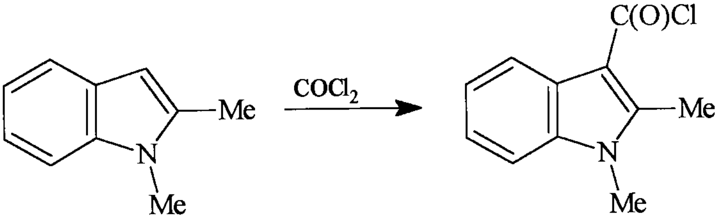
(hmt)

When hmt reacts with $COCl_2$ in inert organic solvents, irrespective of the temperature and reactant proportions, it forms a white, crystalline, high-melting compound with a formula corresponding to $(hmt)_2.COCl_2$ [548,1592,1606,1669,1670]. The compound is reported to be soluble in water and to give a precipitate of silver(I) chloride on addition to an aqueous solution of silver(I) nitrate. These observations could be consistent with the formulation $[(C_6H_{12}N_4)_2CO]Cl_2$. According to other sources, however, hmt forms a molecular compound with phosgene in the ratio of 1:1, $hmt.COCl_2$ [1247a,1589b]. Upon standing in trichloromethane under a slow current of dinitrogen, this material polymerizes to form a tacky substance, whose chloride analysis also corresponds to $hmt.COCl_2$ [1589b].

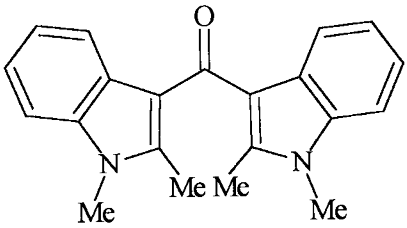
Hexamethylenetetramine has been employed in gas masks as a means of absorbing phosgene [1670]. Its dispersion in aluminium(III) hydroxide gel is also reported to be effective for the absorption of phosgene gas [1592].

10.2.1.6 Indole derivatives

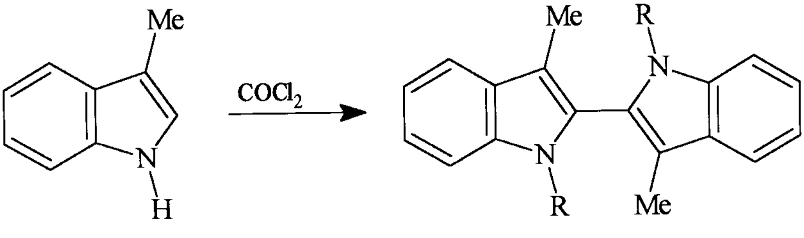
Addition of a toluene solution of phosgene to a solution of 1,2-dimethylindole in dichloromethane at about 10 °C gave the 3-(carbonyl chloride) derivative [177]:



At higher temperature the symmetrical ketone is produced:

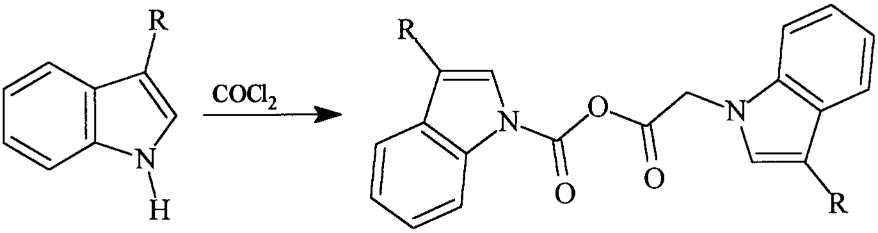


Reaction of 3-methylindole with $COCl_2$ in 1,4-dioxane gave a dimeric product (R = COCl), isolated as the *N,N*-dimethylamide ($R = CONMe_2$) derivative [177]:

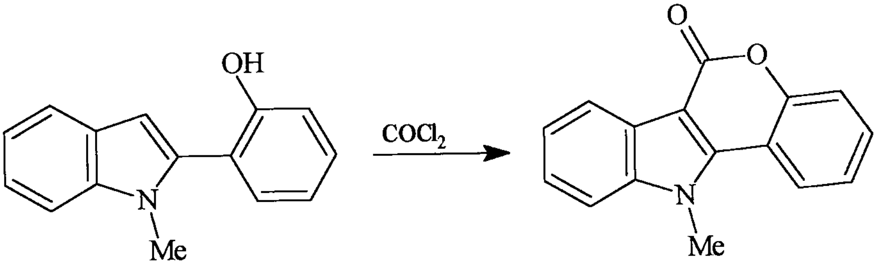


(R = COCl)

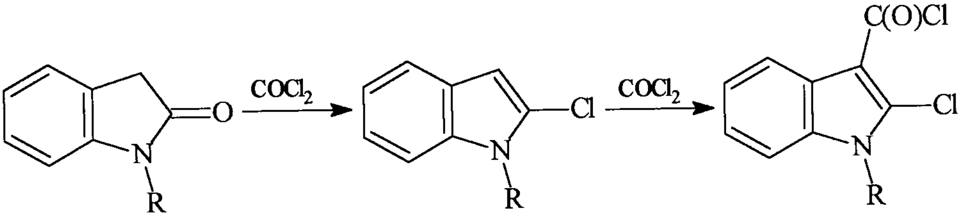
In the presence of a base such as pyridine, however, 3-R-indole (R = Me or Ph) reacts with phosgene in a different manner [177]:



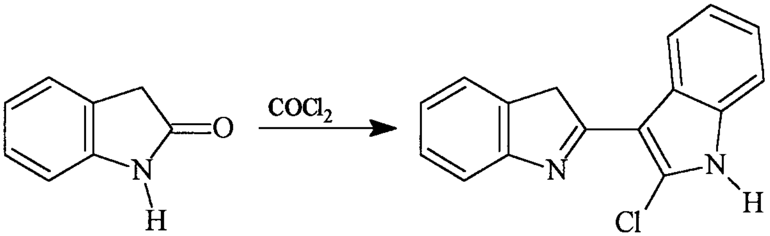
Indolo-fused heterocycles were also prepared by cyclization reactions [177]:



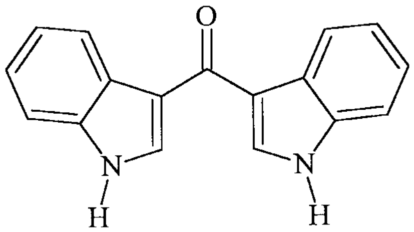
Oxindoles (R = H, Me or Pr) also react with phosgene [177]:

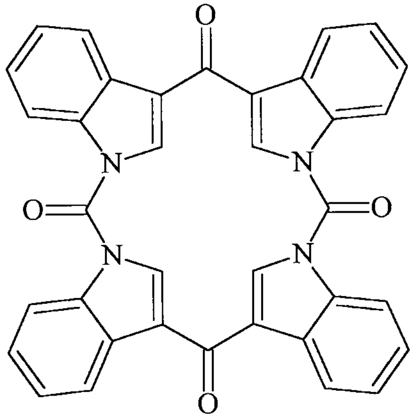


At a slightly higher temperature of 45 °C, however, oxindole (R = H) interacts with $COCl_2$ to give a dimeric indole [177]:



Treatment of indolylmagnesium bromide {*cf*. Section 9.9.1} with phosgene under reflux in diethyl ether gave, after work-up, a mixture of the following compounds [177]:





The above dimer could be carbonylated to the tetramer by further treatment with phosgene in the presence of triethylamine [177].

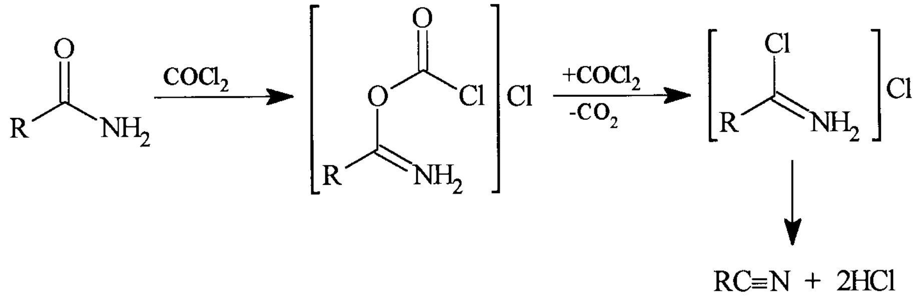
10.2.1.7 Quaternary ammonium salts

Tetraethylammonium chloride is insoluble in liquid phosgene, whilst tetrabutylammonium chloride undergoes solvolysis, possibly releasing an amine [1012].

10.2.2 Carboxamides

10.2.2.1 Primary amides

When primary amides are combined with phosgene, an efficient dehydration occurs to form the corresponding nitrile [1928a]:



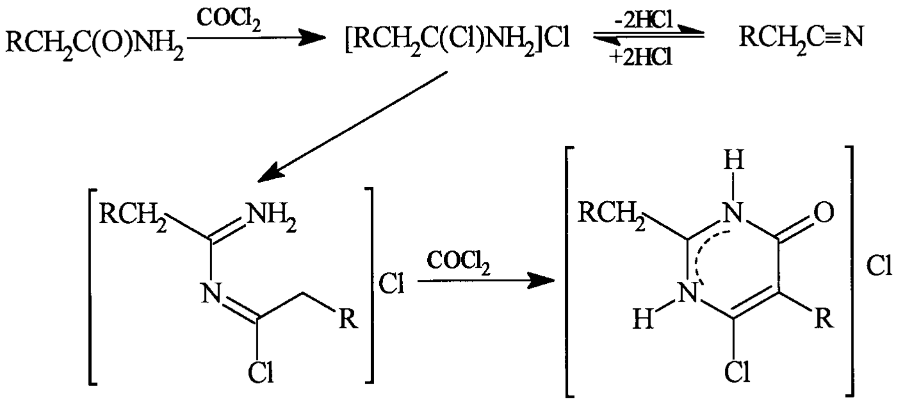
The reaction of $COCl_2$ with methanamide, $HCONH_2$, at 0 °C in $CHCl_3$/1,4-dioxane solution gave a compound with an empirical formula of $C_2H_7ClN_2O_2$, claimed to be $(HCONH_2)_2.HCl$ [237]. The reaction of a series of *N*-(hydroxyalkyl)methanamides with phosgene results in their dehydration to the corresponding isonitriles [634a]:

$$HC(O)NH(CH_2)_nOH \xrightarrow{COCl_2} C{\equiv}N(CH_2)_nOH \quad (n = 2,\ 3 \text{ or } 5)$$

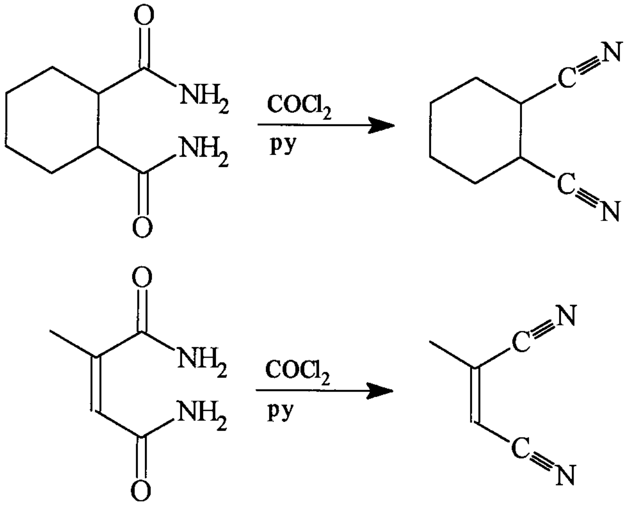
The earliest account [1801a] of the reaction of phosgene with ethanamide (in a sealed tube at 50 °C) gave ethanenitrile as only a minor product, and the reaction is considered to be most suitable for longer chain (saturated and unsaturated) amides having at least eight carbon atoms [822]:

$$C_7H_{15}CONH_2 + COCl_2 \longrightarrow C_7H_{15}CN + 2HCl + CO_2$$

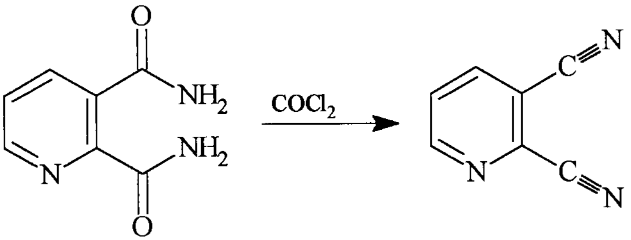
Under pressure, and with an excess of phosgene in the presence of HCl, primary amides give pyrimidine derivatives [2226a]:



In the presence of pyridine, diamides have also been dehydrated to give nitriles [281a,649a]:

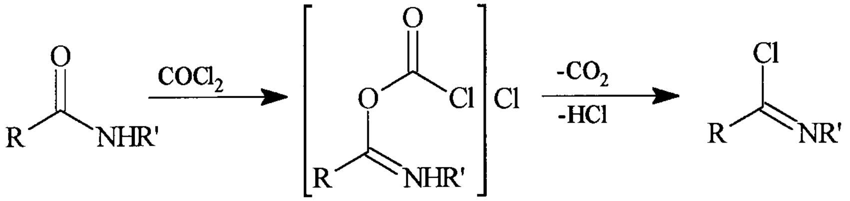


In dmf solution, a similar reaction occurs in the absence of pyridine [451a]:

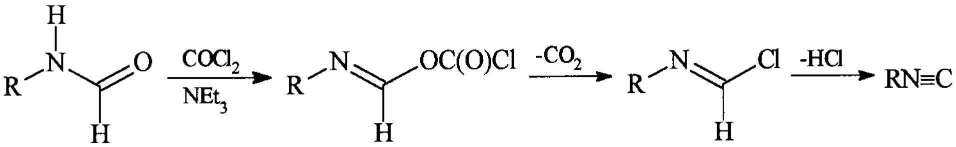


10.2.2.2 Secondary amides

The *N*-monosubstituted carboxamides, on reaction with phosgene, form imidoyl chlorides [2083a]:

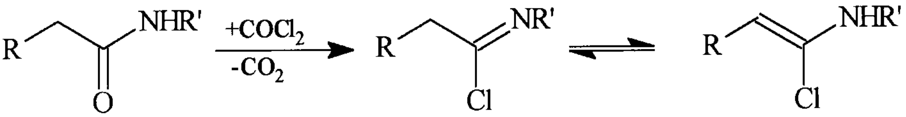


For HC(O)NHR', the reaction can take one of two courses depending upon the absence or presence of added base. In the presence of base, such as triethylamine, the *N*-alkyl-substituted compound is dehydrated to form an isonitrile [2081]:

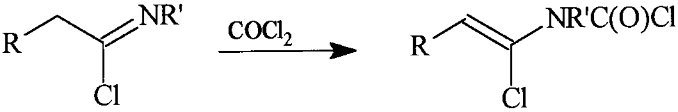


Methanamide salts, [RNH=CHNRCHCl$_2$]Cl or [RNH=CHNRH]Cl, are produced (in the absence of added base) as a result of the reaction of RNHCHO with the imidoyl chloride intermediate [1040].

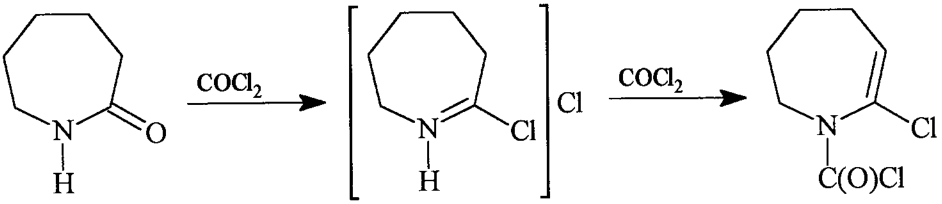
Secondary amides containing a hydrogen in the 2-position (adjacent to the carbonyl group) are chlorinated by phosgene at the carbonyl carbon atom [1574]:



This compound is then chlorocarbonylated at the nitrogen atom [1574]:

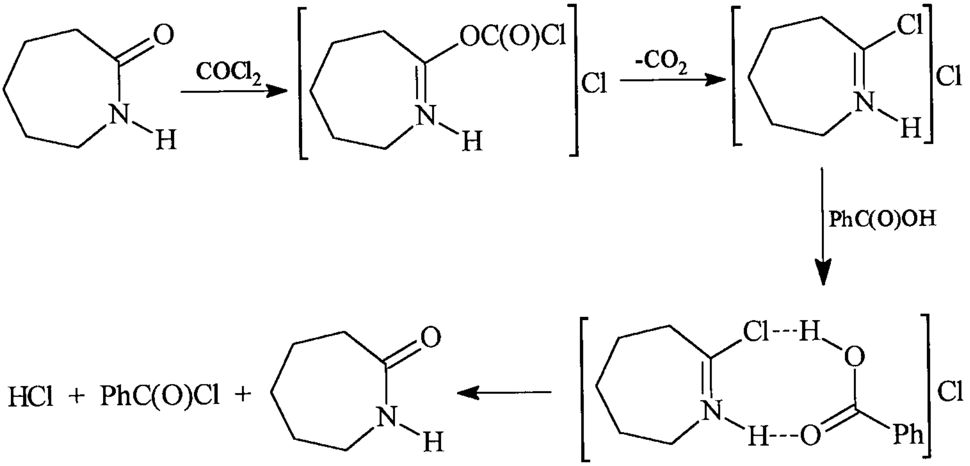


A notable example of this type is the reaction of 6–hexanelactam (ϵ–caprolactam) with phosgene in toluene at elevated temperature [369]:

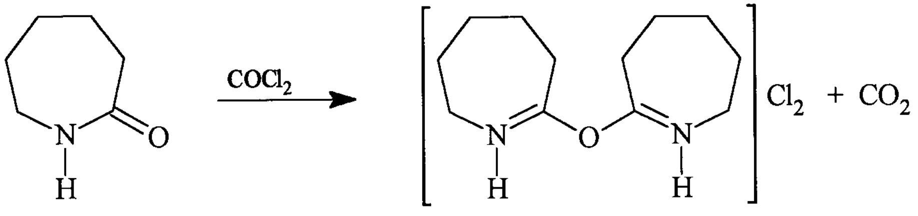


The 3–chloro derivative of ϵ–caprolactam behaves similarly [1574].

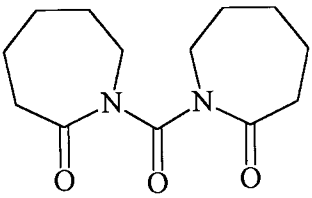
The catalytic effect of ϵ–caprolactam in the production of benzoyl chloride from phosgene and benzoic acid has been explained in terms of the following scheme [1495]:

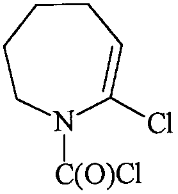


At room temperature, phosgene reacts with ϵ–caprolactam dissolved in benzene to give an ether [1392]:



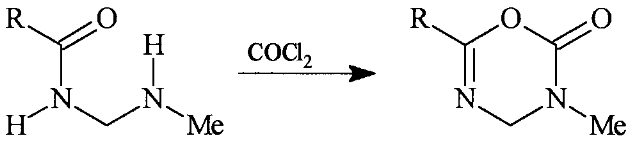
The following compounds are formed as by–products [1392]:



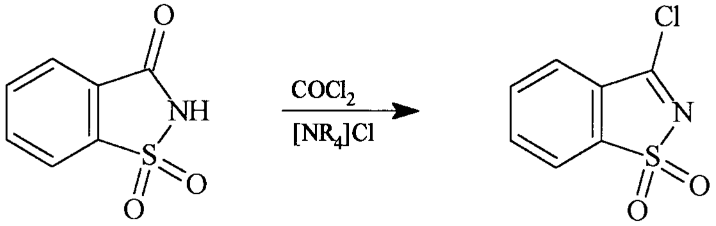


Under a variety of conditions, $COCl_2$ and polycaprolactam gave insoluble chlorine-containing polymers [1392].

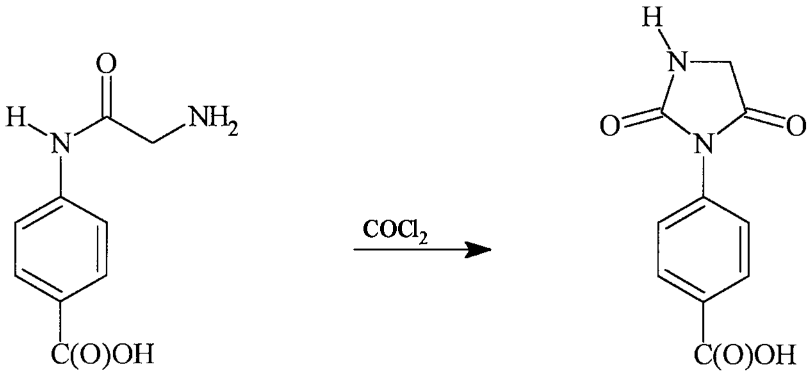
The reaction of $MeNHCH_2NHCOR$ (R = CMe_3, Et or $CHMe_2$) with $COCl_2$ proceeds according to [991]:

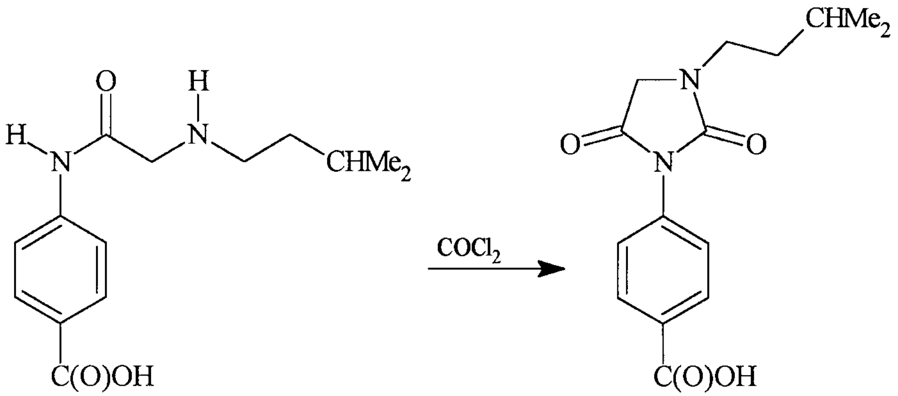


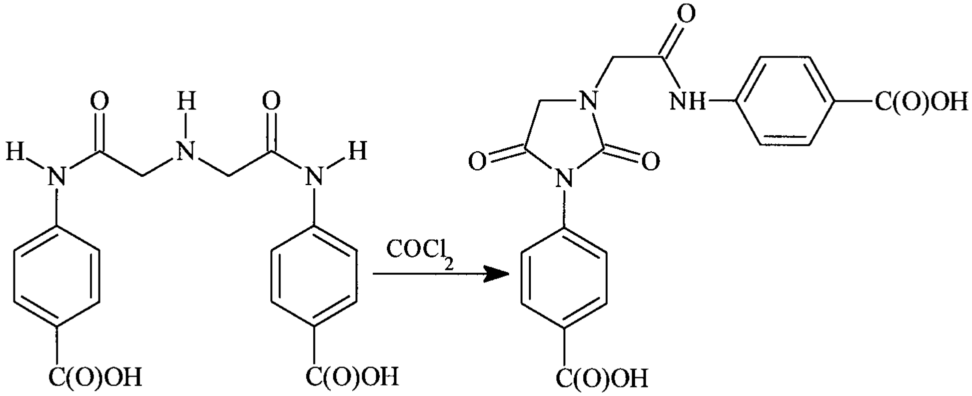
Saccharin also combines with $COCl_2$ [596]; the reaction takes place at about 110 °C over 10 h to give the product material in both high yield and purity:



Finally, the following secondary amides undergo cyclization when treated with $COCl_2$ in the cold to give substituted hydantoins, rather than ureas [2055]:







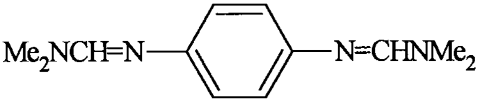
10.2.2.3 Tertiary amides

The reaction of phosgene with *N,N*-disubstituted carboxamides proceeds generally according to:

$$\mathrm{RCONR'_2 + COCl_2 \longrightarrow [RC(Cl){=}NR'_2]^+Cl^- + CO_2}$$

This reaction (R = H, R' = Me [80]; R = R' = Me [172]; R = $CHMe_2$, R' = Me [446]; R = MeCHSMe, R' = Me [750]; R = CH_2Cl, R' = Et [1760]) results in the formation of a series of important reagents, the uses of which include replacement of hydroxy, alkoxy or other related groups with chloride. The reaction of the simplest member of the series, $HCONMe_2$ (dmf) with phosgene is particularly well documented [80,237,585,1333,2251,2253]; its rôle as a catalyst [1117] is known, for example, in the preparation of SO_2Cl_2 from SO_2 and Cl_2 [2208], and the salt $[CHCl{=}NMe_2]Cl$ is commonly referred to as the Vilsmeier reagent (*cf*. the salt formed by the reaction between dmf and $POCl_3$ in a reaction discovered by Vilsmeier and Haack in the 1920s [2118a]). Its preparation is considered to proceed *via* the intermediate $[CHCl{=}NMe_2][OCOCl]$, and a kinetic study of the mechanism has been reported [1334]. The activation energies associated with the formation of $[CHCl{=}NMe_2][OCOCl]$ and $[CHCl{=}NMe_2]Cl$ are 27.6 and 29.7 kJ mol^{-1}, respectively [1334].

Reaction of 1,4-$(NH_2)_2C_6H_4$ with phosgene in the presence of dmf results in the preparation of the following derivative [1929]:



Selenoformates, HC(=Se)OR (R = CMe_3, CEt_3 or cholesteryl) have been prepared according to the reaction scheme [1012a]:

$$\mathrm{HC(O)NMe_2} \xrightarrow{\mathrm{COCl_2}} \mathrm{[HC(Cl){=}NMe_2]Cl} \xrightarrow[\mathrm{py}]{\mathrm{ROH}} \mathrm{[HC(OR){=}NMe_2]Cl} \xrightarrow{\mathrm{NaHSe}} \mathrm{HC(Se)OR}$$

Some applications of $RCONR'_2$-phosgene reagents are illustrated in Table 10.2; other examples (for dmf-$COCl_2$) have been reviewed elsewhere [1117]. Although the reaction of other dehydrating agents, such as $POCl_3$, $SOCl_2$ or $(COCl)_2$, with *N*,*N*-disubstituted carboxamides can produce the same iminium chloride species, the reactions with phosgene are clean, and (since the crystalline solids are hygroscopic and often prepared immediately before use) beneficially rapid [2251]. An NMR study of the intermediates involved in the reaction between carboxamides and $COCl_2$ has been performed [1336].

N,*N*-dialkyl substituted carboxamides containing a hydrogen atom in the 2-position (adjacent to the carbonyl group) react initially with $COCl_2$ to give salts, but when these are heated under reflux with base, enamines are formed [913]:

$$\mathrm{RR'CHC(O)NR''R'''} \xrightarrow{\mathrm{COCl_2}} \mathrm{[RR'CHCCl{=}NR_2''R''']Cl} \xrightarrow{\mathrm{NEt_3}} \mathrm{RR'C{=}CClNR''R'''}$$

R	R'	R''	R'''
Me, Ph, H	H	Me	Ph
CMe_3, Me, Ph	H, Me	Me	Me
Me	Me	$(CH_2)_5$	
$(CH_2)_5$		Et	Et
Me	Cl	$(CH_2)_4$	
Me	$(CH_2)_4$		Me

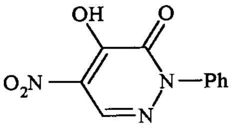
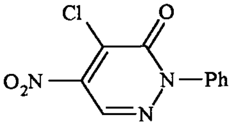
Compounds with two hydrogen atoms adjacent to the carbonyl group can undergo further reaction with phosgene [315]:

$$\mathrm{RCH_2C(O)NR'_2} \xrightarrow{\mathrm{COCl_2}} \mathrm{RC(COCl){=}C(Cl)NR'_2}$$

Phosgene has been used as a condensation agent in the reactions of acid amides with dialkylanilines (R = Me or Bu) [585]:

TABLE 10.2

SOME TYPICAL APPLICATIONS OF $[CR(Cl){=}NMe_2]Cl$ IN ORGANIC SYNTHESIS [a]

Reaction type	R	Substrate	Product	Ref.
Chloro–dehydroxylation	H			1696b
Cyclization	Me	(S)-(−)-PhCH=NCHMePh	$Ph\overline{CHCH_2C(O)N}CHMePh$ [b]	172
Cyclization	Me_2CH	$Cl_2C{=}CClCH{=}CH_2$	$Cl_2C{=}Cl\overline{CHCH_2C(O)C}Me_2$	929
Dehydration	H	$MeO_2C(CH_2)_nC({=}CH_2)C(O)NH_2$ [c]	$MeO_2C(CH_2)_nC({=}CH_2)CN$	117
Dichloro–demethoxylation	H	$CH_3OCH_2CH(OMe)_2$	$CH_3OCH_2CHCl_2$	1663a
Dichloro–deoxygenation	H	$CH_3\overline{CHCH_2O}$	$CH_3CHClCH_2Cl$	2253a
Formylation	H	4–methylpyrimidine	4–$CH(CHO)_2$–pyrimidine	267
Ring–opening	H	thf	$Cl(CH_2)_4Cl$	2253b

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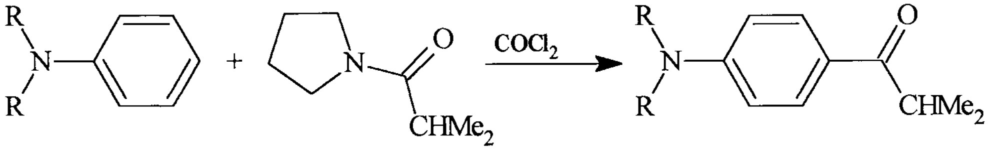
[a] In some cases, only a catalytic amount of amide is required. [b] In this example, n = 1, 2 or 3. [c] An uneven distribution of diastereoisomers is produced.



The reaction of phosgene with *N*,*N*-dimethylbenzamide at room temperature results in the substitution of two atoms of chlorine for the oxygen atom [870b]:

$$PhC(O)NMe_2 \xrightarrow{COCl_2} PhCCl_2NMe_2 + CO_2$$

Finally, it should be noted that Vilsmeier intermediates can be used to generate nitriles. Thus, the nitrile compounds $Me_2NCR(CN)_2$ (R = H, Me, Ph, SMe or NMe_2) were prepared by the reaction of a tertiary carboxamide with phosgene to form the $[Me_2N{=}CRCl]Cl$ salt, followed by treatment with copper(I) cyanide suspended in MeCN [81].

10.2.3 Imines

Most of the chemistry involving the interactions of phosgene with imines is comparatively recent. Although the aldimines, RCH=NH, and ketimines, RR'C=NH (and their substituted derivatives, RCH=NR' and RR'C=NR") are formally the analogues of aldehydes and ketones, the similarities in their behaviour towards phosgene – where this has been investigated – is only superficial.

10.2.3.1 Ketimines

The unsubstituted ketimines, RR'C=NH (R = CMe_3, Ph or 1-np; R' = CMe_3, Me-3-C_6H_4, MeO-2-C_6H_4, MeO-3-C_6H_4, CF_3-3-C_6H_4, CF_3-4-C_6H_4 or 1-np [1771]: R = CMe_3; R' = Ph [1773]: R = R' = Ph [1770]), react with phosgene, initially, to give an *N*-chlorocarbonyl ketimine [1771]:

$$RR'C{=}NH + COCl_2 \longrightarrow RR'C{=}NCOCl + HCl$$

These compounds are in tautomeric equilibrium, between a ketimine form (**10.4**) and an isocyanate form (**10.5**), the predominant form depending upon the nature of the substituents R

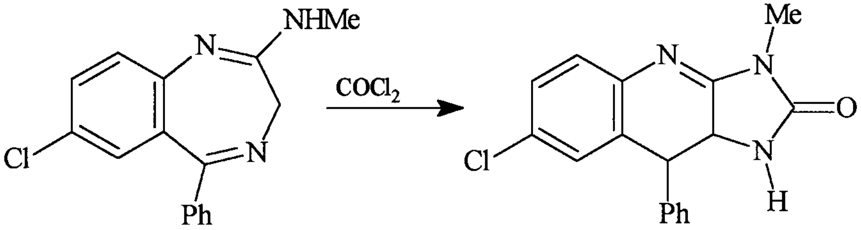
$$\underset{(10.4)}{RR'C{=}NC(O)Cl} \rightleftharpoons \underset{(10.5)}{RR'C(Cl){-}N{=}C{=}O}$$

and R'. When these substituents take part in conjugation, form (**10.4**) is preferred; when R = R' = Ph, similar proportions of (**10.4**) and (**10.5**) are observed; for R = CMe_3, R' = Ph, the isocyanate form (**10.5**) dominates [1773]. Tautomer (**10.5**) also tends to be favoured at higher temperatures.

Ketimines containing a hydrogen atom adjacent to the C=NH group form alkenyl isocyanates upon treatment with phosgene [1772]:

$$R'(R_2CH)C{=}NH + COCl_2 \longrightarrow R'(R_2C{=})C{-}N{=}C{=}O + 2HCl$$

Treatment of a benzodiazepine with $COCl_2$ proceeds with rearrangement [695]:

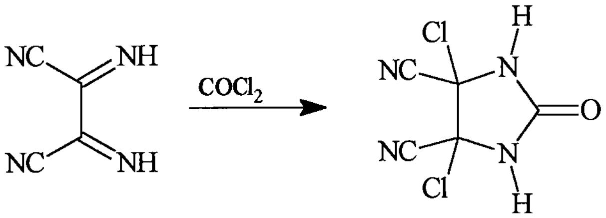


The related imino ester $Cl_3CC(OMe){=}NH$ reacts with $COCl_2$ in the expected manner [1770]:

$$Cl_3CC(OMe){=}NH + COCl_2 \longrightarrow Cl_3CC(OMe)C{=}N{-}C(O)Cl$$

Similarly, the iminocarbonate $(EtO)_2C{=}NH$ reacts initially to give $(EtO)_2C{=}NC(O)Cl$, but then reacts further with the diethyliminocarbonate to give $(EtO)_2C{=}NC(OEt){=}NCO_2Et$ [173].

The diimino compound shown below reacts readily with phosgene at 0 °C to give a 1:1 adduct which has been assigned an imidazolidene structure [153a].



10.2.3.2 Aldimines

Treatment of the substituted aldimine RCH=NR' (*e.g.* R = R' = Me; R = $CHMe_2$, R' = Me; R = Ph, R' = Pr) with phosgene results in the addition of $COCl_2$ to the C=N bond [1105,1150a]:

$$RCH{=}NR' + COCl_2 \longrightarrow RCH(Cl)NR'(COCl)$$

Condensation of RR'CHCHO (R = H or alkyl; R' = H, alkyl, $CH_2{=}CH$, Ph or $PhCH_2$) with Me_3CNH_2, followed by the reaction of the resultant aldimine with phosgene and thermal elimination of Me_3CCl and HCl from the acid chloride, gave α,β-unsaturated isocyanates [1150a]:

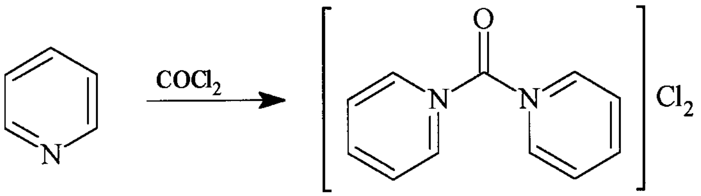
$$\mathrm{RR'CH{-}CH{=}NCMe_3} \xrightarrow{\mathrm{COCl_2}} \mathrm{RR'CH{-}CHCl{-}N(COCl)CMe_3} \xrightarrow{\Delta} \mathrm{RR'C{=}CH{-}N{=}C{=}O}$$

When R' is unsaturated and in the presence of base, however, 2,3-unsaturated alkenylcarbamoyl chlorides were formed [1105]:

$$\mathrm{CH_3CH{=}CHCH{=}NCMe_3} \xrightarrow{\mathrm{COCl_2}} \mathrm{CH_2{=}CHCH{=}CH{-}N(COCl)CMe_3}$$

10.2.3.3 Heterocyclic imino derivatives

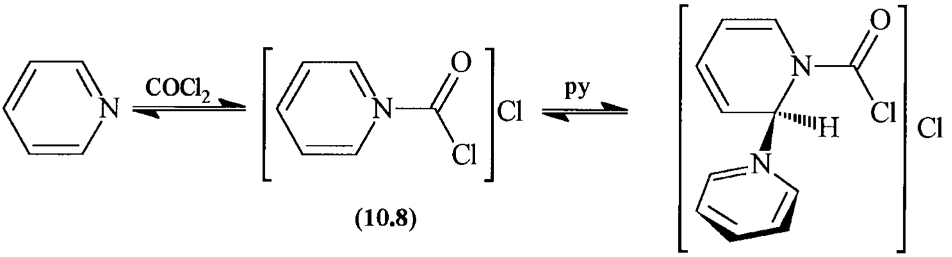
Phosgene was originally thought to react with pyridine as though it were a conventional tertiary amine [364b,973,2042b]:



(10.6)

Interestingly, the chloroformate (diphosgene) and the carbonate (triphosgene) react with pyridine to give the same product (see also Chapter 12). The material described as (py)$_{2\cdot5}$COCl$_2$, prepared from the reaction of phosgene with pyridine in benzene solution, was noted to lose half a molar equivalent of pyridine upon standing over P_2O_5 *in vacuo* [1809a].

Although the structure of the 2:1 adduct of pyridine with phosgene was originally [1809a] assumed to be (**10.6**), largely on the basis of analogy, it has recently been reevaluated on the basis of modern spectroscopic techniques [1107ab]. The use of ^{1}H, ^{13}C (variable temperature and solid state) and ^{15}N (variable temperature) NMR spectroscopy has revealed that the structure of the salt is rather more complex than originally thought, and is that represented in (**10.7**) [1107ab]:



(10.8)

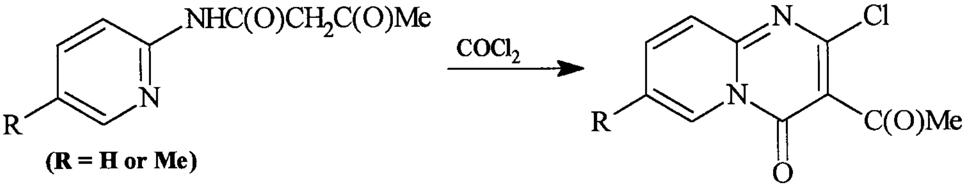
(10.7)

Dissolution of the 2:1 adduct in dichloromethane results in its dissociation: IR spectra show the presence of free phosgene at room temperature, whilst at low temperature (*ca.* −60 °C) new ν(C=O) and ν(C=C) bands indicated the presence of the 1:1 adduct, (10.8). The facile manner in which the hygroscopic solid 2:1 adduct reverts to its starting materials in solution is considered to signal a possible convenient storage system for phosgene. The solid salt can be stored at room temperature for over one year with essentially no loss of chemical activity, providing that it is kept in a moisture-free environment [1107ab].

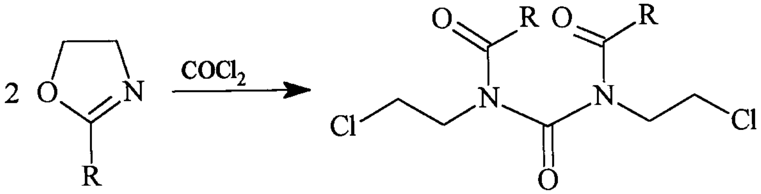
This phosgene-pyridine salt can react with other amines. For example, with aziridine, a stoicheiometric amount of pyridine is displaced to produce pyridinium chloride and equimolar amounts of pyridine and 2-chloroethyl isocyanate [2042b].

A series of addition products are formed when 2,2'-, 3,3'-, 4,4'-, or 2,3'-bipyridines are combined with an excess of $COCl_2$ in dry $CHCl_3$ at room temperature [669]. The compositions of the hygroscopic solids may be represented by the general formula $\{C_{10}H_8N_2.COCl_2\}_2$. The adducts were noted to react with alcohols in a similar way to phosgene, to give the corresponding carbonates.

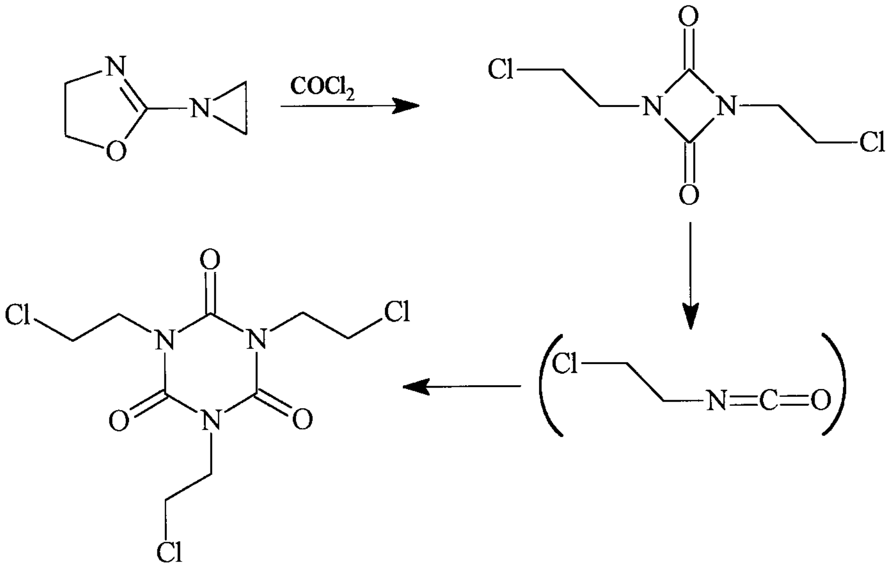
Aminopyridine derivatives undergo cyclization upon reaction with phosgene to give pyridopyridinones [2221]:



The cyclic imino esters, 2-oxazolines, undergo ring opening when treated with phosgene [1826a,2042a]. Thus, 2-alkyl-2-oxazoline reacts with $COCl_2$ to give the urea derivative [1826a]:



Finally, in an intriguing reaction, phosgene reacts with 2-aziridinyl-2-oxazoline to form the trimer of 2-chloroethyl isocyanate [2042a]:



10.2.4 Nitriles, isonitriles and cyanamides

10.2.4.1 Nitriles

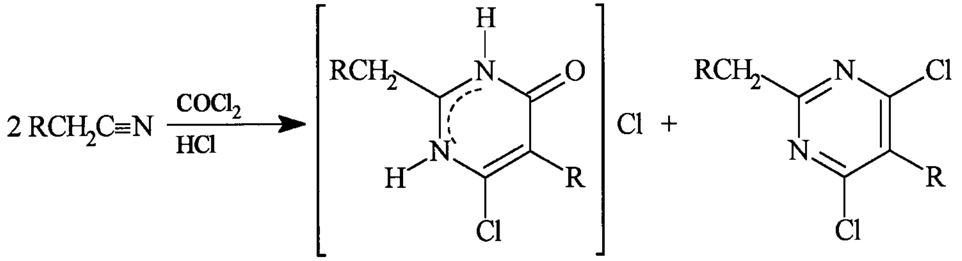
The reactions of phosgene with nitriles have been the subject a series of publications [1543,1544,2227,2228,2230] and the general reactions of acyl chlorides (including the special case of phosgene) with nitriles (in the presence of hydrogen chloride) have been thoroughly reviewed [2229].

Although early work [937a] described the reaction of phosgene with ethanenitrile to give a 1:1 adduct, it was later considered that only dissolution had occurred [578]. Similarly, propanenitrile, when treated with $COCl_2$, is reported [937a] to give a clear colourless product, the chloride analysis of which corresponds to $C_3H_5N.COCl_2$ (erroneously recorded as $C_6H_5N.C_2O_2Cl_2$), but again these results should be regarded with suspicion. Phosgene, free of HCl, was found not to react with propenenitrile even when attempts were made to photoinitiate the reaction [1149].

Nitriles react with phosgene only in the presence of hydrogen chloride, to give either 1,2-unsaturated isocyanates or *N*-heterocyclic derivatives. The reactions are really those between $COCl_2$ and the imidoyl chlorides or 1-chloroenamines, since these are the materials formed, reversibly, as equilibrium mixtures when hydrogen chloride adds to nitriles [2229]:

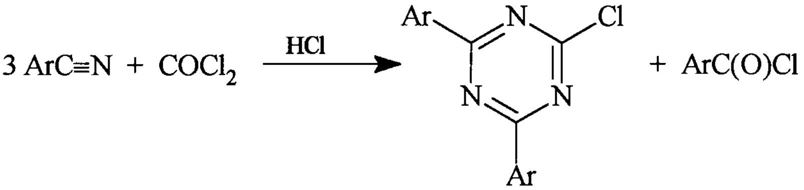
$$\mathrm{RC{\equiv}N} \underset{-\mathrm{HCl}}{\overset{+\mathrm{HCl}}{\rightleftharpoons}} \mathrm{RC(Cl){=}NH} \underset{-\mathrm{HCl}}{\overset{+\mathrm{HCl}}{\rightleftharpoons}} [\mathrm{RC(Cl){=}NH_2}]\mathrm{Cl}$$

Aliphatic nitriles, RCH_2CN {R = H, Me, Et, $Me(CH_2)_2$, $Me(CH_2)_5$, Me_2CH, Cl, $Cl(CH_2)_2$ or $MeCH_2O(CH_2)_2$} combine with phosgene and HCl in a sealed tube at 60–65 °C to give pyrimidinonium chlorides: small amounts of pyrimidines are also formed [2228,2230]:



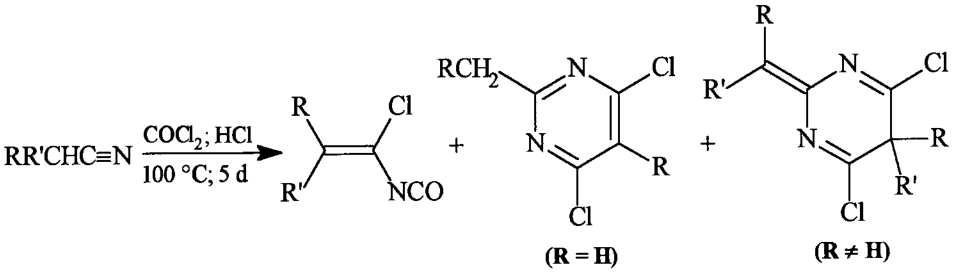
The mechanism for the reaction is given in Fig. 10.2.

ArCN (Ar = Ph, Me-4-C_6H_4 or MeO-4-C_6H_4) react with $COCl_2$ at 100 °C (200 h) in the presence of hydrogen chloride to give 2-chloro-4,6-diaryl-1,3,5-triazines, according to [2227]:



No cyclization occurs in the absence of HCl [2227]. When an excess of $COCl_2$ was employed in the reaction with PhCN, a small quantity of a ketimine, PhCCl=N-C(O)Cl, was produced [1543]. Treatment of 4-ClC_6H_4CN or 4-$NO_2C_6H_4CN$ with phosgene, however, resulted in no reaction [2227].

With hydrogen chloride in a benzene solution, phosgene combines with CH_2ClCH_2CN, $CH_2ClCHClCN$, Me_2CHCN or $MeCH(CH_2Cl)CN$ to form the corresponding *cis*- and *trans*-isomers of 1-chloro-1,2-unsaturated isocyanates, along with pyrimidine derivatives [1543]:



EtCN and PrCN gave the pyrimidine derivatives as major products, and $PhCH_2CH_2CN$ gave the isocyanate as the major product when the quantity of benzene solvent was increased. Isocyanates may be considered to be produced *via* the formation of the imidoyl chloride and subsequent reaction to give the corresponding *N*-carbamoyl chloride, followed by the loss of hydrogen chloride.

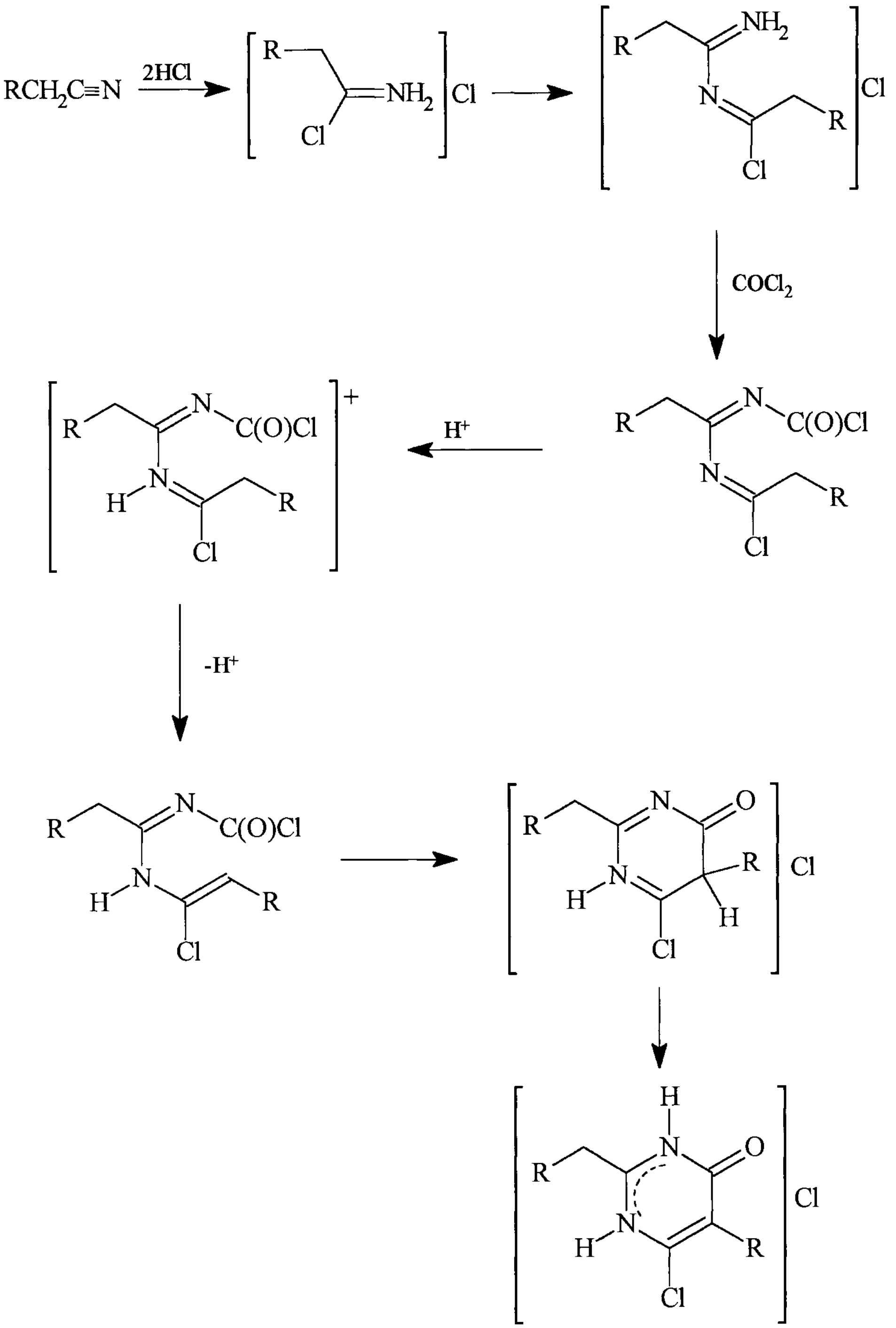
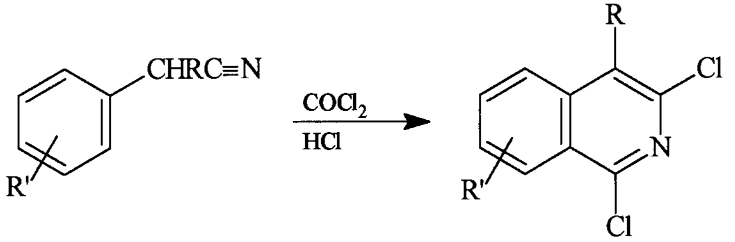


Fig. 10.2 The mechanism for the reaction between nitriles and phosgene [2228,2230].

Reaction of ArCHXCN (bearing at least two methyl groups on the 2- and 6- positions of the benzene ring) with $COCl_2$ and HCl gives an isocyanate [1544]:

$$\mathrm{ArCHX{-}C{\equiv}N + COCl_2 \xrightarrow{HCl} ArCX{=}C(Cl)N{=}C{=}O}$$
$$\mathrm{(X = H\ or\ Cl)}$$

Isocyanates are also formed as intermediates in the reactions of $C_6H_5CH_2CN$ or $C_{10}H_7$-1-CH_2CN with HCl and $COCl_2$ to give 1,3-dichloroisoquinolines [2227a]:



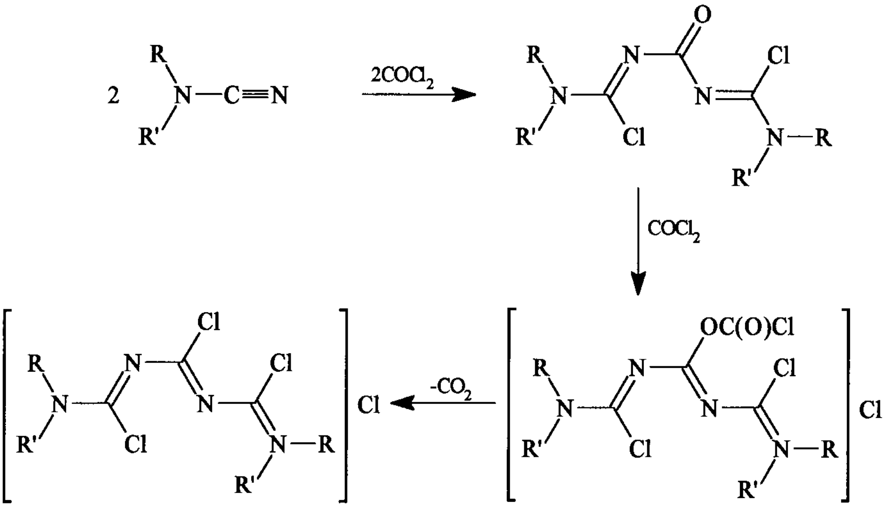
10.2.4.2 Isonitriles

In the reaction of isonitriles and phosgene, bis(imidoyl chlorides) are formed (R = Ph or Me-2-C_6H_4) [1492]:

$$\mathrm{2RNC + COCl_2 \longrightarrow (RN{=}CCl)_2C{=}O}$$

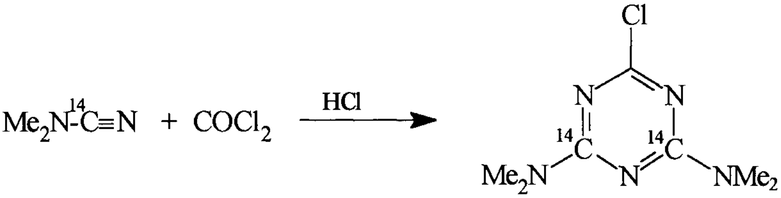
10.2.4.3 Cyanamides

The disubstituted cyanamides, RR'NC≡N, including dimethylcyanamide (R = R' = Me), *N*-cyanopiperidine (R,R' = $-(CH_2)_5-$) and *N*-cyanomorpholine (R,R' = $-(CH_2)_2$-O-$(CH_2)_2-$) react with phosgene not to add to the cyano group, but to give salt-like products [267a]:



The reaction proceeds *via* the formation of an isolable tetrasubstituted urea derivative, the carbonyl group of which reacts with phosgene to give an intermediate chloroformyl group, which then undergoes decarboxylation. Other derivatives (R = R' = Et, Pr, Me_2CH, or $Me(CH_2)_3$; R = Me, R' = Ph) were found to behave in a similar way [433].

The labelled compound $Me_2N^{14}CN$ was cyclocondensed with phosgene in the presence of HCl at about 100 °C (200 h) to give a triazine [542]:



Finally, the action of phosgene on the potassium salt of phenyl cyanamide at room temperature is to give the *N*-chlorocarbonyl derivative [1606]:

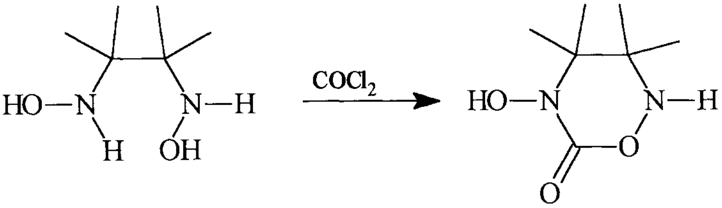
$$K[PhN(C{\equiv}N)] + COCl_2 \longrightarrow PhN(C{\equiv}N)\{C(O)Cl\} + KCl$$

10.2.5 Compounds containing nitrogen-oxygen bonds

10.2.5.1 Hydroxylamines

The urea derivatives $(HONR)_2C{=}O$ were prepared from the reaction of phosgene with RNHOH (R = CMe_3, cych, 1-adamantyl, Ph, $PhCH_2$ or Ph_2CH) [2255]. In contrast, with RNHOH (R = CMe_3, cych or Ph), RNHC(O)NROH is said to be formed as the major product and $(HONR)_2C{=}O$ as the minor product [1802].

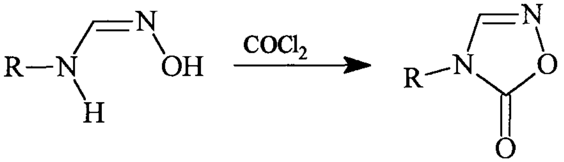
The dihydroxylamine $(NHOHCMe_2)_2$ reacted with $COCl_2$ to give a cyclic derivative [2255]:



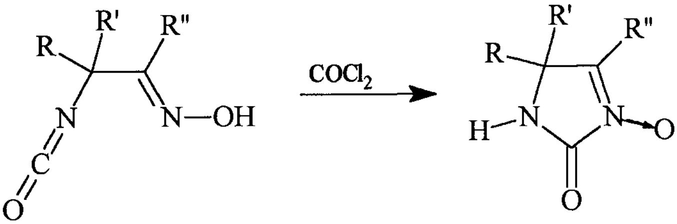
10.2.5.2 Oximes

In general, oximes react as though they were primary alcohols. Thus, treatment of RR'C=NOH (R = CN, R' = Ph, 4-ClC_6H_4 or 1-naphthyl; R = CO_2Et or $CH_3C(O)$, R' = CO_2Et; R = R' = Ph) with $COCl_2$ in inert solvents and in the presence of base results in the formation of RR'C=NOCOCl, which was then treated *in situ* with Me_3COH to give the corresponding oxime carbonate [1014].

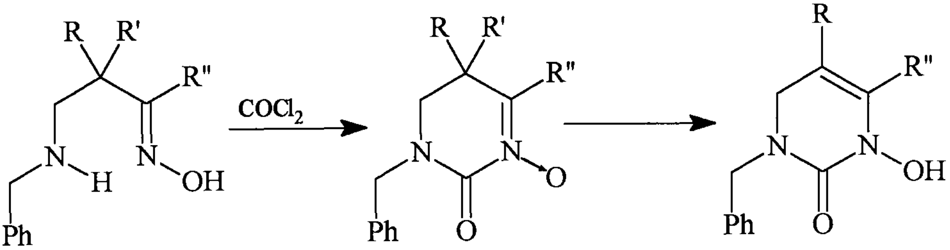
Cyclizations can take place when amino oximes are treated with phosgene. RNHCH=NOH (R = Ph, Me_3C or cych) in pyridine reacts according to [1559]:



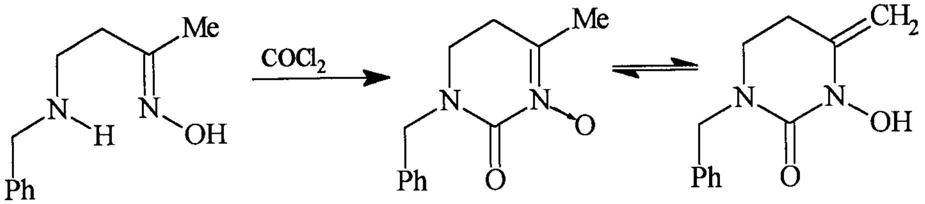
Scission to RNHCN and CO_2 occurs when the above product oxadiazolinone is treated with NEt_3. Condensation of 2-amino oximes $H_2NCRR'CR''=NOH$ (R = Me or Et; R' = Me, Et or Ph; R" = Me or Ph) with $COCl_2$ gave intermediate isocyanate derivatives, which then cyclized to form imidazoline oxides [786]:



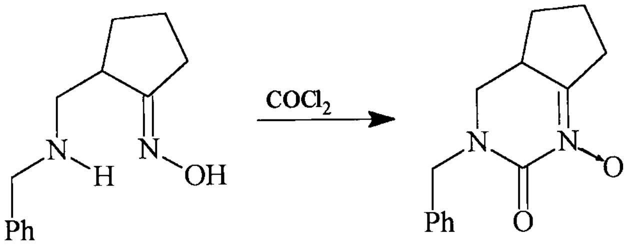
Similarly, reaction of *anti*-amino ketoximes with phosgene results in the formation of intermediate 2-pyrimidone *N*-oxide derivatives [785]:



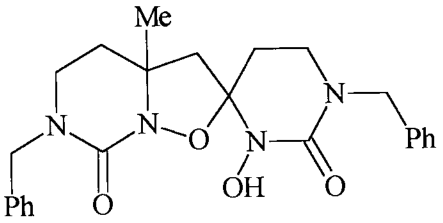
(R = Ph, R' = H, R" = CH_2Ph;
R = R' = Me, R" = $CHMe_2$)



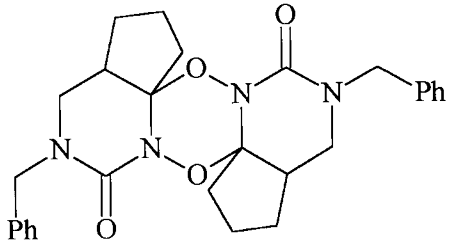
(10.9) **(10.10)**



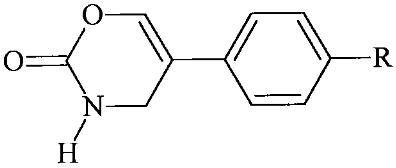
1,3-Dipolar cycloaddition of the 2-pyrimidone *N*-oxide (**10.9**) to its tautomer (**10.10**) results in a spiro compound [785]:



whereas the [3+3] cycloaddition of the *N*-oxide product of the last equation gives the following dimer [785]:

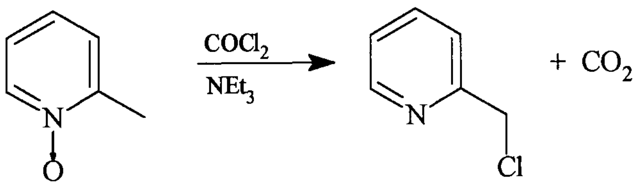


Reaction with $H_2NCH_2C(=NOH)C_6H_4$-4-R (R = H, Me or OMe), however, gave a simple six-membered heterocycle [787]:

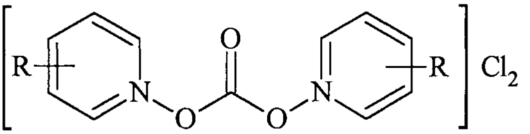


10.2.5.3 *N*-Oxides

Although *N*-oxides are the products or intermediates of reaction of phosgene with some oximes (see Section 10.2.5.2), they can themselves react with phosgene in the presence of base, undergoing deoxygenation. In this manner, treatment of 2-methylpyridine *N*-oxide with phosgene at 25 °C in dichloromethane or ethanenitrile in the presence of a stoicheiometric quantity of NEt_3 gave 2-chloromethylpyridine [83]:



In contrast, the reaction of pyridine *N*-oxide, or its 3-methyl or 4-methyl derivative) with phosgene in dichloromethane, in the absence of added base, gives hydrolytically unstable carbonate salts [811aa]:



(R = H, 3-Me or 4-Me)

10.2.5.4 Nitrones

N-Aryl nitrones combine rapidly with phosgene to give imine hydrochlorides that are chlorinated in the ring (predominantly at the 2- position). Reaction occurs at room temperature in benzene and is accompanied by the evolution of CO_2 and immediate precipitation of product [1257]:

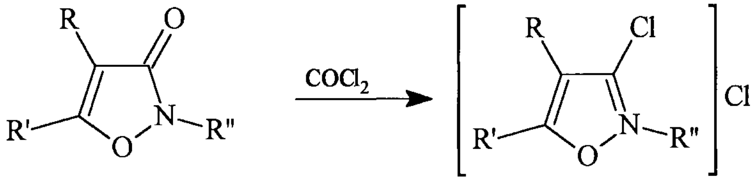
$$\text{ArCH=N(O)Ar'} + \text{COCl}_2 \longrightarrow [\text{ArCH=NHAr''Cl}]\text{Cl} + \text{CO}_2$$

(Ar,Ar' = Ph, Ph; PhCHCH, Ph; NO_2-4-C_6H_4, Ph; Ph, Me-4-C_6H_4; Ph, Cl-4-C_6H_4; MeO-4-C_6H_4, Cl-4-C_6H_4; or Ph, EtO_2C-4-C_6H_4: Ar" = Ar'-H)

The reaction mechanism proposed for this system, illustrated for Ar = Ar' = Ph, is shown in Fig. 10.3 [1257], and accounts for the formation of both 2- and 4-chloro- isomers.

10.2.5.5 Isoxazole derivatives

A large variety of 3-chloroisoxazolium chlorides were prepared by stirring 4-isoxazolin-3-ones with a two-fold molar excess of phosgene in benzene [2043]:



(R = H or Me; R' = H, Me or Ph;
R" = Me, Et, allyl, $PhCH_2$ or Ph)

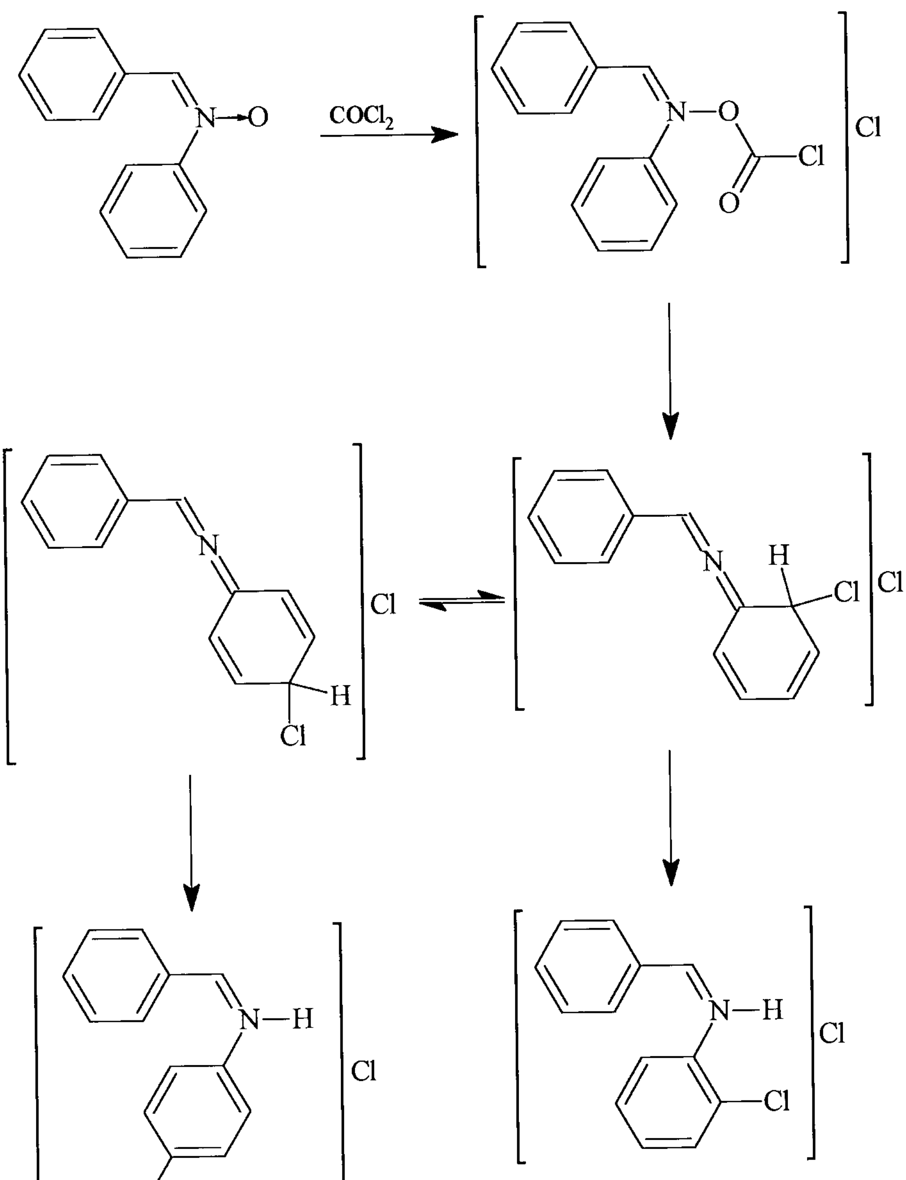


Fig. 10.3 The proposed mechanism for the reaction between phosgene and *N*-aryl nitrones.

10.2.5.6 Nitrosamines

Reaction of the acylarylnitrosamine, PhN(NO)C(O)Me with phosgene, formed *in situ* from oxidation of CCl_3Br, gave $[PhN_2]Cl$, CO_2 and $\{MeC(O)\}_2O$ as the reaction products (see Fig. 10.4) [318].

$$\begin{aligned}
2PhN(NO)C(O)Me &\longrightarrow PhN_2O\cdot + Ph\cdot + N_2 + \{MeC(O)\}_2O \\
Ph\cdot + CCl_3Br &\longrightarrow PhBr + Cl_3C\cdot \\
PhN_2O\cdot + Cl_3C\cdot &\longrightarrow PhN_2OCCl_3 \\
PhN_2OCCl_3 &\longrightarrow [PhN_2]Cl + COCl_2 \\
PhN_2O\cdot + COCl_2 &\longrightarrow PhN_2OCOCl + Cl\cdot \\
PhN_2OCOCl &\longrightarrow [PhN_2]Cl + CO_2 \\
2[PhN_2][MeC(O)O] + COCl_2 &\longrightarrow 2[PhN_2]Cl + CO_2 + \{MeC(O)\}_2O \\
[PhN_2]Cl &\longrightarrow PhCl + N_2
\end{aligned}$$

Fig. 10.4 **The reaction of PhN(NO)C(O)Me with phosgene.**

10.2.6 Compounds containing N-N bonds

10.2.6.1 Diazo derivatives

The reaction of phosgene with diazomethane in a molar ratio of 1:2 gives the previously unknown diazo compound, $N_2CHC(O)Cl$ [185]:

$$CH_2N_2 + COCl_2 \longrightarrow ClC(O)CHN_2 + HCl$$

Both chloroethanoyl chloride, $ClCH_2C(O)Cl$, and 1,3-dichloropropanone, $ClCH_2C(O)CH_2Cl$, are formed as by-products. The former is a result of the combination of $N_2CHC(O)Cl$ with liberated HCl, and the latter is formed by the reaction of the former with the excess of diazomethane to give the diazoketone, $N_2CHC(O)CH_2Cl$, which then itself reacts with HCl [185]. In the presence of triethylamine, using a $COCl_2$:CH_2N_2 ratio of 1:4, the diazoketone, $N_2CHC(O)CH_2Cl$, is the sole product [185].

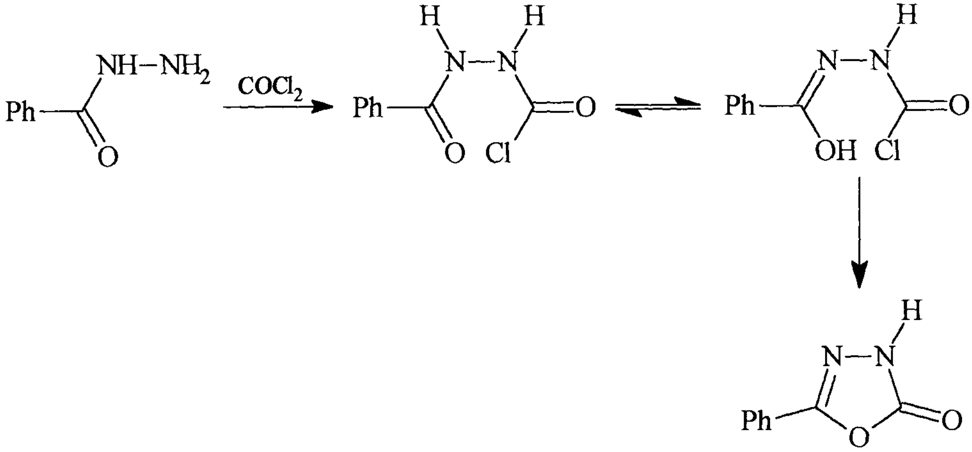
A solution of 2,2,2-trifluorodiazoethane in dichloromethane was treated with finely powdered dipotassium hydrogenphosphate and phosgene at room temperature to give 2-diazo-3,3,3-trifluoropropanoyl chloride [375]:

$$CF_3CHN_2 \xrightarrow{COCl_2} CF_3C\{C(O)Cl\}N_2$$

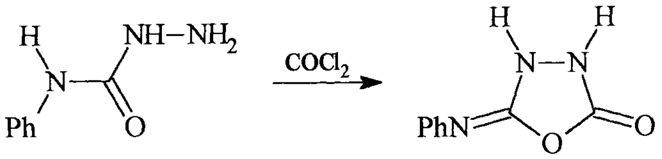
10.2.6.2 Hydrazine derivatives

Phosgene reacts vigorously with hydrazine [1224], and in boiling chlorobenzene phosgene reacts with hydrazine hydrate to give $[(H_3NNH)_2CO]Cl_2$ [1252]. When passed into a boiling chlorobenzene solution of $[PhNHNH_3]Cl$, however, phosgene gives PhNCO and an unidentified residue [1252]. Reaction of $PhNHNH_2$ with EtOCOCl, followed by $COCl_2$, gave $ClCONPhNHCO_2Et$ [1621]. Early work describes the reaction of phosgene with Ph_2NNH_2 to give $Ph_2NNHCOCl$ and $(Ph_2NNH)_2CO$ [4a].

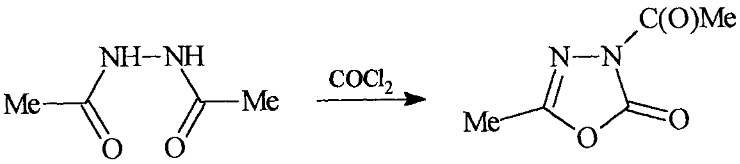
The treatment of acyl hydrazine derivatives with phosgene gives 1,3,4-oxadiazole-5-ones [1252]:



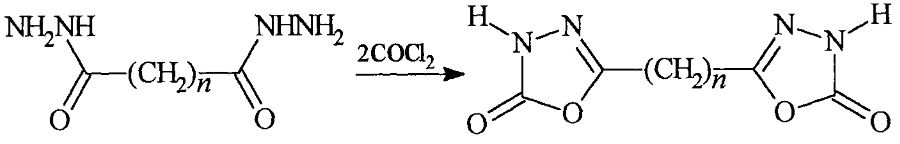
Similarly, a related cyclization of $PhNHC(O)NHNH_2$ with phosgene occurs [2254]:



and treatment of MeC(O)NHNHC(O)Me with $COCl_2$ proceeds according to [1252]:

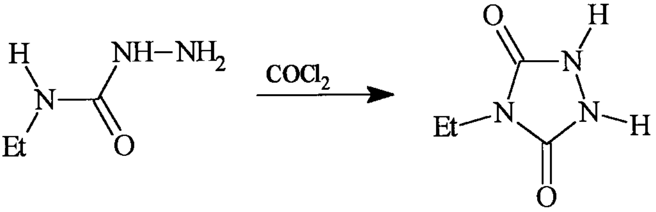


The related dihydrazides of the dicarboxylic acid series also react with phosgene [1252]:

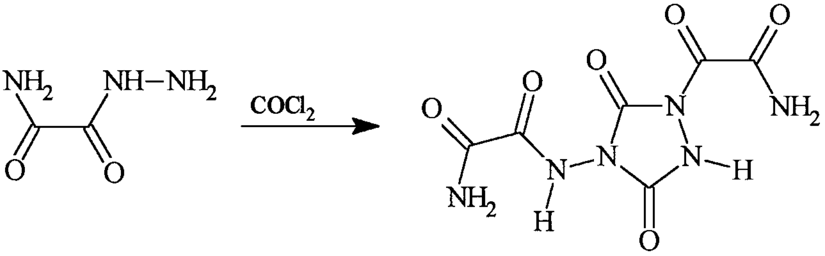


(n = 0, 1, 2 or 4)

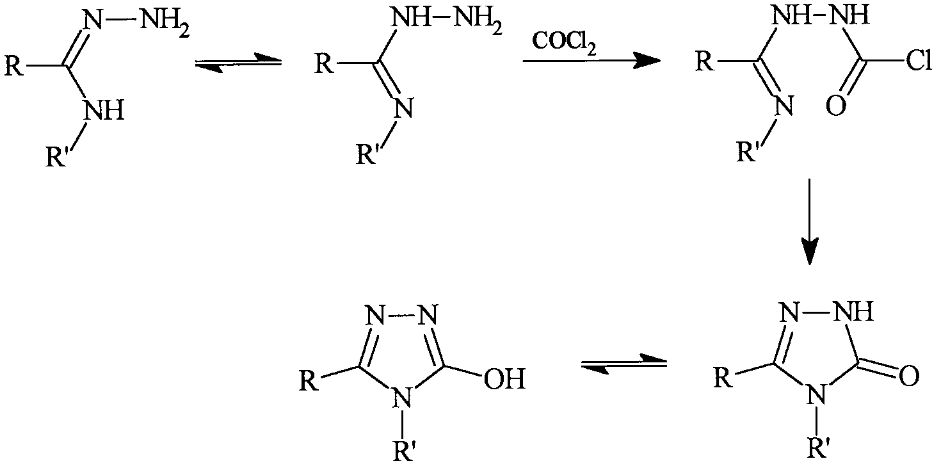
Treatment of semicarbazides with phosgene results in the formation of 1,2,4-triazoles [1074a]:



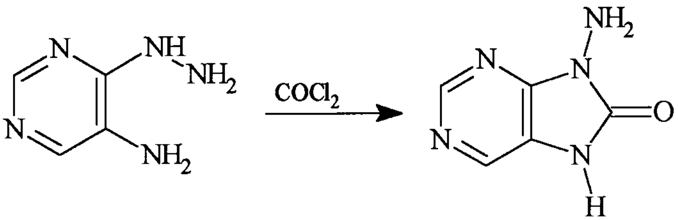
A related compound is derived from the reaction of oxamic acid hydrazide with phosgene [1686]:



3-Substituted 1,2,4-triazoles may be prepared from the reactions of amidrazones with phosgene according to the following general scheme [1700a]:

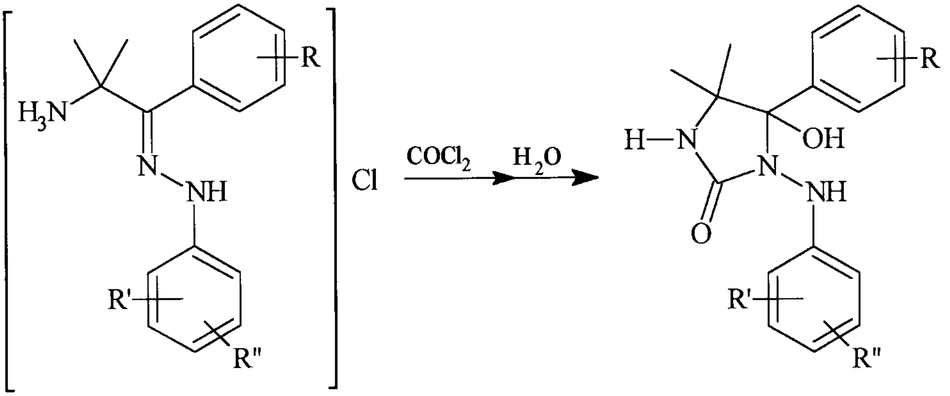


Purine derivatives have also been formed by the reaction of phosgene with heterocyclic hydrazine derivatives [1161b]:



10.2.6.3 Hydrazone derivatives

Cyclization of the depicted hydrazones (R = H, 4-Me or 3-NO_2; R' = H, 2-Me, 2-NO_2 or 4-NO_2; R" = H or 4-NO_2) with phosgene, followed by hydrolysis, gave the following intriguing products [784]:



Benzophenone hydrazone, in the presence of pyridine, combines with $COCl_2$ according to [2168a]:

$$2Ph_2C{=}NNH_2 + COCl_2 \longrightarrow Ph_2C{=}NNHCONHN{=}CPh_2 + 2HCl$$

Further reaction of this product can take place with an excess of phosgene to give a product of undefined constitution.

10.2.7 Urea derivatives

Phosgene can react with *N,N'*-disubstituted ureas at either the oxygen or the nitrogen atom. When attack occurs at the nitrogen atom, allophanoyl chlorides are formed [2087a]:

$$RNHC(O)NHR' + COCl_2 \longrightarrow [RN(COCl)HC(O)NHR']Cl \xrightarrow{-HCl} RN(COCl)C(O)NHR'$$

(R,R' = alkyl)

The reaction of 1-(arylsulfonyl)-3-alkylureas with $COCl_2$ takes place according to the following stoicheiometry [2087a]:

$$R\text{-}C_6H_4\text{-}SO_2NHC(O)NHR' + COCl_2 \longrightarrow R\text{-}C_6H_4\text{-}SO_2NCO + R'NCO + 2HCl$$

(R,R' = CH_3-4-C_6H_4, $CH_3(CH_2)_3$; CH_3-4-C_6H_4, $CH_3CH_2OCH_2CH_2$; or Cl-4-C_6H_4, Pr)

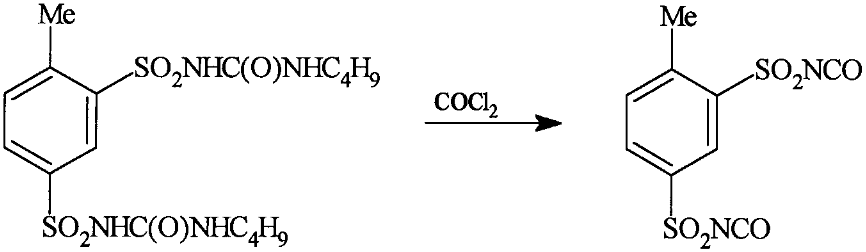
Attack occurs at the alkyl-substituted nitrogen atom owing to the higher acidity of the proton adjacent to the sulfonyl group and the resulting allophanoyl chloride decomposes spontaneously to form the depicted isocyanates [2087a]. This reaction can be employed for the preparation of isocyanates which cannot otherwise be prepared directly from amines. The lower boiling alkyl isocyanates are easily separated from the sulfonyl isocyanates by fractional distillation.

Alkylenebis(3–arylsulfonyl ureas) react readily with phosgene in a similar way to produce the corresponding sulfonyl isocyanate and diisocyanate [2087a]:

$$RSO_2NHC(O)NH(CH_2)_nNHC(O)NHSO_2R + 2COCl_2 \longrightarrow 2RSO_2NCO + OCN(CH_2)_nNCO$$

$(R = Me\text{-}4\text{-}C_6H_4;\ n = 3\text{–}6)$

In a related reaction, a bis(sulfonyl isocyanate) has been prepared by treating phosgene with a bis(sulfonyl urea):



Reaction at the oxygen atom proceeds [585,2087a] to form Vilsmeier–type (chloroformamidinium) salts (see also Section 10.2.2.3):

$$RNHC(O)NHR' + COCl_2 \longrightarrow [RNHC(OCOCl)\text{=}NHR']Cl \xrightarrow{-CO_2} [RNHC(Cl)\text{=}NHR']Cl$$

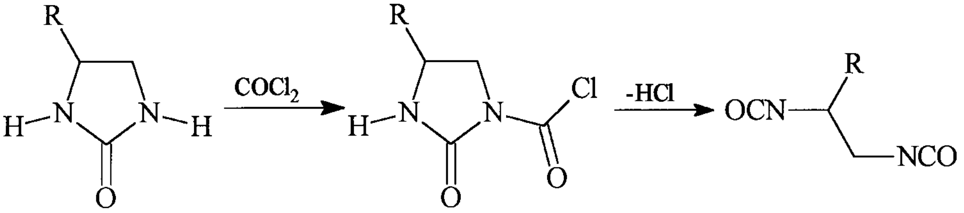
For *N,N'*–dialkyl ureas, steric considerations are primarily responsible for governing the course of the reaction. Secondary or tertiary alkyl substituents tend to give predominantly the products of reaction at the nitrogen, whilst straight–chain alkyl groups give mainly the products of reaction at the oxygen [2087b]. The reaction of phosgene with $(Me_2N)_2CO$ has been employed to give the synthetically useful material, $[Me_2NC(Cl)NMe_2]^+Cl^-$ [554,1065], and treatment of the unsymmetrical urea, $Et_2NC(O)N(CHMe_2)_2$ with $COCl_2$ in Et_2O at room temperature also gave a Vilsmeier salt, which on heating under reflux with Me_3CNH_2 gave $Et_2NC(\text{=}NCMe_3)N(CHMe_2)_2$ [127].

At higher temperatures, in an inert solvent such as chlorobenzene, *N,N'*–disubstituted ureas react with $COCl_2$ to give guanidine derivatives, RNHC(=NR)NHR (R = various alkyl or aryl substituents) [724a], formed from the further reaction of the Vilsmeier salt with an excess of urea. With an excess of phosgene present, *N*–chloroformyl derivatives may be obtained [724a]:

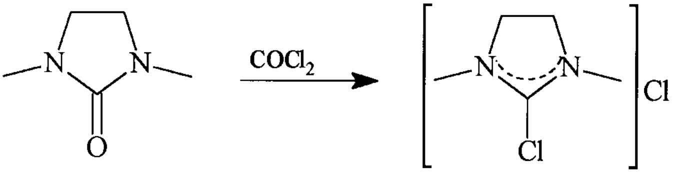
$$[RNHC(Cl)\text{=}NHR]Cl + COCl_2 \longrightarrow [RN(COCl)C(Cl)\text{=}NHR]Cl$$

In the presence of dmf, $(RNH)_2CO$ reacts with phosgene in $CHCl_3$, *via* the complex $[ClCH\text{=}NMe_2]Cl$ (see Section 10.2.2.3), to give $[RNHC(O)NRCH\text{=}NMe_2]Cl$ (R = Ph, Me-3-C_6H_4 or cych). At 60-70 °C, decomposition to [RNHCH=NMe_2]Cl and RNCO occurs [434]. $(PhNH)_2CO$ reacts with phosgene in the presence of $(Me_2N)_2CO$ to give PhNHC(Cl)=NPh [434].

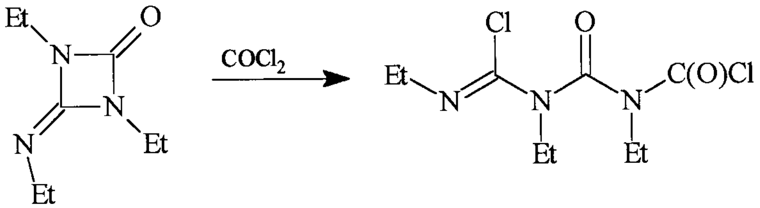
Five-membered cyclic ureas (2-imidazolidinones) react with $COCl_2$ exclusively at the nitrogen atom to form cyclic allophanoyl chlorides, 2-imidazolidinone-1-(carbonyl chloride). In the presence of a base, dehydrochlorination results in the production of isocyanates [2087a]:



Since the cyclic ureas can be obtained from 1,2-diaminoalkanes and CO_2, this reaction represents a potentially useful method for the industrial production of diisocyanates. In contrast, a cyclic chloroformamidinium chloride is obtained from 1,3-dimethylimidazolidine-2-one and phosgene; this reaction is reported to be considerably slower than the corresponding reaction of the tetrasubstituted acyclic urea [2083a]:

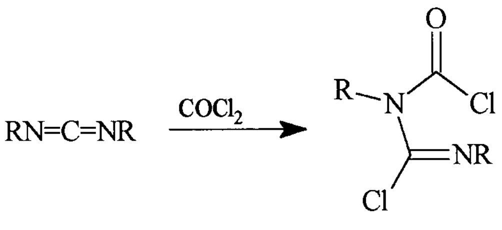


The reaction of a uretone imine with phosgene proceeds *via* ring opening to give a chloroformamidine [615a]:



10.2.8 Carbodiimides

Phosgene adds to the carbodiimides, RN=C=NR (R = Bu, cych or CH_3-2-C_6H_4), at room temperature [2087]:



10.3 REACTIONS WITH OXYGEN COMPOUNDS

10.3.1 Alcohols, phenols and their derivatives

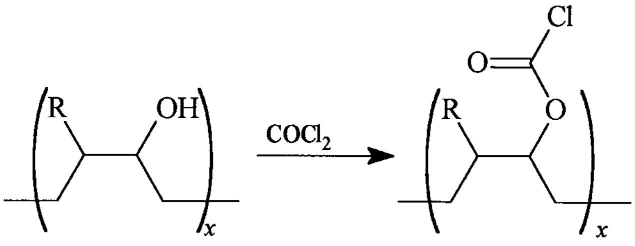
The study of the interaction of phosgene with the alcohols is as old, almost, as systematic organic chemistry itself. The first reaction of this type was observed only some six years following Wöhler's pioneering synthesis of urea [2204a], which marked the demolition of Berzelius' "vital force theory" and the dawning of modern organic chemistry. Not surprisingly, then, the literature is replete with a voluminous quantity of patent descriptions which, at least, verify the commercial importance of this reaction system. In the present review, we have included at least one example of each reaction type for each generic class and any unusual or novel features have been stressed. This approach has been adopted in the light of a number of excellent reviews which have been published [96,1098a,1358]. In particular, a review of the chemistry of chloroformates was published [1358] about twenty years ago (which can be considered recent for chemistry of this type), in which complete coverage of the literature up to 1962 was attempted. Details of the methods of synthesis of chloroformates from phosgene are very adequately described therein, with over three hundred references to about one hundred and fifty chloroformates of the aliphatic type alone.

10.3.1.1 Monohydric alcohols

Phosgene combines readily with most primary and secondary monohydric alcohols at, or below, ambient temperature to produce high yields of chloroformates (chloromethanoates) according to Equation (10.11):

$$ROH + COCl_2 \longrightarrow ROC(O)Cl + HCl \qquad (10.11)$$

This reaction is common to a wide range of R groups [1358], including Me, Et [565c,565d], $CH_3(CH_2)_{11}$ [1376], $CH_2{=}CHCH_2$ [1468], $CH_2{=}C(CH_3)CH_2$ [1467], CF_3CH_2 [286,883], $CF_2H(CF_2)_9CH_2$ [882], $Me_3Si(CH_2)_n$ {n = 2 or 3} [1406a,2214], 4-$Me_3SiC_6H_4CH_2$ [665], $O_2NC(CH_3)_2CH_2$ [200] and $\overline{CH_2CH_2CH_2C}HCH_2$ [252]. Polymers containing chloroformate groups have also been prepared by treatment of low molecular weight, $\{CH_2CHMeCH(OH)CH_2\}_x$ or $\{(CH_2)_2CH(OH)CH_2\}_x$, with an excess of $COCl_2$ [1619]:



(R = H or Me)

Organic carbonates are often formed as by-products in the preparation of chloroformates as a result of further reaction between the alcohol and the chloroformate [1358,2079]:

$$\mathrm{ROH + ROC(O)Cl \longrightarrow (RO)_2C{=}O + HCl}$$

By using higher temperatures, longer reaction times, and an excess of the alcohol, the carbonate can be formed in a one-pot reaction according to the stoicheiometry shown in Equation (10.12) [3]:

$$\mathrm{2ROH + COCl_2 \longrightarrow (RO)_2C{=}O + 2HCl} \qquad (10.12)$$

These reactions are often carried out using dry liquid alcohols and anhydrous phosgene. Owing to the commercial importance of both the chloroformates and carbonates (see Section 4.7.2), many examples are to be found in the patent literature which describe other, often obscure or elaborate, means of preparation or production [*e.g.* 1748,1995].

Both reactions (10.11) and (10.12) can be promoted, and the yields improved, by using a stoicheiometric quantity of a base, such as a tertiary amine [1358]. The reactions can also be catalysed; for example, pyridine, 4-nitropyridine and pyridine *N*-oxide have been used to catalyse the formation of bis(2,2,2-trinitroethyl)carbonate [870a].

In the absence of a base, the cyanohydrin $(CF_3)_2C(CN)OH$ ($pK_a = 4.1$) was found not to react with phosgene and it was concluded [1323] that any alcohol with $pK_a \leqslant 6$ will not react with $COCl_2$ unless the reaction is promoted.

The rate constant for the reaction of 2-chloroethanol ($pK_a = 14.3$) with phosgene (to give $ClCH_2CH_2OCOCl$) has been determined [1584] using a large excess of $ClCH_2CH_2OH$ in 1,4-dioxane. At 5 °C, $k = 0.037\ \mathrm{min}^{-1}$; at 15 °C, $k = 0.055\ \mathrm{min}^{-1}$. These values correspond to half-lives of 18.7 and 12.6 min, respectively. Trichloroethanol possesses hypnotic and anæsthetic properties, but its volatile character, pungent odour and acrid taste render the material unsuitable for therapeutic use. By reaction with phosgene, the material may be converted into the carbonate, $(CCl_3CH_2O)_2CO$, which has low volatility and no taste, but retains its pharmaceutical properties with the added advantage that it can be tableted or encapsulated [1987]. However, owing to the large inductive effect of the three chlorine atoms in the 2-position, trichloroethanol ($pK_a = 12.2$) does not react at all easily with phosgene [1916]. The reaction is not catalysed by activated charcoal and only low yields are produced in the liquid phase reaction at ambient temperature and in the presence of a base. When catalysed by tertiary nitrogen-containing compounds (such as dmf) the reaction to give $Cl_3CCH_2OC(O)Cl$ is reported to be zero-order with respect to both reactants, the rate depending only upon temperature [1916].

Group 1 metal alkoxides, M[OR], can be converted into chloroformates, Equation (10.13), or carbonates, Equation (10.14), by treatment with phosgene [242,1323,1432]

$$M[OR] + COCl_2 \longrightarrow ROC(O)Cl + MCl \tag{10.13}$$

$$2M[OR] + COCl_2 \longrightarrow (RO)_2CO + MCl \tag{10.14}$$

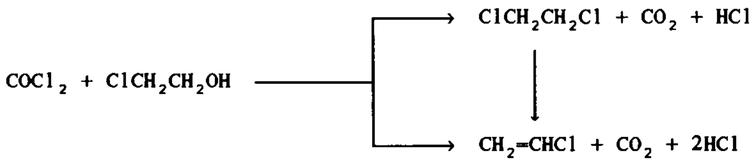
The salts of tertiary alcohols, however, such as $K[OCPh_3]$, may be converted instantly to the chloride upon treatment with $COCl_2$ [242]:

$$K[OCPh_3] + COCl_2 \longrightarrow Ph_3CCl + KCl + CO_2$$

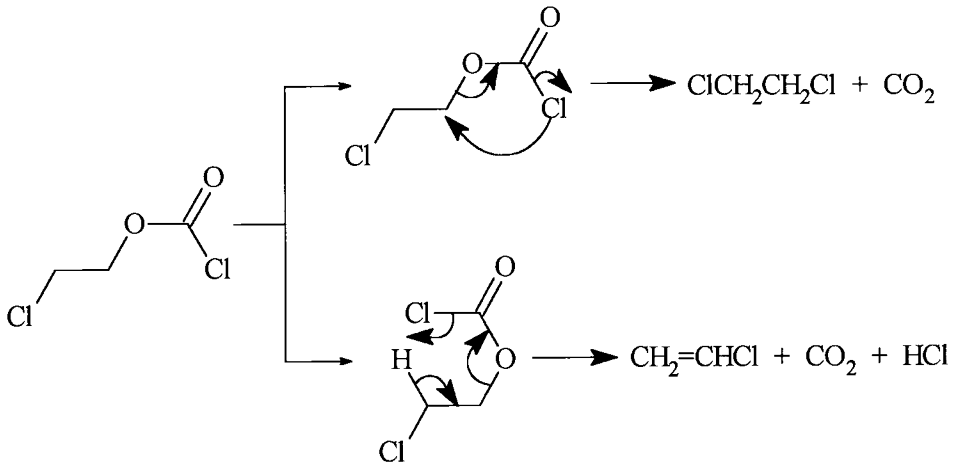
This last reaction appears to be particularly useful when the parent alcohol is especially acidic, for example, $(CF_3)_2C(CN)OH$ [1323], $C_6H_5C(CF_3)_2OH$ [1432] or $(CF_3)_3COH$ [990].

Phosgene also reacts with alcohols in the gas phase [1783]. With an excess of phosgene, the major products of the reactions with primary and secondary alcohols were the corresponding chloroformates. When an excess of propanol was used, however, the carbonate was formed in good yield. Between 100 and 250 °C, C_1–C_8 primary aliphatic alcohols were found to react with $COCl_2$ to give the chloroformates in yields of 50–80%, based on the alcohol. Secondary alcohols were noted to have a similar reactivity to primary alcohols, but the tertiary alcohol 2-methyl-2-butanol, when combined with phosgene at about 150 °C, was converted into 2-methyl-2-chlorobutane, no chloroformate being isolated [1783]. Although chloroformates derived from primary or secondary alcohols can be decarboxylated thermally [1046] or catalytically [129,1500], the chloroformates initially derived from tertiary alcohols or their salts are much less thermally stable and may be converted directly by $COCl_2$ into the corresponding chloroalkane [242,1358]. Moreover, with some tertiary alcohols, phosgene acts as a dehydrating agent resulting in the formation of alkenes. For example, tertiary butanol may be converted into 2-methylpropene [973].

Chloroalkanes have been prepared, in a single step, from the reactions of primary alcohols with phosgene [ICI83,ICI86]. Thus, 1,2-dichloroethane was produced, without isolation of the intermediate chloroformate, by the reaction of phosgene with a molar equivalent of gaseous 2-chloroethanol in a flow system over an activated charcoal catalyst, in the temperature region of 130–350 °C [ICI83]. Chloroethene (CH_2=CHCl) is a by-product of the reaction and is found at temperatures above 200 °C:



The quantity of chloroethene generated in this reaction was considered too high to be accounted for solely on the basis of the catalysed pyrolysis of the 1,2-dichloroethane, and the mechanism of the formation of the products can be explained on the basis of the charcoal-catalysed decomposition of the common intermediate chloroformate:



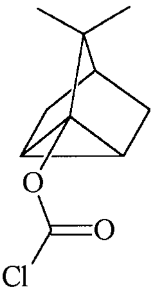
Fluoroalkanes have also been prepared from the vapour phase reactions of fluoroalcohols, $CF_3(CF_2)_nCH_2OH$ (n = 0, 1 or 2), with phosgene and HF over an HF-activated γ-alumina catalyst, at temperatures above 250 °C. The products of these reactions are $CF_3(CF_2)_nCH_2F$, and are potential CFC replacements [1481b]. The related compounds $CHF_2(CF_2)_nCH_2F$ (n = 1 or 3) have also been prepared under similar conditions from $CHF_2(CF_2)_nCH_2OH$. However, when the fluoroalcohol contains more than one methylene unit between the OH and CF_2 groups, reaction with $COCl_2$ and HF results in dehydration to the alkene [1481b]:

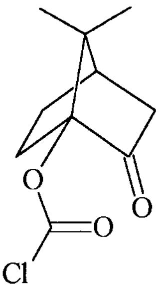
e.g.

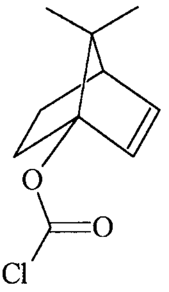
$$CF_3(CF_2)_5CH_2CH_2OH + COCl_2 \longrightarrow CF_3(CF_2)_5CH{=}CH_2 + CO_2 + 2HCl$$

Treatment of the alcohol, $Me_2C{=}CHCH(OH)CCl_3$, with phosgene in the presence of dmf gave a mixture of $Me_2C{=}CHCH{=}CCl_2$, *trans*-$Me_2CClCH{=}CHCCl_3$, $Me_2CClCHClCH{=}CCl_2$, $Me_2C{=}CHCHClCCl_3$ and $ClCH_2CMe{=}CHCH{=}CCl_2$ [1992].

The alicyclic alcohols, ROH {R = $\overline{CH_2CH_2CH_2CH}$, $\overline{CH_2CH_2CH(Me)CH}$ or $\overline{CH_2CH_2CH_2CH_2CH(Me)CH}$} react with $COCl_2$ to give the expected chloroformates [252]. Similarly, the bridgehead 1-chloroformyl derivatives of apotricyclyl, apocamphor and apobornenyl have been prepared from their corresponding alcohols [144]:



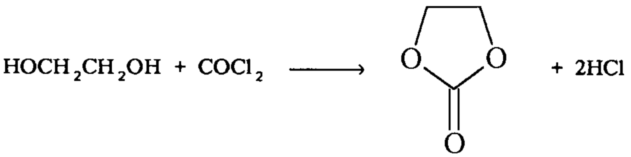




10.3.1.2 Polyhydric alcohols

The gas phase reaction of phosgene with ethane-1,2-diol over activated charcoal results in the formation of 1,2-dichloroethane with a yield of about 70% at 210 °C: higher temperatures caused the decomposition of the diol [ICI86].

Reaction of ethane-1,2-diol with phosgene in the liquid phase gives the bis(chloroformate), $ClC(O)OCH_2CH_2OC(O)Cl$ [1176], the pyrolysis (~450 °C) of which gives $CH_2{=}CHOCOCl$ [1180]. On prolonged contact, the action of phosgene on $HOCH_2CH_2OH$ produces a cyclic carbonate [2131a]:



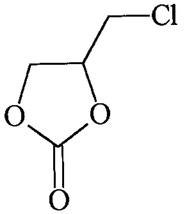
Other bis(chloroformates) have been produced similarly from the reactions of phosgene with $HO(CH_2)_4OH$ [957c], $CH_3CH(OH)CH(OH)CH_3$ [1792], $HOCH_2CH_2OCH_2CH_2OH$, $HO(CH_2CH_2O)_2CH_2CH_2OH$, $\{CH_3CH(OH)CH_2\}_2O$ and $HO(CH_2CH_2O)_3CH_2CH_2OH$ [1469,1625], and the treatment of poly(tetramethylene glycol) with $COCl_2$ gave the bis(chloroformate) [2226]:

$$HO\!-\!\!\left[(CH_2)_4O\right]_n\!H \xrightarrow{COCl_2} ClOCO\!-\!\!\left[(CH_2)_4O\right]_n\!COCl$$

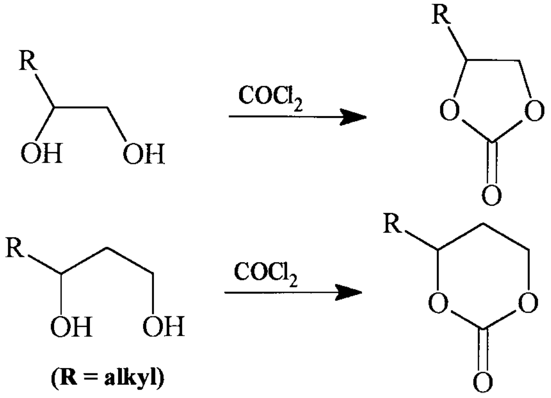
Macromolecules containing reactive chloroformate end-groups are, indeed, prepared quantitatively by treatment of polyloxyethenes with excess of $COCl_2$ in an aprotic medium [714]. The reaction gives a quantitative determination of the –OH content of the polymer and thus an estimation of the average molecular weight, since no modification or degradation of the chain is involved.

A tris(chloroformate) results from the reaction of $COCl_2$ with 1,3,5-hexanetriol [1176]. The thio compound $S(CH_2CH_2OH)_2$, when treated with $COCl_2$ at only ~50 °C, gave $S(CH_2CH_2Cl)_2$ (**WARNING**: Mustard gas) [355]. Phosgenation of a castor oil (composed chiefly of ricinolein) at 100 °C is reported to give $CH_3CH_2C\{O_2C(CH_2)_{16}OC(O)Cl\}_3$ [1626].

Phosgene does not react at normal temperature and pressure with glycerol, $CH_2(OH)CH(OH)CH_2OH$, or the dichloro- derivative, $CH_2ClCH(OH)CH_2Cl$. It does, however, react easily with the monochloro- derivative, $ClCH_2CH(OH)CH_2OH$, to give a cyclic carbonate [408]:



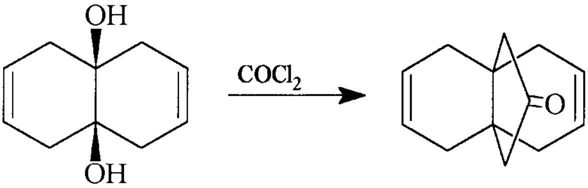
Because of the ease with which this cyclization reaction occurs, phosgene has been used as a reagent for the enantiomeric resolution of 1,2- and 1,3-diols [1151,1152]:



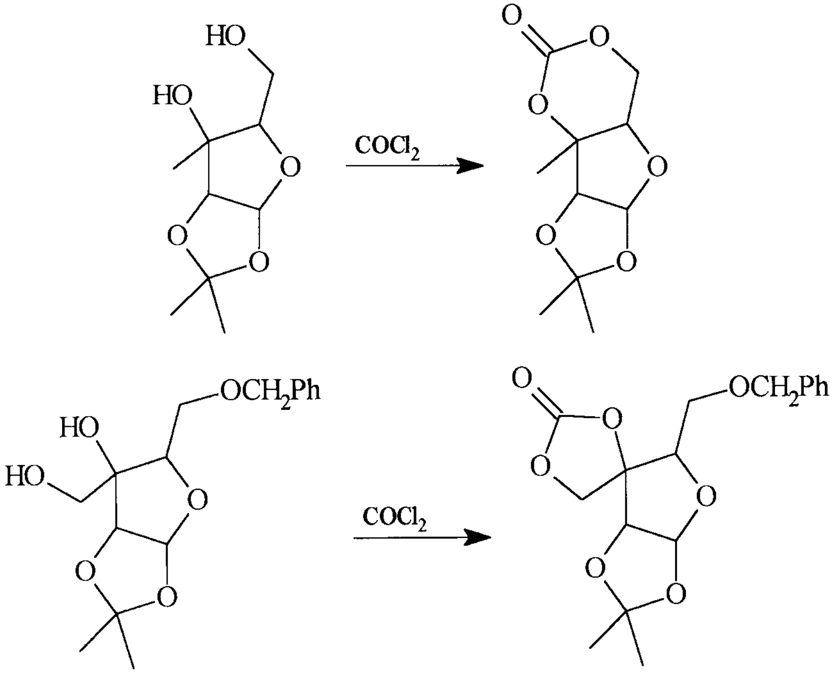
(R = alkyl)

The resulting enantiomers can be separated by chromatography.

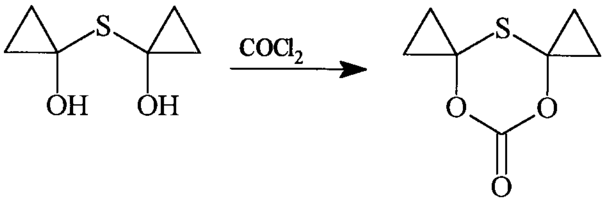
Reaction of the following fused-ring *cis*-diol with phosgene gives a bridged carbonate [84]:



Phosgene reacts with xylofuranose derivatives according to [2054]:

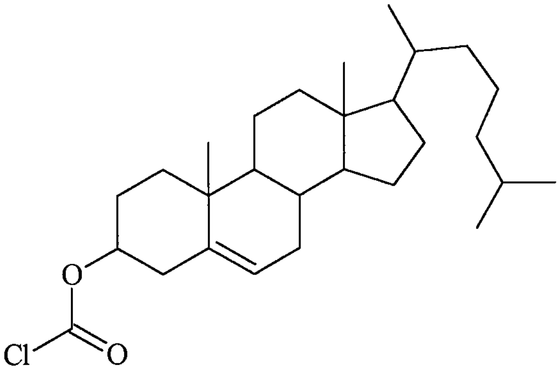


Similarly, in a solution containing pyridine, the sulfur-containing diol shown below reacts with an excess of phosgene to give a cyclic carbonate [1054].



10.3.1.3 Steroid derivatives

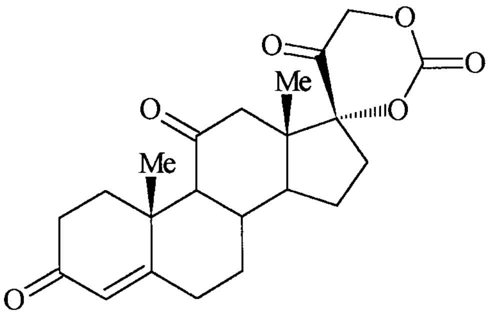
Cholesteryl chloroformate (**10.11**) is produced [1125] from reaction of cholesterol and



(10.11)

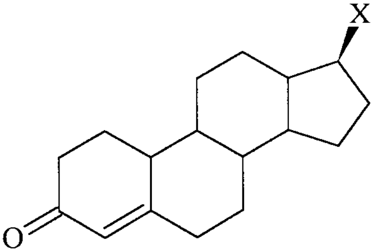
$COCl_2$, and 11-deoxycortisol also reacts with an excess of $COCl_2$ to give the corresponding chloroformate [1240].

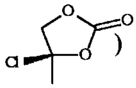
Reaction of cortisone with an excess of $COCl_2$ gives the 17,21-cyclic carbonate (**10.12**)



(10.12)

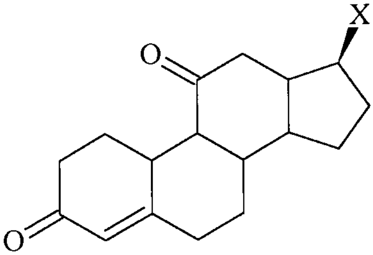
in 36% yield [1240], and the analogous reaction of the 11-deoxycorticosterone (4-pregnen-21-ol-3,20-dione) with $COCl_2$ gave (**10.13**) in *R* and *S* forms as major products and (**10.14**) as a minor product [1241].



(10.13; X = )

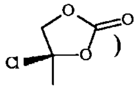
(10.14; X = $C(O)CH_2Cl$)

In contrast, reaction of (10.15) with phosgene gave (10.16) as the major product, and *R* and *S* forms of (10.17) as the minor products.

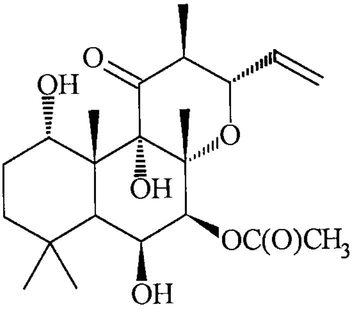


(10.15; X = $C(O)CH_2OH$)

(10.16; X = $C(O)CH_2Cl$)

(10.17; X = )

Forskolin (10.18) with $COCl_2$ in the presence of pyridine resulted in the formation of a carbonate function at the 1,9 positions [189].



(10.18)

10.3.1.4 Phenols

Unlike the majority of alcohols discussed in the two preceding Sections, phenols are relatively inert to phosgene even at elevated temperatures [1080]. Yields of the products can be increased, however if a stoicheiometric equivalent of an organic base is used in the reaction [294,846,1358], or if controlled amounts of alkaline solution are added to the reactants in a suitable solvent [36b,1568]. The effect of tertiary amine in the promotion of the reaction is regarded not to be only a result of its ability to scavenge HCl: it is considered, in addition, to form an ionic complex with phosgene, $[R_3NC(O)Cl]^+$, which acts as a powerful chloroformylating agent towards phenol [1358].

Quaternary ammonium salts such as $[NMe_4]Cl$ have been used to catalyse the reaction according to Equation (10.15):

$$\mathrm{ArOH + COCl_2 \longrightarrow ArOC(O)Cl + HCl} \qquad (10.15)$$

but larger chain R groups are preferred since they are more soluble in organic solvents, such as chlorobenzene. Stearyltrimethylammonium and distearyldimethylammonium chlorides were noted to catalyse reaction (10.15), and these materials also catalysed the preparation of a variety of aromatic bis(chloroformates) in quantitative yield [423]. Lewis acids such as aluminium(III) chloride are reported to catalyse the reaction of phosgene with phenols to produce diarylcarbonates [2056a], Equation (10.16), although pyridine has also been used

$$\mathrm{2ArOH + COCl_2 \longrightarrow (ArO)_2C{=}O + 2HCl} \qquad (10.16)$$

successfully in catalysing the formation of diphenyl carbonate from phenol and phosgene [176]. The standard free energy of formation of crystalline diphenyl carbonate has been derived from combustion enthalpy and low temperature heat capacity measurements. $\Delta G^{\bullet}_{298}$, for the reaction given in the following equation was calculated to be −54 kJ mol^{-1} [1892].

$$\mathrm{2C_6H_5OH_{(s)} + COCl_{2(g)} \longrightarrow (C_6H_5O)_2CO_{(s)} + 2HCl_{(g)}}$$

A general method of synthesis of the aryl chloroformates involves the reaction of phosgene with phenoxide, M[OAr], dissolved in a suitable solvent at low temperatures [1442]:

$$\mathrm{M[OAr] + COCl_2 \longrightarrow ArOC(O)Cl + MCl}$$

This reaction is particularly suitable for phenols, since this type of compound is sufficiently acidic to easily form an alkali metal salt by addition to a solution of an alkali metal hydroxide [1358].

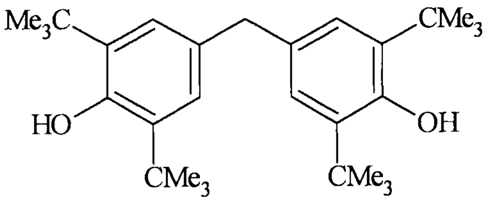
Reactions of the phenoxides with phosgene have also been used to produce diaryl carbonates:

$$\mathrm{2M[OAr] + COCl_2 \longrightarrow (ArO)_2C{=}O + 2MCl}$$

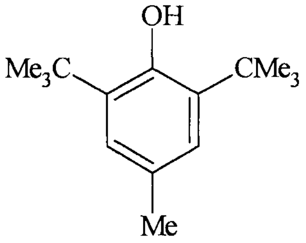
The perhalogenated diarylcarbonates, $(C_6X_5O)_2C{=}O$ (X = Cl or Br) were prepared from the corresponding phenoxides, in the presence of *N*-ethylpiperidine or NEt_3 [28].

The reaction of $[4\text{-}O_2NC_6H_4O]^-$ with phosgene has been studied at the two-phase interface between the aqueous and organic solvents. For maximum yield of the carbonate, an excess of phosgene, NEt_3 and $[OH]^-$ are said to be necessary.

The compounds (10.19) and (10.20) were found not to react with phosgene under



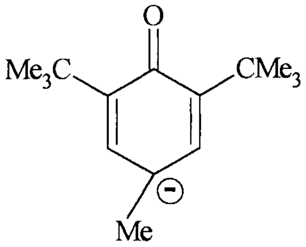
(10.19)



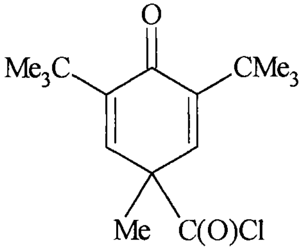
(10.20)

normal conditions [423,1936]. Even in the presence of a catalyst which effected a yield of chloroformate of 94% from phosgene and bisphenol A, $HO-4-C_6H_4CMe_2C_6H_4-4-OH$, only the starting materials were recovered from phosgene and **(10.19)** [423]. Details of the preparation of the industrially significant bis(chloroformate) derived from phosgene and bisphenol A, using stearyltrimethylammonium chloride as the reaction catalyst, have been given elsewhere [423].

The hydroxy group in **(10.20)**, and thus presumably in **(10.19)** too, is considered to be sterically protected by the CMe_3 groups [1936]. Treatment of **(10.20)** with potassium hydroxide to give the phenoxide, and subsequent rearrangement to the keto form **(10.21)**, followed by reaction with $COCl_2$ caused the formation of **(10.22)**, but not the expected chloroformate.

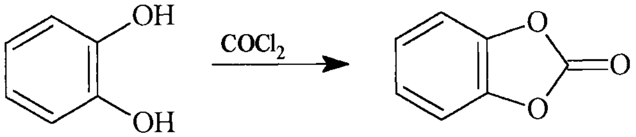


(10.21)



(10.22)

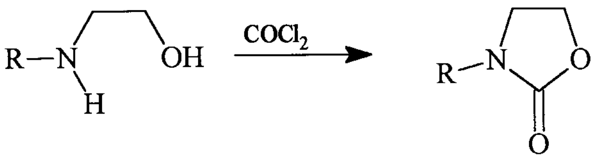
Catechol is readily converted into a cyclic carbonate using two molar equivalents of phosgene in the presence of a sodium hydroxide solution [879a]:



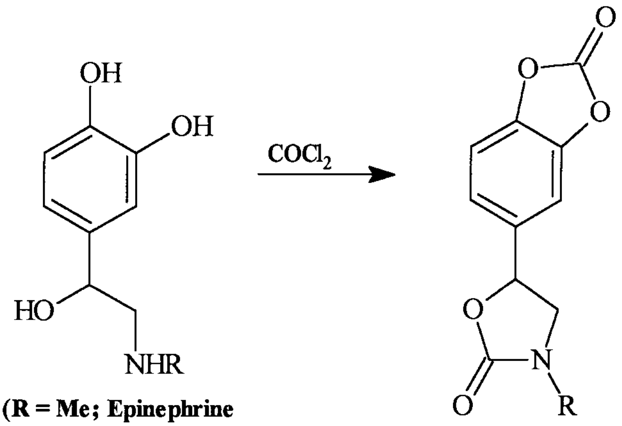
Despite the presence of the N–H group in the substituted catechol $3,4-(HO)_2C_6H_3CH_2CH_2NHCO_2Et$, its reaction with $COCl_2$ affords the corresponding cyclic carbonate [421].

10.3.1.5 Amino alcohols and amino phenols

The reaction of phosgene with a primary [1209] or secondary 2-amino alcohol is a general method [575a] for the preparation of 2-oxazolidone, and this reaction has been employed for the enantiomeric resolution of amino alcohols [855b,1151,1152]:

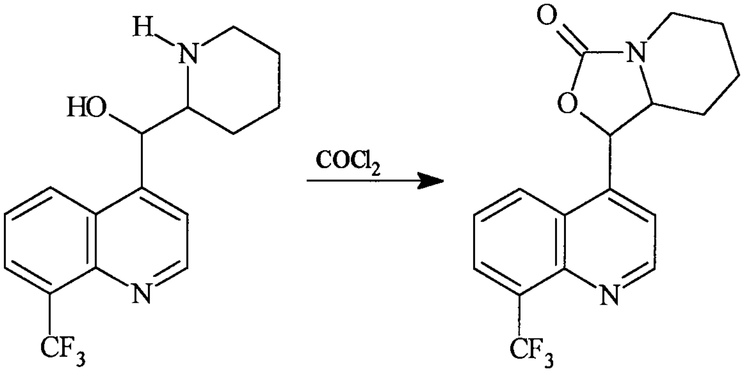


Treatment with phosgene of other 2-aminoalcohols, such as metoprolol ($MeOCH_2CH_2$-4-$C_6H_4OCH_2CH(OH)CH_2NHCHMe_2$; used in the treatment of heart disease), readily forms cyclic 2-oxazolidones {such as (3.3)} [856a]. Epinephrine and Norepinephrine combine with phosgene to give the anticipated cyclized derivatives [856b]:



**(R = Me; Epinephrine
R = H; Norepinephrine)**

Mefloquine, used in the treatment of malaria, reacts with phosgene to give a cyclized derivative, even though the amino group is part of a ring [856a]:

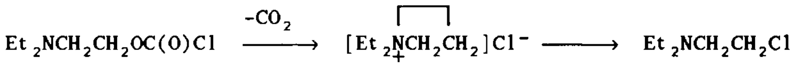


(Mefloquine)

The gas chromatographic determination of the chemically important compound, Alprenolal, $CH_2{=}CHCH_2{-}4{-}C_6H_4OCH_2CH(OH)CH_2NHCHMe_2$, and its 4-hydroxy metabolite, has been performed after cyclization with phosgene [855a].

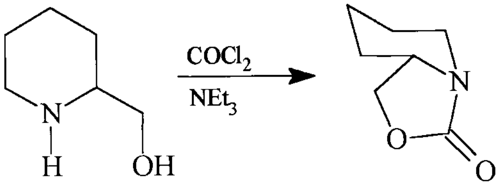
Phosgene reacts with $Et_2NCH_2CH_2OH$ as its hydrochloride to give the corresponding chloroformate, which decomposes readily *via* an aziridine intermediate to $Et_2NCH_2CH_2Cl$:

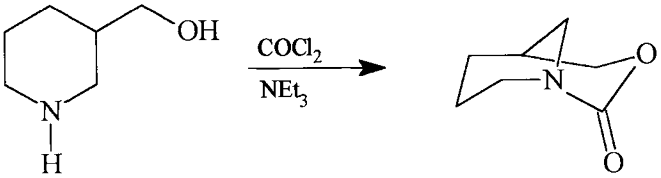
$$Et_2NCH_2CH_2OH + COCl_2 \longrightarrow Et_2NCH_2CH_2OC(O)Cl$$



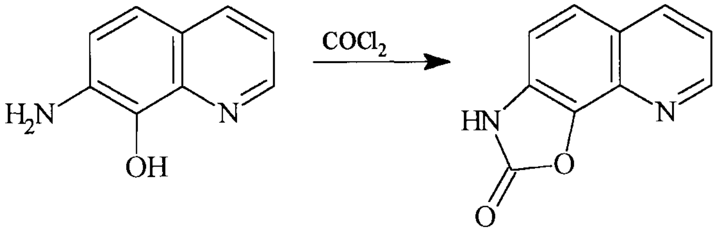
$$Et_2NCH_2CH_2OC(O)Cl \xrightarrow{-CO_2} [Et_2\overset{+}{N}CH_2CH_2]Cl^- \longrightarrow Et_2NCH_2CH_2Cl$$

Reaction of phosgene with the following two amino alcohols at ⩽ −30 °C in CH_2Cl_2 gives the corresponding *N*-carbamoyl chlorides; cyclization was induced by treatment with NEt_3 to give bicyclic urethanes [870]:

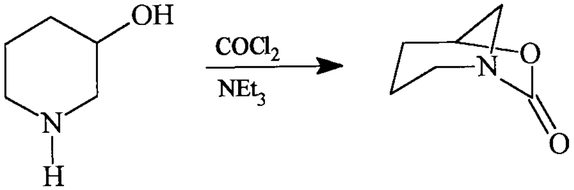




The amino function is usually so much more reactive than the phenolic or naphtholic −OH group that isocyanatophenols (for example $HO{-}4{-}C_6H_4NCO$) and isocyanatonaphthols have been prepared by adding the respective aminophenol or aminonaphthol to an excess of $COCl_2$ in ethyl ethanoate solution at 0–5 °C [2085]. Where the −OH and $-NH_2$ groups are attached to adjacent carbon atoms on the ring, cyclization occurs as illustrated below [1752,2050]:



although where puckering of the ring is possible, cyclization can occur between the 1,3-positions [870]:



10.3.2 Cyclic ethers

The reactions of phosgene with cyclic ethers provides a convenient means, in some cases, of preparing chloroalkyl chloroformates. The reactions are usually fast and, unlike those of the alcohols, do not co-produce hydrogen chloride.

$COCl_2$ reacts vigorously with 1,2-epoxides to give either chloroformate or carbonate derivatives depending upon the reaction conditions. In the absence of a catalyst [1309], or in the presence of a catalytic amount of pyridine, and with an excess of phosgene [1052], ring opening of the epoxide occurs:

$$R\overline{CHCH_2O} + COCl_2 \longrightarrow RCH\{OC(O)Cl\}CH_2Cl$$
$$(R = H,\ Me,\ CH_2Cl,\ \text{or Ph})$$

With two molar equivalents of the epoxide, further reaction ensues to give the corresponding bis(2-chloro-1-alkylethyl) carbonates, providing that pyridine or some other suitable catalyst is present in the reaction solution [1052].

The direction of ring opening of some unsymmetrically substituted epoxyalkanes has been established and takes place as indicated above, without formation of the 2-chloroalkylchloroformate isomer [1052]. A continuous process for the production of 2-chloroalkylchloroformates has been patented [128,454] based upon the reaction of phosgene with $R\overline{CHCH_2O}$ (R = organic group) in the presence of a tertiary amine catalyst, such as $PhCH_2NMe_2$. However, only the reaction of the symmetrical $\overline{CH_2CH_2O}$ was provided as an example, and the implied direction of ring opening, which contrasts with that reported in earlier work [1052], is not substantiated.

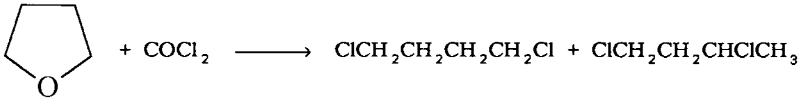
The addition of phosgene to 1,2-epoxy-2,4,4-trimethylpentane did not result in the formation a chloroformate, but instead proceeded with the formation of pentene and pentanol derivatives [1052]:

$$\begin{tikzcd}
Me_3CCH_2C(Me)\overline{CH_2O} \arrow[r, "COCl_2"] \arrow[d, "+HCl"] & Me_3CCH_2C(Me)\{OC(O)Cl\}CH_2Cl \arrow[d, "\begin{array}{l}-HCl\\ -CO_2\end{array}"] \\
Me_3CCH_2C(Me)(OH)CH_2Cl & Me_3CCH{=}C(Me)CH_2Cl
\end{tikzcd}$$

The reaction of 1,2-epoxycyclohexane with phosgene resulted in the formation of the *trans*-2-chlorocyclohexyl chloroformate isomer [1052], and *trans*-2,3-epoxybutane, on treatment with $COCl_2$, gave a mixture of the *erythro*-stereoisomers of 2-chloro-1-methylpropyl chloroformate [1052].

Processes for the continuous production of chloro-substituted chloroformates, $CH_2ClCHROCOCl$ (R = H, Me, $CH_2OCH_2CH{=}CH_2$ or CH_2OPh) from the reaction of phosgene with 1,2-epoxides have been disclosed, in which activated carbon is used as a catalyst, and the reaction is conducted at an operating temperature of 75-115 °C in a circulating stream of pre-formed chloroformate [229].

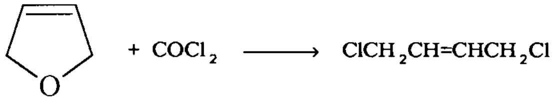
Tetrahydrofuran combines with phosgene in a sealed tube at 100 °C in the presence of hydrogen chloride (or a hydrogen chloride donor):



$$+ \ COCl_2 \longrightarrow ClCH_2CH_2CH_2CH_2Cl + ClCH_2CH_2CHClCH_3$$

1,3-dichlorobutane is the major product of the reaction [378,385], and is probably formed as a result of the rearrangement of the carbenium ion derived from the intermediate chloroformate. When zinc(II) chloride [1287b], dmf (see Section 10.2.2.3) [2253a], or tertiary amines are used as catalysts, tetrahydrofuran is converted by phosgene into the expected product, 1,4-dichlorobutane.

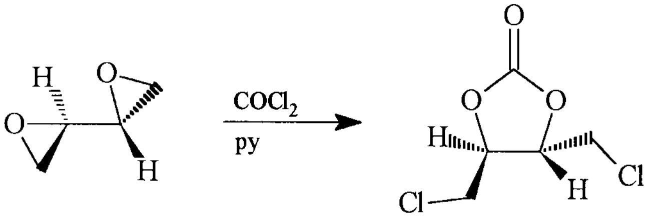
The reaction between 2,5-dihydrofuran and phosgene proceeds according to the following equation [2253a]:



$$+ \ COCl_2 \longrightarrow ClCH_2CH{=}CHCH_2Cl$$

In contrast, phosgene reacts with the 6-membered oxygen heterocycle, 2,3-dihydro-4*H*-pyran, at the double bond, rather than by ring opening [914]. This reaction is described more fully in Section 10.1.2.

Phosgene reacts with the diepoxide derived from butadiene, in the presence of pyridine at room temperature, to form a cyclic carbonate [1107aa]:



10.3.3 Compounds containing the carbonyl group

10.3.3.1 Reactions with aldehydes

The early chemical literature concerning the reactions of phosgene with aldehydes is fraught with confusion. The product of the reaction of phosgene with ethanal, for example, has been variously reported as a polymer [1078b], a *gem*-dichloride [582], a chloroformate [322], or (ludicrously) a material isomeric with vinyl chloride (chloroethene) [685c,887,1164a]. Only recently has this situation been satisfactorily resolved [1765].

Curiously, the reaction of phosgene with the first member of the aldehyde series, methanal, was not properly investigated until the 1980s, the system only then becoming the subject of patent disclosure [1559aa,1762].

Phosgene does not react with gaseous methanal, either thermally or photochemically, and the action of u.v. light is said only to cause dissociation of the phosgene [1164]. At low temperatures in hexane solution, phosgene and methanal are reported to give only poorly defined polymers [1031a], and copolymerization of CH_2O and $COCl_2$, induced by γ-irradiation, results in the incorporation of only a minute fraction of phosgene into the polymer [1490]. However, whilst it is confirmed [1764] that CH_2O and $COCl_2$ do not react by simple heating, in the presence of carbon catalysts phosgene combines with methanal in the gas phase according to Equation (10.17) [1762]:

$$COCl_2 + HCHO \xrightarrow{C} CH_2Cl_2 + CO_2 \qquad (10.17)$$

This reaction, examined in a flow system at atmospheric pressure, occurs rapidly and selectively, with almost complete conversion of the reactants over the temperature range 130-230 °C [1762,ICI95,ICI96]. Above ~200 °C, carbon monoxide is formed: it is believed [ICI96] to be generated according to the stoicheiometry of Equation (10.18):

$$COCl_2 + HCHO \xrightarrow{C} 2CO + 2HCl \qquad (10.18)$$

Conventional processes for the manufacture of dichloromethane are based upon the chlorination of methane or of chloromethane. These reactions have the disadvantage of generating hydrogen chloride as a by-product, and of producing a mixture of all chloromethanes, in addition to dichloromethane. The simple reaction between methanal and phosgene thus provides a potential industrial preparation of CH_2Cl_2 [1762] without the concomitant problems of the traditional processes.

An investigation of the mechanism of the charcoal catalysed reaction (10.17) reveals that the reaction proceeds *via* a strongly absorbed intermediate, identified as chloromethyl chloroformate, $CH_2ClOC(O)Cl$ [1765]. This compound is found to form rapidly above 100 °C in co-adsorption/desorption experiments, and decomposes rapidly above ~170 °C without significant desorption [1765], to give the final products, CH_2Cl_2 and CO_2. The rate-determining step in the reaction is the formation of the chloroformate, so that it is normally only present on the catalyst surface at low coverages, and hence not observed in the gas phase. The catalysis is considered to be a result of the polar surface groups on the charcoal [1765,ICI97]. From kinetic and thermodynamic considerations, an energy profile diagram was constructed, Fig. 10.5, representing the absorption-reaction-desorption sequences in the reaction scheme [1765,ICI97].

Authentic chloromethyl chloroformate has been synthesised by the passage of gaseous methanal (diluted in a stream of dinitrogen) into a solution of phosgene in dichloromethane containing a small quantity of pyridine and held at -5 °C [1765], Equation (10.19).

$$COCl_2 + CH_2O \longrightarrow CH_2ClOC(O)Cl \qquad (10.19)$$

Other compounds, such as quaternary ammonium halides or tetrasubstituted ureas, are reported to catalyse this reaction [1559aa].

The reaction of phosgene with ethanal was first reported by Harnitz-Harnitzky in 1859 [887]. A substance melting at 0 °C and boiling at 45 °C was said to be formed which was believed to be isomeric with chloroethene (!), and which was given the name "chloroacetene". Apparently, these findings were said to be confirmed by Friedel [685c] and by Kraut [1164a], but an investigation by Kekulé and Zincke [1078b] indicated that the action of phosgene on ethanal was consistent only with the polymerization of the ethanal. To add to the confusion, Kempf [1080] claimed that liquid phosgene reacted with ethanal to produce $CH_3C(O)C(O)Cl$ and HCl, and Hofmann [973], without providing experimental detail, reported that aldehydes combine with phosgene to form monoaldehyde or dialdehyde chlorocarbonyls. Subsequently, Eckenroth [582] claimed that 1,1-dichloroethane was formed when phosgene gas was passed into ethanal, with cooling, according to the Equation (10.20):

$$CH_3CHO + COCl_2 \longrightarrow CH_3CHCl_2 + CO_2 \qquad (10.20)$$

Paraldehyde (2,4,6-trimethyl-1,3,5-trioxane) was claimed to behave in a similar way [582]. An early German patent, published after Eckenroth's note [582], claimed that no reaction occurs between $COCl_2$ and aldehydes at normal temperatures [612], and attempts to repeat Eckenroth's preparation [582] have not been successful [1763]. However, by combining the vapours of phosgene and ethanal at atmospheric pressure in a flow system over an activated charcoal catalyst, 1,1-dichloroethane and carbon dioxide are found to be co-produced, especially in the temperature range of 150-200 °C [1763,ICI98,ICI99]. It was confirmed that no reaction occurs in the absence of a catalyst between 25 and 400 °C [1763].

Although methods for the manufacture of 1,1-dichloroethane are well established, they usually involve a combination of a multi-stage process and severe conditions. In one method of manufacture, ethene is chlorinated to give 1,2-dichloroethane, which is then cracked to give chloroethene, and finally treated with hydrogen chloride to give the 1,1-isomer. The catalysed

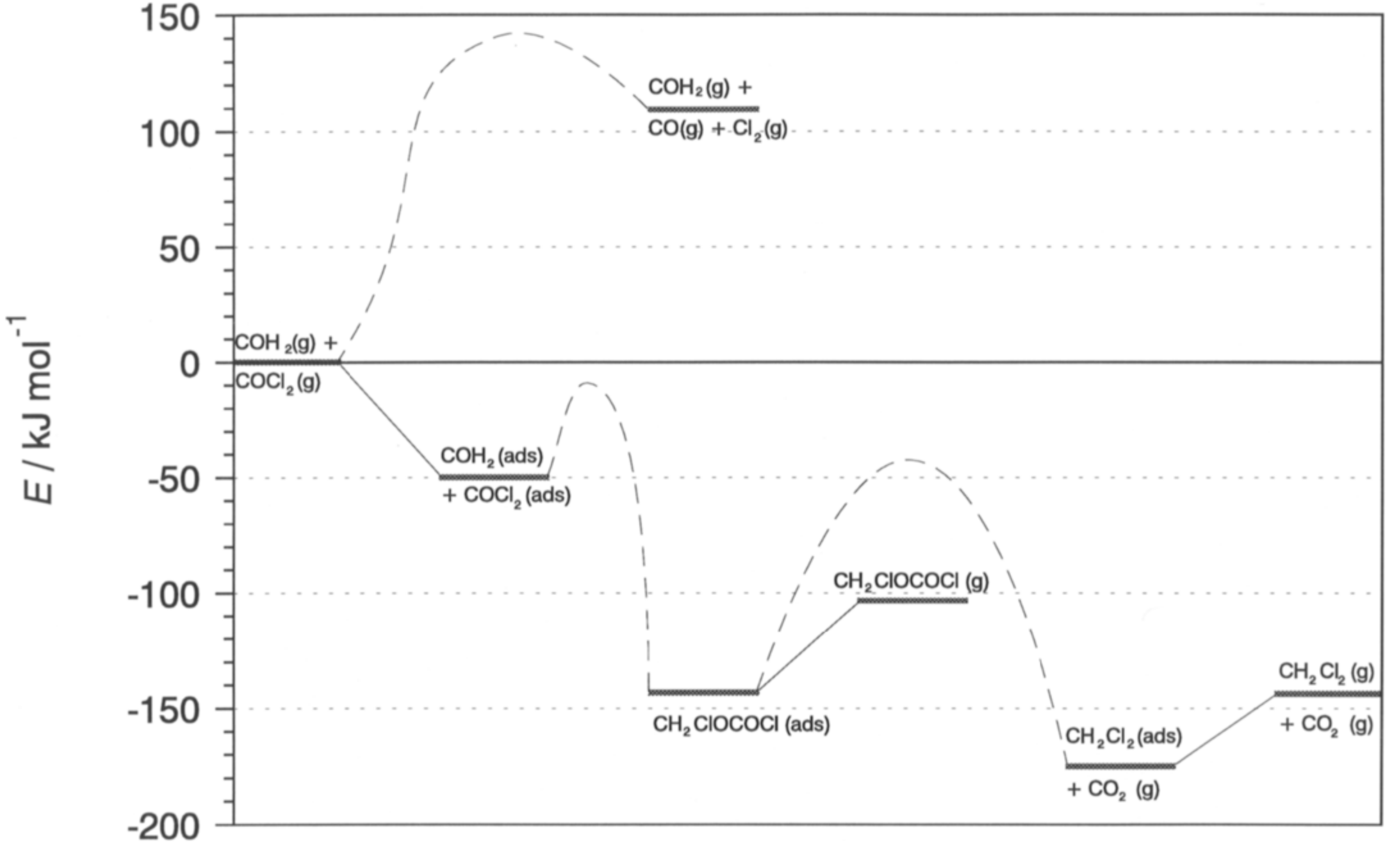


Fig. 10.5 Energy profile for the carbon–catalysed reaction: $COH_{2(g)} + COCl_{2(g)} \longrightarrow CO_{2(g)} + CH_2Cl_{2(g)}$ [1765,ICI97].

reaction of phosgene with gaseous ethanal has the potential advantage of providing a single reaction step and relatively mild reaction conditions for the production of the 1,1-dichloroethane. Phosgene has an advantage over other potential chlorinating agents in this system, and this is expanded upon in Section 4.7.6. Furthermore, since ethanal is a material which is potentially obtainable from synthesis gas (CO/H_2) [862a], it is an attractive starting material, not subject to the uncertainties associated with oil-based materials such as ethene [ICI87].

The reaction of phosgene with butanal under substantially similar conditions to those used for the reaction of phosgene with ethanal gave smaller yields of the 1,1-dichloro-derivative, and the reaction of phosgene with gaseous chloral, CCl_3CHO, over activated charcoal at 200–350 °C gave (in addition to decomposition products) only small amounts of tetrachloroethene – possibly formed as a result of the simultaneous decarboxylation and dehydrochlorination of the intermediate chloroformate, $CCl_3CHClOC(O)Cl$ [1763,ICI100].

Chloral reacts with a molar proportion of phosgene in benzene solution at room temperature in the presence of *N,N*-dimethylaniline to produce $CCl_3CHClOC(O)Cl$ [612], the corresponding dialkyl carbonate is formed if the molar ratio of chloral:$COCl_2$ is increased to 2:1. Similarly, the reaction of C_6H_5CHO and $COCl_2$, under the conditions described as for chloral, results in the formation of the chloroformate, $C_6H_5CHClOC(O)Cl$ or the carbonate $\{C_6H_5CH(Cl)O\}_2C{=}O$, depending upon the reactant proportions [612]. When heated with liquid phosgene to 120–130 °C, however, C_6H_5CHO is reported to be converted into $C_6H_5CHCl_2$ [1080]. The reaction of a mixture of CCl_3CHO, C_6H_5CHO and $COCl_2$ in a benzene solution of quinoline results in the formation of the mixed carbonate, $C_6H_5OC(O)OCCl_3$ [612].

Phosgene does not react with $C_6H_5CH{=}CHCHO$ in the cold, but a violent reaction takes place readily between $COCl_2$ and $Me_2NC_6H_4CHO$ at room temperature, with the liberation of carbon dioxide and the formation of $Me_2NC_6H_4CHCl_2$ [1937]: this reaction forms the basis of an analytical method for the detection of phosgene (see Section 3.2.3.1.1). Similarly, O_2N-4-C_6H_4CHO reacts with phosgene in the presence of Ph_3PO, at 120–140 °C, to give O_2N-4-$C_6H_4CHCl_2$ [316].

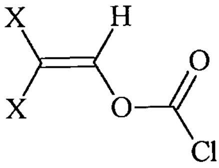
In a recent patent disclosure, ethanal is reported to react with phosgene at low temperatures in tetrachloromethane solution, or other chlorinated solvent, containing $(Bu_2N)_2CO$. The product was 1-chloroethyl chloroformate, $CH_3CH_2ClOC(O)Cl$. Other catalysts used for this reaction were $P(NMe_2)_3$, py, $[N\{(CH_2)_6Me\}_4]Br$, and $[NBu_3(CH_2C_6H_5)]Cl$ [322]. This reaction is apparently a general one for the preparation of 1-chloroalkyl chloroformates, Equation (10.21), and a large variety of salt-like catalysts have

$$COCl_2 + RCHO \longrightarrow RCHClOC(O)Cl \qquad (10.21)$$

been claimed to be effective in the conversion for an equally large variety of R groups, including C_1–C_{12} alkyl groups, aryl, alkenyl, alkynyl and aralkyl. The proposed general mechanism for the reaction, in which A^+ represents an organic or inorganic cation, is illustrated below [322,1557a]:

$$A^+Cl^- + RC(O)H \longrightarrow A^+[RC(O^-)(H)Cl] \xrightarrow{COCl_2} RCHClOC(O)Cl + A^+Cl^-$$

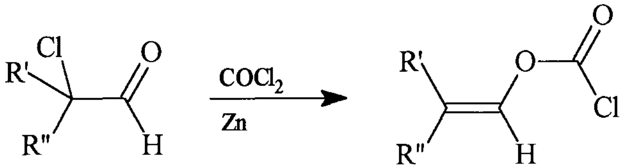
This is consistent with the increased nucleophilicity of the chloride ion resulting from its association with a large cation. Distillation of the simple alkyl chloroformates at atmospheric pressure results in their decomposition to *gem*-dichlorides, $RCHCl_2$. Most of the benzylic chloroformates decompose below 60 °C in a similar fashion, but the chloroformates derived from chloral, $CCl_3CHClOC(O)Cl$, and bromal, $CBr_3CHClOC(O)Cl$, decompose thermally back into phosgene and the parent aldehyde [1557a]. On addition of zinc dust, however, the following dihalovinyl chloroformate is formed [242b]:



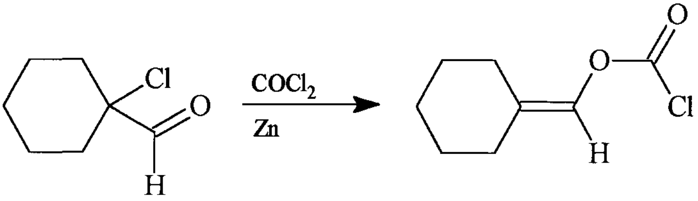
(X = Cl or Br)

These compounds can also be prepared directly by the treatment of chloral or bromal with phosgene and zinc (or magnesium) dust in $MeOC(O)Me/OEt_2$ [242b].

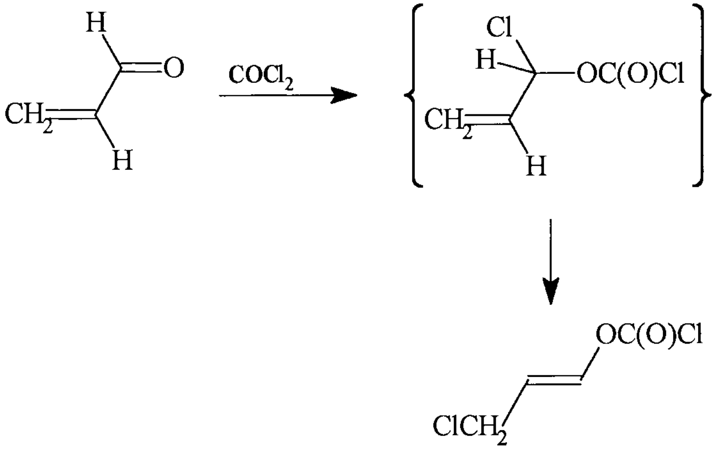
Vinyl chloroformates with the general formula R'R"C=CHOC(O)Cl (R' = R" = Me; R' = Me, R" = Cl; R' = Me, R" = Pr) have been prepared by the addition of phosgene to an aldehyde group adjacent to a 1-chloro atom, followed by removal of chlorine *in situ*, using zinc dust [242c]:



Cyclic derivatives will undergo similar transformations:
e.g.



The chloroformate formed between 2-propenal (acrolein) and phosgene readily rearranges in the presence of a zinc(II) chloride catalyst [1557a]:



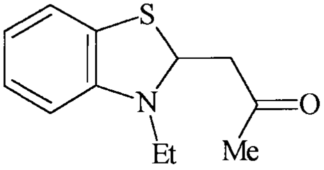
Details of this reaction are sparse, however [1557a].

10.3.3.2 Ketones

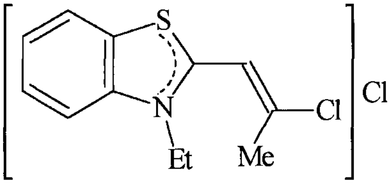
Surprisingly little work has been published on the reactions of phosgene and ketones. Unlike phosphorus(V) chloride, phosgene is reported not to react with ketones to replace the carbonyl oxygen with chlorine, even at elevated temperatures [1704].

Early accounts of the reaction of propanone with gaseous [1080] or liquid [2213a] phosgene suggest the formation of the asymmetrical dichloropropanone, $CH_3C(O)CHCl_2$. The action of phosgene on an excess of propanone at room temperature was later reported to give the chloroformate $CH_2{=}C(Me)OCOCl$, and no evidence for the formation of the dichloropropanone reported by the earlier workers could be found [1355]. However, this reaction itself could not be repeated at room temperature, even when the reactants were in contact for over 24 h [1622].

The reaction of propanone with phosgene appears to be typical of a ketone that is in tautomeric equilibrium with its enol. For example, the heterocyclic derivative (**10.23**) was found to combine with $COCl_2$ to give (**10.24**). In this example, the reaction also proceeded with the liberation of CO_2 [1984a].

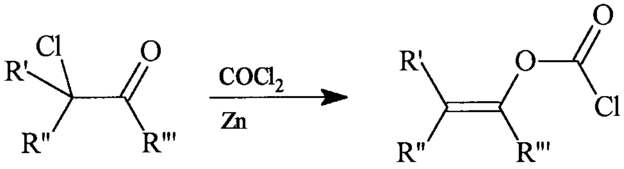


(**10.23**)

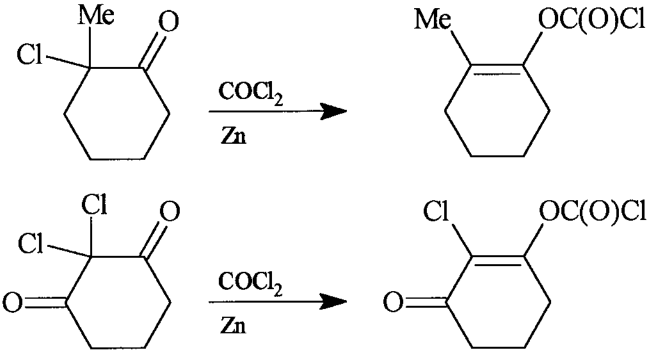


(**10.24**)

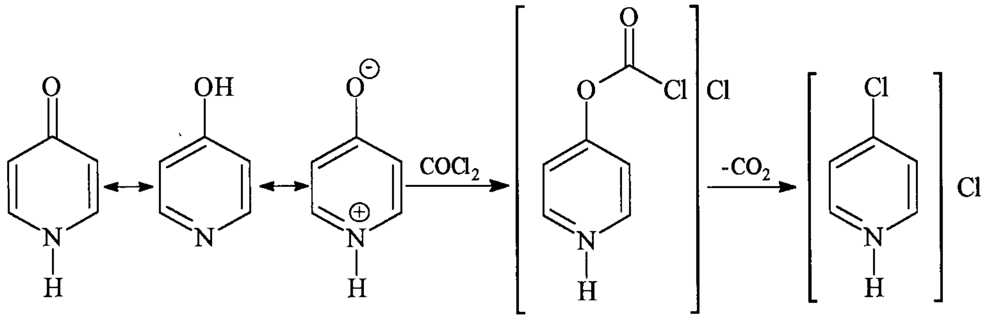
In the presence of zinc dust (*cf*. Section 10.3.3.1), a large number of ketones bearing a 1-chloro substituent react with phosgene to form vinyl chloroformates of general formula R'R"C=CR"'OC(O)Cl (R' = R" = Cl, R"' = Me or Ph; R' = R" = Me, R"' = P(O)(OMe)$_2$, P(O)(OEt)$_2$, or CN) [242c]:



The following cyclic species react in a similar manner [242c]:



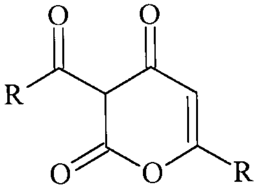
Although it exists predominantly in the keto form, 4-pyridone reacts with phosgene at between 140 and 190 °C, in the absence of a solvent or catalyst, to give 4-chloropyridinium chloride [ICI101]:



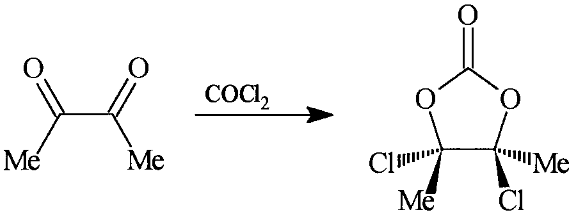
The reaction may be considered to take place either through the enol-form of the pyridone, or its zwitterionic form. The herbicide intermediates 2-chloropyridine [607] and 2,3,5-trichloropyridine [606a] have been prepared from 2-pyridone and 3,4-dichloro-2-pyridone, respectively, using a solution of phosgene in the presence of dmf [606a,607].

Reaction of $COCl_2$ with a suspension of the copper(II) salts of $(RCOCH_2)_2CO$ (R =

Me, Et or Bu) in benzene is reported to give the following lactone (see also Section 9.12) [193a,1298]:

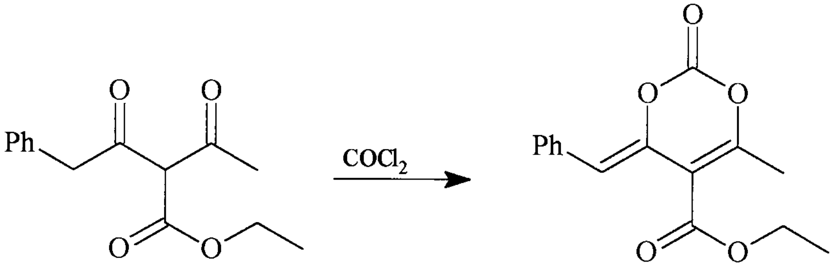


Phosgene reacts with an equimolar quantity of butane-2,3-dione, in the presence of pyridine, to form *trans*-4,5-dichloro-4,5-dimethyl-1,3-dioxalano-2-one in high yield [1107aa]:



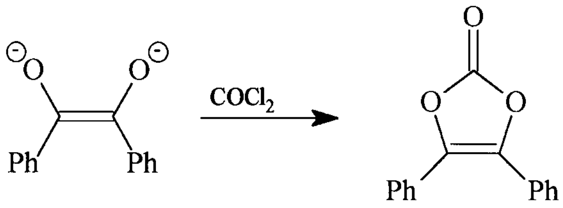
This reaction is understood to proceed through a 4,5-dimethylene intermediate. 1,2-Cyclohexadiene reacts similarly to give the bicyclic 4,5-dichloro-1,3-dioxalan-2-one derivative, although C(O)ClC(O)Cl, C(O)PhC(O)Ph and EtOC(O)C(O)OEt were found to be unreactive under the conditions employed [1107aa].

A cyclic carbonate is formed from the dione (**10.25**) according to [229a]:

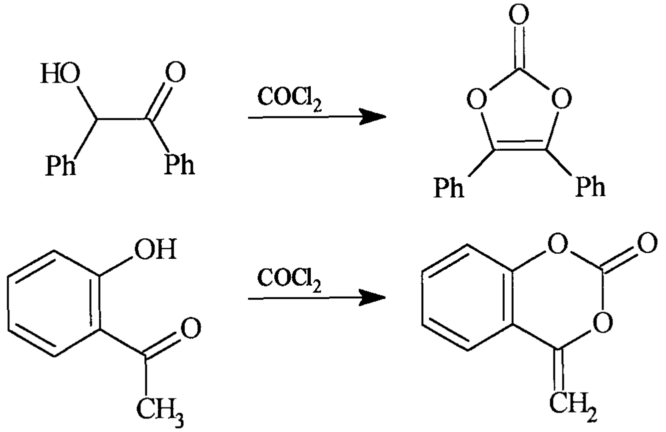


(10.25)

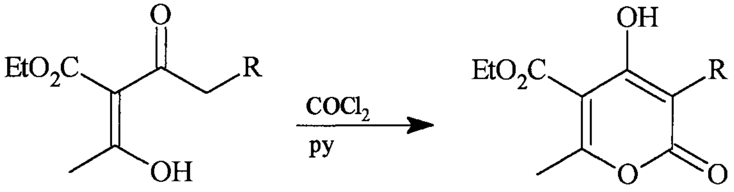
The carbonylation of the sodium salt of an enediolate, prepared *in situ* from PhC(O)C(O)Ph, with $COCl_2$ gives the 1,3-dioxol-2-one derivative [270]:



Compounds containing adjacent C–OH and C=O groups are capable of cyclizing when treated with phosgene, as a result of enolization, as illustrated below [851,1272]:

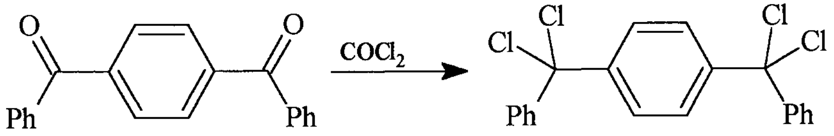


A less common type of cyclization of a keto-alcohol is demonstrated by the reaction of phosgene with (10.26) in the presence of pyridine [229a]:



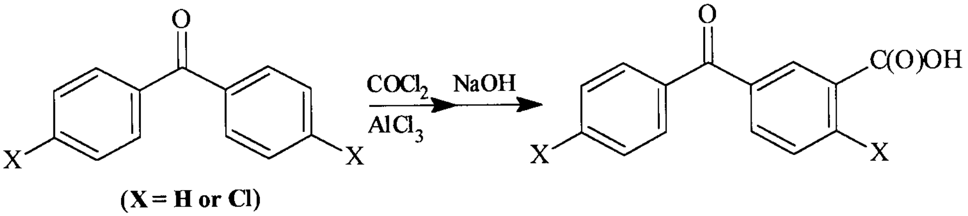
(10.26)

Gem-dichlorides can be obtained from ketones that are not capable of conversion into an enol form by using phosgene in the presence of an organic phosphorus compound [316]. For example, $Ph_2C=O$ was converted into Ph_2CCl_2 in the presence of one of a wide variety of phosphine or phosphine oxide catalysts between 100 and 190 °C. Further, PhC(O)C(O)Ph, when treated with $COCl_2$ in the presence of PPh_3O at 130–140 °C, resulted in the conversion of one of the CO groups into a CCl_2 moiety. PhC(O)-4-C_6H_4C(O)Ph reacted in the presence of PPh_3 to give the tetrachloro- derivative, $PhCCl_2$-4-$C_6H_4CCl_2Ph$ [316]:



PPh_3O was also used to catalyse the reaction between $COCl_2$ and Cl-4-C_6H_4C(O)Ph or O_2N-3-C_6H_4C(O)Ph to give Cl-4-$C_6H_4CCl_2Ph$ or O_2N-3-$C_6H_4CCl_2Ph$, respectively [316].

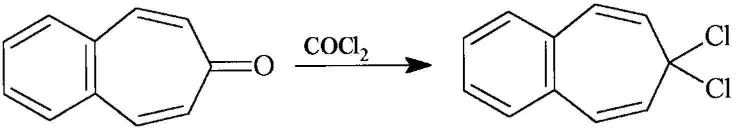
In fused anhydrous aluminium(III) chloride, $Ph_2C=O$ and Cl-4-C_6H_4-C(O)-C_6H_4-4-Cl react with phosgene to give, after saponification, the corresponding 3-carboxylic acid derivatives [265]:



No reaction between $Ph_2C=O$ and phosgene was detected under different temperature conditions, when aluminium(III) chloride was used simply as a solute, and attempts to prepare anthraquinone by this method were not successful [2196].

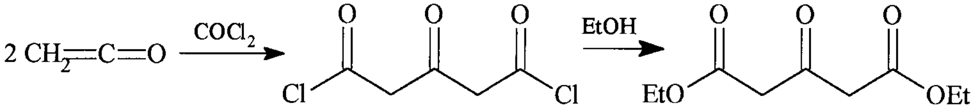
The aniline derivatives $(Me_2N-4-C_6H_4)_2C=O$ and $(Me_2N-4-C_6H_4CH=CH)_2C=O$ may also be dichlorodeoxygenated with phosgene. Although the former compound requires heating to 100 °C for the reaction to proceed, it then does so quantitatively [1937]. $(C_6H_5CH=CH)_2C=O$ and $(CH_3OC_6H_4CH=CH)_2C=O$ (unspecified isomers) appear not to react with phosgene in a toluene solution until heated to a sufficient temperature for decomposition to occur [1937].

Finally, the ability of phosgene to engage in dichlorodeoxygenation extends to tropolone derivatives, such as 7*H*-benzocyclohepten-7-one [664]:

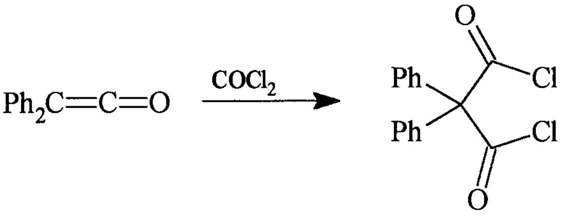


10.3.3.3 Ketenes

Attempts to react unsubstituted ketene, $CH_2=C=O$, with phosgene were not successful [176a]. However, a product of the reaction of $COCl_2$ with an excess of ketene has been claimed to have been prepared *in situ*, and its reaction product with ethanol has been isolated [293,956,1273]:

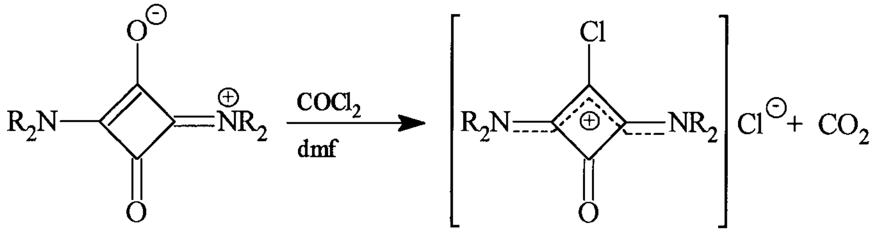


In contrast to the reactions of some ketones, ketenes do not give the products of dichlorodeoxygenation. The reaction of dialkyl ketenes, $R^1R^2C=C=O$, with phosgene results in the formation of $R^1R^2C(COCl)_2$ [595a]. These materials (R_1,R_2 = Me,Me; Me,Et; Me,Pr; or Et,Bu) are advantageously distilled over stabilizing agents to avoid their decomposition [1489]. The result of heating (~120 °C) phosgene with $Ph_2C=C=O$ is illustrated below [1938]:



10.3.3.4 Oxocarbons

Phosgene reacts with "squaric acid" (3,4-dihydroxy-3-cyclobutene-1,2-dione) derivatives according to [1831,1832]:



$\{R_2 = Me_2, (CH_2)_4, (CH_2)_5,$ or $(CH_2)_2O(CH_2)_2\}$

10.3.4 Carboxylic acids and derivatives

10.3.4.1 Carboxylic acids

Carboxylic acids do not react with phosgene easily, and the reactions require promotion with catalysts in order to avoid the need to use excessively high temperatures. The situation may be compared to the reactions of the highly acidic (for example fluorinated) alcohols.

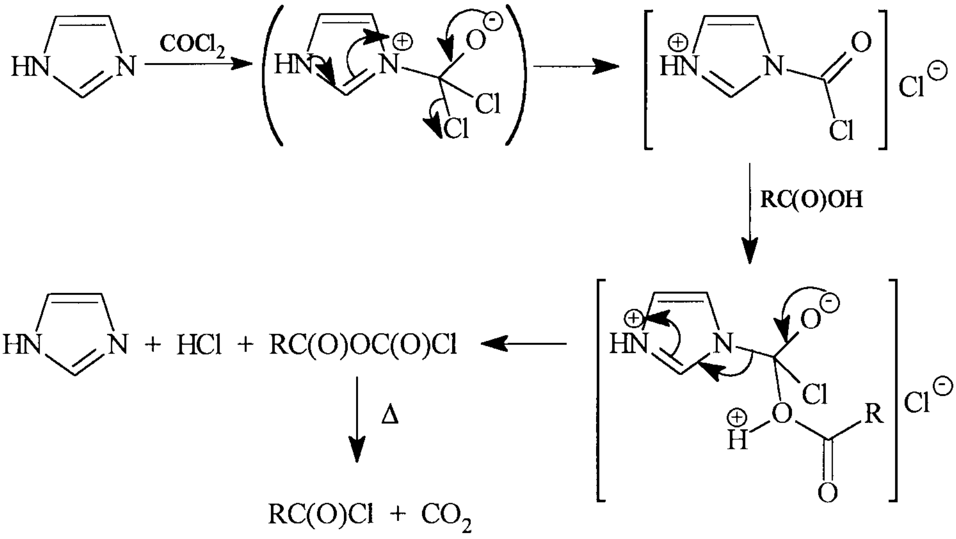
The action of phosgene on a carboxylic acid in the absence of other reactive functional groups is to form the corresponding acid chloride, consistent with Equation (10.22):

$$RC(O)OH + COCl_2 \longrightarrow RC(O)Cl + CO_2 + HCl \qquad (10.22)$$

Although acid chlorides can be produced in a similar way from the reactions of sulfinyl chloride ($SOCl_2$) or phosphorus(V) chloride with RC(O)OH, the by-products obtained from the phosgene reaction are less troublesome and are more amenable to disposal.

Phosgene does not react with ethanoic acid at normal temperatures, but ethanoyl chloride is produced according to Equation (10.22) when the reactants are combined in a Carius tube at ~120 °C [1080]. Long-chain acids, such as $CH_3(CH_2)_nCOOH$ (n = 10, 14 or 16) have been treated in the molten state at ~150 °C, and the unsaturated material, $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$, behaves similarly {*i.e.* according to Equation (10.22)} [1658].

A large variety of aliphatic and aromatic carboxylic acids are claimed to be converted into the corresponding acid chloride in the presence of tertiary amines [1919] or amides [585], and reactions may be catalysed by thiocarboxamides [336], quaternary ammonium, quaternary phosphonium, or ternary sulfonium salts [335]. Imidazoles and several related materials have been found to be very effective catalysts for the preparation of lauroyl chloride {dodecanoyl chloride; $CH_3(CH_2)_{10}C(O)Cl$} from lauric acid (dodecanoic acid) and phosgene. These catalysts are recycled, and result in high yields of product at temperatures below 100 °C [910a]. The mechanism of this reaction is thought to occur *via* the formation of an intermediate *N*-(chlorocarbonyl) derivative, which then reacts with the carboxylic acid to yield the corresponding acyl chloroformate, decomposition of which generates the acid chloride and carbon dioxide [910a]:



The reaction of chloroethanoic acid with phosgene has been studied in the liquid phase using dmf [ICI12], $AlCl_3$ [ICI11] or charcoal [968c] catalysts. The $AlCl_3$-catalysed reaction is believed to occur by the following mechanism [ICI11]:

$$\begin{tikzcd}
CH_2ClC(O)OH + AlCl_3 \arrow[r] & CH_2ClC(O)OAlCl_2 + HCl \arrow[d] \\
& CH_2ClC(O)OAlCl_2.COCl_2 \ \{cf.\ \text{Section } 9.1.2.5\}
\end{tikzcd}$$

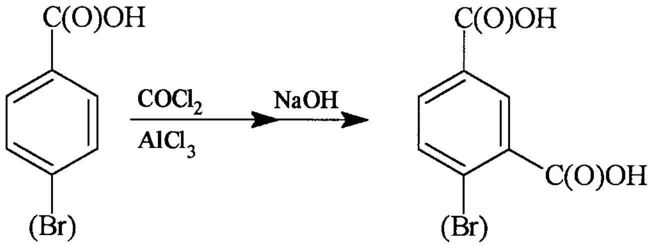
$$CH_2ClC(O)OAlCl_2 + CH_2ClC(O)OAlCl_2.COCl_2 \longrightarrow \{CH_2ClC(O)\}_2O + 2AlCl_3 + CO_2$$

$$\{CH_2ClC(O)\}_2O + COCl_2 \longrightarrow 2CH_2ClC(O)Cl + CO_2$$

Anhydrous $(COOH)_2$ is claimed to react with phosgene in the presence of NEt_2Ph, at room temperature and atmospheric pressure, to give ethanedioyl dichloride [1919]. The ammonium salt of ethanedioic acid dissolved into anhydrous HCOOH also reacts with phosgene at room temperature to give $(COCl)_2$ [1919]. Other dicarboxylic acids have been converted to the bis(acid chlorides) by using high pressures (≥ 1 MPa) and temperatures above 100 °C [329]. Thus, $HO(O)C(CH_2)_4C(O)OH$ and $COCl_2$ in the molar proportions of 1:3 were transformed into $Cl(O)C(CH_2)_4C(O)Cl$, with a yield of 92% under autogenous pressure at 125 °C.

The kinetics of the reaction of $C_6H_5C(O)OH$ with phosgene in the presence of caprolactam 2-oxohexamethyleneimine, $\overline{CH_2(CH_2)_4NHCO}$ to give $C_6H_5C(O)Cl$ (see Section 10.2.2.2) have been evaluated [1495]. The reaction is found to be zero-order in the acid and, at low concentration, first-order in $COCl_2$. At higher concentrations of phosgene, the order becomes greater than one. The activation energy of the uncatalysed reaction over the temperature range 120-160 °C is 113 kJ mol^{-1}; this value is considerably reduced, to 27 kJ mol^{-1}, in the presence of the catalyst. An empirical relationship was derived between the reaction rate and the reactant concentrations and temperature [1495].

In fused anhydrous $AlCl_3$, aromatic carboxylic acids with at least one free 3-position, when treated with $COCl_2$ at about 100-150 °C, followed by treatment with sodium hydroxide, are converted to dicarboxylic acids [265]:



The silver(I) salt of benzenecarboxylic acid also reacts with phosgene, to give C_6H_5COCl [870b]:

$$Ag[C_6H_5COO] + COCl_2 \longrightarrow CO_2 + AgCl + C_6H_5C(O)Cl$$

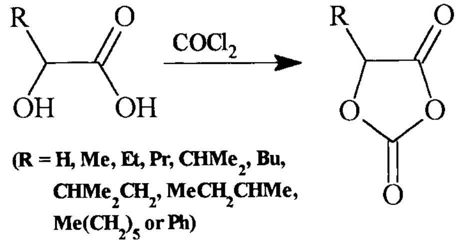
In contrast, reaction with the potassium salt of $[Me_3COC(O)]^-$ results in the production of a tricarbonate according to [1647]:

$$K[Me_3COC(O)O] \xrightarrow{COCl_2} Me_3COC(O)OC(O)OC(O)OCMe_3$$

This tricarbonate is readily decarboxylated by base to give the dicarbonate, $Me_3COC(O)OC(O)OCMe_3$.

Aromatic dicarboxylic acids, $1,4\text{-}C_6H_4(COOH)_2$ in particular, have been treated with phosgene using weakly basic tertiary amines ($pK_b \geq 9$) at 10-50 °C. Use of stronger bases is reported to result in lower yields of the product bis(acid chlorides) [105].

Carboxylic acids (or their alkali metal salts [1170]) possessing a 2-hydroxy group undergo cyclization with $COCl_2$ [465]:



(R = H, Me, Et, Pr, $CHMe_2$, Bu, $CHMe_2CH_2$, $MeCH_2CHMe$, $Me(CH_2)_5$ or Ph)

This reaction has been used to obtain enantiomeric derivatives from their racemic precursors by separating them on a chromatographic column [1152]

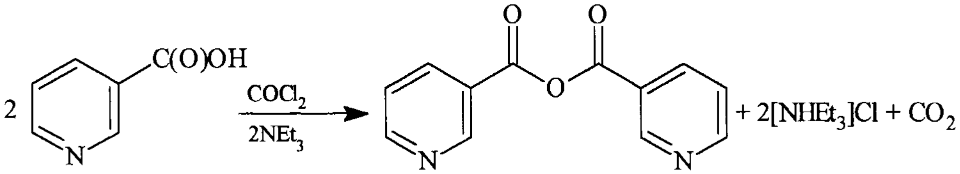
The reaction of phosgene with a mixture of perfluoro acid salts, $K[CF_3(CF_2)_nCO_2]$ (n = 0, 1, 2 or 6) and $K[OC(CF_3CF_2)_3]$ results in the preparation of perfluorocarboxylic esters [1045]:

$$K[R_fC(O)O] + K[OC(C_2F_5)_3] \longrightarrow R_fC(O)OC(C_2F_5)_3 + 2KCl + CO_2$$
$$(R_f = CF_3(CF_2)_n;\ n = 0,\ 1,\ 2 \text{ or } 6)$$

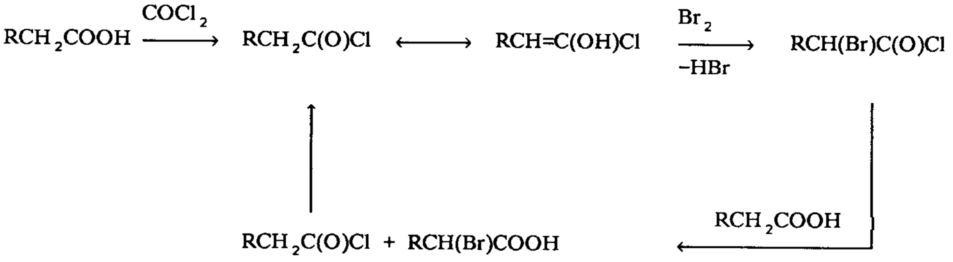
Acrylic and methacrylic anhydrides have been synthesized from the acids (stabilized by a polymerization inhibitor) by the addition of $COCl_2$ in a non-aqueous solvent (containing at least one molar equivalent of triethylamine) at −5 to +20 °C [278c]:

$$2CH_2{=}C(R)C(O)OH + COCl_2 + 2NEt_3 \longrightarrow CH_2{=}C(R)C(O)OC(O)C(R){=}CH_2 + CO_2 + 2[NHEt_3]Cl$$

Carbon dioxide is evolved and triethylammonium chloride is precipitated at, or upon warming to, room temperature. Under rigorously dry conditions, the anhydride of 3-pyridine carboxylic acid can be prepared [1716a]:



Phosgene can act as a catalyst for the bromination of long-chain aliphatic acids at the 2-position [2029]. Carboxylic acids have negligible enol content, and are thus resistant to chlorination. Acid chlorides, however, are slightly enolic. The rôle of phosgene is probably to convert some of the acid to the corresponding acid chloride. The enol form of the acid chloride is then brominated and, by exchange reactions, the brominated acid chloride results in the formation of the acid, brominated in the 2-position, more acid halide being generated in the process. The reaction is thus a modification of the Hell-Volhard-Zelinsky reaction, using phosgene in the place of phosphorus. The reaction is illustrated below:



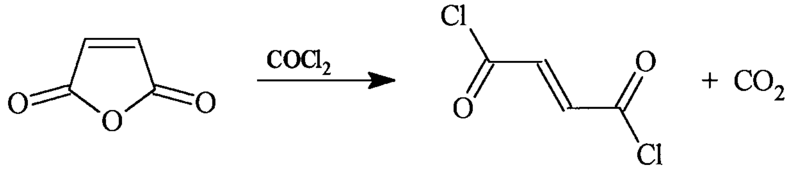
$$\begin{tikzcd}
RCH_2COOH \arrow[r, "COCl_2"] & RCH_2C(O)Cl \arrow[r, leftrightarrow] & RCH{=}C(OH)Cl \arrow[r, "Br_2", "-HBr"'] & RCH(Br)C(O)Cl \arrow[dll, "RCH_2COOH"] \\
 & RCH_2C(O)Cl + RCH(Br)COOH \arrow[u] & &
\end{tikzcd}$$

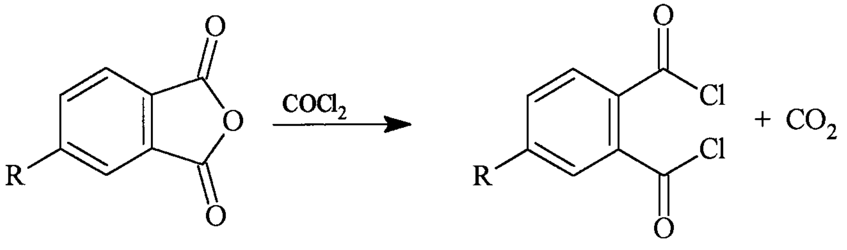
10.3.4.2 Acid anhydrides

Only a limited amount of work has been published concerning the reactions of phosgene with carboxylic acid anhydrides, despite the fact that the product acid chlorides, formed as illustrated in Equation (10.23), are generated without concomitant formation of co-product hydrogen chloride, as in the case for the corresponding reaction of the carboxylic acids.

$$RC(O)OC(O)R + COCl_2 \longrightarrow 2RC(O)Cl + CO_2 \qquad (10.23)$$

Reaction (10.23) (R = Me, Bu, Me_2CHCH_2, or Ph) may be catalysed by *N*,*N*-dialkylcarboxamides, such as dmf, at between 40 and 150 °C [388]. Using iron(III) catalysts, such as iron(III) chloride, in a sealed tube, the intramolecular anhydrides were efficiently converted into their acid chlorides [278a]:

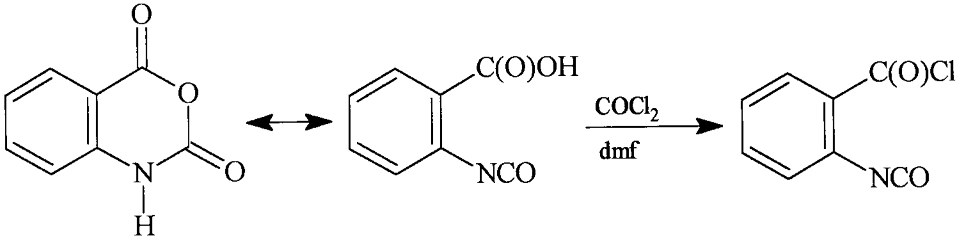




(10.27; R= H)

Both anhydride and acid functions were converted into –C(O)Cl groups when phosgene was passed into a solution of (**10.27**; R = COOH) in benzene containing dmf at 65 °C [1415,2084].

Another interesting example of catalysis by dmf involves the reaction of phosgene with isatoic anhydride [2087c]:



2-Isocyanatobenzoic acid is the most likely intermediate of this reaction [2087c].

10.3.4.3 Esters

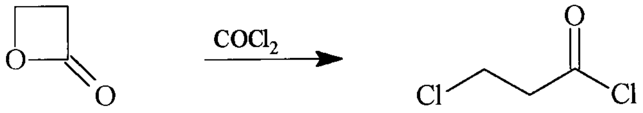
Esters are frequently used as solvents in reactions involving phosgene, but in the presence of catalysts, reaction can be induced according to the Equation (10.24) [4b]. For

$$RC(O)OR' + COCl_2 \longrightarrow RC(O)Cl + R'Cl + CO_2 \qquad (10.24)$$

example, $PhC(O)O(CH_2)_3Me$ was converted into $PhC(O)Cl$ and $Me(CH_2)_3Cl$ by reaction with $COCl_2$ over 6 h at *ca.* 140 °C [4b].

10.3.4.4 Lactones

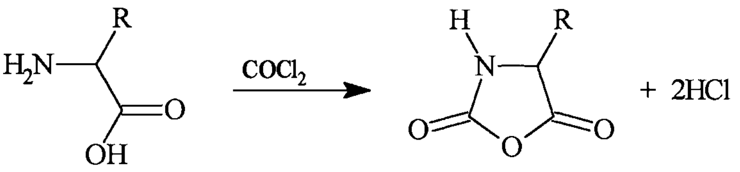
Lactones undergo ring-opening when treated with phosgene. In the presence of HCl or $AlCl_3$ at 50 °C, 3-propanolide reacts with $COCl_2$ according to [1474]:



Treatment of 4-butanolide with $COCl_2$ and a catalytic amount of pyridine at 120 °C gave 4-chlorobutanoyl chloride [4b]. The reactions of phosgene with 4-butanolide, 4-methyl-4-butanolide, or 5-pentanolide to give the corresponding acid chlorides are claimed to be catalysed by tertiary amines, heavy metals, sulfuric acid, phosphoric acid, phosphorus chlorides, $POCl_3$, $AlCl_3$, SO_2Cl_2 or chlorosulfonic acid [4b], although some of these materials, in addition to $ZnCl_2$ and $BF_3.OEt_2$, are known to give rise to polymers [1474].

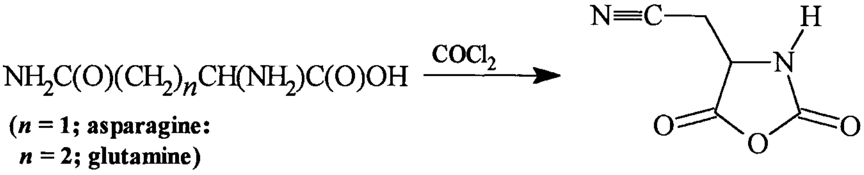
10.3.4.5 Amino acids (and esters)

Phosgene reacts with 2-amino acids (usually suspended in an ether solvent) to give oxazolidine-2,5-diones (*N*-carboxy anhydrides) [562,626,702,957,1064,2003]:



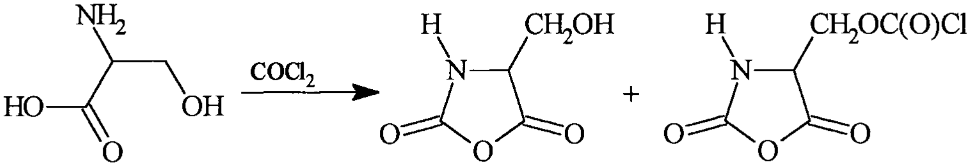
The *N*-substituted carbamoyl chloride is considered to be the intermediate of this reaction [626]. *N*-methyl-2-amino acids [1152] and *N*-benzyloxy-2-amino acids [22] react similarly to give the corresponding oxazolidine-2,5-diones. Phosgene has been used as a reagent for the enantiomeric resolution of *N*-methyl-2-amino acids by gas chromatography [1152].

The dehydration of asparagine, glutamine, and derivatives, with phosgene results in the formation of nitriles [2187]:

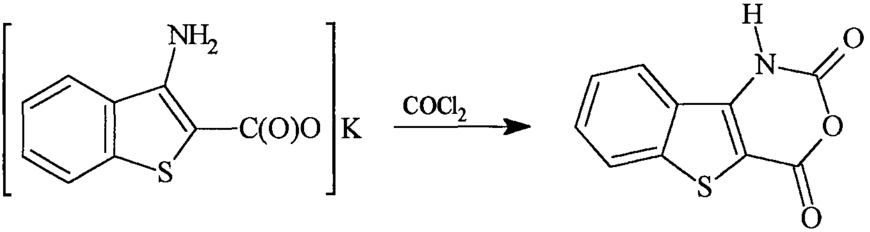


(*n* = 1; asparagine:
***n* = 2; glutamine)**

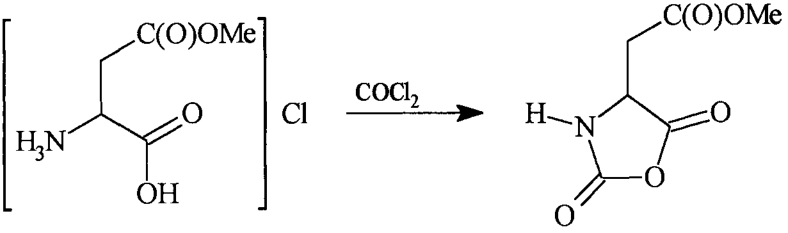
Amino acids containing a hydroxyl group can give the corresponding chloroformate derivative as a co-product; hence, serine reacts with $COCl_2$ according to [1029]:



Reaction of the potassium salt of 3-aminobenzo[*b*]thiophene-2-carboxylic acid with phosgene gave the corresponding anhydride [412]:



and the chloride salt of a protonated methyl ester of aspartic acid cyclizes upon treatment with phosgene to give an aspartame precursor [2045a]:



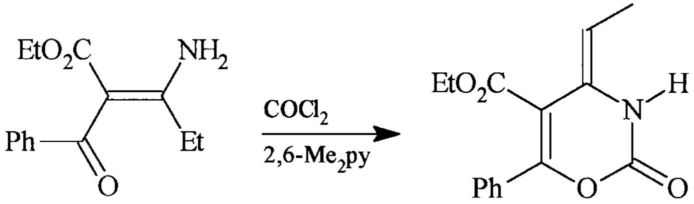
Phosgene has been used as a condensing agent in peptide synthesis [2183], and its effect on the polypeptide hormone, insulin, has been examined [1422,1423]. It is assumed that the $COCl_2$ reacts preferentially with the amino groups of the insulin, and that inter- or intra-molecular linkages are created [1423]:

$$2(Ins)NH_2 + COCl_2 \longrightarrow (Ins)NHC(O)NH(Ins) + 2HCl$$

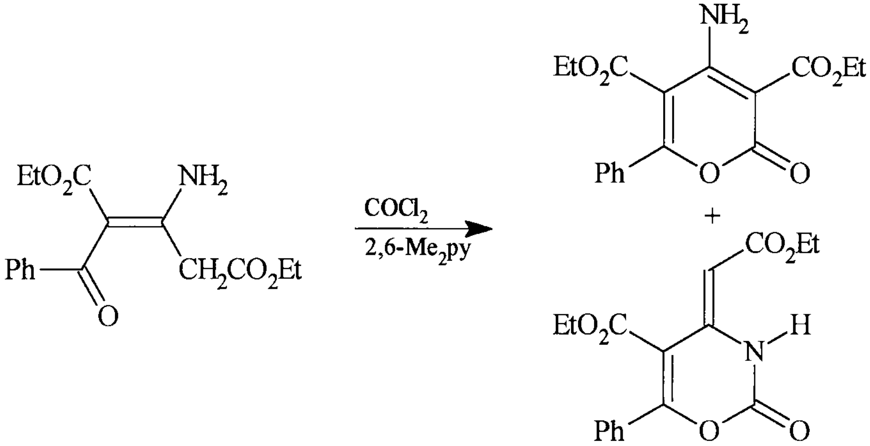
Esters of 2-amino acids, $RCH(NH_2)CO_2R'$, do not cyclize, but rather give the corresponding isocyanate, $RCH(NCO)CO_2R'$ ($R = PhCH_2SCH_2$, $R' = CH_2Ph$) [1276]. The treatment of amino acid esters with phosgene has been used as a method for the separation of the parent amino acids; the resulting isocyanato esters being readily separated by fractional distillation *in vacuo* [1062]. In the presence of pyridine, however, $COCl_2$ and $EtO_2CCH(NH_2)CO_2Et$ give a urea [1264]:

$$2EtO_2CCH(NH_2)CO_2Et + COCl_2 \longrightarrow \{(EtO_2C)_2CHNH\}_2C{=}O + 2HCl$$

Phosgene, in the presence of 2,6-dimethylpyridine, reacts with the alkyl esters of 3-amino-2-benzoylcrotonic acid to give 1,3-oxazin-2-ones as the major products [2148]. These products are derived from the reaction of the two molar equivalents of the amino ester with two or three equivalents of phosgene. The reaction of phosgene/2,6-dimethylpyridine with ethyl 3-amino-2-benzoyl-2-pentenoate gave a small yield of 1,3-oxazin-2-one:



whereas reaction with an analogous alkene gave a mixture of products [2148]:



10.4 REACTIONS WITH ORGANOSILICON COMPOUNDS

Since the mid-sixties, over a hundred papers have been published concerning the use of phosgene in the synthesis of organosilicon compounds, revealing the preparation of many new substances, some of which have potential commercial value in the growing area of silicone chemistry. A review dealing specifically with the rôle of phosgene in the chemistry of organosilicon compounds has appeared recently [1409], summarizing much of the original (largely Russian) work. This section has therefore drawn heavily on that work, and provides an update of the literature since its publication.

10.4.1 C-silyl-substituted compounds

The reactions of phosgene with organosilicon compounds in which the reactive functional group is attached to carbon are not fundamentally different from the parent carbon-substituted materials [1409]. Hence the aminoalkylsilanes and the hydroxyalkylsilanes (or their thio analogues) react according to Equations (10.25) [1161a,1406a,1409], (10.26) [1161a,1406a,1409], and (10.27) [1406a,1409]:

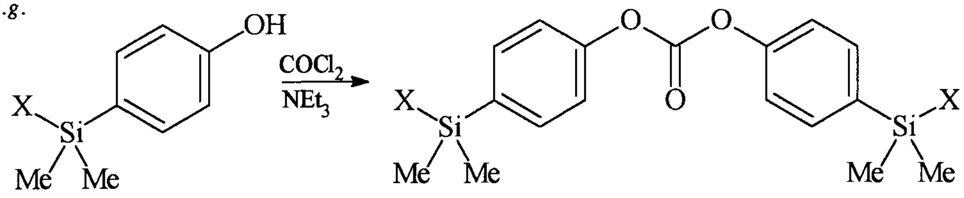
$$R_3Si(CH_2)_nNH_2 + COCl_2 \longrightarrow R_3Si(CH_2)_nNCO + 2HCl \qquad (10.25)$$
$$(n = 1 \text{ or } 3)$$

$$R_3Si(CH_2)_nOH + COCl_2 \longrightarrow R_3Si(CH_2)_nOC(O)Cl + HCl \qquad (10.26)$$
$$(n = 1, 2 \text{ or } 3)$$

$$Me_3Si(CH_2)_3SH + COCl_2 \xrightarrow{NEt_3} Me_3Si(CH_2)_3SC(O)Cl \qquad (10.27)$$

Secondary and tertiary amines react with $COCl_2$ to give the corresponding organosilicon carbamoyl chlorides [1409] and, as with conventional alcohols and phenols, the organosilicon analogues (when present in excess, at higher reaction temperatures, and by using HCl acceptors) can be converted into carbonates [1405a,1408,1409]:

e.g.



(X = H, Cl or OR)

As with conventional phenols, silicon-substituted phenols are unreactive towards phosgene at room temperature [1408]. In the presence of NEt_3, $HMe_2Si\text{-}2\text{-}C_6H_4OH$ and $HMe_2Si\text{-}4\text{-}C_6H_4OH$ were converted into the expected chloroformate derivatives.

The disiloxane diols, typified by $HOCH_2SiMe_2OSiMe_2CH_2OH$, give the corresponding chloroformates upon treatment with phosgene [793].

The nitrile, Me_3SiCN, interacts with $COCl_2$ to give carbonyl dicyanide, $CO(CN)_2$, which reacts with a further molecule of Me_3SiCN to form $Me_3SiOC(CN)_3$ [1250]:

$$COCl_2 + 2Me_3SiCN \longrightarrow CO(CN)_2 + 2Me_3SiCl$$

$$CO(CN)_2 + Me_3SiCN \longrightarrow Me_3SiOC(CN)_3$$

10.4.2 N*-silyl-substituted compounds*

10.4.2.1 Silylamines

Reactions of phosgene at the Si-N bond frequently result in the formation of isocyanates with concomitant cleavage of the Si-Cl moiety, Equation (10.28) [1408a,1409]:

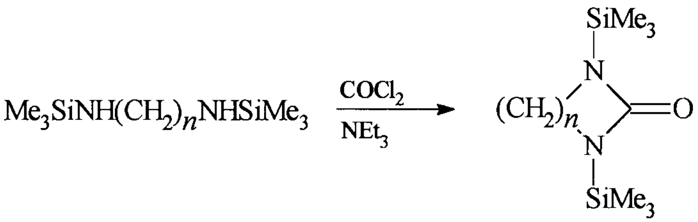
$$R_3Si(CH_2)_3NHSiMe_3 \xrightarrow{COCl_2} R_3Si(CH_2)_3NCO + HCl + Me_3SiCl \qquad (10.28)$$

The reactions of phosgene with primary *N*-silyl-substituted amines take place at lower temperatures than the corresponding unsilylated amines and, in the case of lower alkyls, the unstable *N*-silylcarbamoyl chloride intermediate is irreversibly decomposed to the isocyanate at low temperatures, consistent with Equation (10.29):

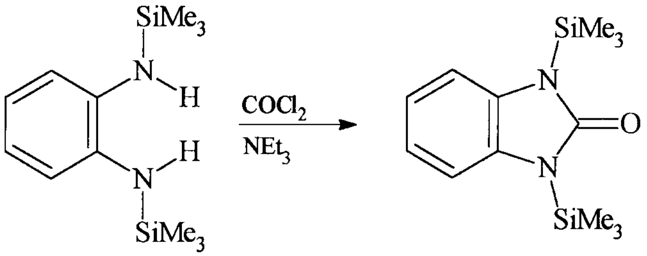
$$RNHSiMe_3 \xrightarrow[0\ ^\circ C]{COCl_2} Me_3SiN(R)C(O)Cl \longrightarrow RNCO + Me_3SiCl \qquad (10.29)$$

In contrast, the corresponding alkyl carbamoyl chlorides are relatively stable, and require the presence of base and temperatures of *ca.* 100 °C in order to undergo dehydrochlorination efficiently [1409].

With certain silylated diamines, phosgene reacts to form the corresponding substituted urea, Equations (10.30) (n = 3 or 4) and (10.31) [197a]. However, for longer chains, *viz.* $Me_3SiNH(CH_2)_nNHSiMe_3$ when n = 6, the expected diisocyanate, $OCN(CH_2)_6NCO$ is formed [2133].



(10.30)



(10.31)

N,*N*-disilyl-substituted amines react with $COCl_2$ at low temperatures (*ca.* 0 °C) to give the corresponding monoisocyanate [1409]:

$$(Me_3Si)_2NR \xrightarrow{COCl_2} Me_3SiN(R)C(O)Cl \longrightarrow RNCO + Me_3SiCl$$

However, when R = H, a mixture of products is formed [1409]:

$$4(Me_3Si)_2NH + 3COCl_2 \longrightarrow 5Me_3SiCl + 3Me_3SiNCO + [NH_4]Cl$$

The sodium salt of $(Me_3Si)_2NH$, in contrast, reacts with phosgene to produce a carbodiimide [1409]:

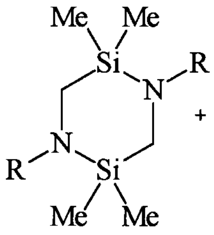
$$2[(Me_3Si)_2N]Na + COCl_2 \longrightarrow Me_3SiN{=}C{=}NSiMe_3 + (Me_3Si)_2O + 2NaCl$$

Diisocyanates, OCN-X-NCO {X = $(CH_2)_6$, CH_2-3-$C_6H_4CH_2$, or 4-$C_6H_4CH_2C_6H_4$-4}, are formed from the reactions of $(Me_3Si)_2NXN(SiMe_3)_2$ with phosgene [2133].

N-silyl-substituted secondary amines combine with phosgene, as illustrated in Equation (10.32), to give a carbamoyl chloride [1409]. This proceeds at a faster rate with phosgene

$$R_2NSiMe_3 + COCl_2 \longrightarrow R_2NCOCl + Me_3SiCl \qquad (10.32)$$

than with acyl halides or chloroformates. Reactions with 2,5-disilapiperazine derivatives also result in the formation of the corresponding carbamoyl chlorides, Equation (10.33) [1409], although when an excess of phosgene is not employed, ureas are produced as illustrated in Equation (10.34) [1409]. For R = $SiMe_3$, the reaction proceeds further to give the isocyanate, $ClMe_2SiCH_2CNO$ [1409].



$$+ 2COCl_2 \longrightarrow 2ClMe_2SiCH_2N(R)C(O)Cl \qquad (10.33)$$

$$\xrightarrow{COCl_2} ClMe_2SiCH_2N(R)C(O)N(R)CH_2SiMe_2Cl \qquad (10.34)$$

10.4.2.2 *N*-silyl-substituted carboxylic acid amides (or silylamides)

At temperatures below ambient, *N*-silyl-substituted amides react with phosgene to give nitriles, Equation (10.35) [1409].

$$\mathrm{RC(O)NHSiMe_3 + COCl_2 \longrightarrow RCN + Me_3SiCl + CO_2 + HCl} \qquad (10.35)$$

The *N*-alkyl- and *N*-aryl-*N*-(trimethylsilyl)amides have been noted to react with phosgene to give a novel class of carbamoyl chlorides [1409]:

$$\mathrm{RC(O)NR'SiMe_3 + COCl_2 \longrightarrow RC(O)NR'C(O)Cl + Me_3SiCl}$$

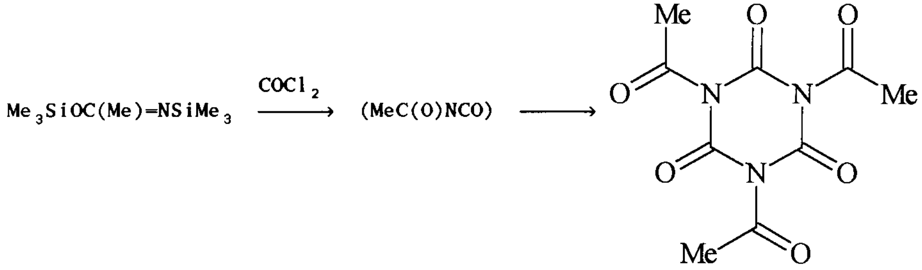
$$\mathrm{RC(O)NR'C(O)Cl \xrightarrow{150\ ^\circ C} RC(Cl){=}NR' + CO_2}$$

Disilyl-substituted amides react with phosgene according to the following scheme [1409]:

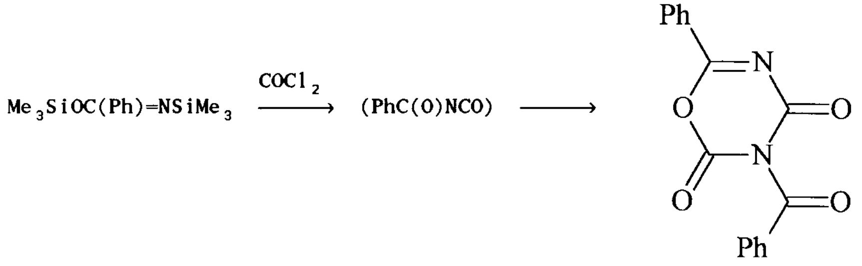
$$\begin{tikzcd}
\mathrm{RC(O)N(SiMe_3)_2} \arrow[r, shift left] \arrow[d, "\mathrm{COCl_2}"] & \mathrm{RC(OSiMe_3){=}NSiMe_3} \arrow[l, shift left] \arrow[d, "\mathrm{COCl_2}"] \\
\mathrm{RC(O)N\{C(O)Cl\}SiMe_3} & \mathrm{RC(OSiMe_3){=}NC(O)Cl}
\end{tikzcd}$$

10.4.2.3 *N*-silyl-substituted imines (or silylimines) and derivatives

The reactions of *N*-silyl-substituted ketimine derivatives with phosgene result in the formation of acyl isocyanates, which trimerize or dimerize under the reaction conditions [1854]:

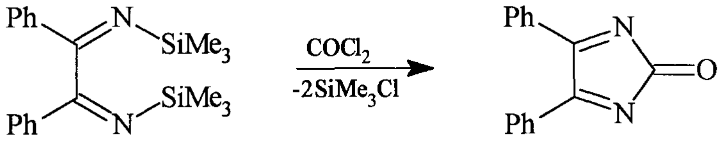


$$\mathrm{Me_3SiOC(Me){=}NSiMe_3 \xrightarrow{COCl_2} (MeC(O)NCO) \longrightarrow}$$



$$\mathrm{Me_3SiOC(Ph){=}NSiMe_3 \xrightarrow{COCl_2} (PhC(O)NCO) \longrightarrow}$$

The *N*-silyl-disubstituted diimine, $Me_3SiN{=}C(Ph)C(Ph){=}NSiMe_3$, reacts with phosgene to form an imidazolidone [2066a]:



Addition of phosgene to silyl substituted iminoesters results in the formation of *N*-chlorocarbonyl-iminoesters, which are decomposed thermally into acylisocyanates [1409]:

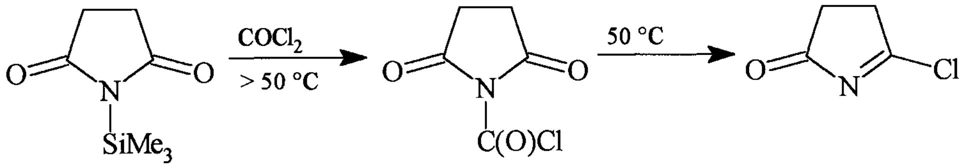
$$RC(OR''){=}NSiR'_3 + COCl_2 \longrightarrow RC(OR''){=}NC(O)Cl + R'_3SiCl$$

$$\downarrow \Delta$$

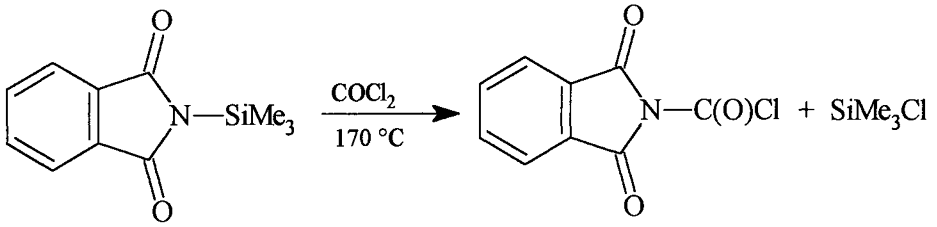
$$RC(O)NCO + R''Cl$$

10.4.2.4 *N*-silyl-substituted imides (or silylimides)

N-Trimethylsilylbutanimide combines rapidly with $COCl_2$ to give the *N*-chlorocarbonyl derivative, which readily decomposes [1409,1855a]:



In contrast, *N*-trimethylsilylphthalimide reacts with phosgene only under forcing conditions to produce the carbamoyl chloride [1409,1855a]

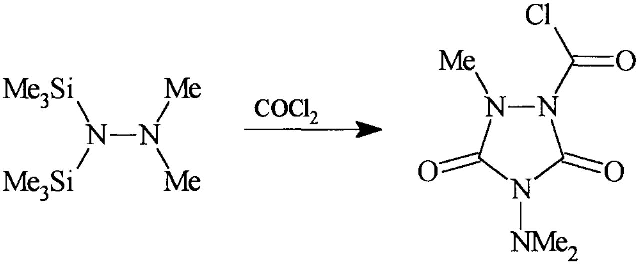


10.4.2.5 Silyl hydrazine derivatives

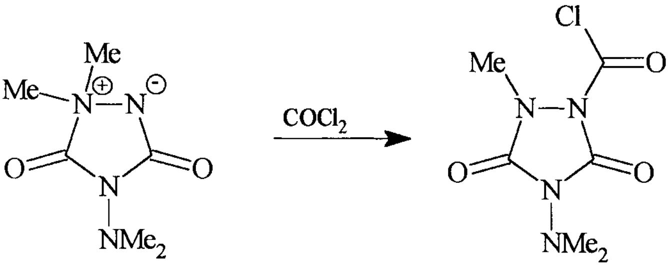
Whereas the reaction of Me_2NNH_2 with phosgene results in the formation of the urea, $Me_2NNHC(O)NHNMe_2$, protection with a silyl group prior to reaction with phosgene results in the formation of an isocyanate dimer in almost quantitative yield [1409]:

$$2Me_2NNH(SiMe_3) + 2COCl_2 \longrightarrow Me_2NN\{\mu\text{-}C(O)\}_2NNMe_2 + 2Me_3SiCl + 2HCl$$

An identical reaction product was obtained with $Me_2NN(SiMe_3)_2$ [1853]; however, treatment of $Me_2NN(SiMe_3)_2$ with phosgene at −30 °C proceeded according to [2256]:

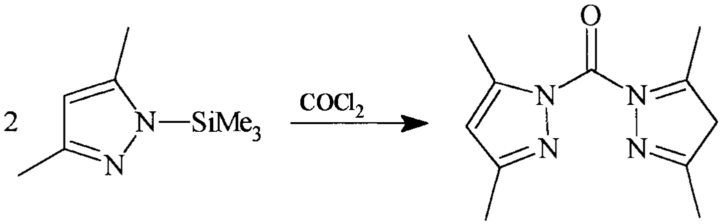


A clue to the reaction mechanism can be obtained by noting that the azoniaimidazolide (prepared by treatment of $Me_2NN(SiMe_3)_2$ with COF_2) reacted with phosgene according to [2256]:

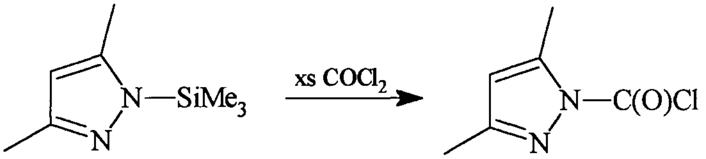


10.4.2.6 *N*-silyl-substituted azoles (or silylazoles)

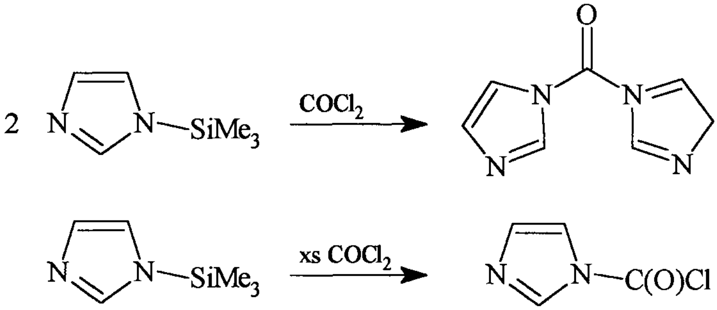
The *N*–$SiMe_3$–substituted diazoles react with phosgene to give products which depend sensitively upon the reaction conditions [1409]. For example, where a substituted pyrazole is in an excess, the substituted urea is produced:



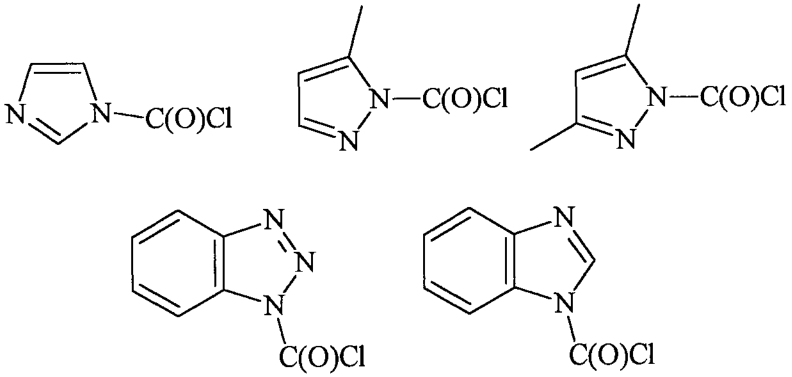
With an excess of phosgene, however, carbamoyl chlorides are formed [1409]:



Analogous reactions are found for imidazole derivatives [1409]:



The reactions of *N*-SiMe$_3$-substituted derivatives of imidazole, 3(5)-methylpyrazole, 3,5-dimethylpyrazole, benzotriazole and benzimidazole (see below, X = SiMe$_3$) with an excess of phosgene have been examined recently [1855], and are found to give high yields of the *N*-chloroformyl derivatives illustrated below:



Symmetrical *N*,*N*'-carbonylbisdiazoles are formed as by-products.

10.4.2.7 *N*-silyl-substituted ureas (silylureas) and urethanes (silylurethanes)

Reactions of phosgene with trialkyl(trimethylsilyl) ureas in toluene, at low temperatures, give trialkyl(chloroformyl) ureas [1406]:

$$R_2NC(O)N(Me)SiMe_3 + COCl_2 \longrightarrow R_2NC(O)N(Me)C(O)Cl + Me_3SiCl$$
(R = Me or Et)

On heating to 150–220 °C, the chloroformyl ureas decompose into carbon dioxide, chloromethane and 2,4,6-tris(dialkylamino)-1,3,5-triazine.

The treatment of *N*-silyl-substituted carbamate esters with phosgene at room temperature results in the formation of a thermally stable *N*-chloroformyl derivative [1406]:

$$\mathrm{NMe(SiMe_3)C(O)OEt + COCl_2 \longrightarrow NMe(COCl)C(O)OEt + Me_3SiCl}$$

10.4.3 O-Silyl-substituted compounds

10.4.3.1 Silanols

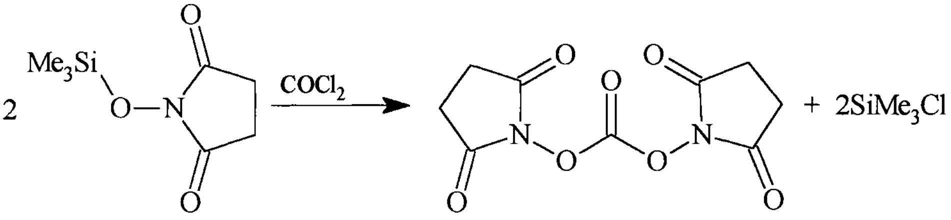
There appears to be no reports of any silyl chloroformate derivatives, $R_3SiOCOCl$. Although these materials may be postulated as reaction intermediates, the corresponding silyl chlorides are the thermodynamically and kinetically favoured products of the reactions between phosgene and silanols, Equation (10.36) [1407,1407a,1409]:

$$\mathrm{R_3SiOH \xrightarrow{COCl_2} (R_3SiOC(O)Cl) \xrightarrow{\Delta} R_3SiCl + CO_2} \qquad (10.36)$$

By using an excess of the silanol (in the presence of NEt_3), or its sodium salt, $[R_3SiO]Na$, disilyl carbonates are formed according to Equation (10.37), in which the chloroformate may again be regarded as an intermediate [1409]:

$$\begin{array}{l} \mathrm{2R_3SiOX + COCl_2 \longrightarrow R_3SiOC(O)OSiR_3} \\ \mathrm{(X = H\ or\ Na)} \end{array} \qquad (10.37)$$

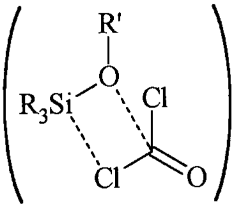
The trimethylsilyl-substituted *N*-hydroxysuccinimide (depicted below) reacts with $COCl_2$ in thf at 0 °C with cleavage at the Si–O bond to give *N,N'*-disuccinimidyl carbonate [1539]:



10.4.3.2 Silyl ethers

The reactions of phosgene with silyl ethers, R_3SiOR', give R_3SiCl and $R'OCOCl$ as products [1102,1409,1852]. The reactivity of $-SiMe_3$ derivatives of saturated alcohols decreases as the alkyl group lengthens ($Me_3SiOMe > Me_3SiOEt > Me_3SiOPr > Me_3SiOBu$), as the degree of branching increases ($Me_3SiOPr > Me_3SiOCHMe_2$; $Me_3SiOBu > MeSiOCH_2CHMe_2$), and upon replacement of acyclic groups with cyclic groups ($MeSiOCHMe_2 > Me_3SiOC_6H_{11}$). The reactivity of $-SiMe_3$ derivatives of unsaturated alcohols falls as the degree of unsaturation increases ($Me_3SiOCHMe_2 > Me_3SiOCH_2CH{=}CH_2 > Me_3SiOCH_2C{\equiv}CH$) and as the length of the branching group increases ($Me_3SiOCH_2CH{=}CH_2 > Me_3SiOCH_2CH{=}CHPh > Me_3SiOCH_2C(Me){=}CH_2$) [1852]. In a non-polar solvent, the mechanism is considered to involve the transition state illustrated in Equation (10.38) [1409]. This reaction has been used

$R_3SiOR' + COCl_2 \longrightarrow$

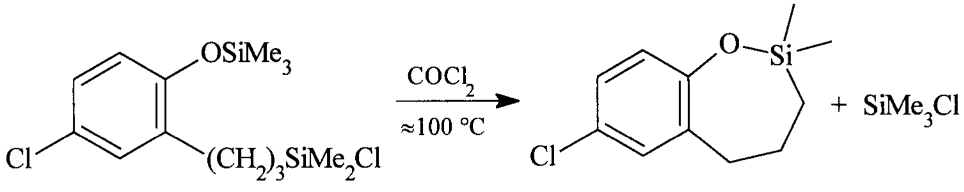


$\longrightarrow R_3SiCl + R'OC(O)Cl$ (10.38)

to prepare bis-chloroformates [1852]:

$$Me_3SiOCH_2SiMe_2OSiMe_2CH_2OSiMe_3 + 2COCl_2 \longrightarrow ClC(O)OCH_2SiMe_2OSiMe_2CH_2OC(O)Cl + 2Me_3SiCl$$

However, reaction of substituted silylated phenols with phosgene does not always give the chloroformate product, owing to the faster reaction represented below [1102]:

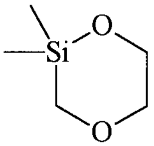


Cyclic silyl ethers undergo ring opening with phosgene to produce chloroformates [1409]:

$$\overline{R_2Si(CH_2)_nO} + COCl_2 \longrightarrow ClR_2Si(CH_2)_nOC(O)Cl$$
$$(n > 3)$$

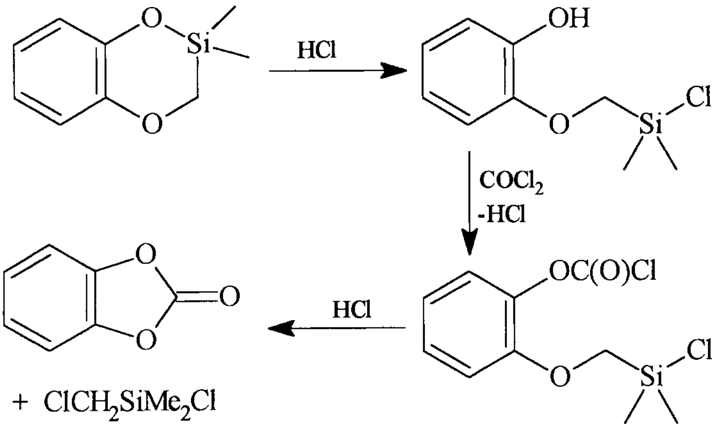
This reaction is most vigorous for $n = 3$, and reactivity falls dramatically with increasing ring size. The reaction may, however, be catalysed by Lewis acids and is accelerated sharply by increasing the temperature. The polymerization products of these cyclic ethers, having a general formula $-\!\![\, O(CH_2)_3SiMe \,]\!\!-_n$, react much more sluggishly with $COCl_2$. At high temperatures, using a zinc(II) chloride catalyst, only low yields of the corresponding chloroformate were obtained [1409].

The dioxane derivative, illustrated below, reacts vigorously with phosgene to give high yields of chloroformate [1102]:

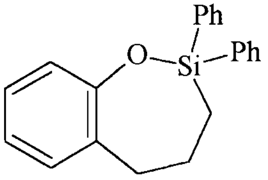


$+ COCl_2 \longrightarrow ClMe_2SiCH_2OCH_2CH_2OC(O)Cl$

However, the related phenylene derivative reacts with phosgene only when the ring is opened on heating to 120–140 °C in the presence of gaseous HCl [1102]:



The inertness of phosgene towards compounds containing the Si–O–aryl linkage is a general observation, and is extended to the compound (**10.28**) for which no reaction occurs with HCl/$COCl_2$ mixtures at temperatures as high as 200 °C for prolonged periods [1102].



(10.28)

10.4.3.3 Siloxane derivatives

Organosilicon diols of the disiloxane series can react with phosgene with cleavage of the siloxane and ether linkages occurring, in addition to the formation of the bischloroformates [793,1408]:

$$O(SiMe_2XOH)_2 \xrightarrow{COCl_2} O(SiMe_2XOC(O)Cl)_2 + ClSiMe_2XOC(O)Cl + ClSiMe_2XCl$$
$$\{X = CH_2 \text{ or } (CH_2)_3\}$$

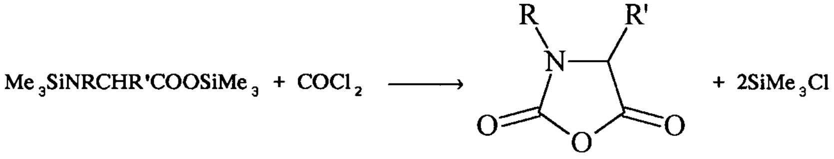
The mono-chloroformate, however, is formed as a result of the action of HCl (liberated in the reaction) on the disiloxane linkage, rather than by the action of phosgene itself. Indeed, phosgene has no action upon passing into the boiling $Me_3SiOSiMe_3$ for a prolonged period [1161a,1409].

Organosilicon diols possessing ether linkages combine with phosgene to give a large spectrum of products (arising both by reaction with $COCl_2$ and with HCl):

$$\begin{aligned}O(SiMe_2CH_2OCH_2CH_2OH)_2 \xrightarrow{COCl_2} \; & O(SiMe_2CH_2OCH_2CH_2OCOCl)_2 + \\ & ClSiMe_2CH_2OCH_2CH_2OCOCl + O(SiMe_2CH_2OCOCl)_2 + \\ & O(SiMe_2CH_2Cl)_2 + ClSiMe_2CH_2Cl + ClCH_2CH_2Cl + \\ & ClCOOCH_2CH_2OCOCl + ClCOOCH_2CH_2Cl\end{aligned}$$

10.4.3.4 Amino acid derivatives

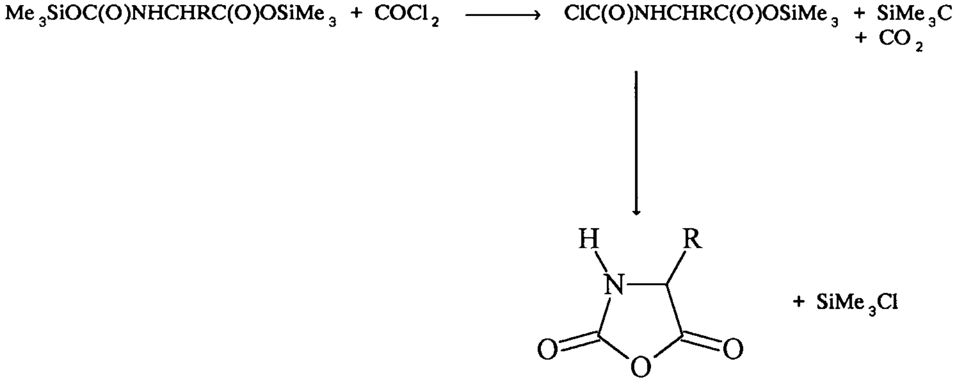
Trimethylsilyl esters of *N*-trimethylsilylamino acids react with phosgene to give the products illustrated below [1169]:



(R = H, Me or CO_2Et; R' = H, Me_2CHCH_2, Bz, $MeSCH_2CH_2$ or Me_3SiO-4-$C_6H_4CH_2$)

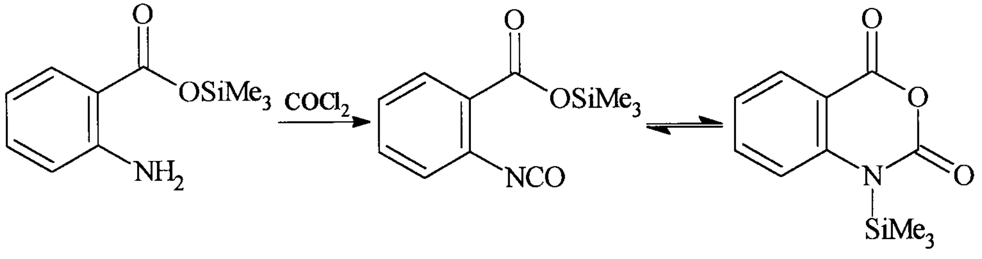
With excess of the silyl compound, or at lower temperatures, urea derivatives, such as $(Me_3SiOCOCHRNH)_2CO$, are formed [1169]. The corresponding esters of *N*-siloxycarbonylamino acids combine easily with phosgene at temperatures above 0 °C, also to give oxazolidine-2,5-diones [1169a]:

e.g.



These methods of synthesis of the *N*-carboxyanhydrides do not involve elimination of hydrogen chloride, and thus permit retention of configuration of the ester groups. The silyl esters can be vacuum distilled without decomposition, and since (unlike their unsilylated analogues) they are readily soluble in non-polar solvents, the silylation methods constitute a suitable means of preparing this important class of compounds [1409].

The trimethylsilyl derivatives of aminobenzoic acids (H_2N-*n*-$C_6H_4COOSiMe_3$; n = 2, 3 or 4) react with phosgene at 0–10 °C in solutions containing triethylamine, to give the corresponding isocyanate, OCN-*n*-$C_6H_4COOSiMe_3$. The 2-isomer, however, exists in equilibrium with the cyclic anhydride [1161]:



10.4.3.5 Amino ester derivatives

The addition of phosgene to amino esters, silylated at the nitrogen atom, gives the expected isocyanate derivative [1409]:

$$Me_3SiNHCHRC(O)OEt \xrightarrow{COCl_2} OCNCHRC(O)OEt$$

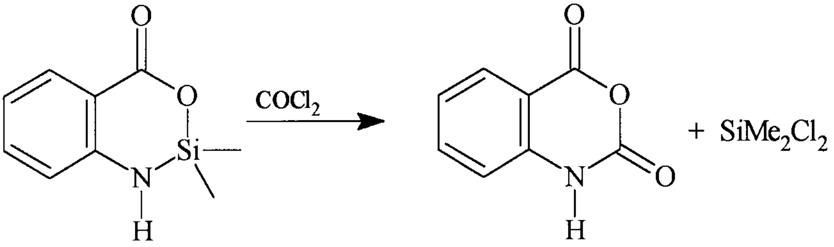
(R = Me or CMe_2H)

In the presence of at least an equimolar amount of NEt_3, this reaction was extended to the preparation of *N*–carbonyl–α–amino acid esters derived from a wide variety of amino acids [460].

N,*O*–bis(trimethylsilyl)carbamate, $Me_3SiNHC(O)OSiMe_3$, with phosgene at 60–70 °C, gave Me_3SiNCO [1160]:

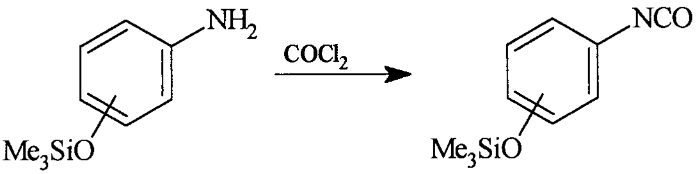
$$\begin{tikzcd}
Me_3SiNHC(O)OSiMe_3 \arrow[r, "+COCl_2", "-Me_3SiCl"'] & (ClC(O)NHC(O)OSiMe_3) \arrow[r, "-HCl"] & (OCNC(O)OSiMe_3) \arrow[d, "-CO_2"] \\
 & & O{=}C{=}NSiMe_3
\end{tikzcd}$$

The *N*,*O*–silyl derivative shown below is converted into an anhydride on treatment with phosgene [1409]:

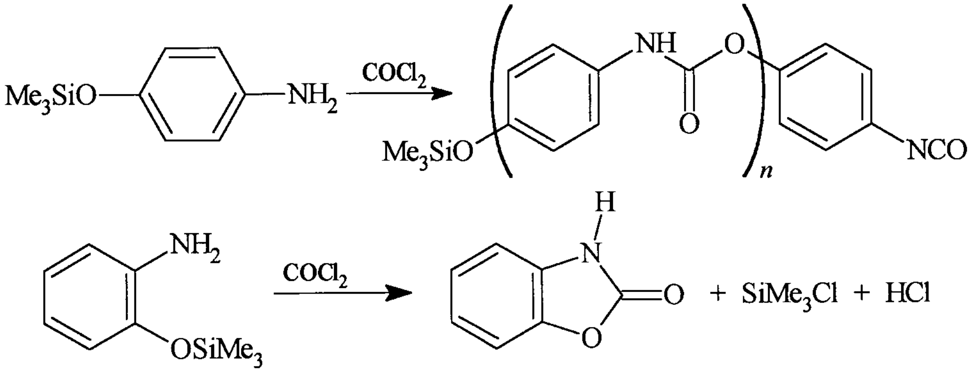


10.4.3.6 Amino phenol derivatives

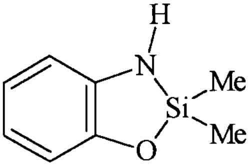
Under mild conditions, and in the presence of NEt$_3$, silyl derivatives of aminophenols are converted by phosgene into the corresponding isocyanates [1159a]:



The Si–O bonds are cleaved at higher temperatures; the 4–OSiMe$_3$ isomer reacting to give an oligomer and the 2–isomer giving a cyclic derivative [1159a]:

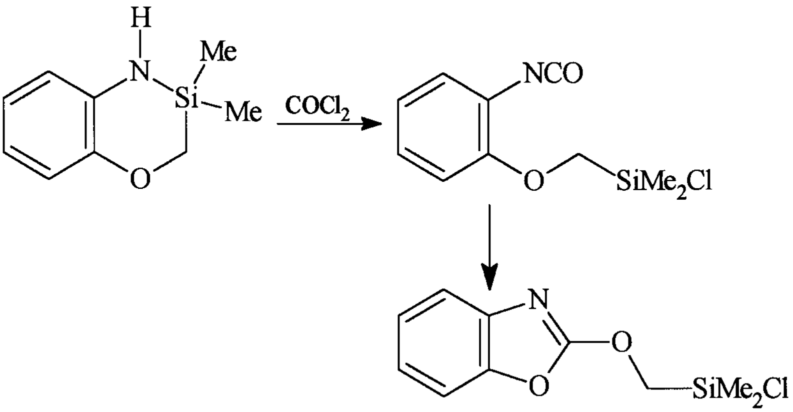


The cyclic product is also formed readily from the reaction of phosgene with compound (10.29) [1409]. Reaction of a related compound containing a six-membered ring, however,



(10.29)

results in the formation of a five-membered heterocyclic compound *via* the rearrangement of an unstable isocyanate [1409]:

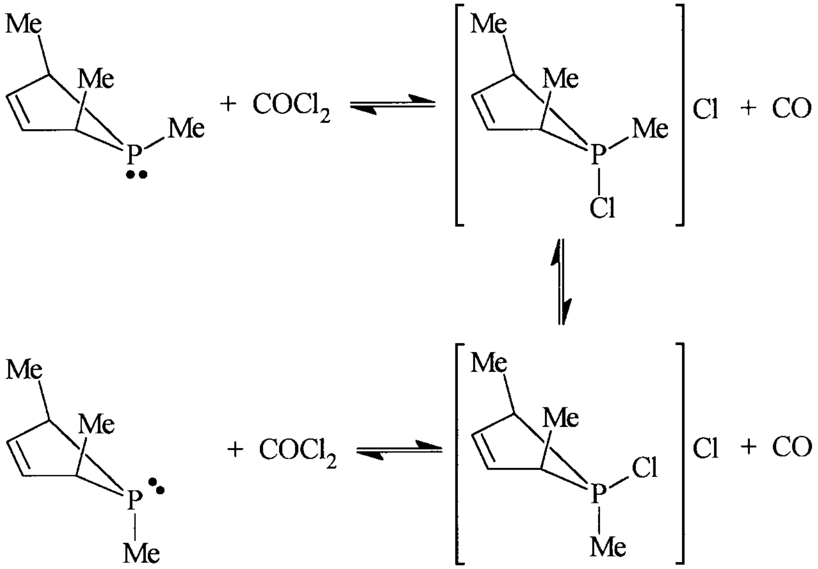


10.5 REACTIONS WITH ORGANOPHOSPHORUS AND RELATED COMPOUNDS

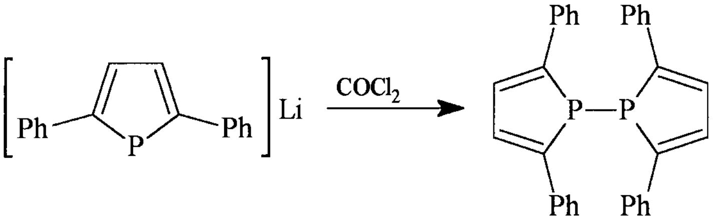
10.5.1 Heterocyclic derivatives

The relatively stable carbon–phosphorus bond is resistant to cleavage by phosgene in a way that is similar to a carbon–carbon bond in a hydrocarbon chain. The phosphorus atom, in its formal oxidation state of +3 in an organic compound, however, may react by virtue of its unshared electron pair.

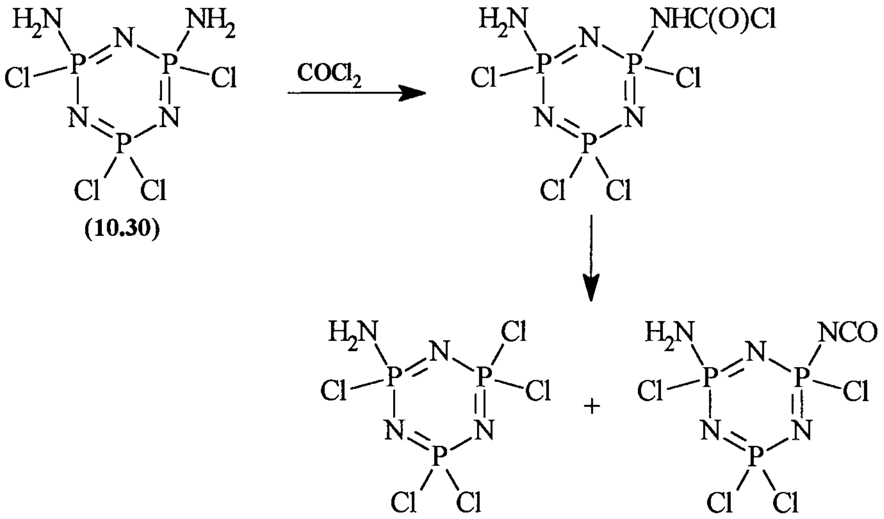
Cis–1–alkyl(or aryl)–2,5–dimethyl–3–phospholenes were noted to isomerise to the *trans*–isomers in $CDCl_3$, the isomerization being a result of small quantities of $COCl_2$ in the solvent. Addition of an excess of phosgene to the *cis*– isomer gave the quaternary salt depicted in the following scheme, which quickly equilibrated to another salt (which could also be prepared from the reaction of the *trans*– isomer with an excess of phosgene [877]:



Phosphido salts are particularly reactive towards halogen–containing compounds. Not surprisingly, therefore, the lithium salt of the 2,5–diphenylphospholyl anion reacts with phosgene to give 2,2',5,5'–tetraphenylbiphospholyl [359]:



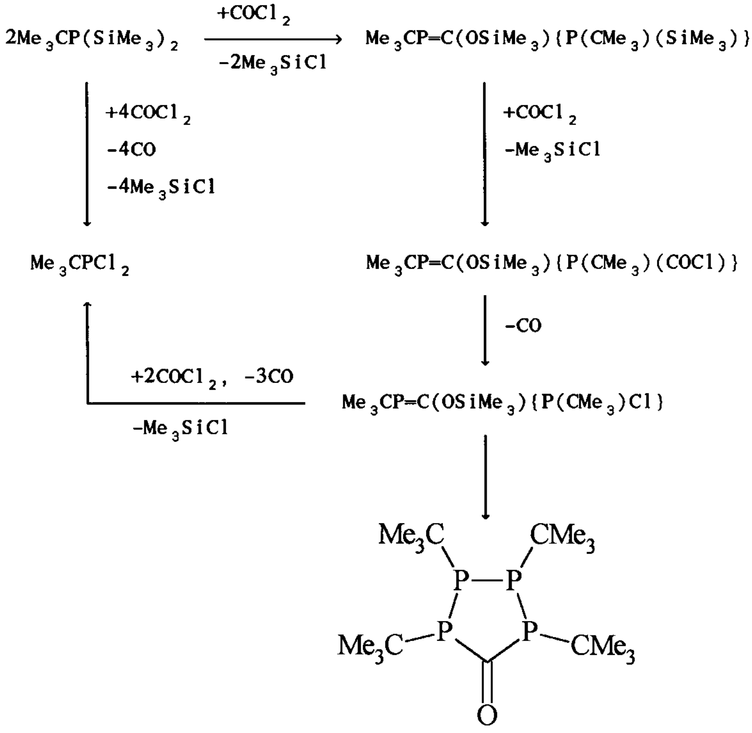
Treatment of the tetrachlorodiaminocyclotriphosphazene (**10.30**) with a cold solution of phosgene in chlorobenzene gives the carbamoyl chloride as an intermediate. Heating this solution under reflux for several hours gave both a pentachloro derivative and an isocyanate [2018]:



(10.30)

10.5.2 Silyl phosphanes

The reaction of $Me_3CP(SiMe_3)_2$ with phosgene occurs with the elimination of Me_3SiCl and CO, and the formation (*via* several detectable intermediates) of a cyclic phospha-urea derivative, **(10.31)**, as illustrated in the following scheme [71]:

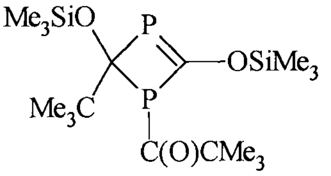


(10.31)

The heterocycle **(10.31)** may also be formed by the reaction of phosgene with the tetraphosphorus compound depicted below [71]:

$$(Me_3Si)P(CMe_3)P(CMe_3)P(CMe_3)P(CMe_3)(SiMe_3) + COCl_2 \longrightarrow \mathbf{(10.31)} + 2SiMe_3Cl$$

Treatment of $Me_3SiP{=}C(OSiMe_3)(CMe_3)$ with $COCl_2$ gave an unexpected reaction product, a diphosphacyclobutene, **(10.32)** [70]:



(10.32)

10.5.3 Phosphine oxide derivatives

Phosphine oxides, possessing a wide variety of R groups, are transformed into dichlorophosphoranes upon treatment with phosgene in anhydrous CH_3CN, Equation (10.39).

$$R_3PO + COCl_2 \longrightarrow R_3PCl_2 + CO_2 \qquad (10.39)$$

Ph_3PCl_2, in particular, is a useful material for the conversion of ketonic carbonyl groups into the corresponding dichlorides, and phosgene is a cheap and effective reagent which may be used, on an industrial scale, to convert the triphenylphosphine oxide back to starting material [1704]. Ph_3PCl_2 (prepared *in situ* from phosgene and $Ph_3P{=}O$ in toluene) has been employed, for example, to react with the hydroxyl groups of 2,3,6,3',4'-penta-*O*-acetylsucrose to give 4,1',6'-trichloro-4,1',6'-trideoxy-2,3,6,3',4'-penta-*O*-acetylgalactosucrose [1534a], an important precursor in the preparation of chloro-sugar sweetening agents.

In contrast, the reaction of $(HOCH_2)_3PO$ with phosgene at 70–150 °C gives only $(ClCH_2)_3PO$ [1707].

10.5.4 Phosphinic and phosphonic acid derivatives

The mechanism of the reaction of phosgene with alkyl phosphinates, Equation (10.40),

$$R_2P(O)OR' + COCl_2 \longrightarrow R_2P(O)Cl + CO_2 + R'Cl \qquad (10.40)$$

has been elucidated by following the reaction of $R_2P(O)^{18}OCH_2Ph$ (R_2 = Ph,Me) with a saturated solution of $COCl_2$ in CCl_4 [816,817]. The results indicate that the mechanism proceeds *via* a *quasi*phosphonium intermediate with phosphoryl oxygen atom as the nucleophilic centre:

$$\begin{tikzcd} R_2P(=O)^{18}OCH_2Ph \arrow[r, "COCl_2"] & {[R_2P(OCOCl)^{18}OCH_2Ph]Cl} \arrow[r, "-CO_2"] & {[R_2P(Cl)^{18}OCH_2Ph]Cl} \arrow[d] \\ & & R_2P(=^{18}O)Cl + PhCH_2Cl \end{tikzcd}$$

The reaction of $COCl_2$ with (+)-1-methylheptyl methylphenyl phosphinate gave (+)-1-methyl-1-chloroheptane and methylphenyl phosphinyl chloride [816]. This indicates that the alkyl chloride is produced by an S_N2 displacement on a *quasi*phosphonium intermediate by chloride ions.

The dialkyl alkylphosphonates, $(RO)_2P(O)R'$ (R,R' = Et,Me; Et,Et; Me_2CH,Me; Me_2CH,Et) react with phosgene to form phophonochloridates, according to Equation (10.41) [397a]. Only one ester group is replaced, and high yields of the co-produced chloroalkane

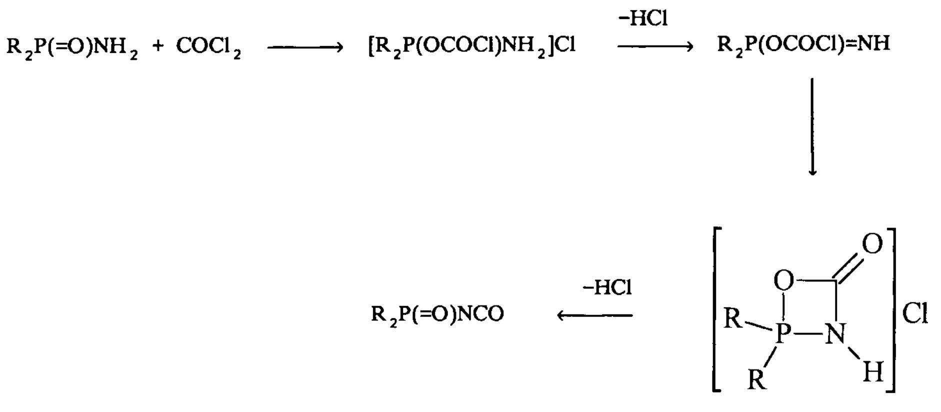
$$(RO)_2P(O)R' + COCl_2 \longrightarrow (RO)P(O)(Cl)R' + CO_2 + RCl \tag{10.41}$$

are isolated [817]. As for the analogous phosphinates, initial attack is believed to occur on the phosphoryl-oxygen atom.

Amines of phosphonic and phosphinic acids, on reaction with phosgene, are partially cleaved at the P-N bond. Thus, in addition to the formation of isocyanates, Equation (10.42), a number of by-products (such as the chlorides of the corresponding acids)

$$R_2P(O)NH_2 + COCl_2 \longrightarrow R_2P(O)NCO + 2HCl \tag{10.42}$$

are formed [508]. Both the amine and phosphoryl groups in these compounds are centres of nucleophilicity. However, the most probable course of the reaction is believed to be [508]:



10.5.5 Phosphorous and phosphoric acid derivatives

Treatment of the phosphite triesters, $P(OR)_3$ (R = Me, Et, $(CH_2)_3Me$ or CH_2CHMe) with $COCl_2$ resulted in the formation of $(RO)_2P(O)Cl$, according to Equation (10.43) [1059,1666].

$$(RO)_3P + COCl_2 \longrightarrow (RO)_2P(O)Cl + CO + RCl \tag{10.43}$$

The reaction for R = Me_2CH apparently proceeds *via* the formation of an acid chloride intermediate, $(Me_2CHO)_3P(COCl)Cl$ [666a]. This later work [1666] refutes that published earlier [1058] in which the product of the reaction of $(MeO)_3P$ with $COCl_2$ was reported to be $(MeO)_2P(O)(COCl)$ (accompanied by the elimination of MeCl). Furthermore, the addition of a second molar equivalent of $(MeO)_3P$ to the product of reaction (10.43) proceeded according to Equation (10.44) [1666] rather than forming the ester of carbonylphosphinic acid, as reported previously [1058].

$$(MeO)_2P(O)Cl + (MeO)_3P \longrightarrow (MeO)_2P(O)OP(O)(OMe)(Me) + MeCl \tag{10.44}$$

In a recent paper [1678], the mechanisms of the reactions of phosgene with the *N*-methylpyridinium salts of diphenyl phosphate and of 1,2-dimethylethenylene phosphate - a cyclic enediol phosphodiester (4,5-dimethyl-2-oxido-2-oxo-1,3,2-dioxaphosphole) - were reported. The products of the reactions (studied by ^{31}P NMR spectroscopy) are mixtures of pyrophosphates and phosphorochloridates, the proportions depending on both the structure of the phosphodiester and the experimental conditions. The free acid, diphenyl hydrogenphosphate, $(PhO)_2P(O)(OH)$, does not react appreciably with phosgene at room temperature in dichloromethane, but the *N*-methylpyridinium ($[NMepy]^+$) salts react at much lower temperatures to give, initially, the corresponding chloroformate as an intermediate:

$$[NMepy][(PhO)_2P(O)O] + COCl_2 \longrightarrow (PhO)_2P(O)OC(O)Cl + [NMepy]Cl$$

This chloroformate then either decomposes to give $(PhO)_2P(O)Cl$ and CO_2, or reacts with the starting material to form the corresponding pyrophosphate, $(PhO)_2P(O)OP(O)(OPh)_2$. Less of the phosphorochloridate is formed in the reaction of phosgene with the cyclic phosphodiester, although the mechanism is believed to follow the same general pathway [1678].

Aliphatic aminoesters of phosphoric (and thiophosphoric) acid react with phosgene, Equation (10.45), under milder conditions (*ca.* 0 °C) than do the aromatic aminoesters. Only

$$\begin{array}{l}(RO)_2P(E)NH_2 + COCl_2 \longrightarrow (RO)_2P(E)NCO + 2HCl \\ (E = O \text{ or } S)\end{array} \tag{10.45}$$

small amounts of the isocyanates are generally obtained, however, because the corresponding hydrochloride adducts are formed, which are unreactive towards phosgene under these conditions [508].

Diethyl esters of *N*-alkylamino phosphoric acid react readily with phosgene. Carbon dioxide and chloroethane are liberated, reaction occurring at the phosphoryl group in preference to the nitrogen atom [508]:

$$\mathrm{(EtO)_2P(O)NHR + COCl_2 \longrightarrow (EtO)P(O)(Cl)NHR + CO_2 + EtCl}$$

Treatment of the hexamethylphosphoric triamide, hexamethylphosphoramide, $\mathrm{(Me_2N)_3PO}$, with $\mathrm{COCl_2}$ gives $\mathrm{[(Me_2N)_3POCOCl]Cl}$, which decarboxylates to $\mathrm{[(Me_2N)_3PCl]Cl}$ – an intermediate in the preparation of the peptide coupling reagent known as the BOP reagent [341,342,778].

10.5.6 Thiophosphorus acid derivatives

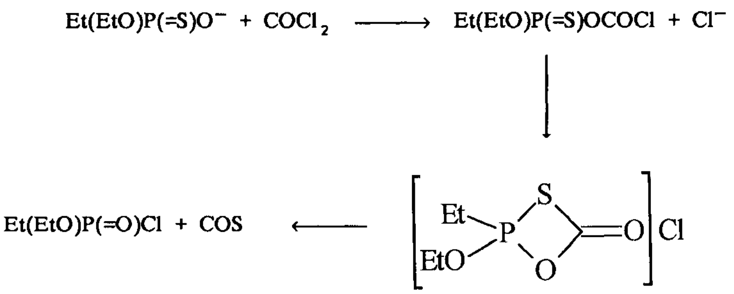
$\mathrm{R_3P{=}S}$ (R = Ph or Bu) is transformed into $\mathrm{R_3P{=}O}$ by $\mathrm{COCl_2}$ in MeCN over 24 h; hydrolysis occurs by the presence of adventitious traces of water in the solvent [294a]:

$$\begin{tikzcd}
\mathrm{R_3P{=}S} \arrow[r, "\mathrm{COCl_2}"] & \mathrm{[R_3PSC(O)Cl]Cl} \arrow[r, "\mathrm{H_2O}"] & \mathrm{[R_3P(OH)]Cl + HCl + COS} \arrow[d] \\
 & & \mathrm{R_3P{=}O + HCl}
\end{tikzcd}$$

The thiophosphinic acid derivative, $\mathrm{(RO)_2P(S)Me}$, reacts with phosgene in a similar way to the analogous phosphoryl compound {see Equation (10.41)}, except that COS is eliminated in place of $\mathrm{CO_2}$, Equation (10.46) [317]:

$$\mathrm{(RO)_2P(S)Me + COCl_2 \longrightarrow (RO)P(O)(Cl)Me + COS + RCl} \qquad (10.46)$$

Reaction of $\mathrm{COCl_2}$ with the sodium salt of the optically active $\mathrm{[Et(EtO)P(S)O]^-}$ proceeds with inversion of configuration, to give the chloridate Et(EtO)P(O)Cl. The mechanism of this reaction, and of the formation of chloridates in general, is thus considered to proceed *via* the four-membered cyclic intermediate illustrated in the following scheme [1]:



Reaction of phosgene with EtO(EtS)P(O)Me results in the elimination of carbon dioxide, Equation (10.47), whereas reaction with the isomeric thionate, $(EtO)_2P(S)Me$, is accompanied by the loss of sulfur, Equation (10.48) [317]:

$$EtO(EtS)P(O)Me + COCl_2 \longrightarrow Cl(EtS)P(O)Me + EtCl + CO_2 \quad (10.47)$$

$$(EtO)_2P(S)Me + COCl_2 \longrightarrow Cl(EtO)P(O)Me + EtCl + COS \quad (10.48)$$

This observation is consistent with the greater reactivity of the thiophosphoryl group compared to that of the phosphoryl group. Prolonged contact with EtO(EtS)P(O)Me at room temperature, however, also resulted in the formation of the product of Equation (10.48).

Salts of the thiolate anions represented in Equation (10.49) combine with phosgene with the loss of the sulfur, rather than the loss of the oxygen atom [317]. Reaction between $COCl_2$ and the anion of the corresponding dithionic acid, however, gives the readily isolated product of Equation (10.50) [317].

$$[(EtO)_2P(O)S]^- + COCl_2 \longrightarrow (EtO)_2P(O)Cl + Cl^- + COS \quad (10.49)$$

$$[(EtO)_2P(S)S]^- + COCl_2 \longrightarrow (EtO)_2P(S)OC(O)Cl + Cl^- \quad (10.50)$$

Highly moisture-sensitive phosphonium chloride derivatives are produced from the reactions of phosgene with $(Me_2N)_2P(S)NH_2$ or $(Et_2N)P(S)(NH_2)_2$, Equations (10.51) and (10.52) [778]. $[(Et_2N)P(Cl)(NH_2)_2]Cl$ was noted to react further with phosgene, as illustrated in Equation (10.53) [778].

$$(Me_2N)_2P(S)NH_2 + COCl_2 \longrightarrow [(Me_2N)_2P(Cl)NH_2]Cl + COS \quad (10.51)$$

$$(Et_2N)P(S)(NH_2)_2 + COCl_2 \longrightarrow [(Et_2N)P(Cl)(NH_2)_2]Cl + COS \quad (10.52)$$

$$[(Et_2N)P(Cl)(NH_2)_2]Cl + COCl_2 \longrightarrow (Et_2N)P(O)(NH_2)Cl + [Cl_2C{=}NH_2]Cl \quad (10.53)$$

10.6 REACTIONS WITH ORGANOSULFUR COMPOUNDS

There is little to distinguish between the reactions of phosgene at an oxygen or at a sulfur centre. Certainly, the thiols are more acidic (C_2H_5SH, $pK_a = 10.6$) than the corresponding alcohols (C_2H_5OH, $pK_a = 15.9$), and this would suggest that their reactions would be somewhat slower. However, because of their higher acidity, the thiols easily form salts by reaction with alkali metal hydroxides, which in turn can be easily combined with phosgene to produce chlorothioformates, RSC(O)Cl, or dithiocarbonates, RSC(O)SR. The dithiocarbonates are a common impurity formed during the preparation of chlorothioformates from thiols and phosgene and, owing to the relative strength of the S-S bond, dialkyl disulfides are also to be found as reaction products.

Sulfur compounds exist in various forms of coke. The concentration of sulfur can be considerably reduced by contacting with phosgene at high temperatures [1287].

10.6.1 Simple thiols

By analogy with the behaviour of alcohols, thiols react with phosgene to give chlorothioformates, Equations (10.54) and (10.55)

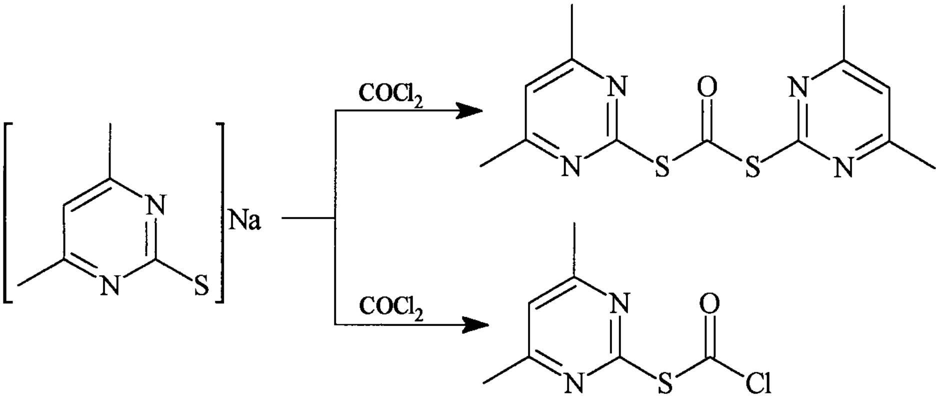
$$\mathrm{RSH + COCl_2 \longrightarrow RSC(O)Cl + HCl} \qquad (10.54)$$

$$\mathrm{ArSH + COCl_2 \longrightarrow ArSC(O)Cl + HCl} \qquad (10.55)$$

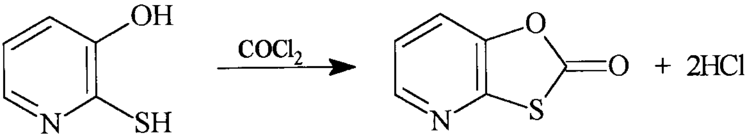
These reactions may be catalysed by amides, such as $HC(O)NMe_2$ (R = Et, Pr, Me_2CH, $Me(CH_2)_3$, Me_3C, $Me(CH_2)_7$; Ar = Ph) [2036], activated carbon (R = Et) [27], or NEt_3 [1406a]. EtSC(O)Cl has been prepared by treating a benzene solution of EtSH with phosgene in the presence of a 20 % aqueous solution of NaOH [1785]. As with chloroformates derived from tertiary alcohols, the chloroformates derived from tertiary thiols may be expected to be much less thermally stable than those derived from primary or secondary thiols. Hence, in some cases, the reaction of phosgene with a thiol might lead directly to the formation of the corresponding simple chlorocompound with concomitant formation of COS, even in the absence of a catalyst [355]. Symmetrical *S*,*S'*-dialkyl thiocarbonates have been prepared by converting the thiol (R = alkyl) to a Group 1 metal salt and then treating with phosgene in an organic solvent, Equation (10.56) [1602a].

$$\mathrm{[RS]M + COCl_2 \longrightarrow RSC(O)SR + 2MCl} \qquad (10.56)$$

Similarly, the sodium salt of a pyrimidine thiol derivative gives a symmetrical carbonate when treated with phosgene in the ratio $COCl_2$:thiol = 2:1; when equimolar amounts of reactants are used, a chlorothioformate is formed [2122]:

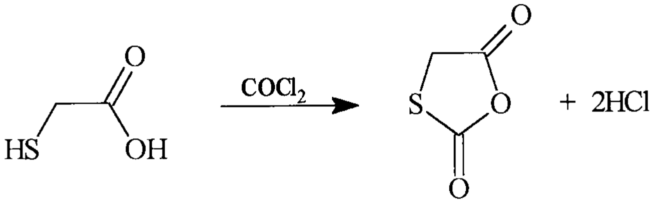


Thio alcohols, in which SH and OH groups are adjacent, are subject to cyclization when treated with $COCl_2$ [1075]:



Amino thiols behave similarly [2078].

Carboxylic acids containing an SH group in the 2-position (*e.g.* $HSCH_2CO_2H$) are similarly subject to cyclization upon treatment with $COCl_2$ [465]:

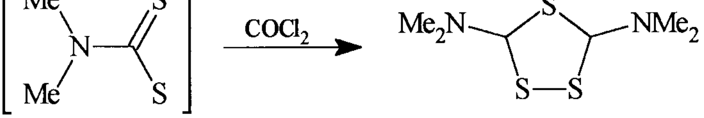


10.6.2 Dithiocarboxylic acids, dithiocarbamates, dithiols, and related compounds

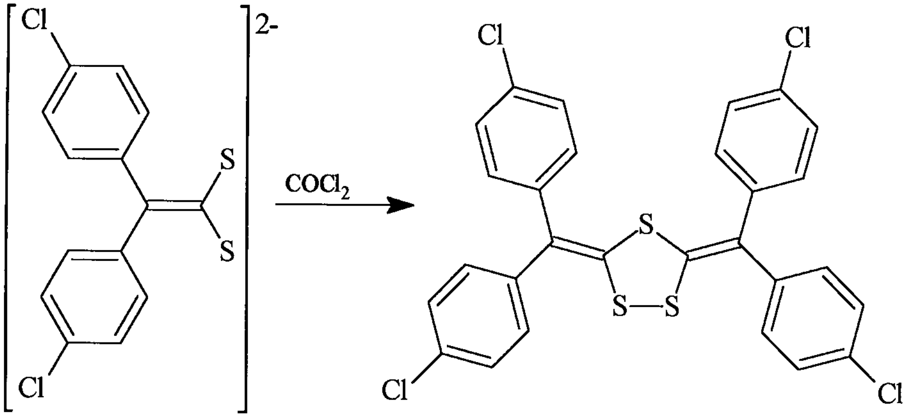
The alkyl and aryl dithioacids, RC(S)SH (R = Me, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$ or 2-thienyl), react with $COCl_2$ in organic solvents, followed by the thermolysis at reduced pressure, to give RC(S)Cl. The reaction mechanism is believed to be [2119]:

$$RC(S)SH + COCl_2 \xrightarrow{-HCl} RC(S)SC(O)Cl \xrightarrow{-COS} RC(S)Cl$$

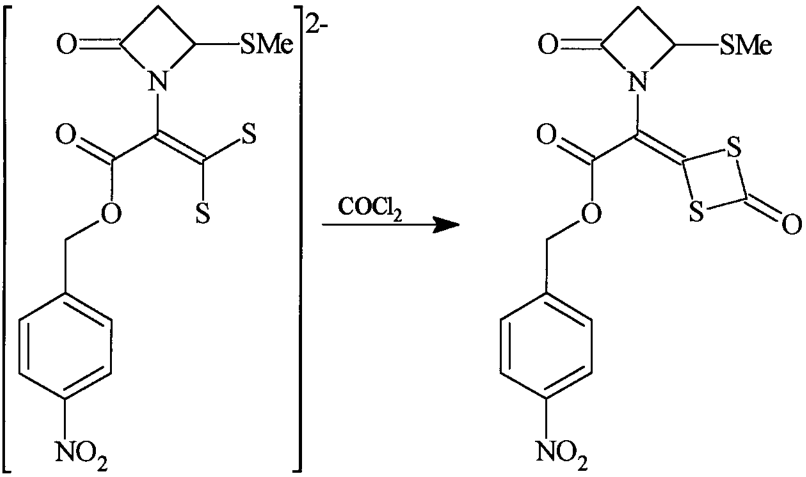
Treatment of an aqueous solution of $Na[S_2CNMe_2]$ with phosgene between 25 and 50 °C resulted in the formation of compound **(10.33)** [2056], and the $[NEt_4]^+$ salt of the dithiolate anion **(10.34)** gave compound **(10.35)** on treatment with $COCl_2$ at −78 °C [1793]. In contrast, the lithium salt of the dithiolate anion **(10.36)**, upon treatment with $COCl_2$ at −78 °C in thf, gave compound **(10.37)** [2006].



(10.33)

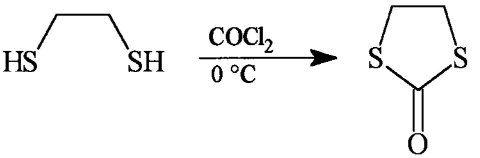


(10.34) **(10.35)**



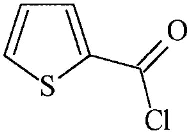
(10.36) **(10.37)**

Similarly, with 1,2-ethanedithiol in the presence of pyridine, phosgene gives 2-oxo-1,3-dithiolane [1781a]:



10.6.3 Thioethers and thiophene derivatives

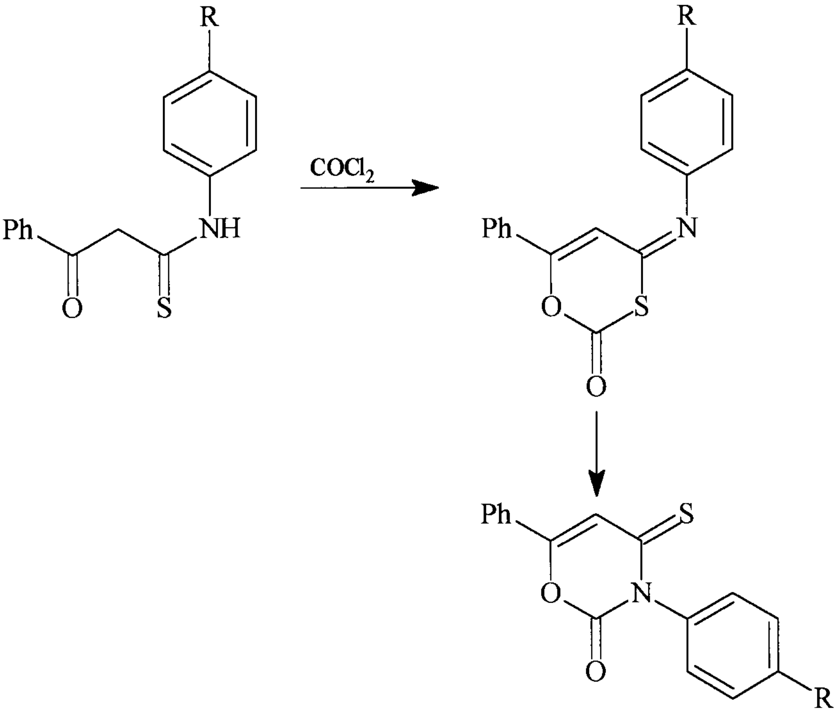
Ring-opening occurs on addition of phosgene to ethylene sulfide, CH_2CH_2S; in the presence of a catalytic amount of pyridine at -10 to +20 °C, $ClCH_2CH_2SC(O)Cl$ was formed [451]. Without a catalyst, the reaction gives the same product but takes a little longer [597]. Ring-opening does not occur in the aromatic compound thiophene, C_4H_4S. Reaction of this compound with phosgene in the presence of $AlCl_3$ in an inert organic solvent (such as CH_2Cl_2) at low temperatures results in an attack at the 2-position to give the carbonyl chloride derivative, C_4H_3S-2-C(O)Cl [1909]:



10.6.4 Sulfur- and nitrogen- containing compounds

10.6.4.1 *N*-monosubstituted thiocarboxamides

The *N*-monosubstituted thiocarboxamide (R = H, Me or Cl) illustrated in Equation (10.57) combines with $COCl_2$ to give a cyclic derivative, which rearranges in acid solution at room temperature to give a thioketone [2244].



(10.57)

10.6.4.2 Thiourea derivatives

Owing to the greater nucleophilic character of sulfur relative to oxygen, reaction of 1,3-disubstituted thioureas with phosgene usually occurs at the sulfur atom, to give high yields of chloroformamidinium chlorides [2083a,2087]:

$$\text{RNHC(S)NHR'} + COCl_2 \longrightarrow [\text{RNHC(Cl)=NHR'}]\text{Cl} + \text{COS}$$

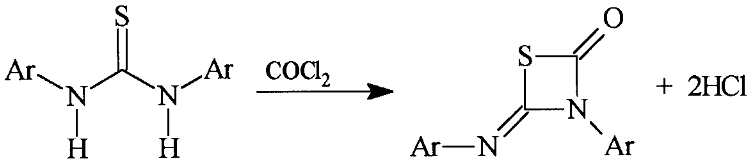
In a non-polar solvent, which retards the elimination of COS, it is possible to isolate the initial reaction product [585]:

$$\text{RNHC(S)NHR'} + \text{COCl}_2 \longrightarrow [\text{RNHC\{SC(O)Cl\}=NHR'}]\text{Cl}$$

Significant formation of allophanoyl chlorides, RNHC(O)NR'C(O)Cl, does not take place. Further, the formation of the gaseous co-product COS gives this reaction a considerable advantage over the corresponding use of phosphorus(V) chloride, the co-product, liquid $P(S)Cl_3$, being very difficult to remove [2083a].

Reaction of thioureas with phosgene is usually performed at room temperature in an inert solvent (such as benzene, chlorobenzene or 1,2-dichloroethane) in which the thiourea is soluble. By-products, if formed, are readily separated with ethoxyethane in which the chloroformamidinium chloride salts are insoluble.

The loss of two molecules of HCl (often at room temperature) from the chloroformamidinium salts results in the formation of carbodiimides, RN=C=NR' [2087,2087a]. The use of an excess of $COCl_2$ should therefore be avoided, since carbodiimides themselves can react with phosgene to give chloroformamidine-*N*-carbonyl chlorides, see Section 10.2.8. Indeed, in early work [2189a], diarylthioureas were found to react with an excess of $COCl_2$ to form cyclic compounds:

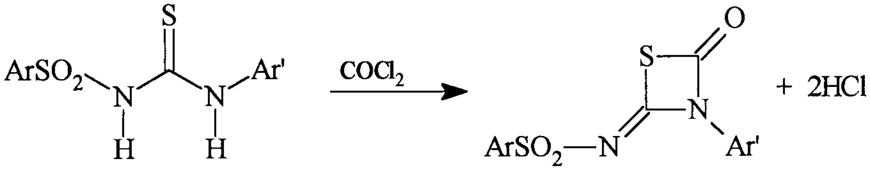


These materials were noted to form only in minor amounts when an excess of phosgene was not employed [585].

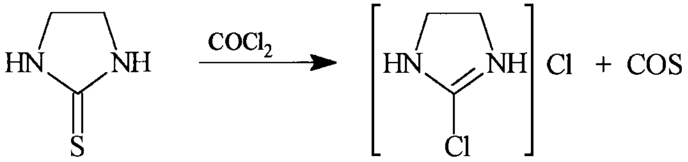
The reaction of 1-alkyl-3-arylsulfonyl thioureas with $COCl_2$ proceeds according to [2087a]:

$$\text{ArSO}_2\text{NHC(S)NHR} + \text{COCl}_2 \longrightarrow \text{ArSO}_2\text{N=C(Cl)NHR} + \text{COS} + \text{HCl}$$

In contrast, 1,3-diarylsulfonyl thioureas are transformed into 1,3-thiazetidin-2-ones [2087a]:



Cyclic thioureas react predictably with $COCl_2$ [2083a]. In the following example, the chloroimidazolidinium chloride is formed, accompanied by the production of carbonyl sulfide:



The reactions of tri- and tetra- substituted thioureas with $COCl_2$ give high yields of the corresponding chloroformamidines [127,2083a]:

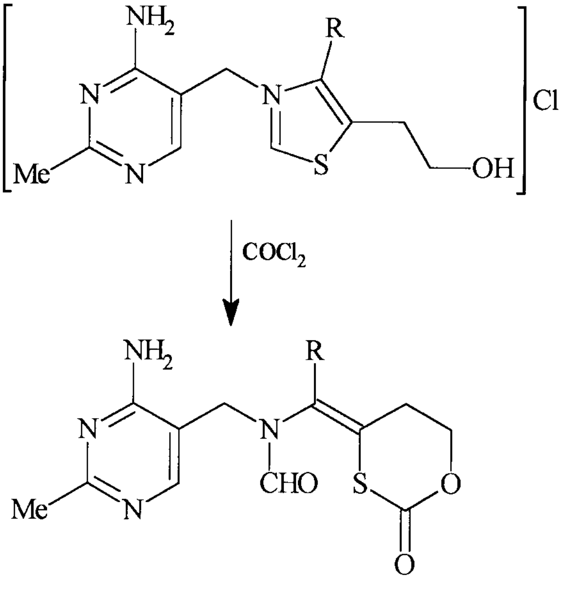
$$RNHC(S)NR'R'' + COCl_2 \longrightarrow RN{=}C(Cl)NR'R'' + HCl + COS$$

$$RR'NC(S)NR''R''' + COCl_2 \longrightarrow [RR'NC(Cl)NR''R''']Cl + COS$$

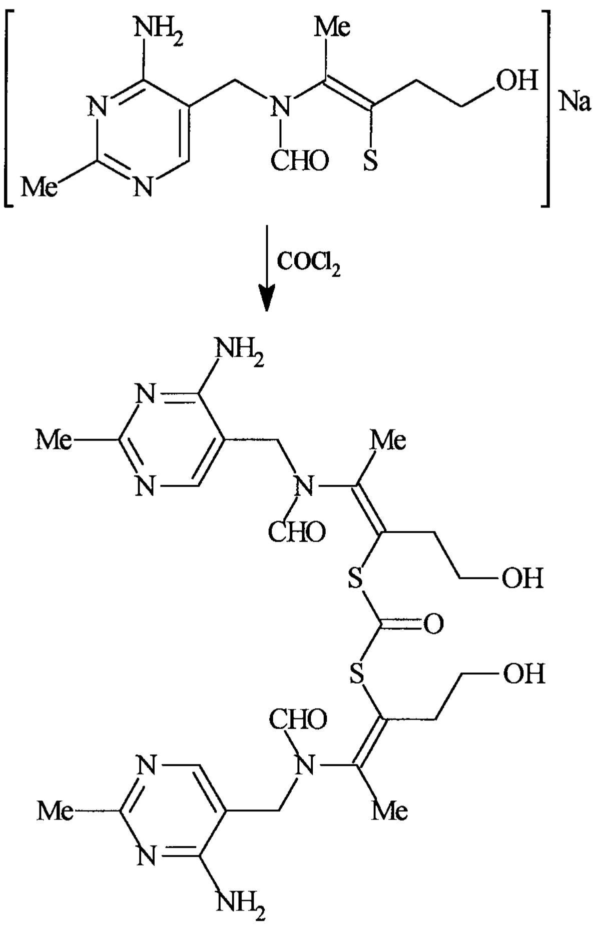
1-(5-dihydrocyclopentadienyl)-3,3-dimethyl urea has been prepared by treating the analogous thiourea with phosgene in thf, followed by hydrolysis [301].

10.6.4.3 Thiamine and its derivatives

In an ice-cooled alkaline solution, thiamine (R = Me) reacts with $COCl_2$ to give cyclocarbothiamine [1462]:



Hydroxyethylthiamine {R = MeCH(OH)} reacts similarly. When the sodium salt of thiamine was treated with phosgene at −20 °C in aqueous ethanol, *S,S'*-carbodithiamine was formed [1462]:



This material could also be obtained by treating the sodium salt of *O*-(2-tetrahydropyranyl)-thiamine with phosgene, and eliminating the tetrahydropyranyl group with aqueous hydrochloric acid solution [1462].

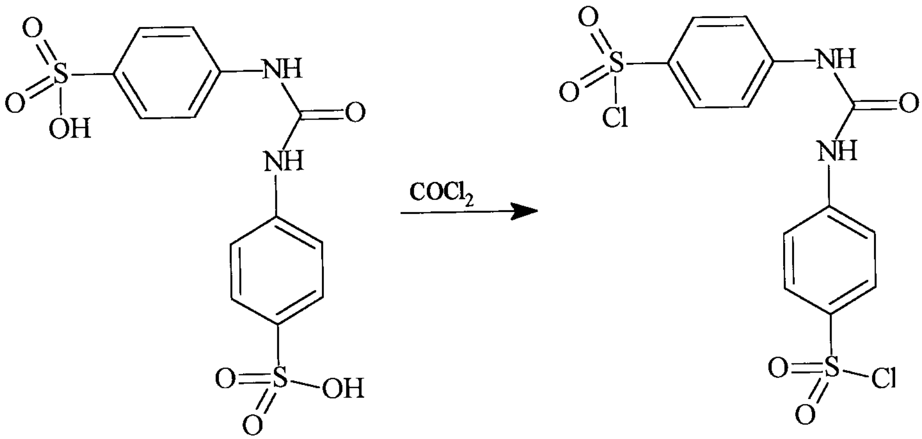
10.6.5 Sulfur- and oxygen- containing compounds

10.6.5.1 Sulfoxides

Dimethyl sulfoxide, when treated with a CH_2Cl_2 solution of phosgene, gives the chlorosulfonium salt, $[Me_2SCl]Cl$, stable at temperatures below 0 °C and rearranging to $MeSCH_2Cl$ at higher temperatures [724].

10.6.5.2 Sulfonic acids

Reaction of $PhSO_3H$ with phosgene, in the presence of dmf and sulfuric acid, gave $PhSO_2Cl$ in a yield of 98.5% [204]. Similarly, treatment of the bisbenzenesulfonic acid illustrated in Equation (10.58) with $COCl_2$ in benzoyl chloride and dmf at 55-70 °C results in the formation of the corresponding sulfonyl chloride [1977].



(10.58)

10.6.5.3 Sulfonamides

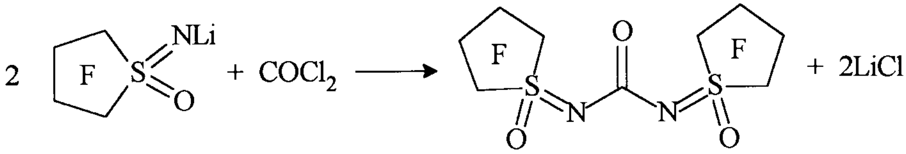
Sulfonamides only combine with phosgene with difficulty. Reaction only occurs at temperatures in excess of 200 °C, with the result that low yields of the corresponding sulfonyl isocyanates are obtained (because of cleavage of the S–N bond) [2087a]:

$$RSO_2NH_2 + COCl_2 \longrightarrow RSO_2NCO + 2HCl$$

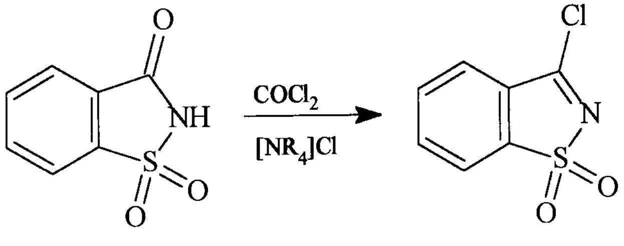
Arylsulfonyl isocyanates (*e.g.* R = Ph, Me–4–C_6H_4, F–4–C_6H_4 or Cl–4–C_6H_4) have been prepared under milder conditions, however, by addition of catalytic quantities of an isocyanate to the corresponding sulfonamide/phosgene mixture [2087a].

10.6.5.4 Sulfoximide derivatives

The *N*–substituted sulfoximide salt, $\overline{CF_2CF_2CF_2CF_2S}(O)=NLi$, was treated with $COCl_2$ to produce a disubstituted derivative [1c]:



The isothiazole derivative, saccharin, in the presence of a quaternary ammonium salt, is converted into 3–chloro–1,2–benzisothiazole 1,1–dioxide {*cf.* Section 10.2.2.2} [596]:

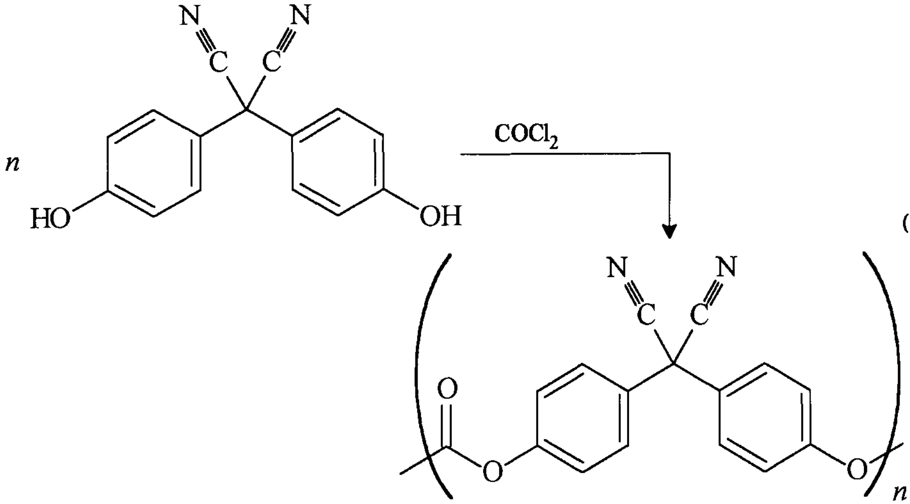


10.7 POLYMER CHEMISTRY

Phosgene is very commonly employed in polymerisation reactions. Its *rôle* in the synthesis of polyurethanes and of polycarbonates has been described in Chapter 4, and reactions in which polymers are modified by post-treatment with $COCl_2$ have been described in Chapter 10 (under the Section most appropriate to the type of functional group involved). This Section is mainly concerned with the reactions of phosgene to give novel polymers.

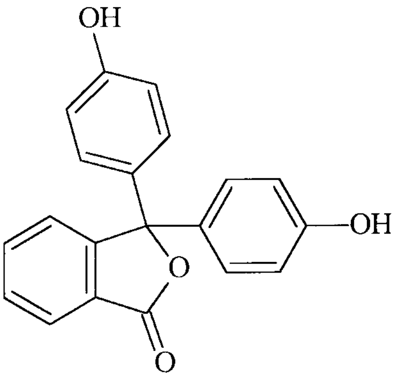
Probably the simplest polymer formation reaction involving phosgene is that with the dihydric aliphatic alcohols, such as ethylene, propylene or butylene glycol (*viz.* ethane-1,2-diol, propane-1,3-diol or butane-1,4-diol): this reaction results in the formation of linear, wax-like polymers suitable for the impregnation of materials requiring water barrier properties [1133].

Over a thousand patents have been issued concerning polycarbonates, and phosgene features in many of these disclosures. The synthesis of these polymers, particularly aromatic polymers, from phosgene has been adequately described in the literature [388a,676,841,2016], and the industrially important materials have been described in Chapter 4, although many novel materials are being added to this list at regular intervals. For example, new organosilicon polycarbonates have been prepared from 1,1-bis(4-hydroxyphenyl)cyclohexane, phosgene and organosilicon bis(chloroformates) [1903]. Copolymer films of such materials showed chemical resistance to strong alkali solutions, and gave good adhesion to mineral glass [1903]. Bisphenol A derivatives, such as the novel polycarbonate illustrated in Equation (10.59), have been described [114].



(10.59)

As a final example, phenolphthalein (**10.38**) and related compounds react with phosgene to give high molecular weight linear polycarbonates [1434].



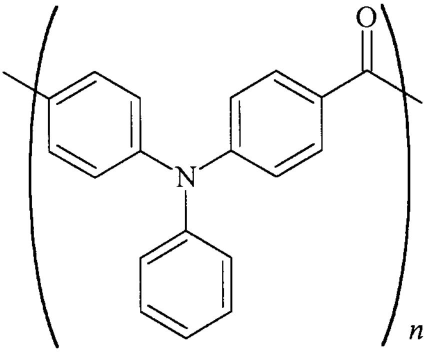
(10.38)

A number of novel process methods have been described. For example, ultrasound [1142] and phase-transfer catalytic techniques [1085] have been employed to increase reaction rates in the synthesis of polycarbonates.

In the presence of organometallic compounds of Groups 12 or 13, such as $ZnEt_2$, phosgene reacts with H_2CO in hexane at low temperatures (−78 °C) to form a polymer of undefined structure containing 4% chlorine. The yields of polymer and the respective chlorine contents were notably increased by the addition of relatively small amounts of organic compounds containing oxygen, sulfur, or nitrogen groups [1548].

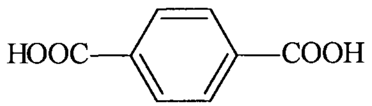
The copolymerization of H_2CO and phosgene can be induced by irradiation with γ-rays, to give materials with $COCl_2$:H_2CO = (0.001–0.005):1. The thermal stability of these co-polymers was not improved relative to the homopolymer of H_2CO [1490].

Phosgene undergoes a condensation reaction with NPh_3 in the presence of aluminium(III) chloride to form a polymer, m.pt. 189–245 °C, in a yield of 22% [675]. A possible structure of this material is:

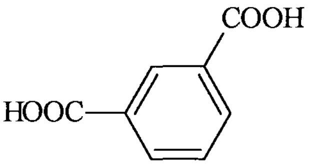


No reaction was observed when the aluminium(III) chloride was replaced by zinc(II) chloride.

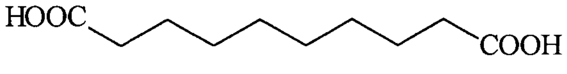
Polyanhydrides of terephthalic acid (**10.39**), isophthalic acid (**10.40**), and sebacic acid (**10.41**), were prepared by reaction with phosgene in toluene in the presence of NEt_3 [1865]. The polymers all have the general structure {**10.42**; X = 1,4-C_6H_4, 1,3-C_6H_4 or $(CH_2)_8$}.



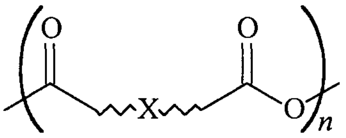
(10.39)



(10.40)



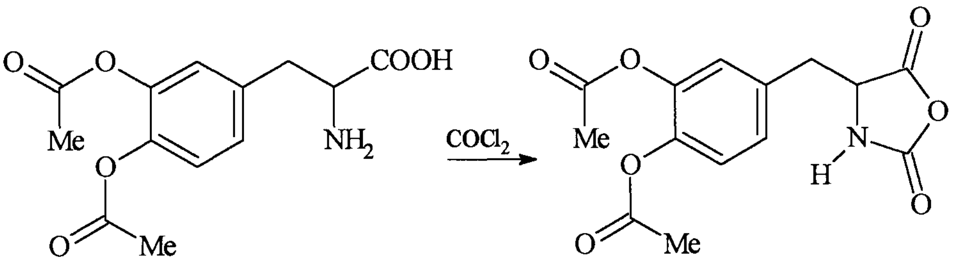
(10.41)



(10.42)

The common problem of contamination of the product with $[NEt_3H]Cl$ was overcome by performing the reaction in trichloromethane, using an insoluble base (*e.g.* poly(4-vinylpyridine) or potassium carbonate) [547a]. Alternatively, a solvent in which $[NEt_3H]Cl$ was insoluble, but in which the polymer dissolved was selected; thus, **(10.41)** reacts with phosgene to give a pure polymer in dmf or toluene [547a].

High molecular weight poly(L-DOPA) was prepared by treating *O,O'*-diethanoyl-L-DOPA **(10.43)** with $COCl_2$, and polymerizing the resulting *N*-carboxyanhydride, **(10.44)**, in dioxane containing Na[OMe], followed by deethanoylation of the resulting poly(*O,O'*-diethanoyl-L-DOPA) with $H_2N(CH_2)_nOH$ (n = 2 or 3) [703].



(10.43) **(10.44)**

Phosgene can be used as an initiator for the living cationic polymerization of isobutene or styrene. Aluminium(III) chloride was used as the co-initiator, but the proposed mechanisms for its involvement are "imaginative", and do not take into account the known chemistry of the $AlCl_3$-$COCl_2$ system (see Section 9.1.2.5) [2255a].

10.8 SYNTHESIS OF RADIOLABELLED COMPOUNDS

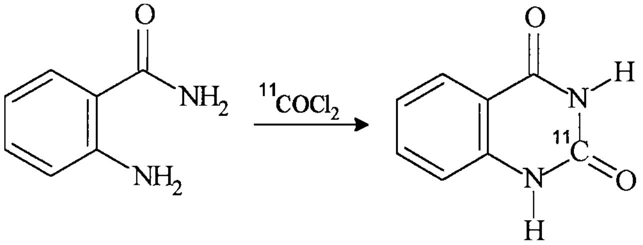
Phosgene is a versatile reagent for the isotopic labelling of organic molecules and its use for the preparation of a variety of radiopharmaceuticals is well established. In particular, the synthesis of ^{11}C-labelled compounds is possible owing to the frequently rapid reactions involving phosgene which are necessary because of the short lifetime ($t_{\frac{1}{2}}$ = 20.4 min [1730]) of ^{11}C. Carbon-11 is a short-lived positron-emitting radionuclide useful for *in vivo* measurements with positron emission tomography (PET) [519]. Because of the short half-life of ^{11}C, it can be administered without excessive radiation damage. Moreover, the ability to label with a high specific activity also permits the facility to inject only small amounts of the pharmaceutical [428].

The preparations of labelled phosgene, $^{11}COCl_2$, $^{13}COCl_2$ or $^{14}COCl_2$, have been described in Section 5.8.

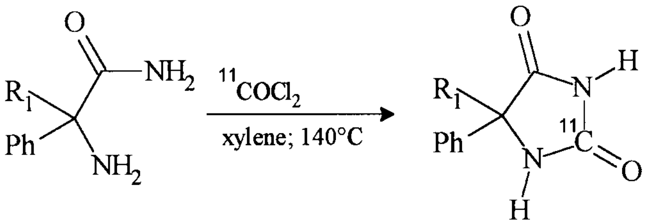
10.8.1 Reactions with nitrogen compounds

^{11}C-urea, suitable for biological or pharmacological applications, has been rapidly synthesised in a high state of radiochemical purity by the action of $^{11}COCl_2$ on aqueous ammonia solution [1730]. The method may be easily extended to primary or secondary amines for the labelling of pharmacologically-useful substituted ureas [1729,1730]. Diphenyl urea containing ^{11}C incorporated into the carbonyl group can be quantitatively prepared by reaction of $^{11}COCl_2$ with aniline in toluene [519,1732,1734]. The anti-tumour drug, 1,3-bis(2-chloroethyl)-[2-^{11}C]nitrosourea (BCNU), has been prepared with a high specific activity from CH_2ClCH_2NH-^{11}CO-$NHCH_2CH_2Cl$, derived from the reaction of $^{11}COCl_2$ with aziridine (ethyleneimine) [518a]. The *in vivo* pharmacokinetics of BCNU have been examined by PET [518a].

Labelled 5,6-benzouracil in a radiochemical yield of 85% has been prepared from the $^{11}COCl_2$-induced ring closure reaction illustrated below [275]:

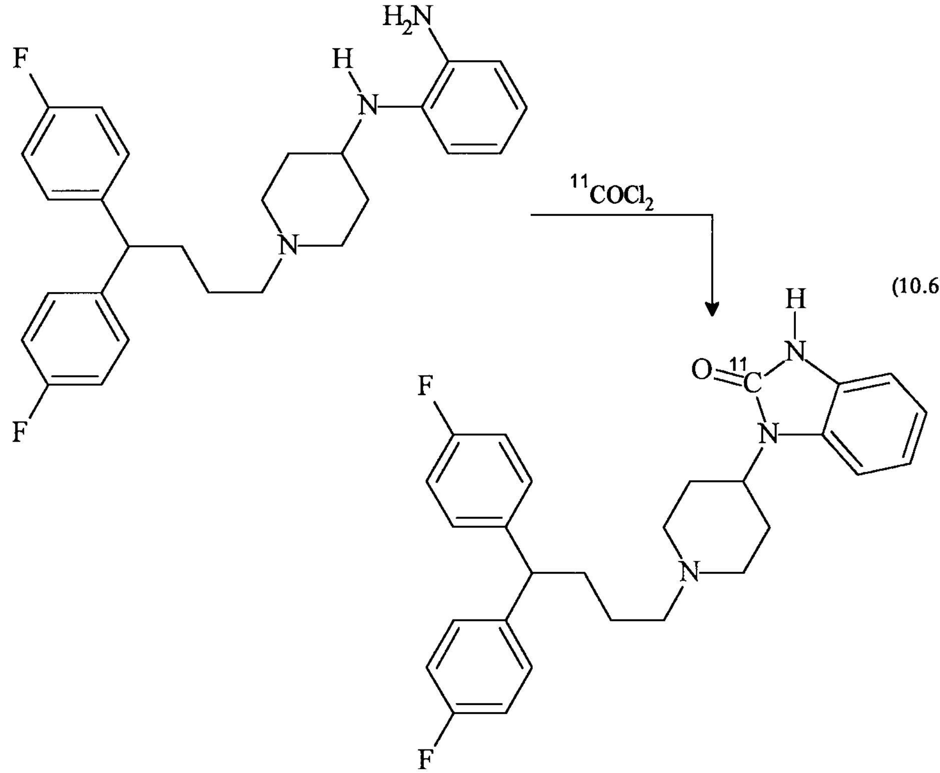


Other fast ring closure reactions have been employed for the synthesis of ^{11}C-labelled hydantoins (used in epileptic treatments), Equation (10.60) [1729,1732,1733], and for the synthesis of the ^{11}C-labelled neuroleptic drug, pimozide, Equation (10.61) [428].



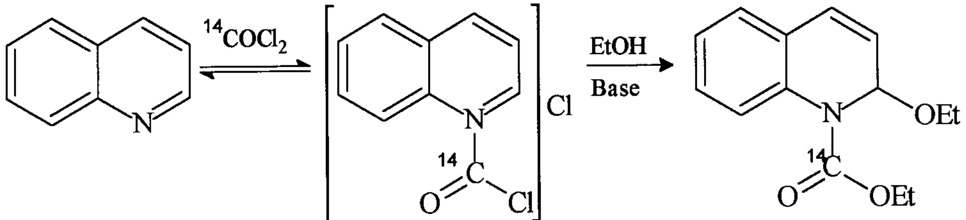
(R_1 = Et or Ph)

(10.60)



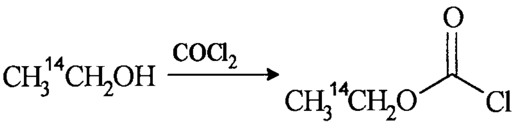
(10.61)

$^{14}COCl_2$ reacts with quinoline, followed by treatment with ethanolic base, to give a poor yield of the ester **(10.45)**, labelled at the carbonyl carbon atom [1725]:

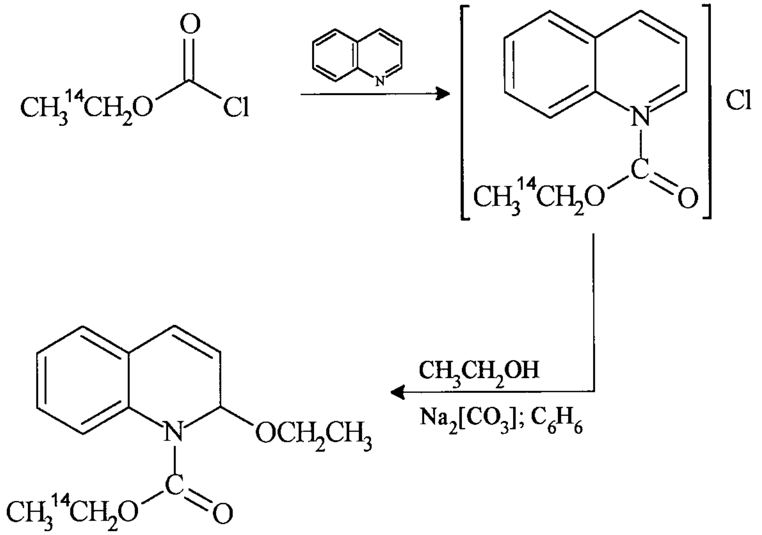


(10.45)

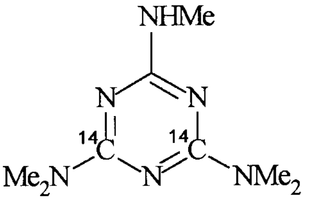
This material is preferably prepared, with the label in a different position, from the reaction of quinoline with $CH_3{}^{14}CH_2OCOCl$ [1725]. This is itself prepared by the reaction of specifically labelled ethanol with unlabelled phosgene:



$$CH_3{}^{14}CH_2OH \xrightarrow{COCl_2} CH_3{}^{14}CH_2O\text{–}C(=O)\text{–}Cl$$



Of course, unlabelled phosgene can be employed as a reagent in the chemically normal sense to prepare a radioactively labelled material, where the co-reactant itself is labelled. Thus, the antitumour agent, **(10.46)**, was synthesised by the cyclocondensation of $Me_2N^{14}CN$ with $COCl_2$ in the presence of HCl (see Section 10.2.4.3), followed by condensation with methylamine, to give the molecule labelled at the positions shown. The reaction with $^{14}COCl_2$ resulted in total labelling of the carbon atoms in the triazine [542].

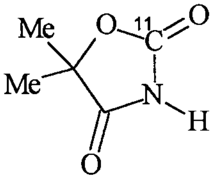


(10.46)

10.8.2 Reactions with oxygen compounds

Ethyl chloroformate, labelled at the methylene or at the chloroformyl carbon atom, is readily prepared from $CH_3{}^{14}CH_2OH$ and phosgene [1725], or from ethanol and $^{11}COCl_2$ [1732,1734], respectively. ^{11}C-diethyl carbonate can also be made directly by introduction of $^{11}COCl_2$ into a solution of NaOEt in ethanol [1732,1734]. Dimethyl carbonate, ^{11}C-labelled at the carbonyl group, is similarly prepared using a methanolic solution of Na[OMe] [759].

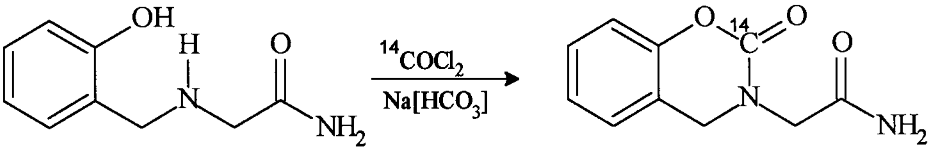
The compound [2-^{11}C]5,5-dimethyloxazolidine-2,4-dione **(10.47)**, used for the estimation of intracellular pH, is prepared by reaction of $^{11}COCl_2$ with a dry ethanolic solution containing 2-hydroxy-2-methylpropanamide and sodium ethoxide [180,181]. This procedure involves the synthesis of diethyl carbonate *in situ*, which reacts in turn with the hydroxy amide [759].



(10.47)

10.8.3 Reactions at nitrogen and oxygen centres

Labelled caroxazone (**10.48**) was prepared from $^{14}COCl_2$ according to the following reaction [178]:



(10.48)

This material, which is said to have potential antidepressant activity, was administered to human subjects and the metabolites (recovered from urine samples) identified by radioassay and chromatographic methods [178].

11 PHOSGENE AS A NON-AQUEOUS SOLVENT

It is rather unfortunate to have to record that there are almost as many reviews and discussions concerning the use of phosgene as a non-aqueous solvent [46,90a,358,850d,997a, 1030,1285a,1925a,2026] as there are original research papers investigating the topic, and that the majority of the original work (from Germann and coworkers [735–746]) predates the renaissance in inorganic chemistry which occurred in the middle of this century. It has been stated in one of the most recent reviews that the utility of phosgene as a non-aqueous solvent is limited by its "unfavorable liquid range" and is "further limited by its intolerable odor [*sic*], extremely poisonous character, sensitivity to moisture [*sic*] and general high chemical reactivity" [90a]. A much more perceptive view was expressed by J.S. Anderson [46]: "Further data on this interesting system are lacking, and it clearly offers rich material for future investigations". This was written in 1943, and (apart from Huston's excellent study [997–998]) little has changed since then. The existence of so many reviews mitigates against the need to discuss the early, and largely misinterpreted, literature data in any detail here.

11.1 PHYSICAL PROPERTIES OF LIQUID PHOSGENE

The thermodynamic and physical properties of phosgene have been discussed at length in Chapter 6, but it is apposite to summarize some of the properties which relate to the use of liquid phosgene as a non-aqueous solvent in Table 11.1. Phosgene possesses an attractive liquid range (being slightly larger than water, and three times greater than that of liquid ammonia), but a rather low dielectric constant. This makes it a good solvent for covalent molecules (*e.g.* BCl_3 and $SOCl_2$), but a rather poorer solvent for ionic salts [151]. 0 °C is an extremely useful and practical working temperature for isothermal studies.

11.2 CONDUCTIVITY OF LIQUID PHOSGENE

Phosgene has a very low measured specific conductivity, 7 x 10^{-7} S m^{-1} [736,738], and this value (as the author himself clearly warns) represents an *upper limit*, as "no effort was made to prepare a product of the highest purity" and traces of hydrogen chloride would give conducting solutions. Germann [738] concluded that "the conductivity of pure phosgene is undoubtedly very much lower than the value given". The elegant work of Huston and coworker [997,998] is summarised in Section 9.1.2.5, and clearly demonstrates that phosgene

TABLE 11.1

PHYSICAL PROPERTIES OF LIQUID PHOSGENE

Property	Value	Ref.
Melting point (Phase I)	-127.78 °C	752
Boiling point	+7.92 °C	649
Density (0 °C)	1.418 g cm^{-3}	462
Conductivity (25 °C)	$\leqslant 7 \times 10^{-7}$ S m^{-1}	736,738
Dielectric constant (0 °C)	5.131	461
Dipole moment (0 °C)	1.175 D (3.919×10^{-30} C m)	461
Molar susceptibility (c.g.s.)	-48.0×10^{-6} cm^3 mol^{-1}	1104
Molar susceptibility (S.I.)	-6.03×10^{-10} m^3 mol^{-1}	1104
Viscosity (0 °C)	5.90×10^{-4} Pa s	1284
Surface tension (0 °C)	22.6 mN m^{-1}	715

shows no significant autoionization:

$$COCl_2 \rightleftharpoons [COCl]^+ + Cl^-$$

This result, like that found for sulfur dioxide, is somewhat ironic, as phosgene played an important *rôle* in the development of Franklin's theory of the acid-base behaviour of non-aqueous solvents [736,738a,850d,1285a]. There has been a very recent suggestion, however, that $[COCl]^+$ is stabilized by a zeolite framework [641], and exhibits ν(CO) at 1790 and 1710 cm^{-1} [641]. This claim requires substantiation, however.

Electrolysis of conducting solutions of aluminium(III) chloride [738] liberates a mixture of carbon monoxide and dichlorine [736].

11.3 PHOSGENE AS A NON-AQUEOUS SOLVENT

Phosgene represents an intriguing reaction medium. The lack of a detectable autoionization process guarantees no solvolysis complications. The combined evidence of the reactions described in Chapter 9 testifies not only to the low tendency that phosgene has to form stable complexes, but also to the high solubility exhibited by many covalent halides and oxohalides in it. Moreover, although phosgene is thermodynamically unstable with respect to dismutation (see Chapter 8), it is remarkably unreactive towards inorganic compounds at

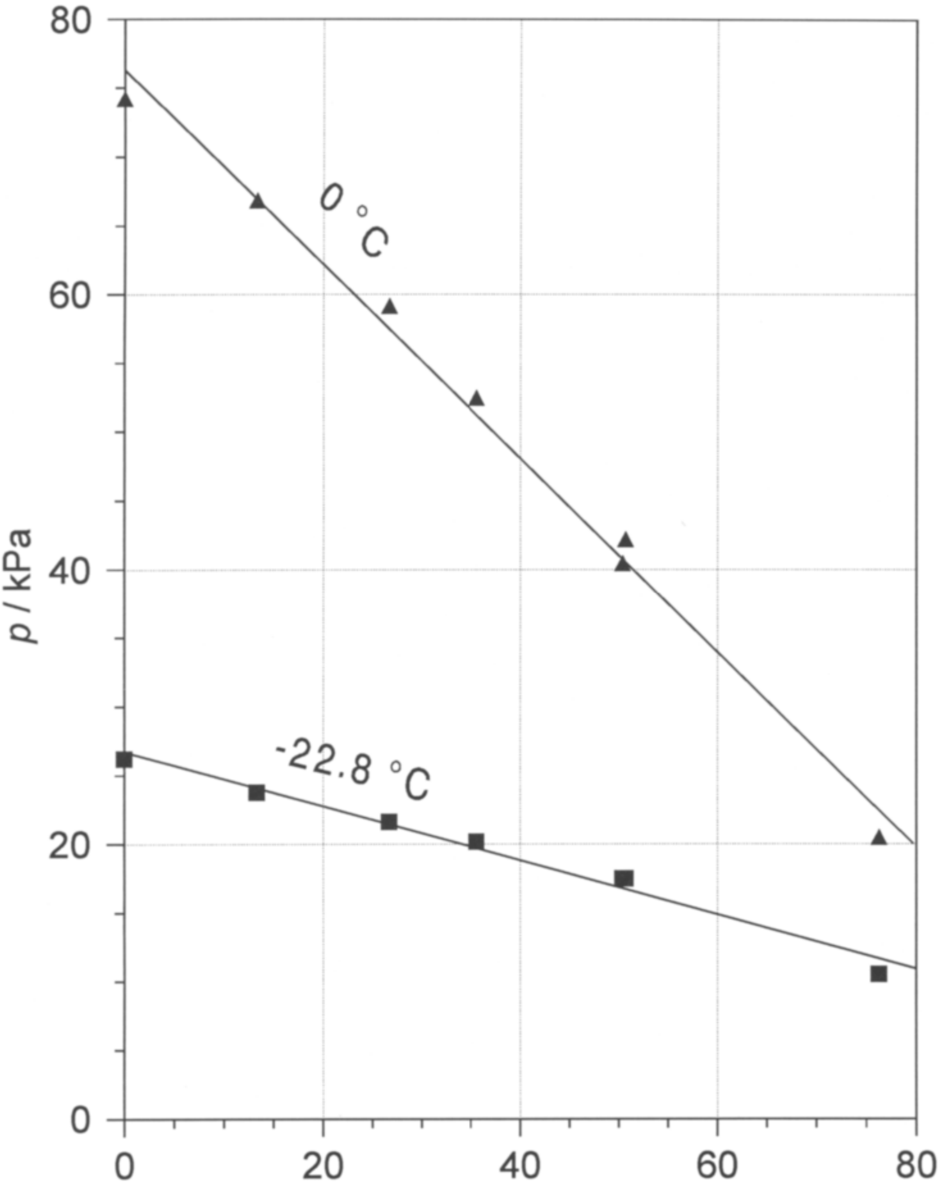


Fig. 11.1 The vapour pressure – composition isotherms for solutions of $CO(CN)_2$ in phosgene at (a) 0 °C, and (b) −22.8 °C [772].

temperatures below ambient. Indeed, it has been used as a solvent for cryoscopic measurements [742,1203] and ebullioscopic molecular weight determinations [151,1787a] for both inorganic and organic molecules.

Early measurements indicate that the solubility of gases in phosgene is surprisingly low, the solubilities of CO, CO_2, Cl_2 and HCl not exceeding 5% at −10 °C (*vide infra*) [1168]. The solubility of O_2 in phosgene is 0.136 mol% at −30 °C and 0.083 mol% at −10 °C [ICI19]; the solubility of CO_2 in phosgene is 6.9 mol% at −30 °C and 4.2 mol% at −10 °C [ICI19]. The vapour pressure – composition isotherms for carbonyl dicyanide in phosgene are given in Fig. 11.1 [772].

Phosgene dissolves large quantities of various other toxic agents. Thus, at 0 °C, it will form a solution of chlorine containing 6.63% of the latter, and at −15 °C, 20.57%. At higher temperatures, the solubility of Cl_2 in $COCl_2$ is apparently less. Mustard gas and diphenylchloroarsine also dissolve in phosgene [2146]. More details of the important $COCl_2$–Cl_2 and $COCl_2$–HCl systems will be found in Sections 6.6.3 and 6.6.4, respectively.

Group 1 and Group 2 metal chlorides, MCl or $M'Cl_2$, dissolve in solutions of aluminium(III) chloride in phosgene to give $M[AlCl_4]$ or $M'[AlCl_4]_2$, respectively [198,738a, 740,741,745,746]: there is evidence for both solvation and association of the salts [198,740]. Lead(II) chloride reacts similarly to give a compound described as $Pb[AlCl_4]_2$ [198]. Metallic magnesium, calcium, zinc, cadmium and tin react (in order of decreasing reactivity) with solutions of aluminium(III) chloride in phosgene, according to [741]:

$$M + [Al_2Cl_6] + COCl_2 \longrightarrow M[AlCl_4]_2 + CO$$

Metallic potassium, which does not react with pure phosgene, also reacts in a similar manner [735].

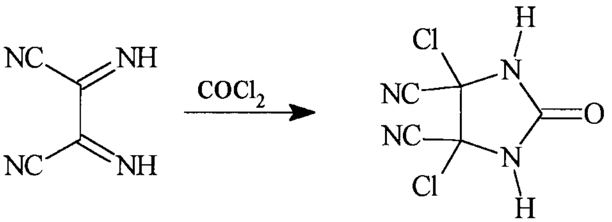
This represents the sum total of the studies upon the use of phosgene as a solvent for inorganic chemistry, apart from the solubility determinations and complex formation studies described in Chapters 6 and 9. This has been a very short chapter; more a reflection of missed opportunities and ill-informed neglect than a paucity of chemical interest. To echo the sentiments expressed by J.S. Anderson in 1943 [46], there is a vast potential for phosgene as a solvent for the study of inorganic reactions which still remains to be exploited.

12 PHOSGENE SUBSTITUTES AND HOMOLOGUES

Because of its reputation as a noxious material, there is occasionally an advantage to be obtained by using a phosgene substitute or homologue. This Chapter describes some of the alternatives that are available, and considers what possible advantages may be gained by their use.

12.1 PHOSGENE SUBSTITUTES

Despite its cheapness, extensive chemistry, and ease of use, phosgene is undoubtedly a highly toxic material. As a result, deaths have occurred from the use of the material both in the factory and the laboratory (see Chapters 2 and 3). Inherently safer reagents, that are less toxic (in the chronic as well as the acute sense), should be used in place of phosgene where possible, providing any reduction in reaction efficiency by using the alternative reagent is not offset by providing the extra safety precautions required for phosgene handling. In some cases, phosgene, despite its high inhalation toxicity, can provide a safer alternative to those reagents that would be considered as phosgene alternatives. In one example, potentially dangerous complications can result from the preparation of *N,N*-dimethylchloromethyleniminium chloride from sulfinyl chloride and dmf. This reaction is more easily controlled by substitution of the $SOCl_2$ with phosgene, which removes the possibility of forming unstable adducts [80a,2250a]. It is suggested that the acute risk should be accepted over the chronic risk, so that acylations might be preferably performed with phosgene rather than dimethylcarbamoyl chloride [1930]. Alternative, non-phosgene, processes for the manufacture of isocyanates have been mentioned in Chapter 4, and substitutes for phosgene in organic syntheses have been the subject of a recent review [806]. Clearly, reactions in which the whole of the phosgene molecule is incorporated into the substrate are usually only possible when phosgene is used [*e.g.* 153a]:

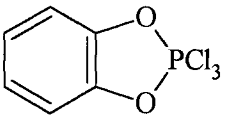


Exceptions to this rule-of-thumb may occur if either diphosgene (trichloromethyl chloroformate) or oxalyl chloride (ethanedioyl dichloride) are used. In the last example, the elements of phosgene may be incorporated into a product with the concomitant formation of carbon monoxide.

The principal uses of phosgene in organic synthesis are in the areas of chlorination, chloroformylation, carbonylation and dehydration, and possible substitutes will now be considered in each of these areas.

12.1.1 Chlorination

In many cases, phosgene provides a unique method for chlorination, and many examples of this are provided in Chapter 10. In particular, the use of phosgene to convert aldehydes, RCHO, to the corresponding *gem*-dichloride, $RCHCl_2$, has been compared with the possible alternative chlorinating agents, dichlorine, hydrogen chloride, and sulfinyl chloride (see Chapter 4). Of these materials, only phosgene is effective in giving the required conversion. Although phosphorus(V) chloride is well known to effect the dichlorodeoxygenation of aldehydes, this reagent has the disadvantage of giving troublesome co-products. An interesting and extremely versatile chlorine transfer reagent, catechol phosphorus trichloride (**12.1**), reacts with compounds containing C=O, P=O, S=O, RO-, PO- and SiO- groups to give the corresponding chloro-derivative [779]. The chemistry of this compound has been recently reviewed, and offers a most promising alternative to phosgene for many selective chlorinations on the small preparative scale. Specific examples, *inter alia*, include the conversion of carboxylic acids into acid chlorides, ketones into *gem*-dichlorides, and alcohols into alkyl chlorides [779].



(12.1)

In combination with dmf, phosgene reacts with anhydrides, such as those based on phthalic anhydride, to give the corresponding acid chloride [806]. In contrast, $SOCl_2$/dmf does not produce this reaction. Apart from these and one or two related examples (see Chapter 10), other reagents than phosgene can be employed for the purposes of chlorination. For example, sulfinyl chloride can be used to convert carboxylic acids into the corresponding acid chloride; PCl_5, PPh_3/CCl_4, or $SOCl_2$ can be used for the conversion of mono-substituted amides, RC(O)NHR', to RC(=N-R')Cl; and disubstituted amides, RC(O)NR'R", can be converted into the corresponding imidium chloride salt, [RC(Cl)NR'R"]Cl using $SOCl_2$, oxalyl chloride (ethanedioyl dichloride), or PPh_3/CCl_4 [806]. Similarly, phosgene can be replaced by

PCl_5 or PPh_3/CCl_4 in the following reaction:

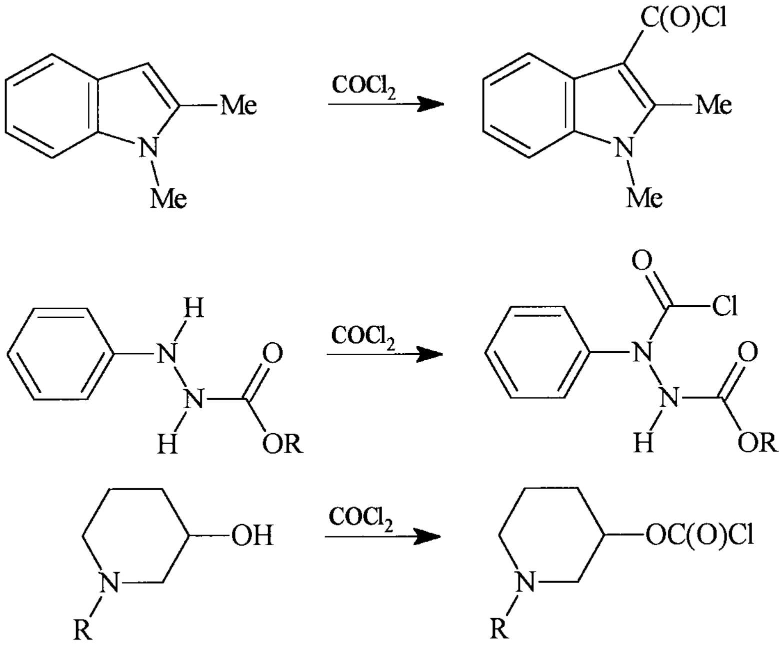
$$\mathrm{RR'NC(O)NHR''} \longrightarrow \mathrm{RR'NC(=N{-}R'')Cl}$$

12.1.2 Chloroformylation

Oxalyl chloride (ethanedioyl dichloride) can be an effective, alternative, chloroformylating agent to phosgene. The reaction of oxalyl chloride with diphenyl ketene, for example, proceeds under milder conditions than with phosgene to give the identical organic product [1938]:

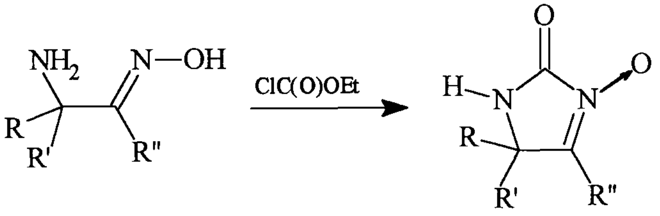
$$\mathrm{Ph_2C{=}C{=}O} \longrightarrow \mathrm{Ph_2C(COCl)_2}$$

Where the carboxylic acid group can be introduced into a molecule, its subsequent conversion to the acid chloride should be possible by using the alternative chlorinating agents described earlier. In many cases, however, such derivatives are difficult, or impossible, to make, in which case phosgene has to be employed. Three examples demonstrate this point rather well [177,806,1621]:

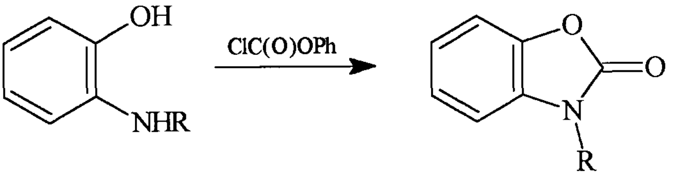


12.1.3 Carbonylation

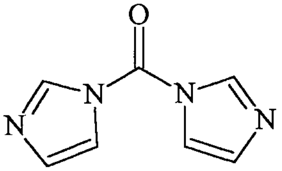
Phosgene is a particularly useful carbonylating agent, but even here it is not unique in its ability to effect carbonylation reactions. In particular, ethyl chloroformate has been described for its suitability as a ring-closing reagent in the synthesis of imidazoline derivatives [786]:



Yields are improved in this reaction, relative to phosgene, where the R substituents are small alkyl groups such as methyl or ethyl, although in other cases the reaction was found to be better when phosgene was used. Ring-formed carbamic acid derivatives have been similarly prepared using phenyl chloroformate [806]:

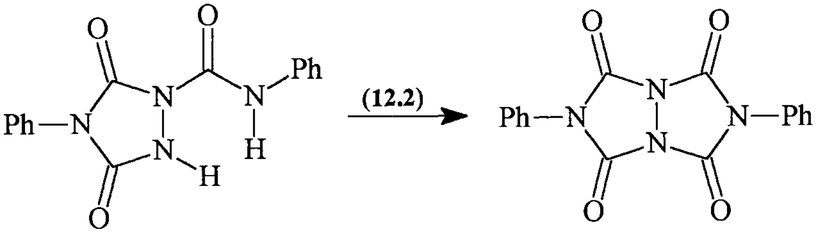


N,*N*'-carbonyldiimidazole (**12.2**) may be used as a phosgene replacement for certain



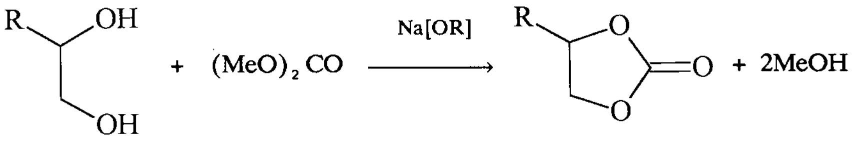
(12.2)

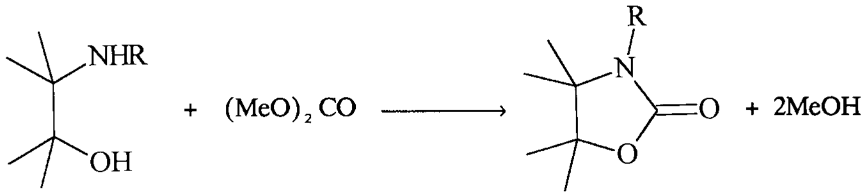
carbonylations, giving yields of about 80% of that achieved with phosgene [806]:



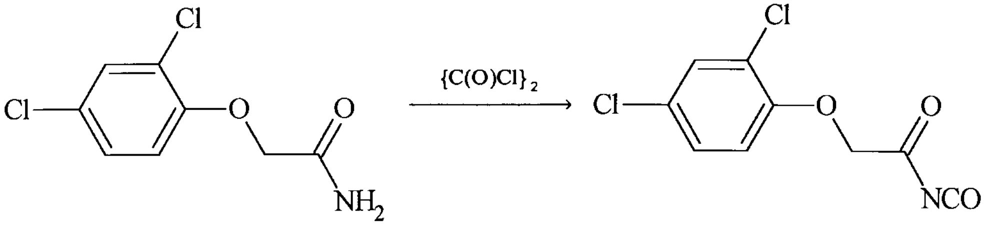
Dimethyl carbonate, $(MeO)_2CO$, is a recognized substitute for phosgene in many carbonylation and ring-closing reactions [595]. For example [595]:

$$(MeO)_2CO + 2PhOH \longrightarrow PhOC(O)OPh + 2MeOH$$

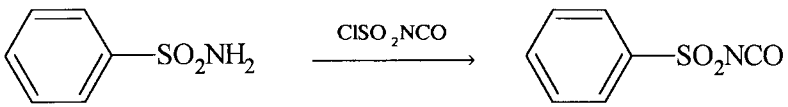




Although there are many alternative routes [806] to the synthesis of the isocyanates, none are as simple or as attractive as the carbonylation of primary amines with phosgene (see Chapter 10). This is reflected by the widespread employment of phosgene in the industrial manufacture of isocyanates; the use of phosgene continues despite numerous attempts to find suitable alternatives (see Chapter 4). However, acyl isocyanates cannot be normally prepared from the reaction of phosgene with carboxylic acid amides, since the phosgene causes dehydration of the $C(O)NH_2$ group to the corresponding nitrile. In this case, oxalyl chloride is effective [806]:



Sulfonyl isocyanates may be prepared using the reaction of sulfonamides with chlorosulfonyl isocyanate, $ClSO_2NCO$, in place of $COCl_2$ [806]:



12.1.4 Dehydration

Many compounds, other than $COCl_2$, can be employed for the conversion of amides, $RC(O)NH_2$, into nitriles, RCN. Examples of effective dehydrating agents include $SOCl_2$, $POCl_3$ or P_2O_5 [860], although on an industrial scale pyrolysis at around 250 °C is commonly used. Similarly, dehydration of *N*-monosubstituted formamides, HC(O)NHR, to isonitriles, RNC, can be effected using PPh_3/CCl_4, although the product must be then separated from the co-produced phosphine oxide [806]. The catechol phosphorus trichloride reagent, (**12.1**), is effective in converting oximes (*e.g.* PHCH=NOH) into the nitrile dehydration product (*e.g.* PhCN) [779].

Metal chloride hydrates, such as $CrCl_3.6H_2O$, can be efficiently dehydrated to the anhydrous material in the laboratory by heating under reflux in the presence of an excess of $SOCl_2$ (*cf.* Section 9.10.3.1).

12.2 HOMOLOGUES

12.2.1 "Diphosgene"

Diphosgene – trichloromethyl chloroformate, $CCl_3OC(O)Cl$ – is a frequently cited substitute for phosgene. In many ways, it can be regarded as being equivalent to two phosgene molecules (into which it is readily decomposed, see Chapter 5) in terms of its chemistry and stoicheiometry. Thermal dissociation of diphosgene occurs homogeneously – with only slight influence from the glass walls – at about 300 °C, but over iron(III) oxide, iron(III) chloride, aluminium(III) chloride or activated charcoal the decomposition is catalysed, and occurs at room temperature [781,867].

Diphosgene can be prepared by the complete chlorination of methyl formate (or methyl chloroformate) [862a]. Unlike phosgene, diphosgene is a liquid, b.pt. 128 °C. It thus has a lower vapour pressure (1.3 kPa at 20 °C) than $COCl_2$, so that some of the safety hazards associated with phosgene could be removed by the general availability of diphosgene [862a]. The compound reacts with alcohols, phenols and amines to form products similar to those obtained from the corresponding reaction with $COCl_2$ [1358]. Depending upon the conditions and stoicheiometry, carbonates and chloroformates [612,1380], carbamates [1380], isocyanates [1184] and ureas [938] can be obtained with diphosgene, in addition to more complicated products such as carbamoyl chlorides, imidic chlorides, carboxylic acid chlorides, isonitriles and *N*-carboxy-α-amino acid anhydrides [1358].

However, despite the attraction of diphosgene as a phosgene substitute in a chemical sense, it is itself a toxic material [1443,2039] with a lingering lachrymatory effect, and has also been used as a war gas [1824b]. Indeed, in one study [2039] to determine the toxic mode of action of phosgene, diphosgene was employed (for ease of handling) since it was argued that the two compounds behave, in essence, identically! Although the physical state of diphosgene, under normal temperature and pressure conditions, imparts some handling advantages over phosgene, spillages of the material are more persistent and the cost of the material may be prohibitive for anything other than small-scale use.

Diphosgene has not been prepared from phosgene itself, but its detailed preparation from the action of dichlorine on methyl chloroformate has been described [1184]. However, diphosgene is now readily available commercially from regular suppliers.

12.2.2 "Triphosgene"

Triphosgene (hexachloromethyl carbonate, or bis(trichloromethyl) carbonate, $Cl_3COC(O)OCCl_3$) is a solid, decomposing quantitatively at 250–300 °C into three molar equivalents of phosgene. At lower temperatures, such as during its distillation, triphosgene decomposes into phosgene and diphosgene, but when mixed with powdered activated carbon (or with Lewis acids [867]) and heated to the melting temperature of the carbonate (78 °C), rapid decomposition to $COCl_2$ occurs [781]. Slow dissociation to phosgene is said to occur even at ambient temperature, however, since crystalline triphosgene is inherently unstable. The formation of triphosgene from phosgene, *per se*, is unknown. Nevertheless, triphosgene can behave in its reactions like three molecules of phosgene [399a,1006a,1458b]. Where laboratory, or other small-scale, quantities are required, triphosgene can provide a degree of handling convenience. In this respect, the reactions of triphosgene with a range of aldehydes has been studied in order to produce experimental quantities of 1-chloroalkyl chloroformates [399a].

Triphosgene, prepared by the chlorination of dimethyl carbonate (a potential large-scale gasoline anti-knock additive), has been claimed to be usable as an alternative to phosgene, for preparation of isocyanates (*e.g.* MDI), chloroformates and polycarbonates [582a]. It is conceivable that triphosgene could gain importance if legislation emerges to prohibit non-captive usage of phosgene. However, the modern trend to produce phosgene captively, and on demand (therefore minimizing storage), coupled with the inevitably higher manufacturing costs of triphosgene relative to phosgene, would make this rather unlikely.

SECTION B

RELATED CARBONYL HALIDES

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13 CARBONYL DIFLUORIDE

Carbonyl difluoride is not an esoteric material; simple methods for its synthesis are well documented, and patents describing its economic preparation on a commercial scale are currently in force. Evidence for its synthetic utility is overwhelming (*vide infra*), and the potential exists for the displacement of much traditional (and rather unpleasant) chemistry, based on F_2 and/or HF, by the use of COF_2. Despite this, COF_2 has only been typically available (until very recently) from commercial suppliers in research quantities ($\leqslant$100 g). The commercial price of the material has fluctuated wildly, from year to year, reflecting more its availability, or scarcity, rather than the cost of its preparation: at one time, a small laboratory cylinder of COF_2 retailed at £2000! Most recently, a bulk supply of COF_2 has been made available (from a Russian source), resulting (at least temporarily) in a reduction of its price to more realistic levels. One supplier (Fluorochem; UK), at 14/2/92, quoted the following prices: 25 g, £165; 100 g, £275; 1 kg, £980; 10 kg, £4690; 100 kg, £20,000–30,000. We would anticipate that a consistent supply of COF_2, in quantities suitable for research and pilot studies, would result in a burgeoning growth in its chemistry and commercial utilization.

It is notable that the chemistry and properties of COF_2 can be summarized in one chapter, whereas twelve chapters were required to describe the chemistry and properties of phosgene. However, examination of this chapter reveals that, if anything, the chemistry of COF_2 is even more interesting, and potentially more wide-ranging, than that of phosgene. We fervently hope that this chapter will rekindle interest in this much neglected molecule.

The structure of this chapter mirrors the ordering of material in Section A.

13.1 BIOLOGICAL ACTIVITY OF CARBONYL DIFLUORIDE

13.1.1 Symptoms of COF_2 poisoning

It has been suggested that carbonyl difluoride has a lower toxicological activity than phosgene owing to the greater stability of the C–F bond relative to C–Cl [393a]. However, it is much more likely that, unlike phosgene, which is not readily soluble in water, carbonyl difluoride owes its toxicity to its rapid hydrolysis giving hydrogen fluoride:

$$COF_2 + H_2O \longrightarrow CO_2 + 2HF \tag{13.1}$$

It is hydrogen fluoride acting on the tissues of the body that produces the recognised symptoms of COF_2 poisoning [76,254,393a,1787]. Consequently, unless the exposure dose has been very high, most of the toxic activity of COF_2 occurs in the upper respiratory passages and other moist surfaces such as the eyes. Phosgene, by contrast, exerts its effects predominantly in the deepest regions of the lungs.

The initial symptoms experienced, on exposure to carbonyl difluoride, are irritation of the eyes, skin, nose and respiratory tract [253,255,277,2197]. However, the response is dose related and severe exposure can result in inflammation and congestion of the lungs, followed by cardiovascular collapse leading to death [39,255]. The skin may also be burned if brought into direct contact with carbonyl difluoride vapour or liquid, causing deep sores that are slow to heal [255]. This is the result of progressive chemical burning of the tissues if the condition is unchecked [255].

Long-term toxic effects have also been observed in animals. They are believed to be caused by the liberation of fluoride ions from the hydrolysis of COF_2 *in vivo* [39], the fluoride ion affecting not just the target organ of the lung, but also the liver and kidneys [2235]. The activity of the fluoride-sensitive enzyme succinic dehydrogenase activity is also inhibited by the generation of fluoride ions [277]. The subsequent metabolic disturbance contributes significantly to the toxic response of the exposed individual [39].

13.1.2 Effects of carbonyl difluoride on the respiratory system

Upon entering the respiratory passages, carbonyl difluoride immediately hydrolyses in the moisture present to form hydrogen fluoride and carbon dioxide [76,254,393a,1787,1893]. The HF then attacks the exposed tissues causing progressive chemical burning, resulting in serious inflammation.

In high doses, some of the gas can penetrate further into the main lung passages (bronchi and bronchioles), eventually reaching the alveoli. Here, the blood-air barrier may be disrupted by the action of HF, so resulting in leakage of fluid into the alveolar space to produce an accumulating œdema, showing the usual symptoms [255]. For this reason, affected persons should be kept under observation for 48 h (*cf.* phosgene, see Section 2.5.2).

Focal hæmorrhage and pulmonary œdema are typical of the acute toxic effects, but there does not appear to be extensive permanent damage from non-fatal doses. However, residual focal emphysema and interstitial fibrosis remaining after the initial lesions have cleared are possible long term results of the injury [1794,2235].

13.1.3 Evaluation of exposure

There are insufficient data in the literature to give a useful correlation between exposure dose and the degree of toxic response in humans, although animal experiments do provide an indication of the types of reactions that might be expected with slight or severe exposure (see Section 13.1.4).

There have also been reports indicating that raised or abnormally high concentrations of fluoride have been found in the urine of individuals exposed to carbonyl difluoride [1553,1643]. However, although this observation may be taken as a sign of exposure to

COF_2, it cannot be used as a reliable indicator of the extent of exposure [39,1486a, 1553,1643].

13.1.4 Animal experiments

The effects of carbonyl difluoride on humans is recorded in case histories but, for obvious reasons, there are few quantitative data in the literature. Consequently, the toxicity of COF_2 has been investigated by many workers using a variety of vertebrate animals other than man. These investigations are summarised in Table 13.1. From the literature, it is possible to describe the toxic effects as being dose related, with irritation of nose, eyes and skin initially, followed by severe respiratory impairment as a result of acute lung damage. Since 100 p.p.m. of COF_2 is equivalent to 200 p.p.m. of HF {see Equation (13.1)}, this is noted to correspond to within the lethal range for HF for rats exposed for just less than 4 h [393a]. Damage to the kidneys and liver is also frequently recorded.

No reports were found in the literature to show that any conditions of carcinogenicity, mutagenicity or teratogenicity result from exposure to carbonyl difluoride [1486a].

13.1.5 Treatment of carbonyl difluoride poisoning

Remove the victim from the toxic atmosphere, and summon medical aid whilst the victim is kept warm and rested [253,277]. For cases of mild exposure, oxygen should be administered immediately and at half-hour intervals for 3-4 h. However, if the exposure dose has been high, then oxygen should be administered under slight positive pressure for half-hour periods for at least 6 h, until breathing is regular and skin colour is normal. If necessary, mild sedatives and pain killers may be given, but under no circumstances must morphine or barbiturates be administered, as they may have a depressant effect on the respiratory system. Artificial respiration should only be given if breathing has ceased. Generally the victims of carbonyl difluoride poisoning should be treated as if they had been exposed to hydrogen fluoride [253,254,255,277].

In cases of severe exposure, pulmonary œdema may occur several hours later and appropriate treatment for this condition must be available [253,254,255,277].

If the eyes have come into contact with COF_2, they should be flushed with water for at least 15 min. Ice compresses may also be used to help relieve the irritation. Pain relief may be provided using 2-3 drops of 0.5 % tetracaine [253,254,255,277].

Contaminated skin should be drenched with water until completely clean. Clothing should be removed whilst washing. The affected part may then be treated with a highly effective HF Antidote Gel of 2.5% calcium gluconate (which is now commercially available), or immersed in an ice-cold saturated solution of magnesium sulfate, iced 70% ethanol, or an aqueous or ethanolic solution of ™Hyamine (a high molecular weight quaternary ammonium compound). The treated area should be removed from the bathing solution for 2-3 min every ten minutes, in order to relieve discomfort. Fresh compresses may be applied every two minutes, if the affected area cannot be immersed. Treatment should continue for up to 4 h,

TABLE 13.1

THE EFFECTS OF COF_2 POISONING UPON VARIOUS ANIMAL SPECIES

Species	Source of COF_2	Pyrolysis Temperature/°C	Major Observations	Ref.
Dog	PTFE	550	LC_{50}, 1 h	1794
Guinea pig	PTFE	550	LC_{50}, 1 h	1794
Mouse	PTFE	550	LC_{50}, 1 h	1794
	PTFE	390	hyperæmia cutis,[a] bradypnea,[b] convulsions, œdema and hæmorrhage in lung and brain. Possible that COF_2 is most important toxic compound	1166
Parakeet	PTFE	280	LD_{100}	827
Quail	PTFE	315	No deaths	827
	PTFE	330	LD_{100}	827
Rabbit	PTFE	>450	lung damage	1247
	PTFE	550	LC_{50}, 1 h	1794
Rat	PTFE	490-700	Toxic	403
	PTFE	450	Respiratory damage	403
	PTFE	500-600	LC_{50}	2235
	PTFE	550	LC_{50}, 1 h	1794
	COF_2	not given	LC_{50}, 1 h, 360 p.p.m.	39,2011
	COF_2	not given	LC_{50}, 4 h, 90 p.p.m.	39
	PTFE	390	hyperæmia cutis,[a] bradypnea,[b] convulsions, œdema and hæmorrhage in lung and brain	1166
	PTFE	500-600	toxic	2235
	COF_2	not given	LC_{50}, 1 h, 360 p.p.m.	255
	COF_2	not given	lethal conc. 4 h, 100 p.p.m.	393a,394, 1856c

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[a] Hyperæmia cutis - engorgement of skin with blood. [b] Bradypnea - slowness of breathing.

depending on the extent of the injury. Oil or grease must not be applied, although a paste of powdered magnesium oxide and glycerine may be used. Severe burns may be prevented by infiltrating the skin and subcutaneous tissues with a 10 % calcium gluconate solution, with a local anæsthetic [253,254,255,277].

13.1.6 Rôle of carbonyl difluoride in the toxicity of PTFE

There have been numerous reports of toxic effects caused by the thermal decomposition of poly(tetrafluoroethene), PTFE. The resulting condition, referred to as 'polymer fume fever' is characterised by its distinctive influenza-like symptoms of chills, body aches, joint pains and profuse sweating. Nausea and vomiting may also be in evidence. A general feeling of weakness, particularly in the lower limbs, may occur several hours after exposure. The syndrome appears to clear spontaneously about 48-72 h after exposure, with no long term residual effects [6a,118a,121,255,283,1183,1382,1530,1594,2191,1438,1486a]. However, despite very many investigations into the specific cause of the observed symptoms of polymer fume fever, there is still considerable disagreement as to its cause [1486a].

Experimental evidence has shown that PTFE does not break down significantly at temperatures below 425 °C [403,1217,1285,2246]: at higher temperatures, the breakdown products vary according to temperature [76,403,1581,1794,2192a,2235]. At temperatures from 500 to 800 °C, the principal product of PTFE decomposition has been shown to be carbonyl difluoride, and consequent experiments indicate that this material is primarily responsible for producing the toxic effects [39,76,403,603,1183,1246,1247,1553,1794,2149,2235]. However, other workers have conducted experiments which indicate that it is the particulate matter produced on the thermal decomposition of PTFE that produces the toxic effects, particularly at the lower decomposition temperatures (>200 °C) [1217,2191]. Still further suggestions have been made that the toxicity is due to a combination of both of these materials, either by acting together as particles with carbonyl difluoride adhering [2149,2190,2246], or by carbonyl difluoride producing initial effects, with subsequent effects being the result of particulate presence [1794]. Clearly, the definitive study has yet to be carried out.

It is worth noting that adequate evaluation of the chronic effects of long-term exposure and detailed epidemiological studies have not yet been performed [1486a].

There are many reported instances of polymer fume fever occurring in workers, using PTFE or related materials, who are in the habit of smoking at or near their work place [6a,121,283,293a,394,603,1643,2160,2167,2191]. It appears that contamination of the hands with fluorocarbon telomers represents a hazard to smokers. As cigarettes burn at temperatures ranging from 814-913 °C, it is relatively easy for the pyrolysis of fluorocarbon contaminants to occur. The unfortunate individual is therefore taking into the lungs the pyrolysis products known to cause illness. This theory has, in fact, been informally tested by a chemist at a large industrial plant where PTFE was being used. There had been several cases of polymer fume fever at the plant, and a link had been identified between the individuals most susceptible to this illness and their smoking habits. The chemist decided to test the hypothesis that contamination of smoking materials with PTFE was responsible for causing some incidents of polymer fume fever. He placed one particle of PTFE in a cigarette which he then smoked and (not surprisingly) he developed the classical symptoms of polymer fume fever within 3 h (HEALTH WARNING: Smoking PTFE can seriously damage your health!) [6a]. It has also been reported that victims show an aversion to cigarette smoke for some time afterwards, but whether this is a physical or psychological response has not been determined [1530].

13.1.7 Rôle of carbonyl difluoride in the toxicity of perfluoroisobutene

Perfluoroisobutene {PFIB; $(CF_3)_2C{=}CF_2$} is noted for its high toxicity, and it has been suggested by Danishevskii and Koganov that it is the formation of COF_2 *in vivo* that produces the toxic effects [451aa]. This view is considered doubtful, not least because carbonyl difluoride has been shown to be approximately 130 times less toxic than PFIB [393a]. Further discussion of the likely biological action of PFIB is presented elsewhere [393a,394].

13.2 INDUSTRIAL HYGIENE

A gas data and safety sheet for carbonyl difluoride has been produced by the British Compressed Gases Association [277] and the compound is described in the Matheson publication, "Guide to safe handling of compressed gases" [1347], and the ACGIH Documentation of the Threshold Limit Values for Substances in Workroom Air [38,39].

13.2.1 Potential hazards

Carbonyl difluoride is a poisonous gas, designated as such by the U.S. Department of Transportation [1893]. The vapour is heavier than air. Below about 22 °C (*sic*; *cf.* Section 13.8.1.4), COF_2 exists in containers as a liquid under a pressure of about 55 bar [277]. Above about 23 °C, the material exists under these conditions as a compressed gas [277]. Thus, the equipment used must be rated for this cylinder pressure [1347].

Unlike with phosgene, hydrolysis occurs rapidly (to form HF and CO_2), but the hydrolysis may not be so rapid as to prevent some lung penetration of the COF_2. The material in both liquid and gaseous states is thus extremely corrosive to the eyes and skin, particularly when moist [277].

13.2.2 Occupational exposure limits

The principal source of exposure to COF_2 results from the burning or thermal decomposition of fluorocarbon-based plastics, such as PTFE, in air (see Section 13.7.12). The material has also found use as a reagent in organic synthesis (see Section 13.14). Although its deployment as a military poison gas has been suggested [1893], it is unlikely to be as effective as phosgene, having both a lower order of toxicity and being too volatile.

The ACGIH [39,40a,1893] has proposed a TLV–TWA of 2 p.p.m. (5.4 mg m^{-3}) and a short-term exposure limit of 5 p.p.m. (13.5 mg m^{-3}). Although this could involve an intake of fluorine slightly above that permitted for HF (3 p.p.m.), the retention of COF_2 is expected to be lower than that for HF (since COF_2 is appreciably more volatile) [39].

13.2.3 Personnel protection and safe handling of carbonyl difluoride

The toxic effects of COF_2 are very different to $COCl_2$ (see, for example, [253]), since they originate predominantly with HF rather than COF_2 (see Section 13.1).

13.2.3.1 **Laboratory handling**

Before handling carbonyl difluoride, personnel should be equipped with suitable leak detection equipment and HF Antidote Gel (see Section 13.1.5). A solution of concentrated aqueous ammonia enables the detection of leaks by forming copious white fumes on contact of the respective vapours. Larger leaks are apparent from the formation of white fumes resulting from the hydrolysis of the COF_2 in moist air, and from the detection of the irritating and pungent odour. Any areas of equipment exposed to a COF_2 leakage should be cleaned up to remove any acid formed.

In the laboratory, a fume cupboard with a face velocity of >90 ft min^{-1} (>27.4 m min^{-1}) is considered adequate for toxic materials of this type. It is important, in addition, to keep the fronts of conventional fume cupboards as low as possible during handling operations. As with phosgene, the size of the cylinder should be limited to the smallest amount suitable for the particular purpose to which it is to be put.

Where exposure to the gas in a concentration above the occupational exposure limit would otherwise occur, positive pressure breathing apparatus should be worn along with a protective apron, long rubber gloves, and safety goggles [277].

Containers should be stored in the outside open air, and those in use should be handled only under forced ventilation, with self-contained breathing apparatus available in the event of an emergency. Cylinders containing COF_2 should be protected from heat (to avoid the build-up of pressure) and should be maintained at temperatures below 45 °C. Suck-back traps, or other devices to prevent reverse flow, should be employed to prevent the entry of extraneous material (particularly water) into the cylinder [277].

Cylinders of COF_2 are most commonly available from specialist suppliers, in 1.3 kg or 200 g quantities. Details of cylinder type and pressure regulators are usually provided in the suppliers technical literature.

Since COF_2 is readily hydrolysed, the gas can be scrubbed with a large excess of water (or aqueous KOH [1192]) without the requirement of a catalyst or sophisticated mixing equipment. However, the hydrofluoric acid solution formed as a result of the hydrolysis should be treated with an excess of potassium carbonate before disposal to drain [ICI111].

Owing to the high pressures exerted by the liquified gas in a cylinder of carbonyl difluoride, the use of a suitable pressure regulator is required. Reactors constructed of stainless steel, or ™Inconel, are recommended for containment of carbonyl difluoride, although the dry material has been examined in glass reactors with eventual etching of the glass surface. Glass joints are suitably lubricated and protected by the use of fluorinated greases such as "Fomblin" [84a]. Glass stop-taps fitted with PTFE cores may be also usefully employed.

13.2.3.2 Compatibility of materials

Although, in the anhydrous condition, COF_2 is not corrosive to ordinary metals used for construction, when moist the compound behaves in a highly corrosive manner. In these circumstances, copper, nickel, ™Monel, ™Inconel, or ™Hastelloy C are recommended. For ordinary temperatures, natural rubber, ™Viton, ™Teflon and ™Kel-F are compatible [277,1199]. Steel is acceptable at moderate temperatures [84a]. A corrosion-resistant distillation column made entirely from nickel, bronze and ™Kel-F has been used to separate the corrosive gas mixture: OF_2, COF_2, C_2F_6, C_2F_5Cl, ClO_2, ClO_3, ClO_3F, ClO_2F and HF [1573].

13.2.3.3 Laboratory storage

Freshly prepared and purified COF_2 is advantageously stored at liquid nitrogen temperature, since it is found that storage in a steel cylinder at room temperature results in a steady increase in the carbon dioxide content until an equilibrium concentration of 2% CO_2 is reached [1580].

13.2.4 Legislation, transportation and labelling

The U.S. Department of Transportation Substance Identification No. for carbonyl difluoride is UN 2417 [1893]. The Hazchem code for transportation in the U.K. is 2PE [277]. The RTECS accession number is FG6125000 [2011].

COF_2 is included in the European inventory of existing chemical substances (EINECS) [602a], since it was included in the core inventory [602]: its EINECS number is 206-534-2. The U.S. DOT classifications are as follows [1347]:

DOT Shipping Name	Poisonous Gas	
DOT Hazard Class	Poison A	
DOT Required Label	Poison Gas	
DOT Identification No.	NA 1955	(North America)
DOT Identification No.	UN 2417	(International)

13.3 ANALYTICAL METHODS FOR THE DETERMINATION OF CARBONYL DIFLUORIDE

13.3.1 Classical "wet" techniques

The ready hydrolysis of COF_2 makes it especially amenable to wet analytical methods. Techniques for the measurement of fluoride in aqueous solution are well documented in standard texts [*e.g.* 990a], and will not be covered here.

One method which specifically treats the determination of COF_2 in air involves aspiration through water in a glass absorber, followed by treatment of the dissolved silicate (formed from attack of HF on the glass) with molybdate [1603].

13.3.2 Colorimetric methods

Unlike phosgene, a system for the direct detection of carbonyl difluoride is not commercially available. However, it has been found in our own laboratories that Dräger tubes (see Section 3.2.3.1.2) used for phosgene monitoring also indicate the presence of COF_2. These tubes could thus be calibrated for rough quantitative estimation by using standardized concentrations of COF_2 [ICI111].

In another method, COF_2-containing air is passed through a tube containing silica gel, KBr, $KBrO_3$, and fluorescein. The HF formed by hydrolysis causes the liberation of dibromine, which upon reaction with the fluorescein forms the red compound eosin (tetrabromofluorescein): the length of the stain is a measure of the fluoride concentration [1603].

13.3.3 Gas chromatographic methods

As with phosgene (see Section 3.2.5.1), gas chromatography is a particularly useful technique for the determination of a broad range of concentrations of carbonyl difluoride. The thermal conductivity detector is the only detection system reported to be used for this compound. The detector response for the thermal conductivity detector is shown to be linear over a wide range of COF_2 concentrations [559].

A celite column coated with 20 % perfluorotributylamine has been employed for the determination of COF_2 admixed with tetrafluoroethene oxide, tetrafluoroethene and hexafluorocyclopropane [1230]. With both column and detector held at −20 °C, the COF_2 was determined quantitatively from its decomposition on the column into carbon dioxide. Similarly, COF_2 has been measured in these types of gas mixtures by quantitatively converting to CO_2 on silica gel columns and measuring the CO_2 effluent [928a,1782a]. COF_2 was also converted to CO_2 over ™Porapak T and ™Spherocarb columns [1980], so that the sum concentrations, only, of these materials could be determined in the absence of other analyses. However, by conditioning a composite column consisting of ™Porapak T in series with ™Porapak N, CO_2 and COF_2 were satisfactorily separated and analysed at a column temperature of 23 °C [274,559]. A plot of the peak area as a function of the COF_2 sample partial pressure reveals that the curve passes through the origin, indicating the absence of any significant COF_2 absorption on the column [559]. By using a packed column of silanised ™Silochrome, held at 15–35 °C, CO_2 and COF_2 were determined independently in the decomposition products of tetrafluoroethene oxide [2118]. A mixture of hexafluoropropene oxide, $CF_3C(O)F$, $CF_3CF_2C(O)F$, and COF_2 were similarly analysed [2117].

By using a column (maintained at room temperature) packed partly with 25 % "13F" (a chlorofluorinated liquid phase) on ™Floroplast 4 and partly with 10 % "13F" on ™Polysorb 1, COF_2 was determined in the presence of CO_2 and air with a sensitivity of 0.05 %, using a thermal conductivity detector and helium carrier gas [10].

Group 1 metal fluorides have been employed as column packings for the determination of COF_2 (and other fluorocarbonyl compounds) in mixtures with tetrafluoroethene [967]. By using a column composed of CsF supported upon CaF_2, the tetrafluoroethene is not chemisorbed and is eluted rapidly. The fluorocarbonyl compounds $(CF_3)_2C{=}O$ (b.pt. −28 °C), $CF_3C(O)F$ (b.pt. −59 °C), and COF_2 (b.pt. −84.6 °C), however, are eluted in reverse order of boiling temperatures, so that carbonyl difluoride is eluted last [967]. The chemisorption arises from the reversible chemical process [1692]:

$$CsF + COF_2 \rightleftharpoons Cs[OCF_3]$$

Columns consisting of a high surface area (> 130 $m^2\ g^{-1}$) graphite fluoride, $(CF_x)_n$, in which $0.5 < x < 1.14$, and in which n is an integer, have been used to separate CO, CO_2 and COF_2 in the presence of HF [1988].

Suitable gas chromatographic conditions for the analysis of carbonyl difluoride in mixtures with phosgene, carbonyl chloride fluoride, CO_2 and air are as follows [84a]:

> ™Porapak P; 9 ft. column. Helium carrier gas at 40 $cm^{-3}\ min^{-1}$. Temperature programmed at 70 °C for 2 min; 39 °C min^{-1} to 130 °C. Under these conditions the following retention times were typical:

Eluted component	Time/min
Permanent gases	1.0
COF_2	1.3
CO_2	1.5
COClF	2.8
$COCl_2$	6.0

13.3.4 Infrared spectroscopic methods

Infrared spectroscopy has been used for the quantitative determination of COF_2 in a mixture with tetrafluoroethene and hexafluorocyclopropane, resulting from the thermal decomposition of tetrafluoroethene oxide [1230]. The ν_2 absorption band at *ca.* 950 cm^{-1} was used for COF_2 [1230]; other workers have used ν_1 [427a]. Quantitative measurement of

CO_2 in COF_2 by infrared spectroscopy has been achieved using the 2380 cm^{-1} band [1580].

More recently, very sensitive i.r. techniques have been developed for measuring the low levels of COF_2 in the stratosphere (see Section 13.5).

13.4 TYPICAL ASSAY OF COMMERCIAL CARBONYL DIFLUORIDE

A typical analysis for commercially available COF_2 {BOC Special Gases Catalogue, 1979} is as follows:

Carbonyl difluoride	98.07 %
Carbon monoxide	0.51 %
Tetrafluoromethane	0.12 %
Phosgene	0.98 %
Carbonyl sulfide	0.32 %

In the experience of the authors, however, carbon dioxide is a persistent, common and undesirable impurity.

13.5 ENVIRONMENTAL CONSIDERATIONS

Carbonyl difluoride is not manufactured on any sort of large scale, so that direct industrial emissions of the gas need not be considered as far as the environmental issues are concerned. Natural emissions of COF_2 from volcanoes have been predicted by equilibrium thermodynamic models, but have yet to be experimentally verified [1990a].

Carbonyl difluoride does represent a significant environmental issue, however, as it is generated in the atmosphere from the breakdown of hydrochlorofluorocarbon-22, $CHClF_2$, which is used on a large industrial scale as a refrigerant, and as an intermediate in the production of PTFE and $CBrClF_2$, bromochlorodifluoromethane, a fire-fighting agent [1746a]. $CHClF_2$ reacts with hydroxyl radicals in the lower atmosphere according to:

$$CHClF_2 + \cdot OH \longrightarrow [CClF_2]\cdot + H_2O$$

$$[CClF_2]\cdot + O_2 \longrightarrow COF_2 + [ClO]\cdot$$

$[ClO]\cdot$ is then converted to HCl, which along with COF_2, is removed by rain before either component reaches the stratosphere [36b]. Even if COF_2 were to reach the stratosphere, however, it would not be expected to decompose the ozone there to any significant extent [36b]. The environmental fate of many of the newly proposed hydrofluorocarbons (HFCs – CFC replacements) is alleged to proceed *via* their decomposition to COF_2. However, this research is at an early stage, and remains to be verified.

Dichlorodifluoromethane, CCl_2F_2, undergoes photodissociation in the stratosphere according to the following initial process:

$$CCl_2F_2 \xrightarrow{h\nu} [CClF_2]\cdot + Cl\cdot$$

Chlorine atoms are thus released and are available to attack the environmental ozone. The free radical, $[CClF_2]\cdot$, reacts with dioxygen to release $[ClO]\cdot$ and form COF_2. Further dissociation of COF_2 results in the generation of carbon monoxide, and fluorine atoms, which are ultimately precipitated as HF in the troposphere [36b].

Carbonyl difluoride has been unequivocally detected in the stratosphere by infrared solar absorption spectroscopy instrumentation carried on board Spacelab 3 [624a,1718b], and with an i.r. Michelson interferometer carried in a balloon over New Mexico [1463a]; it has also been detected (by i.r. matrix isolation) in the stratosphere in several flights over Northern Europe, but not in the troposphere (*cf*. phosgene, Section 3.7.2) [932a]. Earlier, stratospheric concentrations of COF_2 were only inferred from transmittance measurements (in the 1240 cm^{-1} region) made by satellite [556]. Previously, the study of COF_2 was said to have been difficult, owing to interference by CH_4, H_2O, and N_2O. The concentrations of COF_2 in the lower stratosphere are increasing, currently, at the rate of 10.3% per year, based on measurements taken over the past decade [1718a]. However, an estimate of the residence time for COF_2 cannot yet be made, owing to the lack of necessary data [932b].

Stratospheric concentrations of HF have been calculated from the photolysis rates and vertical transport coefficients of CF_2Cl_2, $CFCl_3$, COF_2 and COClF [1994]. The atmospheric production rate for COF_2 was assumed to be equal to the photodecomposition rate of CF_2Cl_2, whereas its removal was assumed to be effected by reaction with $O(^1D)$ and by photolysis. The model predicts that HF is the most abundant fluorine-containing species in the stratosphere, with concentrations of COF_2 (and of COClF) calculated to be appreciably less than that of HF. In addition, the model also predicts that the maximum concentration of COF_2 occurs in the stratosphere at about 30 km above sea level [1994].

The recommended rate constant value for the reaction of COF_2 with $O(2\,^1D_2)$ at 298 K is $(3.5 \pm 0.7) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}; for physical quenching, an approximate value of $(1.0 \pm 0.4) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} is suggested [1808].

13.6 POTENTIAL USES OF CARBONYL DIFLUORIDE

There is an obvious and tremendous, but unfulfilled, potential for carbonyl difluoride as a reagent for commercial organic synthesis. COF_2 has a potential industrial utility as a fluorinating agent under conditions where the cheaper and abundantly available hydrogen fluoride is ineffective. For example, in the conversion of alcohols, ROH, to their corresponding fluorides, RF, only certain types of R group (*i.e.* R = CMe_3 or Me) will react with HF, whereas COF_2 combines with alcohols to form the corresponding fluoroformate, FC(O)OR, decarboxylation of which gives RF. Similarly, phenols do not combine with HF to form the corresponding aryl fluorides, but these can be formed by reaction with COF_2, again followed by decarboxylation of the product (see Section 13.14.6.1).

There are also potentially important inorganic applications of COF_2. Most of the industrially important low-oxidation-state metal fluorides are prepared from the reaction of their oxides, hydroxides or carbonates with aqueous or anhydrous HF. However, preparation of fluorides of metals in high formal oxidation states is usually achieved by the use of elemental fluorine on the metal, because of the problem of hydrolysis from the reversible reaction of the oxide with HF:

$$\mathrm{M_2O_5 + 10HF \rightleftharpoons M_2F_{10} + 5H_2O}$$

Indeed, in a recent patent, phosgene was used as a drying agent in this reaction, for the syntheses of niobium(V) fluoride and tantalum(V) fluoride [1481a]. COF_2 can provide a completely anhydrous route to these compounds, generating CO_2 instead of water as the co-product (see Section 13.13.2):

$$\mathrm{M_2O_5 + 5COF_2 \rightleftharpoons M_2F_{10} + 5CO_2}$$

It has also been suggested that COF_2 may be added to CO/O_2 mixtures to enhance the thermal deburring of superalloys, such as Nimonic 90 and Nimonic 80A [1130].

Perhaps the most likely immediate commercial application of carbonyl fluoride, however, arises from its spectroscopic properties. Irradiation of mixtures of COF_2 and H_2 (or D_2), over a wide pressure range and at ambient temperature, with the multiline output of a continuous wave CO_2 laser, results in the generation of excited state HF (DF) which lases [1387]. Energy transfer from the R_{12} line (970 cm^{-1}) of CO_2 (which is close in energy to the ν_2 band of COF_2) causes the dissociation of the COF_2 to CO and two excited state fluorine atoms which subsequently react with the dihydrogen (or dideuterium). However, COF_2 itself has been found to effect rapid vibrational de-excitation of HF^* [239], an observation that suggests that the COF_2/H_2 route to the HF laser may be of limited practicality.

In related experiments, COF_2 (formed *in situ*) has been shown to reduce the output power of DF–CO_2 transfer chemical lasers [553,611]. These lasers, which achieve population inversion by intermolecular energy transfer to the asymmetric stretching mode of CO_2 {*viz.* $\mathrm{DF}(\nu = n) + \mathrm{CO_2}(00^{\bullet}0) \longrightarrow \mathrm{DF}(\nu = n-1) + \mathrm{CO_2}(00^{\bullet}1)$} utilize CO_2, O_2, D_2 and F_2 as reactants, and N_2 or He as diluent gas; the deleterious effects were more marked with dinitrogen as diluent than with helium [553]. A rate constant of (225 ± 30) s^{-1} Pa^{-1} has been determined for the vibrational relaxation of $\mathrm{CO_2}(00^{\bullet}1)$ by COF_2 at 300 K. Its large magnitude has been attributed to resonant vibration-vibration energy transfer involving ν_1 of COF_2 and the $00^{\bullet}1 \longrightarrow 10^{\bullet}0$ transition of CO_2 [411]:

$$\mathrm{CO_2}(00^{\bullet}1) + \mathrm{COF_2} \longrightarrow \mathrm{CO_2}(10^{\bullet}0) + \mathrm{COF_2}(\nu_1) + \Delta E_{\mathrm{V}}$$

where ΔE_{V} is -4 cm^{-1} [411]

COF_2 has attracted some interest recently due its own laser action in the far-infrared/millimetre wave regions [465a,721aa,982a,2017,2040,2041,2041a]. Although there are inconsistencies between the report of Temps and Wagner [2017] and others [465a,2040,2041a], it is clear that COF_2 lases at more than ten wavelengths between 339 and 1900 μm when pumped by lines of the P and R branches of the 10 μm band of CO_2. Three lines - at 478, 700 and 1135 μm - gave an unoptimized continuous-wave power of more than a milliwatt, and particular attention was drawn to the lines at 700 and 1135 μm, as there are no other laser lines at these frequencies that are strong enough for local oscillator applications [2040,2041].

COF_2 (in the pressure regime 80 to 170 Pa) also lases when pumped by the 9-8 P(9,11) and the 10-9 P(12) lines of a CO laser [1494]. The emission (at 10 μm), which has been assigned to either $\nu_1 \longrightarrow \nu_2$ or $2\nu_2 \longrightarrow \nu_2$, is quenched if the COF_2 pressure is raised to 266 Pa, or if helium (1333 Pa) or argon (1866 Pa) are mixed with COF_2 at 80 Pa.

The possibility of using COF_2 as a 'fuel' for a new class of chemical lasers, utilizing electronic transitions in atoms, radicals or molecules excited as a result of oxidation chain reactions, has also been discussed [134a].

13.7 SYNTHESIS AND FORMATION OF CARBONYL DIFLUORIDE

The first authentic preparation of carbonyl difluoride in a pure state (*cf.* Section 13.7.5.4) was described by Ruff and Miltschitsky in 1934, by the interaction of carbon monoxide and silver(II) fluoride [1756]. Although this method still constitutes a convenient laboratory preparation, it is not economical on any larger scale owing to the prohibitive cost of AgF_2, which itself is prepared from silver and elemental fluorine.

Hydrogen fluoride is the most common, accessible, active fluorinating agent, and its interaction with phosgene is known to generate carbonyl difluoride (see Section 9.10.4). However, for reasons described in the appropriate section, it is difficult to separate the products from this reaction using normal distillation methods. Thus, many different sources of fluorine have been explored in the varied synthetic routes described in the following Sections. One of the most promising routes for commercialization is the electrochemical fluorination of carbon monoxide by liquid hydrogen fluoride (see Section 13.7.3.2).

13.7.1 Synthesis of carbonyl difluoride from carbon

13.7.1.1 Reaction with CaF_2/TiO_2 mixtures

Carbonyl difluoride can be prepared from heating approximately stoicheiometric proportions of calcium fluoride (fluorspar), titania, and lampblack or graphite in an electric arc furnace at 2800-3500 °C under a flowing argon atmosphere, according to [1205]:

$$CaF_2 + 2TiO_2 + 2C \longrightarrow COF_2 + CaTiO_3 + TiC$$

Other suitable fluorine-containing salts which could also be usefully employed include: NaF, KF, $Na_3[AlF_6]$, $Na_3[SiF_6]$ and fluorapatite, $Ca_5(PO_4)_3F$. Other suitable oxygen scavengers in the presence of carbon include the oxides of boron, zirconium, hafnium, thorium, aluminium, manganese(II), and lead(IV); borates, such as $K_2[B_2O_4]$, or $K_2[B_4O_7]$; and complex oxides, such as: $Be[Al_2O_4]$, $Fe[Al_2O_4]$, $Fe_3[P_2O_8]$, and ilmenite, $Fe[TiO_3]$.

13.7.1.2 Reaction with difluorine-dioxygen mixtures

Polycarbon monofluoride {graphite fluoride, $(CF)_n$} can be prepared from treating carbon with difluorine at 250–600 °C in the presence of air instead of inert gases. At 350 °C, using the partial pressure ratio of F_2:air = 0.15:0.85, for 90 minutes, a solid product corresponding to $(CF)_n$ was produced along with a residual gas, consisting of COF_2 (2.5 wt %), CO_2 (1.5 wt %), C_1–C_8 perfluorocarbons (4.0 wt %), and other by-products (2.0 wt %) [2083].

13.7.1.3 Reaction with iodine(V) fluoride

IF_5 reacts with the electrode in a carbon arc to give a mixture of fluorocarbons, including CF_4, C_2F_4, C_2F_6 and CF_3I: in addition, COF_2 and SiF_4 were produced in trace amounts [622].

13.7.1.4 Electrolysis of fluoride-containing melts

At an applied potential of 2.2–3.6 V to a graphite electrode in melts of alkali metal fluorides or beryllium fluoride at 500–700 °C, formation of CF_4, C_2F_6 and COF_2 was noted [2249]. The formation of COF_2 has been noted similarly during the electrolysis of oxofluorotitanate melts using graphite anodes [67].

COF_2 (along with CF_4) is evolved during the 'anode effect'† in industrial aluminium production by the electrolysis of bauxite in molten cryolite, $Na_3[AlF_6]$ at a graphitic electrode [66,842], and this has also been detected in fast cyclic voltammetric studies of solutions of Al_2O_3 in $Na_3[AlF_6]$ [1031b].

13.7.2 Synthesis of carbonyl difluoride from methane

COF_2 is produced as a principle combustion product (30–60 % of the composition) during the burning of methane in mixtures of F_2 and O_2 [108].

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†The anode effect consists of a sudden disruption of electrolysis, accompanied by a sharp drop in current, a rise in voltage, and intensive arcing.

13.7.3 Synthesis of carbonyl difluoride from carbon monoxide

13.7.3.1 Reaction with difluorine

Carbonyl difluoride can be synthesised by burning carbon monoxide in an atmosphere of difluorine according to [1193]:

$$CO + F_2 \longrightarrow COF_2$$

The difluorine is flushed through the entire apparatus (constructed of quartz or of copper provided with observation ports) until a piece of oil-soaked fabric can be ignited by the exit stream. The CO stream is then introduced into the reactor after igniting in air and adjusting to give a small flame. The CO and F_2 streams are controlled to provide a constant excess of the difluorine. If the reverse procedure is employed, of burning difluorine in an atmosphere of carbon monoxide, then there exists a risk of explosion in the event of the flame being unexpectedly extinguished. The COF_2 which is formed may be condensed into liquid dinitrogen, and subsequently fractionated and stored in steel cylinders.

Since the difluorine source frequently contains dioxygen, the COF_2 prepared by this method can be contaminated with CO_2, which is difficult to remove from COF_2 by distillation. In addition, the product may be contaminated with tetrafluoromethane (arising as a result of the dismutation equilibrium, $2COF_2 \rightleftharpoons CF_4 + CO_2$), which may be separated from the COF_2 by crystallization and distillation.

COF_2, free from contamination, was prepared by passage of difluorine with a small excess of CO over copper tubing heated to 100 °C, followed by condensation in a trap at −183 °C and removing the more volatile impurities *in vacuo* [1083]. Silver fluoride (supported as a film on copper) is also reported to act as a catalyst for this reaction, permitting the combination to take place rapidly, smoothly, and without explosion [2159a]. Neither caesium fluoride nor aluminium were found to be active [2159a].

Under normal conditions of temperature and pressure, the reaction between carbon monoxide and difluorine takes place only with a slow rate. After passage of equimolar amounts of CO and F_2 through a glass tube, however, an explosion was noted after about 15 min. At low pressures (2.7 kPa), the reaction is imperceptibly slow, and the equimolar gas mixture is not able to be ignited by a high voltage discharge [1756].

The kinetics of the thermal reaction between difluorine, CO and O_2 have been examined at sub-atmospheric pressures between 15 and 45 °C [948,949]. However, since dioxygen is found to strongly inhibit the reaction, only a small amount of COF_2 is formed, according to:

$$F\cdot + CO \longrightarrow [COF]\cdot$$

$$[COF]\cdot + F_2 \longrightarrow COF_2 + F\cdot$$

The main reaction product is the peroxide $(FCO)_2O_2$ [948,949].

In studies of the interaction of fluorine atoms (produced in a low power microwave discharge through NF_3 or CF_4 in argon carrier gas) with CO in an argon matrix (products rapidly quenched at 14 K), prominent infrared absorptions appeared characteristic of COF_2, in addition to those of $[COF]\cdot$ [1021,1022].

13.7.3.2 Reaction with hydrogen fluoride

Carbonyl difluoride is formed electrochemically by introducing CO into the pores of a porous anode (porous carbon) of an electrolysis cell containing anhydrous hydrogen fluoride with a small quantity of a metal fluoride, such as KF, to provide adequate conductivity [368]. Whilst the stoicheiometry corresponds to:

$$CO + 2HF \longrightarrow COF_2 + H_2$$

the mechanism of the process is believed to involve the migration of a fluorine-containing anion, from the HF electrolyte, into the pores of the anode. Here, an electron is discharged and a free radical intermediate is formed, which adsorbs to the anode surface forming a surface complex that is the actual fluorinating species. It has been established that elemental difluorine is not the fluorinating species in the process [368]. Using an electrolyte composition corresponding to KF.2HF, with the cell maintained at a voltage of 7 V at 86 °C, and at a current of 3 A (current density of 1000 A m^{-2}), the effluent volume composition for a CO feed rate of 3.78 dm^3 h^{-1} was 35.4 % COF_2, with 64.6 % unconverted CO [368].

In a similar electrochemical system, CO was injected into anhydrous HF containing a sodium fluoride concentration of 10 g dm^{-3}. Electrolysis, typically at 5–6.5 V with an anodic current density of 220 A m^{-2}, gave an effluent volume composition, for a CO feed rate of 1.56 dm^3 h^{-1}, of 46.4 % COF_2, 4.8 % CF_3OF, 25.6 % CF_4 and 23.2 % CO_2 [1472].

13.7.3.3 Reaction with tetrafluoromethane

The reaction of arc-generated carbon atoms with CF_4 in the presence of dioxygen resulted in the formation of carbonyl difluoride [1670]. COF_2 is also formed when a 4:1 molar ratio of CO and CF_4 (at a pressure of 0.7 kPa) is passed through an electric arc produced between graphite electrodes at 7500 V [1884].

13.7.3.4 Reaction with nitrogen(III) fluoride

At 520 °C, CO and NF_3 react, in equimolar flows through a nickel tube, to give COF_2 in yields of 90–95 %, according to:

$$3CO + 2NF_3 \longrightarrow 3COF_2 + N_2$$

Further reaction of the COF_2 with NF_3 gives small amounts of CF_4, NOF, NO and NO_2.

If an excess of CO is applied using a long reaction contact time (80 min), the yield of COF_2 is almost quantitative [770a].

The co-deposition of CO and NF_3 (having been passed through a microwave discharge) in an argon matrix generates a mixture of [COF]· and COF_2 [1021,1022].

13.7.3.5 Reaction with dioxygenyl hexafluoroantimonate(V)

When carbon monoxide is swept over powdered $[O_2][SbF_6]$ at ambient temperature, a rapid and exothermic reaction takes place producing dioxygen and carbonyl difluoride according to [1944]:

$$CO + 2[O_2][SbF_6] \longrightarrow COF_2 + 2O_2 + SbF_5$$

13.7.3.6 Reaction with oxygen difluoride

At 150–180 °C (and between 13–20 kPa), carbon monoxide reacts with OF_2 according to the overall stoicheiometry:

$$2CO + OF_2 \longrightarrow CO_2 + COF_2$$

The observation of induction periods of varying duration, particularly at the lower reaction temperatures, indicates the existence of a chain mechanism. The reaction is homogeneous, and is unaffected by total pressure, the surface:volume ratio, or the material of construction of the glass vessel. The rate of reaction is not very reproducible, but corresponds to a second order system [81c]:

$$\text{reaction rate} = k_2[CO][OF_2]$$

where,

$$k_2/\text{l mol}^{-1}\ \text{s}^{-1} = 1.45 \times 10^{12} \exp(-106315/RT)$$

The following chain mechanism was assumed, based on the overall stoicheiometry:

$$CO + OF_2 \longrightarrow [COF]\cdot + [OF]\cdot$$

$$[COF]\cdot + OF_2 \longrightarrow COF_2 + [OF]\cdot$$

$$[OF]\cdot + CO \longrightarrow [COF]\cdot + O$$

$$CO + O + M \longrightarrow CO_2 + M$$

$$[COF]\cdot + [OF]\cdot \longrightarrow COF_2 + O$$

Between 180 and 200 °C, carbonyl difluoride reacts further with OF_2 to give CF_3OF as the main reaction product [81c].

The kinetics of the reaction between OF_2 and CO have been studied in shock tubes in the temperature range of 800–1400 K (at about 133–267 kPa) [943]. Significant amounts of COF_2 are produced, in addition to CO_2, O_2 and F_2. COF_2 is understood to be formed from [COF]· as a result of the following elementary steps, the rate constants of which were estimated from thermodynamic and molecular data:

$$OF_2 + M \longrightarrow F\cdot + [OF]\cdot + M$$

$$[OF]\cdot + [OF]\cdot \longrightarrow O_2 + 2F\cdot$$

$$F\cdot + F\cdot + M \longrightarrow F_2 + M$$

$$[OF]\cdot + CO \longrightarrow CO_2 + F\cdot$$

$$OF_2 + CO \longrightarrow [COF]\cdot + [OF]\cdot$$

$$F_2 + CO \longrightarrow [COF]\cdot + F\cdot$$

$$F\cdot + CO + M \longrightarrow [COF]\cdot + M$$

$$OF_2 + [COF]\cdot \longrightarrow COF_2 + [OF]\cdot$$

$$F_2 + [COF]\cdot \longrightarrow COF_2 + F\cdot$$

$$F\cdot + [COF]\cdot + M \longrightarrow COF_2 + M$$

Under the influence of ultraviolet radiation (λ = 365 nm), the reaction between CO and OF_2 proceeds, even at 15–35 °C [1056a]. However, in addition to COF_2 and CO_2, comparable quantities of FC(O)OF and $(FCO)_2O_2$ are also formed. The rate of reaction is proportional to the light intensity, and is barely affected by the reaction temperature, the CO partial pressure, or the system's total pressure. The following elementary reactions contribute to COF_2 formation:

$$OF_2 \xrightarrow{h\nu} F\cdot + [OF]\cdot$$

$$CO + F\cdot + M \longrightarrow [COF]\cdot + M$$

$$[COF]\cdot + OF_2 \longrightarrow COF_2 + [OF]\cdot$$

The [OF]· radicals produced in the last step contribute to the chain–carrying mechanism as a result of the reaction:

$$[OF]\cdot + CO \longrightarrow [COF]\cdot + O$$

but its reaction with [COF]· leads to the formation of the by–product, FC(O)OF [1056a].

Experiments to generate [COF]· in CO or argon matrices by reaction of CO with F· (produced by the photolysis of OF_2, NF_2 or N_2F_2) also produce by–product COF_2 [1401].

13.7.3.7 Reaction with sulfur fluorides and oxide fluorides

The u.v. irradiation of a mixture of SF_4 and CO causes the slow production of COF_2, in addition to SF_6 and a small amount of COS. No reaction occurs, even after prolonged exposure (17 h), in the absence of the u.v. radiation [1345].

No reaction occurs thermally between SF_6 and CO up to 500 °C and 400 MPa [861a]. However, the reaction:

$$SF_6 + CO \longrightarrow COF_2 + SF_4$$

can be initiated by focused infrared radiation of frequency 931 cm^{-1} from a continuous CO_2–N_2–He laser of 16 [1639] or 20 W [1642] output. The reaction takes place in a cylindrical steel cell charged initially with partial pressures of 1.3 kPa SF_6 and 1.3 kPa CO [1639,1642], and was followed by periodically taking the infrared spectrum of the sample. SOF_2 and CF_4 were also formed, in minor amounts, as a result of the reaction between CO and the product SF_4. Whilst no clear explanation can be provided for the formation of CF_4, the other products of the reaction are accounted for in the following scheme [1639,1640]:

$$n_0(SF_6)^{\nu=0} \xrightarrow{h\nu} \sum_i n_i(SF_6)^{\nu\geqslant 0} + n^*SF_6^*$$

$$SF_6^* + CO \longrightarrow COF_2 + SF_4$$

$$SF_4 + CO \longrightarrow SOF_2 + :CF_2$$

By using a commercially available TEA CO_2 laser, the above laser-induced chemical reaction can be made to generate gram quantities of product per hour, which in real laser time could translate into kilograms of product per second [1842a].

Reaction of SF_5Cl with a five molar excess of CO under u.v. irradiation gave a volatile fraction containing COF_2 and COClF, in a ratio of about 1:15 [1345].

When heated at 500 °C over 2 h, SOF_2 combines with an excess of carbon monoxide to give an effluent composed of COS (13 %), CO_2 (11 %) and COF_2 (6 %), the remaining gas being unreacted CO [895]. Equimolar quantities of COF_2 and SOF_4 are produced by heating a mixture composed of equal partial pressures of CO and SF_5OF according to [2193]:

$$CO + SF_5OF \longrightarrow COF_2 + SOF_4$$

The reaction also takes place within two days at room temperature, under high pressure, to give the two uncontaminated products [2193]. In contrast, the photochemical decomposition (253.7 nm) of SF_5OF in the presence of carbon monoxide gave mainly CO_2 and SF_6, but a small amount of COF_2 was found to be one of the by-products of the reaction [641aa].

13.7.3.8 Reaction with bromine(III) fluoride

COF_2 is formed, in conjunction with COBrF, when carbon monoxide is bubbled through bromine(III) fluoride at 8–30 °C, according to [1196a,1596]:

$$2CO + BrF_3 \longrightarrow COBrF + COF_2$$

The reaction is rapid and exothermic (and may be explosive at too high a temperature), and the COF_2 and COBrF are readily separated by condensing out the COBrF into a trap cooled to −78 °C, and subsequently trapping the COF_2 into a trap cooled to −196 °C. To remove the final traces of bromine from the COF_2, it may be passed over antimony powder and recondensed [1193].

13.7.3.9 Reaction with iodine(V) fluoride

CO and IF_5 react under pressure (12 MPa) in an autoclave at normal temperature to give equal molar quantities of COF_2 and COFI (see also Section 16.4.1) [1196]:

$$3CO + IF_5 \longrightarrow 2COF_2 + COFI$$

13.7.3.10 Reaction with silver(II) fluoride

The reaction of carbon monoxide with silver(II) fluoride (prepared from the reaction of silver(I) fluoride and difluorine) is a particularly suitable method for the laboratory preparation of COF_2 {see Equation (13.2)} [611a,624,1756] without the necessity for low-temperature

$$CO + 2AgF_2 \longrightarrow COF_2 + 2AgF \qquad (13.2)$$

distillation. The precise preparative details have been described in *Inorganic Syntheses* [624], and will be described only in outline here. Following evacuation and flushing with helium, a mixture of metered flows of carbon monoxide and helium is passed *via* a pressure release device through a copper reaction tube containing silver(II) fluoride. An exothermic reaction ensues, and the effluent gases are passed *via* copper connections through a smaller tube containing sodium fluoride to remove any hydrogen fluoride produced from any adventitious moisture. A series of two glass traps immersed in liquid dinitrogen serve to condense the product COF_2. When the reaction is completed, the flow of gases is stopped and the apparatus evacuated. The storage cylinder is cooled in liquid dinitrogen (taking care to avoid any mechanical shock when in this condition), and connected to the glass traps which are allowed to warm to room temperature to permit transfer of the carbonyl difluoride. Yields of COF_2 by this method range typically from 70 to 85 % [624]. The principal contaminant is carbon dioxide, which may be present in the carbon monoxide starting material or formed from hydrolysis of COF_2 from traces of moisture in the apparatus. Purification of the CO and rigorous drying of the equipment are thus to be recommended. In addition, CO should be passed only at a slow rate over the silver(II) fluoride, in order to prevent too great a rise in temperature, giving rise to the formation of CO_2 from the dismutation equilibrium, Equation (13.3) [1580].

$$2COF_2 \rightleftharpoons CO_2 + CF_4 \tag{13.3}$$

13.7.3.11 Reaction with mercury(II) fluoride

COF_2 is formed from the reaction of carbon monoxide with mercury(II) fluoride; mercury is co-produced according to [1497]:

$$CO + HgF_2 \longrightarrow COF_2 + Hg$$

13.7.3.12 Reaction with uranium(VI) fluoride

Photoinduced dissociation of UF_6 {irradiated with a CO_2 laser ($\tilde{\nu}$ = 935 cm^{-1}) [985aa] or a Hg lamp ($\tilde{\nu}$ = 39417 cm^{-1}) [323a]} in SF_6-UF_6-CO gas mixtures produces COF_2, along with $\{UF_5\}_n$.

13.7.4 Synthesis of carbonyl difluoride from carbon dioxide or carbonyl sulfide

13.7.4.1 Reaction with tetrafluoromethane and other fluoromethanes

The reversibility of the dismutation equilibrium, Equation (13.3) {*cf.* Section 8.2}, has been proven at high temperatures over a platinum catalyst (see Section 13.13) [1755]. However, when mixtures of CO_2 and CF_4 were heated to 1036 K or 1173 K, no reaction was apparent, even after 3 weeks. The formation of COF_2 from CO_2 and CF_4 is thermodynamically favoured at low temperatures, although the time taken to reach equilibrium may be excessively long.

At temperatures around 900 °C, CCl_2F_2 reacts with carbon dioxide according to [1590]:

$$CO_2 + CCl_2F_2 \longrightarrow COCl_2 + COF_2$$

The reaction proceeds in the reverse direction at lower temperatures (see Section 13.13).

13.7.4.2 Reaction with nitrogen(III) fluoride

Mixing of CO_2 and NF_3, at equal flow rates through a nickel tube at 825 °C, gave a reaction consistent with the equation:

$$CO_2 + NF_3 \longrightarrow COF_2 + NOF$$

The COF_2 is produced with a yield of 80 %, but the contact times required for the reaction are excessively long (>2000 min). Further reaction of the NOF with the CO_2 starting material gives rise to the reaction by-products CF_4, NO_2 and NO [770a].

13.7.4.3 Reaction with oxygen difluoride

Photolysis of OF_2 in the presence of carbonyl sulfide/dioxygen mixtures results in the formation of F_2SO_4 and CO. If, however, irradiation is continued after total conversion of the COS, the products SOF_4, SO_2F_2, COF_2, CF_3OF and $(CF_3)_2O_2$ were formed [1925].

13.7.4.4 Reaction with sulfur fluorides

The high-temperature (500 °C) reaction of SF_4 with CO_2 in the approximate molar ratio of 2:1 over 2 h gave a yield of 10 % COF_2, with CF_4 being the major product formed with a yield of 80 % [895].

$$CO_2 + SF_4 \longrightarrow COF_2 + SOF_2$$

$$COF_2 + SF_4 \longrightarrow CF_4 + SOF_2$$

Quantitative fluorination of CO_2 to COF_2 has been achieved by the laser-induced reaction between SF_6 and CO_2 [1305,1640]:

$$2CO_2 + SF_6 \longrightarrow 2COF_2 + SO_2F_2$$

The method involves the irradiation of a gaseous mixture (2:1) of CO_2 and SF_6 in a reaction chamber at about 1-7 kPa, with a CO_2 laser beam at a frequency of about 940 cm^{-1} (which is strongly absorbed by SF_6; *cf.* Section 13.7.3.7).

13.7.4.5 Reaction with cobalt(III) fluoride

Carbonyl sulfide was fluorinated by a large excess of cobalt(III) fluoride at about 200 °C, using dinitrogen as a diluent and carrier. The condensed product was filtered at -110 °C: the solid material was shown to be SF_6, and the liquid product was a mixture of SF_6 and COF_2 [1881]. The reaction stoicheiometry corresponded to:

$$8CoF_3 + COS \longrightarrow 8CoF_2 + COF_2 + SF_6$$

13.7.5 Synthesis of carbonyl difluoride from phosgene

13.7.5.1 Reaction with difluorine

Related reactions to those described in this Section will be found in Section 9.7.7.

From early work, it is reported that the passage of difluorine and phosgene over granulated CaF_2, heated to 200 °C in a copper vessel, resulted in the formation of a mixture of dichlorine and carbonyl difluoride [992]. However, although the molecular weight determination of the fluorine-containing product corresponded to that of COF_2, analysis of the material for fluorine gave only 9.75 % (COF_2 requires 57.6 %) and the boiling point of the material was closer to that for COClF than for COF_2.

13.7.5.2 Reaction with hydrogen fluoride

Many related reactions to those described in this Section will be found in Section 9.10.4.

The reaction of phosgene with hydrogen fluoride offers a potentially attractive route to the synthesis of carbonyl difluoride. However, the hydrogen chloride co-product of the reaction, represented in Equation (13.4) has a boiling temperature (-83.1 °C) very close to that of COF_2 (-84.6 °C). In addition, azeotrope formation occurs, so that the two materials are only separated with great difficulty using normal distillation techniques. Separation of the two materials may be affected using aliphatic nitriles (such as ethanenitrile) or aromatic hydrocarbons (such as toluene) in which HCl is more readily absorbed relative to COF_2 [629,630]. Alternatively, the separation may be affected by adsorption of the HCl onto a metal fluoride, SO_3 or P_2O_5, which do not react at all readily with the COF_2 [2069].

$$COCl_2 + 2HF \longrightarrow COF_2 + 2HCl \qquad (13.4)$$

COF_2 could not be prepared by passing phosgene into anhydrous HF in the absence of a catalyst. However, the slow passage of phosgene into a mixture of hydrogen fluoride, ethanenitrile and triethylamine (which serves to bind the HCl co-product) between 10 and 40 °C results in the formation of carbonyl difluoride, which passes through a reflux condenser charged with a dry ice freezing mixture (used to contain the reactants) [681]. The yields of COF_2 using this method are in excess of 70 %, with carbon dioxide as the main contaminant.

At higher temperatures (about 150 °C) in an iron autoclave, COF_2 is formed from HF and $COCl_2$ in the molar ratio of 4:1.5 when in contact with activated carbon. After 10-17 h, the COF_2 yield is about 90 % [1196a].

A mixture of phosgene and anhydrous hydrogen fluoride, when passed over activated charcoal at 600 °C in a graphite tube, gives COF_2 as the principal product; at temperatures from 775-850 °C, tetrafluoromethane is the major product (in 20% yield), along with smaller amounts of CF_3Cl, COF_2 and COClF [399]. The reaction when carried out in the presence of activated charcoal or Cr_2O_3 pellets at 300 °C can give conversions to COF_2 of between 60 and 90% [ICI36]. However, much milder conditions are possible. For continuous flow operation, phosgene (or a mixture of CO and Cl_2) and HF may be brought into contact over calcium fluoride or charcoal at 150-300 °C and atmospheric pressure [2069]. Charcoal serves as an efficient catalyst for this reaction, and contact times as short as five seconds can be employed for good feed conversions. Treatment of the effluent gas with an alkali metal fluoride, such as sodium fluoride, at room temperature results in the removal of the co-product HCl or any unconverted HF, according to [2069]:

$$HCl + 2NaF \longrightarrow NaCl + Na[HF_2]$$

$$HF + NaF \longrightarrow Na[HF_2]$$

Similarly, SO_3 can be employed to remove HX (X = Cl or F), by virtue of the formation of XSO_3H. Short contact times are recommended, to avoid the possibility of SO_3 reacting with phosgene to form SO_2Cl_2 and CO_2 [2069]. Phosphorous(V) oxide forms HPO_3 and $POCl_3$ upon contact with HCl, with no detectable reaction between the P_2O_5 and COF_2. Any unconverted HF is also consumed by P_2O_5 to give POF_3 (b.pt. −40 °C) [2069].

Electrochemical fluorination of phosgene bubbled through anhydrous liquid hydrogen fluoride at 12–13 °C produces (in 72% overall yield) COF_2 (82%), CF_3OF (10%) and CF_4 (8%), along with dichlorine and traces of $CClF_3$ and OF_2 [1470], but under static conditions at 0 °C the primary product is COClF (91%) [2132]. Electrochemical fluorination of carbon monoxide under similar conditions (but with added sodium fluoride) produces (in 58% overall yield) COF_2 (71%), CF_3OF (8%), CF_3OOCF_3 (6%) and CF_4 (15%), along with traces of OF_2, CF_3OCF_3 and CO_2 [1470]: at −5 °C (in the absence of NaF), a mixture of COF_2, $C_nF_{2n+1}C(O)F$, C_nF_{2n+2}, CO and CO_2 was produced [2132]. Electrolysis of CO/Cl_2 and CO/HCl mixtures passed through liquid hydrogen fluoride at −5 °C produced COF_2 (80–90%), contaminated with COClF and $COCl_2$ [2132].

Hydrogen fluoride can also be delivered to phosgene as $[HF_2]^-$. Thus, the addition of phosgene over 50 min to a small stoicheiometric excess of $[NH_4][HF_2]$ in ethanenitrile, followed by heating for 1 h at 70 °C and trapping the products at −196 °C, gave COF_2 (89.8 %) and COClF (7.6 %) [1248].

Tertiary amine trishydrofluorides are stable complexes, very convenient for the delivery of hydrogen fluoride. They can be distilled *in vacuo*, and are suitable reagents for the nucleophilic replacement reactions of chlorine by fluorine under mild homogeneous conditions. The reaction of $COCl_2$ with $Et_3N.3HF$ [680] in dry ethanenitrile at room temperature proceeds quantitatively according to:

$$COCl_2 + 2[Et_3N.3HF] \longrightarrow COF_2 + 2[NEt_3H]Cl + 4HF$$

13.7.5.3 Reaction with Group 1 fluorides

Many related reactions to those described in this Section will be found in Section 9.1.1.

Phosgene reacts with a high temperature ionic liquid, LiF–NaF–KF, at 550 °C to give a mixture of COF_2 (70%), CO_2 (25%) and SiF_4 (4–5%), with traces of COClF (from the action of COF_2 on the walls of the glass vessel) [1978,1979]. This reaction is sustainable until the point at which all of the alkali fluorides are converted to the corresponding chlorides. However, under far milder conditions, phosgene will react with anhydrous sodium fluoride in a polar solvent ($\epsilon > 20$, *e.g.* ethanenitrile, nitromethane, dimethyl sulfate, ethylene carbonate or tetrahydrothiophene-1,1-dioxide) at 30 °C to give high yields (*ca.* 80%) of pure COF_2 [631]. Thus, the addition of a solution of phosgene in ethanenitrile, over a period of 1-2 h, to a stirred slurry of a stoicheiometric excess of sodium fluoride in ethanenitrile under reflux at 30-45 °C, gave carbonyl difluoride {see Equation (13.5)} with a phosgene conversion corresponding to 70-80 %. The COF_2 was of 95 % purity, with carbon dioxide as the major impurity. Carbonyl chloride fluoride and phosgene were present in trace amounts [632]. This appears to represent one of the most convenient laboratory-scale preparations of COF_2.

$$COCl_2 + 2NaF \longrightarrow COF_2 + 2NaCl \qquad (13.5)$$

In benzene, no COF_2 was formed [631]; with solid NaF and no solvent, small amounts of COClF were formed [631].

Preparation of COF_2 in a yield of 97 % was obtained by condensing $COCl_2$ on to a suspension of a large excess of NaF in CH_3CN, followed by warming the mixture to, and maintaining it at, 20 °C over 24 h in a sealed tube [1692]. Analysis by infrared spectroscopy revealed only CO_2 and SiF_4 as impurities, with no indication of COClF providing that a sufficient excess of NaF was employed in the preparation.

COF_2 is formed in the reaction between NaF and phosgene in liquid HCN, along with CO(CN)F [2068a,2070], and as a by-product in the reaction between C(O)ClC(O)Cl and NaF in tetramethylene sulfone [2070].

The reaction of phosgene with a two molar equivalent of a potassium fluoride-hexafluoropropanone complex (prepared from the reaction of KF and CF_3COCF_3 in diglyme) was conducted in a stirred reaction vessel cooled to -55 °C over 48 h, during which time the temperature rose to about 5 °C. On vacuum transfer of the volatile materials, carbonyl difluoride was formed in large, but unspecified, amounts [1385].

A solution of KF or CaF_2 in a fused $ZnCl_2$-KCl eutectic has been also found to be suitable for chloride-fluoride exchange with phosgene [1979].

13.7.5.4 Reaction with Group 2 fluorides

Heating equimolar quantities of phosgene and calcium fluoride at 500 °C in a steel bomb gives CCl_nF_{4-n} (n = 0-4) and some COF_2 and COClF [1454]: lowering the temperature to below 400 °C resulted in only mixtures of COClF and COF_2 being formed [1454]. The reaction between phosgene and a mixture of CaF_2 and KCl at 500 °C and 3.45 MPa also gives a mixture containing COF_2, COClF and unreacted $COCl_2$ [1561].

13.7.5.5 Reaction with Group 15 fluorides

Many related reactions to those described in this Section will be found in Section 9.1.4.

NF_3 combines with an equimolar amount of phosgene at 400 °C in a nickel tube to give COF_2 with a selectivity of 100 % [771]:

$$3COCl_2 + 2NF_3 \longrightarrow 3COF_2 + 3Cl_2 + N_2$$

At lower temperatures, the COF_2 selectivity falls and the selectivity to COClF increases (see also Section 9.1.4.1 and Chapter 16).

In early work, dating back to 1920, phosgene was reported to react with AsF_3 to produce COF_2, albeit in small yields [1947]. Although this material was prepared only in an impure form, it was the first account of the existence of COF_2. In the presence of a catalytic quantity of $SbCl_5$, at 130 °C and 5.5 MPa, the major product from the reaction of phosgene with AsF_3 was shown to be COClF with a much smaller amount (4 %) of COF_2 [378].

Both COF_2 and COClF can be prepared from the reaction of phosgene and SbF_3, depending upon the relative proportions and temperature conditions. Thus, phosgene combines with SbF_3 (50 % excess) in a rotating autoclave over 12 h at 200–280 °C (15 MPa) to give COF_2 which was free from hydrogen chloride (for the first time), but contaminated with CO_2 [589]:

$$3COCl_2 + 2SbF_3 \longrightarrow 3COF_2 + 2SbCl_3$$

COClF and unreacted phosgene were removed by passage of the gases through copper traps, cooled by solid carbon dioxide, to give COF_2 of 90–95 % purity. At 135 °C (3.25 MPa), in the presence of a catalytic amount of $SbCl_5$, SbF_3 reacts with phosgene to give COClF with only a minor proportion of COF_2 [589]. In the presence of Cl_2 at 285 °C, over 17 h, the reaction of SbF_3 with $COCl_2$ gave a yield of 80–85 % COF_2 in 95 % purity [900].

13.7.5.6 Reaction with sulfur fluorides and oxide fluorides

Related reactions to those described in this Section will be found in Section 9.1.5.

A three-fold molar excess of SF_4 reacts with phosgene, in the presence of a catalytic amount of TiF_4 at 250 °C over 4 h, to give 90 % CF_4 and 9 % COF_2 [895].

Treatment of phosgene with SOF_2 in the presence of a catalyst (such as $FeCl_3$, $AlCl_3$, UCl_4, LaF_3, WOF_4, or $SbCl_5$) at 300–400 °C and atmospheric pressure in the gas phase gave COF_2 (and COClF) according to the equations [704]:

$$2COCl_2 + SOF_2 \longrightarrow 2COClF + SOCl_2$$
$$COCl_2 + SOF_2 \longrightarrow COF_2 + SOCl_2$$

Passage of a 4:1 gas mixture of SOF_2 and $COCl_2$ through an iron tube filled with $FeCl_3$ and heated to 400 °C (with a contact time of 10 min) gave a COF_2 yield of 95.9 %: minor amounts of COClF and CCl_2F_2 (1-3 %) were also formed.

13.7.6 Synthesis of carbonyl difluoride from carbonyl chloride fluoride

A new and potentially economic route for the preparation of carbonyl difluoride has been found recently. This involves the catalytic disproportionation of carbonyl chloride fluoride over activated charcoal in a flow system at low temperatures (20-177 °C) [85a,ICI110]. The high yields obtained in the process correspond closely to those calculated for the equilibrium reaction:

$$2COClF \rightleftharpoons COF_2 + COCl_2$$

Since COClF can be formed directly from the reaction of phosgene with natural fluorspar, CaF_2 (see Section 9.1.1), the phosgene generated according to the above equation can be recycled so that the overall stoicheiometry represents the formation of COF_2 from calcium fluoride and phosgene. The yields of COF_2 in this reaction are found to closely approach those corresponding to the equilibrium values at temperatures above about 40 °C for contact times of $\leqslant$ 30 s. At room temperature, the equilibrium yields (corresponding to *ca.* 50 % reaction) are approached at higher contact times (*ca.* 125 s). When the activated charcoal catalyst was replaced by a high surface area silica, temperatures of around 200 °C and contact times of more than 30 s were required in order to obtain an extent of reaction of only 1 % [85a,ICI110].

13.7.7 Synthesis of carbonyl difluoride from metal(0) carbonyls

13.7.7.1 Reactions of pentacarbonyliron(0)

Condensation of $[Fe(CO)_5]$ onto CF_3NO in a steel bomb, followed by warming to -20 °C, resulted in the formation of COF_2 (indicated by the precipitation of diphenylurea on passage of the product gases into $PhNH_2$ solution), in addition to CF_4, CO_2, FeF_2, N_2, CO, $CF_3N(O)=NCF_3$ and $CF_3N=NCF_3$ [650].

Small amounts of carbonyl difluoride are produced in the reaction of $[Fe(CO)_5]$ with tetrafluorohydrazine, N_2F_4, in a steel bomb at about -10 °C [594]. In contrast, NF_3 and $[Fe(CO)_5]$ react only at temperatures above 100 °C, and at 200 °C a vigorous combination takes place with the formation of FN=NF, CO, and iron fluorides. Only a small quantity of COF_2 is formed, probably from the reaction of CO with FeF_3 [594].

A vigorous reaction occurs between $[Fe(CO)_5]$ and SF_5Cl at room temperature, in which most of the carbonyl groups of the metal carbonyl are evolved as CO; the remaining volatile material is composed of COF_2, $COCl_2$, COClF and COS [1345].

13.7.7.2 Reactions of tetracarbonylnickel(0)

$[Ni(CO)_4]$ reacts only slowly with SF_5Cl at room temperature, and without the formation of carbonyl dihalides. However, irradiation of the mixture with u.v. light results in the formation of COClF (as the main product), COF_2 and COS [1345].

13.7.7.3 Reactions of metal(0) carbonyl clusters

The reactions of XeF_2 with $[Ru_3(CO)_{12}]$ and $[Ir_4(CO)_{12}]$, in anhydrous hydrogen fluoride, generate COF_2 as one of the major prducts [273a].

13.7.8 Synthesis of carbonyl difluoride from oxygenates

13.7.8.1 Reactions of ketones

The fluorination of Me_2CO with cobalt(III) fluoride at 60 °C results in total cleavage into COF_2, CHF_3, MeF, CH_2F_2, $CH_3C(O)F$ and $CH_2FC(O)F$. Similarly, MeEtCO (at 50 °C) and Et_2CO (at 105 °C) both give COF_2, along with other fluorinated cleavage products [977]. Treatment of Me_2CO with F_2 (diluted with dinitrogen) at about 100 °C over a copper screen gave CF_3COCF_3 and $CH_2FC(O)Me$, along with CF_4, COF_2, $CF_3C(O)F$ and $(COF)_2$ [700].

Photolysis of 1,3-dichlorotetrafluoropropanone at 313 nm, in the presence of O_2 at 25 °C, gave COF_2 and CO_2 in a 2:1 ratio as the only carbon-containing products (no chlorine species could be detected using g.c., i.r., or mass spectrometry, but elemental chlorine is assumed to have been produced) [1980]. COF_2 is believed to be formed as a result of oxidation of $[CF_2Cl]\cdot$ radicals, formed in the primary step:

$$\begin{aligned}
CF_2ClC(O)CClF_2 &\xrightarrow{h\nu} 2[CF_2Cl]\cdot + CO \\
[CF_2Cl]\cdot + O_2 &\longrightarrow [CF_2ClO_2]\cdot \\
2[CF_2ClO_2]\cdot &\longrightarrow 2[CF_2ClO]\cdot + O_2 \\
[CF_2ClO]\cdot &\longrightarrow COF_2 + Cl\cdot
\end{aligned}$$

Passage of 2-heptafluoropropylcyclohexan-1-one saturated with I_2 through a carbon arc gave COF_2, along with a mixture of C_2 and C_3 perfluorinated alkanes [623].

13.7.8.2 Reactions of ureas

At −30 °C, or at room temperature, elemental fluorine (in N_2) reacts with urea to form COF_2, HF, NH_3, CO_2 and $(H_2NCONH)_2$ [773]. The electrolysis of urea in anhydrous HF at −10 °C (6 V, 10 A) gives NF_3 in a yield of about 50 %, but appreciable quantities of COF_2 are formed in addition to CF_4, F_2, CO_2 and NH_3 [1799]. The electrochemical fluorination of thiourea, $NH_2C(S)NH_2$, in molten KF.2HF at 120 °C, using amorphous carbon as the anode, gave COF_2 amongst the products, which consisted also of NF_3, SF_6, CF_4, N_2O, CO_2 and SO_2F_2 [2009].

13.7.8.3 Reactions of carboxylic acids and derivatives

The electrolysis of $CH_2(SH)C(O)OH$ in anhydrous HF (4.2 V, 10 A) gave $SF_3CF_2C(O)OH$, with COF_2 formed as one of the gaseous products [906].

Treatment of $Na[O_2CCF_3]$ with I_2 under a hot flame gave CF_3I, CO_2, COF_2, $CF_3C(O)Cl$ and $(CF_3CO)_2O$ [896]. Reaction of $CF_2(CO_2Ag)_2$ with elemental iodine gave AgI, CO_2, CO, COF_2 and $(CF_3CO_2H)_2$ [633].

Passage of F_2 (15–20 %) in N_2 (contaminated with 5–10 % O_2) into $CF_3C(O)NH_2$ at −6 °C gave NF_3, COF_2, CO_2, and CF_3COF. A similar treatment of $CHF_2C(O)NH_2$ at room temperature gave NF_3, COF_2, CO_2 and $CHF_2C(O)F$ [594a].

The heating of an intimate powdered mixture of equimolar quantities of calcium ethane-1,2-dioate with calcium fluorosulfonate to about 130 °C results in the evolution of CO and COF_2, with no trace of ethane-1,2-dioyl fluoride [1055]:

$$Ca[C_2O_4] + Ca[SO_3F]_2 \longrightarrow 2Ca[SO_4] + CO + COF_2$$

A lower yield of COF_2 is obtained when $Ca[SO_3F]_2$ is reacted with the free ethane-1,2-dioic acid [1055].

Treatment of $CCl_3OC(O)Cl$ with an alkali metal fluoride in MeCN, at 50–80 °C over 5 h, produced COF_2 in a high yield [969,971].

13.7.8.4 Reactions of organic hypofluorites

In an attempt to prepare trifluoromethanol, CF_3OH, trifluoromethyl hypofluorite was treated with an equal flow rate of dihydrogen at about 160 °C in a reaction vessel packed with copper ribbon [1078e]. However, the reaction proceeded to give carbonyl difluoride in accordance with:

$$CF_3OF + H_2 \longrightarrow COF_2 + 2HF$$

Trifluoromethyl hypofluorite reacts with mercury at room temperature to afford COF_2 and Hg_2F_2 [1648]. Lithium reacts similarly, but more slowly at the same temperature, giving COF_2 and lithium fluoride. With sulfur, both COF_2 and SF_4 are produced according to the stoicheiometry [1648]:

$$S + 2CF_3OF \longrightarrow 2COF_2 + SF_4$$

CF_3OF reacts with N_2F_4 at room temperature under u.v. irradiation to form mainly CF_3ONF_2; COF_2, NF_3, and CF_4 were formed as by-products [866a]. COF_2 is believed to have formed over a period of ten days when CF_3OF was in contact with a hydrocarbon stopcock grease at room temperature, although the material was found to be unreactive towards "Kel-F" (fluorothene) grease. On heating above 110 °C, or in the presence of certain (usually CH-containing) chemical initiators, the hypofluorite CF_3CF_2OF undergoes decomposition according to:

$$CF_3CF_2OF \longrightarrow CF_4 + COF_2$$

In the presence of an equimolar amount of methane, CF_3CF_2OF is almost completely decomposed in 24 h [1653b]. The mechanism for the propagation of this reaction is believed to occur as follows:

$$[CF_3CF_2O]\cdot \longrightarrow COF_2 + [CF_3]\cdot$$
$$[CF_3]\cdot + CF_3CF_2OF \longrightarrow CF_4 + [CF_3CF_2O]\cdot$$

In the presence of mercury, CF_3CF_2OF forms $CF_3C(O)F$, carbonyl difluoride and tetrafluoromethane [1653b].

Thermal decomposition of $CF_3CF_2CF_2OF$ behaves in a similar way to that for CF_3CF_2OF, with cleavage occurring at the C–C bond adjacent to the OF group, to give COF_2 and C_2F_6:

$$CF_3CF_2CF_2OF \longrightarrow C_2F_6 + COF_2$$

These products are similarly obtained when $CF_3CF_2CF_2OF$ is added to decomposition initiating agents such as hydrocarbons [1653b].

The substituted derivatives $O_2NCF_2CF_2OF$ and $ClCF_2CF_2OF$ undergo thermal decomposition in a similar manner to that described for the simple fluoroxyperfluoro compounds [1653b]:

$$XCF_2CF_2OF \longrightarrow CF_3X + COF_2$$
$$(X = NO_2 \text{ or } Cl)$$

Dichloro- or trichloro- substituted derivatives also give COF_2 and CF_2Cl_2 or $CFCl_3$, respectively, upon heating [1653b].

The bisfluoroxy compound, $FOCF_2CF_2CF_2OF$, upon heating or in the presence of hydrocarbons, gives tetrafluoromethane and two moles of COF_2 [1653a]:

$$FOCF_2CF_2CF_2OF \longrightarrow CF_4 + 2COF_2$$

13.7.8.5 Decomposition of trifluoromethanol

As seen in the preceding Section, trifluoromethanol has been an elusive synthetic target. However, it has now been prepared by treating CF_3OCl with HCl in CF_3Cl at –120 °C [1128,1842aa]:

$$CF_3OCl + HCl \longrightarrow CF_3OH + Cl_2$$

Trifluoromethanol is colourless, melting at −82 °C; it decomposes slowly at above −20 °C according to [1128,1842aa]:

$$CF_3OH \longrightarrow COF_2 + HF$$

13.7.8.6 Reactions of perfluorinated organic peroxides

COF_2 is a common decomposition product or by-product in many reactions of fluorinated peroxides or trioxides [502,511a,1833,1866]. Decomposition reactions of peroxides which result in COF_2 formation are described in this Section, in addition to Section 13.7.11.

The peroxide $(FCO)_2O_2$ decomposes into CO_2, O_2 and COF_2 above 100 °C. At temperatures above 200 °C, or when mixed with carbon monoxide, the decomposition proceeds explosively [81a,81b].

$$(FCO)_2O_2 \longrightarrow COF_2 + CO_2 + \tfrac{1}{2}O_2$$

$$(FCO)_2O_2 + CO \longrightarrow COF_2 + 2CO_2$$

Reaction of $(FCO)_2O_2$ with NO at room temperature proceeds according to [81a,81b]:

$$(FCO)_2O_2 + NO \longrightarrow NO_2 + CO_2 + COF_2$$

COF_2 was produced as the principal product when nitrogen(II) oxide was combined with CF_3OOCF_3. The reaction follows the rate law [927]:

$$d[COF_2]/dt = 2k[NO][CF_3OOCF_3]$$

over the pressure range 0.4–47 kPa, with $k = 10^{9.2} \exp(-18100/RT)$ l mol^{-1} s^{-1} over the temperature range 25–128 °C. NO_2 is also generated, with SiF_4 resulting from wall reactions. No further reaction occurs between NO and COF_2, even at 128 °C. The pyrolysis of pure CF_3OOCF_3 has also been examined [138]:

$$CF_3OOCF_3 \rightleftharpoons CF_3OF + COF_2$$

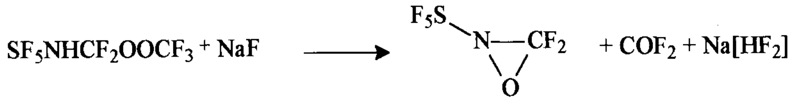
The perfluoroformate $(CF_3)_3COOC(O)F$ combines with ClF over caesium fluoride at −60 to −65 °C to generate a quantitative yield of COF_2 [2240]:

$$(CF_3)_3COOC(O)F + ClF \longrightarrow (CF_3)_3COOCl + COF_2$$

If the reaction is carried out at −78 °C, $(CF_3)_3COOCF_2OCl$ is formed, which decomposes cleanly on warming to give COF_2, O_2, CF_3Cl and $(CF_3)_2CO$ [2240]. Similarly, in the presence of CsF, $R_fOOC(O)F$ ($R_f = CF_3$ or SF_5) adds ClF across the carbonyl group to form the intermediate, R_fOOCF_2OCl which decomposes to eliminate COF_2 [2240]:

$$R_fOOC(O)F + ClF \longrightarrow R_fOOCl + COF_2$$

The dehydrofluorination of $SF_5NHCF_2OOCF_3$ over sodium fluoride at 22 °C gives the oxaziridine (13.1) according to the equation [1835]:



(13.1)

13.7.8.7 Reactions of isocyanates

When a mixture of KF and K[OCN] in cylinders of brass gauze (within a copper reactor) was treated with a F_2/N_2 mixture at 50–55 °C, the principal products were CF_3OF, NF_3 and KF, with small amounts of COF_2 and CO_2 being formed [2220]. However, the analogous reaction with Ag[OCN] produces COF_2 as the principal reaction product, along with AgF_2 [2220].

The alkali metal fluorides, KF, CsF or NaF, catalyse the polymerisation of gaseous chloroisocyanate, ClNCO, but COF_2 is formed as a by-product of the reaction, according to [805]:

$$ClNCO + MF \longrightarrow FNCO + MCl$$

$$2FNCO \longrightarrow COF_2 + N_2 + CO$$

Indeed, FNCO is unstable at room temperature, even in the gas phase, and its reactions and decompositions generally produce COF_2, either as one of the main products, or as a by-product [749a].

13.7.9 Synthesis of carbonyl difluoride from tetrafluoroethene

Carbonyl difluoride is usually the major product of the oxidation of tetrafluoroethene, $CF_2{=}CF_2$, whether the oxidation is induced thermally, photochemically or by ionising radiation.

Serious concern that some of the commonly used fluorocarbons may adversely affect the concentration of ozone in the stratosphere have prompted many studies of the oxidation of tetrafluoroethene to COF_2, with a wide range of oxidizing agents.

13.7.9.1 Oxidation with oxygen atoms

Oxygen atoms, $O(^3P)$, produced from the mercury-photosensitized decomposition of N_2O (253.7 nm), react with C_2F_4 in the presence of molecular oxygen to form carbonyl difluoride and dinitrogen in approximately equal amounts, in addition to smaller quantities of tetrafluoroethene oxide, C_2F_4O, and perfluorocyclopropane [926,928a]. At room temperature, using an excess of N_2O (66.7 kPa) and 0.4–16 kPa C_2F_4, quantum yields for COF_2 were approximately equal to unity, regardless of either exposure time or light intensity. The addition of further amounts of O_2 (0.7–20 kPa), however, generates an increase in the quantum yield for COF_2, up to about 3. At 125 °C, $\Phi(COF_2)$ can increase to about 10 [926]. The reaction mechanism involves a small chain at ambient temperature, although, at 125 °C, the chain is both branched and larger.

In the absence of O_2, the mechanism is given by [400b]:

$$
\begin{aligned}
Hg &\xrightarrow{h\nu} Hg^* \\
Hg^* + N_2O &\longrightarrow Hg + N_2 + O(^3P) \\
O + C_2F_4 &\longrightarrow COF_2 + CF_2 \\
O + C_2F_4 &\longrightarrow C_2F_4O^* \\
2CF_2 &\longrightarrow C_2F_4 \\
CF_2 + C_2F_4 &\longrightarrow cyclo\text{-}C_3F_6 \\
C_2F_4O^* + C_2F_4 &\longrightarrow COF_2 + cyclo\text{-}C_3F_6
\end{aligned}
$$

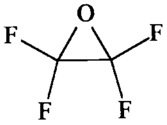
Whereas, in the presence of molecular oxygen the mechanism is proposed to be [926,1782a]:

$$
\begin{aligned}
CF_2\ (\text{triplet}) + O_2 &\longrightarrow CF_2O_2 \\
2CF_2O_2 &\longrightarrow 2COF_2 + O_2 \\
CF_2O_2 + C_2F_4 &\longrightarrow 2COF_2 + CF_2\ (\text{triplet})
\end{aligned}
$$

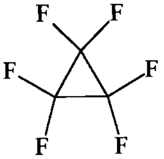
In the presence of ethene, it is noted that C_2F_4 and ethene scavenge the oxygen atoms with equal ease, the rate constant being 0.6×10^9 dm^3 mol^{-1} s^{-1} [1782a].

13.7.9.2 Oxidation with dioxygen

Carbonyl difluoride is the principal product of the oxidation of tetrafluoroethene by molecular oxygen, whether induced thermally, photolytically, or by ionizing (X-ray or γ-ray) radiation. A comparison of the methods has been carried out for the gas phase in a static system, and the results are summarized in Table 13.2 [320]. Tetrafluoroethene oxide, C_2F_4O (13.2), and hexafluorocyclopropane, $(CF_2)_3$ (13.3), are formed as additional gaseous products



(13.2)



(13.3)

of the reactions and a small quantity of polymeric peroxide $(C_2F_4O_2)_x$ is formed in the liquid phase.

TABLE 13.2

REACTION OF C_2F_4 AND O_2 (1:1) UNDER STATIC CONDITIONS; A COMPARISON OF THERMAL AND RADIATIVE TREATMENTS [320]

Compound		Method			
		X-ray[a]	γ-ray[b]	u.v.[c]	Thermal[d]
Conversion / %:	C_2F_4	25.3	22.0	64.2	15.5
	O_2	18.3	15.7	43.0	8.5
Yield[e] / %:	COF_2	47.2	47.5	47.4	41.7
	C_2F_4O	37.2	30.1	40.0	14.7
	$(CF_2)_3$	4.5	5.7	7.0	42.0

[a] Initial pressure 101.3 kPa; dose rate 0.4 Mr h^{-1}; 1.5 h. [b] Initial pressure 86.7 kPa; dose rate 0.4 Mr h^{-1}; 1.5 h. [c] Initial pressure 101.3 kPa; 75 W low pressure Hg lamp; 24 h exposure. [d] Initial pressure 101.3 kPa; 100 °C; 14 h. [e] Yields based on percentage of C_2F_4 consumed.

The gas phase oxidation of tetrafluoroethene with an equimolar amount of dioxygen, Equation (13.6), takes place at 200–450 °C in a flow system at contact times of 1–10 s. The

$$CF_2{=}CF_2 + O_2 \longrightarrow 2COF_2 \qquad (13.6)$$

reaction is highly exothermic (ΔH = −761 kJ mol^{-1}), selective, and almost quantitative: it has consequently been proposed as a potential manufacturing route to COF_2 [413,572]. Only small amounts of by-products {such as CF_4, CO_2, CF_3COF and $CF_3OC(O)F$} are formed.

Carbonyl difluoride itself can be used as a diluent and heat sink for the reaction [413], but fluorinated organic compounds such as HCFC-22 ($CHClF_2$) or CFC-113 ($CClF_2CCl_2F$) can also be used as inert diluents during the reaction and serve to dissolve the COF_2 during condensation, thereby reducing its volatility and making it more convenient to handle [1319].

Reaction of C_2F_4 with O_2–OF_2 mixtures was also noted to produce COF_2 in high yield [2164].

Oxidation of tetrafluoroethene (C_2F_4) by molecular oxygen can be induced by ionizing radiation [320,321,420,959,1013,1997] (^{60}Co γ-ray or 50 kV X-ray) at room temperature and a total pressure, for the 1:1 mixture, equal to atmospheric. The process occurs, *via* a chain reaction, to give the fluorinated gaseous products, COF_2 (as the major product in 27.9 % yield), the epoxide, $(CF_2)_2O$, and perfluorinated cyclopropane [321,420]. A yield of 29.4 % of COF_2, based on equation (13.6), was obtained by exposure of a 10:1 mixture of dioxygen and C_2F_4 to ^{60}Co γ-irradiation at 15 °C and 0.76 MPa [1013].

Kinetic studies of the oxidation of C_2F_4 by molecular oxygen induced by ionising radiation reveal that variation of the dioxygen partial pressure (in the range 14–63 kPa) does not effect the reaction rate. In contrast, the initial rate of formation of COF_2 is strongly dependent upon the partial pressure of C_2F_4. The overall rates of formation of the three gaseous compounds have been estimated from the experimental data. For COF_2, the following equation holds, in which the dose rate, I, is expressed in Mrad h^{-1}, the concentration of C_2F_4 is in mol dm^{-3}, and the overall reaction rate is expressed in mol dm^{-3} h^{-1} [420]:

$$d[COF_2]/dt = (0.26 \pm 0.02)\, I^{0.72}[C_2F_4]$$

The apparent activation energy for the γ-ray induced formation of carbonyl difluoride is calculated to be 18.0 kJ mol^{-1}. The kinetics results indicate a chain mechanism in which primary radicals formed from the irradiation of C_2F_4 induce its copolymerization with O_2. The resulting long-chain peroxide radicals decompose by splitting off COF_2 or C_2F_4O, depending upon whether a carbon–carbon, or oxygen–oxygen bond is broken. The perfluorinated cyclopropane is considered to be formed independently, in a minor side-reaction [420].

The mercury-photosensitized oxidation of C_2F_4 at 253.7 nm to give COF_2 can be explained by two processes [928,928a]. The first is attack of the C_2F_4 by oxygen atoms resulting from the Hg-photosensitized decomposition of O_2:

$$O + C_2F_4 \longrightarrow C_2F_4O \xrightarrow{O_2} 2COF_2 + O$$

and the second involves the reaction of molecular oxygen with an electronically-excited C_2F_4 molecule:

$$C_2F_4^* + O_2 \longrightarrow 2COF_2$$

The u.v.-irradiation (365 nm) of a mixture of C_2F_4 and O_2, in the presence of Cl_2 at 31 °C, gave COF_2 as the exclusive oxidation product formed in a long chain process, according to the following scheme [1776]:

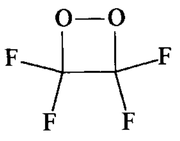
$$\begin{aligned}
Cl_2 &\xrightarrow{h\nu} 2Cl\cdot \\
CF_2{=}CF_2 + Cl\cdot &\longrightarrow [CF_2ClCF_2]\cdot \\
[CF_2ClCF_2]\cdot + O_2 &\longrightarrow [CF_2ClCF_2O_2]\cdot \\
2[CF_2ClCF_2O_2]\cdot &\longrightarrow 2[CF_2ClCF_2O]\cdot + O_2 \\
&\longrightarrow (CF_2ClCF_2O)_2 + O_2 \\
[CF_2ClCF_2O_2]\cdot + [CF_2ClCF_2]\cdot &\longrightarrow (CF_2ClCF_2O)_2 \\
[CF_2ClCF_2O]\cdot &\longrightarrow CF_2ClC(O)F + F\cdot \\
&\longrightarrow COF_2 + [CF_2Cl]\cdot
\end{aligned}$$

Oxidation of $[CF_2Cl]\cdot$ gave COF_2, regenerating the $Cl\cdot$ atom in the process:

$$[CF_2Cl]\cdot + \tfrac{1}{2}O_2 \longrightarrow COF_2 + Cl\cdot$$

This results in very high quantum yields for COF_2, with values ranging from 430–1283:

The reaction of C_2F_4 with $O_2(^1\Delta)$ in a low pressure discharge flow system results in the observation of electronically excited products, formed from the decomposition of the corresponding dioxetane, (13.4) [225].



(13.4)

C_2F_4 in a shock tube forms difluorocarbene, $:CF_2$, which reacts immediately with molecular oxygen to produce COF_2 [1420,1421a]; similarly, $C_2F_4{:}O_2$ (95:5) mixtures in a glow discharge (for the plasma etching of silicon to SiF_4) produce by-product COF_2 [1646].

13.7.9.3 Oxidation with trioxygen (ozone)

C_2F_4 reacts with an excess of trioxygen at room temperature to give COF_2 and O_2. The formation of an intermediate and unstable ozonide, $C_2F_4O_3$, was assumed, although C_2F_4O or CF_3CFO were not detected. The rates of reaction of C_2F_4 with O_3 are fast, and increase with increase of C_2F_4 and O_3 concentrations. However, at large concentrations of O_3, the reaction rate begins to decrease again, probably as a result of diffusion control [923].

Passage of equal flow rates of C_2F_4 and O_2 (the O_2 having been previously passed through an ozonizer) into a reactor at 15 °C and 98.7 kPa resulted in a gaseous effluent composition of 55.4 % C_2F_4, 18.1 % C_2F_4O, 26.0 % COF_2 and 0.5 % C_3F_6 {(13.3)}. Liquid poly(oxyperfluoromethylene), $-(-CF_2O-)_n$, was obtained as a residue [1425]. Similar yields of COF_2 were obtained by performing the reaction in a chlorofluorocarbon solvent {particularly CFC-113a (CF_3CCl_3)} [1426]. The addition of trioxygen initiates the reaction between C_2F_4 and dioxygen [414]. In a flow system, using approximately equal feed rates of C_2F_4 and O_2 in a helium diluent containing 0.53 % of O_3, at 100 °C and atmospheric pressure, contact times of 4–34 s were sufficient to give a yield of COF_2 of 70.8 % based on a C_2F_4 conversion of 57.2 %. Under similar conditions, using 0.26 % of O_3, the yield of COF_2 and conversion of C_2F_4 were 20.9 % and 13 %, respectively. In the absence of O_3, under these conditions, no reaction was observed [414].

13.7.9.4 Oxidation with nitrogen(II) oxide

When a mixture of C_2F_4 and NO in a large excess of argon was heated to 2600 K by reflected shock waves, COF_2 was formed as a result of the following reactions [1418]:

$$C_2F_4 \longrightarrow 2CF_2$$

$$CF_2 + NO \longrightarrow CF_2NO$$

$$CF_2NO + NO \longrightarrow COF_2 + N_2O$$

$$2CF_2NO \longrightarrow 2COF_2 + N_2$$

Because of the high dinitrogen content of the product mixture, the last reaction is considered to be the most important.

13.7.9.5 Oxidation with oxygen fluorides

Condensation of C_2F_4 onto solid dioxygen difluoride at −196 °C is accompanied by flashes immediately upon contact, to give COF_2 and CF_4, along with lesser amounts of C_2F_6, SiF_4 and CF_3OOCF_3 [978]. Under similar experimental conditions, but in the presence of diluent argon, CF_3OF, OF_2 and C_4F_{10} were obtained in addition to the products mentioned above. In the presence of diluent helium, the products included those described above (with the exception of OF_2) along with CO_2, $C_2F_5OCF_3$ and octafluorofuran. The steps necessary to account for COF_2 formation, and its subsequent reactions, are as follows [978]:

$$C_2F_4 + O_2F_2 \longrightarrow CF_3OF + COF_2$$

$$C_2F_4 + O_2F_2 \longrightarrow OF_2 + C_2F_4O \longrightarrow COF_2 + (CF_2)_n \quad (n = 1\text{-}4)$$

$$CF_3OF + C_2F_4 \longrightarrow C_2F_5OCF_3$$

$$CF_3OF + COF_2 \longrightarrow CF_3OOCF_3$$

13.7.9.6 Oxidation with fluorine nitrate

NO_3F reacts almost quantitatively with C_2F_4 at room temperature in the gas phase according to [2038]:

$$C_2F_4 + NO_3F \longrightarrow COF_2 + CF_3NO_2$$

The products are probably formed from the decomposition of $C_2F_5ONO_2$, which in turn results from the addition of $FONO_2$ across the double bond [2038].

13.7.9.7 Oxidation with sulfur dioxide

Photolysis of SO_2 in the presence of C_2F_4 at room temperature with 313 nm radiation gave COF_2, C_3F_6 (13.3), and polymer. For all experiments with C_2F_4 pressures above 2.7 kPa, $\Phi(COF_2)$ was virtually constant at 0.05, whereas at low pressures $\Phi(COF_2)$ decreased with decreasing C_2F_4 or increasing SO_2 concentrations. No change could be observed at SO_2 partial pressures above 10 kPa. The addition of NO suppressed product formation, and the addition of an excess of dinitrogen had no effect, indicating that the emitting states (which are strongly quenched by N_2) are not chemically important in this system. The principal COF_2-forming reaction is as follows:

$$SO_2^* + C_2F_4 \longrightarrow SO + COF_2 + CF_2$$

in which SO_2^* represents the non-emitting singlet or triplet states of SO_2. The CF_2 generated according to the above equation can either dimerize, or add to C_2F_4 to give the observed cyclic product (13.3) [348].

13.7.10 Synthesis of carbonyl difluoride from other halogenated hydrocarbons

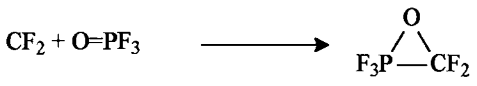
Carbonyl difluoride is formed frequently during the oxidation of many fluorine-containing halocarbons. The "simplest" fluorocarbon, CF_2 (prepared from the decomposition of trifluoromethyl fluorophosphoranes), when generated at 100 °C in the presence of O_2, gives COF_2 [1299].

With OPF_3, CF_2 reacts either as a reducing agent or a fluorinating agent, Equations (13.7) or (13.8), respectively. At 100 °C, reaction (13.7) accounts for 95 % of the

$$CF_2 + OPF_3 \longrightarrow COF_2 + PF_3 \qquad (13.7)$$

$$CF_2 + OPF_3 \longrightarrow CO + PF_5 \qquad (13.8)$$

products and reaction (13.8) for 5 %, whereas, at 25 °C, the relative compositions are reversed. From these product ratios, it was estimated that reaction (13.7) has an enthalpy and entropy of activation of 75 kJ mol^{-1} and 209 J mol^{-1} K^{-1}, respectively, greater than those for reaction (13.8). Addition of CF_2 to the P=O bond is the first step involved for either reaction:



Breakage of the P–O bond or the P–C bond in the cyclic intermediate (above) leads to reaction (13.7), whereas reaction (13.8) requires a series of fluorine shifts from the carbon to the phosphorus atom, to give CO and PF_5 [1300].

Carbonyl difluoride is the principal end-product of the photo-oxidation of a number of CFCs and HCFCs (*e.g.* CCl_2F_2 and $CHClF_2$) in the stratosphere, but is itself relatively inert. The photolysis (λ = 213.9 nm) of CCl_2F_2 in the presence of O_2 results in the formation of COF_2 ($\Phi = 1.0$) and Cl_2 ($\Phi \approx 0.59$) [1037]. COF_2 is also generated ($\Phi \approx 1.09$) by the photo-oxidation of CCl_2F_2 at 184.9 nm [88,2202a]. Similar results were found when either CCl_2F_2 or $CHClF_2$ were oxidized with O(^{1}D) [88,1624]:

$$O(^1D) + CCl_2F_2 \longrightarrow COF_2 + Cl_2$$

$$O(^1D) + CHClF_2 \longrightarrow COF_2 + HCl$$

These reactions proceed with 85% and 50% yield, respectively [1624]. COF_2 has been generated by irradiating mixtures of CHF_3 and O_2 with CO_2 laser pulses ($\tilde{\nu}$ = 1085.8 cm^{-1}), under conditions suitable for the multiphoton dissociation of the trifluoromethane [1501a]. COF_2 is also the primary product from the multiphoton decomposition of mixtures of C_2F_6 and O_2 [1578a].

The mechanism for the photochemical formation of COF_2 by the oxidation of CFCs (and related materials) is of significant interest. Take, for example, the photo-oxidation of CF_3I; the initiation step is clearly [922a]:

$$CF_3I + h\nu \longrightarrow [CF_3]\cdot + I\cdot$$

The oxidation of the trifluoromethyl radical, $[CF_3]\cdot$, has attracted a significant level of attention. One of the two possible mechanisms postulated by Heicklen [922a] involved direct oxidation:

$$[CF_3]\cdot + O_2 \longrightarrow COF_2 + [OF]\cdot$$

However, mass spectrometric studies [1761a] have shown that the reaction proceeds *via* the intermediacy of a peroxyfluoromethyl radical, according to Heicklen's second proposal [922a]:

$$[CF_3]\cdot + O_2 \xrightarrow{M} [CF_3O_2]\cdot$$

This reaction proceeds [1761a] at 295 K with a second-order rate constant, k_2, of 8×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. As the reaction of $[CF_3O_2]\cdot$ with itself is endothermic, its fate in the stratosphere must be to form COF_2 by secondary reactions [2105a,2105b]. A recent matrix isolation study (argon; 4.2 K) has shown that this may occur by reaction with NO, producing equal amounts of COF_2 and FNO_2 from a common intermediate [395b]:

$$\{[CF_3O_2]\cdot + NO\} \longrightarrow CF_3OONO$$

$$\{[CF_3O_2]\cdot + NO\} \longrightarrow \{[CF_3O]\cdot + NO_2\}$$

$$CF_3OONO \longrightarrow COF_2 + FNO_2$$

$$CF_3OONO \longrightarrow \{[CF_3O]\cdot + NO_2\}$$

$$\{[CF_3O]\cdot + NO_2\} \longrightarrow COF_2 + FNO_2$$

$$\{[CF_3O]\cdot + NO_2\} \longrightarrow CF_3ONO_2$$

$$CF_3ONO_2 \longrightarrow COF_2 + FNO_2$$

This overall process is exothermic.

The substrates, and a brief summary of the reaction conditions, leading to COF_2 formation are summarized in Tables 13.3, 13.4 and 13.5, for the C_1, C_2 and C_3 halocarbons, respectively. Of course, COF_2 formation by the oxidation of fluorocarbons is not restricted to these materials, but there have been far fewer examples studied of the oxidation of fluorocarbons containing greater than three carbon atoms than of those containing three or less carbon atoms. One such example is the photochemical oxidation of perfluoro-1,5-hexadiene by atmospheric dioxygen [653a]. Another such example is the room temperature oxidation of octafluorobut-2-ene by trioxygen, which results in the formation of COF_2 and trifluoroethanoyl fluoride in the ratio of 2.8:1 [923]. The mechanism of the reaction was presumed to proceed *via* the formation of an intermediate ozonide [923], with the further reaction of $CF_3C(O)F$ (in

TABLE 13.3

COF_2 FORMATION: OXIDATION OF C_1 HALOGENATED HYDROCARBONS

Halocarbon	Oxidant; Conditions; Products	Ref.
CF_4	O_2; 2450 MHz; CF_4 plasma	153,1646
CF_4	NO; electric arc; 2000 °C	1259
$CBrF_3$	O_2; 450-550 °C	68
$CBrF_3$	O_2; u.v. (>220 nm); 6.0 h; 0.6 MPa	677
$CBrF_3$	O_2; in H_2-O_2-N_2-CF_3Br flame	1225
$CBrF_3$	O_2; in CH_4-O_2-Ar-CF_3Br flame	196
$CBrF_3$	O_2; in CO-H_2-O_2-Ar flame	995
$CBrF_3$	O_2; u.v. (184.9 nm); COF_2 ($\Phi = 1.02$)	2202a
CF_3I	O_2; u.v. (>220 nm); 1.3-4.0 h; 0.2-0.6 MPa	677,922a
$CHClF_2$	O_2; 200-500 °C	143a
$CHClF_2$	O_3; 20 °C	1147
$CHCl_2F$	O_2/Cl_2; u.v. (365.5 nm); COF_2 ($\Phi \in [10,100]$) and HCl	1776a
$CHCl_2F$	O_2; u.v.	1857a
CHF_3	O_2/Cl_2; u.v. (360 nm); COF_2 ($\Phi \in [0.02,0.11]$) SiF_4 and HCl	1776a
CCl_2F_2	WO_2; 525 °C	2159
CCl_2F_2	O_3; 20 °C	1147
CCl_2F_2	O_2; u.v. (welding arc)	1130c
CCl_2F_2	O_2; u.v. (184.9 nm); COF_2 ($\Phi = 1.08$)	2202a
$CBrClF_2$	O_2; u.v. (>220 nm); 6.5 h; 0.6 MPa	677
	O_2; u.v. (248 nm); 20 °C	2067
CBr_2F_2	O_2; u.v. (>220 nm); 1.3-6.5 h; 0.6 MPa	677
CBr_2F_2	O_2; u.v. (206, 248, 302 nm); Br_2 formed	1424

the excited state) with O_3 invoked to account for the production of the excess COF_2:

$$CF_3C(O)F + O_3 \longrightarrow 2COF_2 + O_2$$

However, a more reasonable explanation may be as follows [103a]:

TABLE 13.4

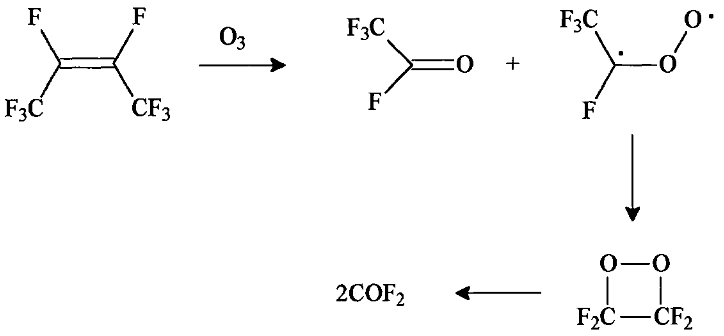
COF$_2$ FORMATION: OXIDATION OF C$_2$ HALOGENATED HYDROCARBONS

Halocarbon	Oxidant/Conditions	Ref.
CF_3CH_2F	O_2/N_2; u.v.; $CF_3C(O)F/HC(O)F$ major products	2066aa
$CF_2ClCFCl_2$	O_2; 500-1000 °C	1325
CF_3CF_2I	O_2; u.v. (313 nm); 25 °C	1326
CH_2CHF	O_2 (1 g); low pressure discharge	225
CF_2CF_2	See Section 13.7.9	
CF_2CFCl	O_2; room temperature	1156
CF_2CFCl	O_2; u.v.; room temperature	908
CF_2CFCl	O_2; laser-induced photolysis (1050 cm^{-1})	1270
CF_2CFCl	O_2; initiated by Cl_2; room temperature	1197
CF_2CFCl	O_2/F_2 mixture; 25 °C	1397
CF_2CFBr	NO; u.v.; 200-500 °C; FCN also formed	849

TABLE 13.5

COF$_2$ FORMATION: OXIDATION OF C$_3$ HALOGENATED HYDROCARBONS

Halocarbon	Oxidant/Conditions	Ref.
C_3F_6	O_2; 300 °C (215 °C, NaF or CsF catalyst)	2174
C_3F_6	RuO_2; inert solvent; room temperature	847
C_3F_6	O_2; 300-700 °C; 0.1 MPa	1872
C_3F_6	O_2; 220-250 °C; metal oxide catalyst	2047
C_3F_6	O_2; u.v. (253.7 nm); Hg vapour; 24 °C	925
C_3F_6	O_2; u.v. (>220 nm); Hg vapour; 25 °C	924
C_3F_6	O_2; ^{60}Co γ-rays (0.35 Mr h^{-1}, 25 h); 25 °C	1229
$CF_3CF_2CFCl_2$	O_2; $h\nu$ (>220 nm); 0.15-2 MPa; 6-28 h	677
$CF_3CF_2CFClBr$	O_2; $h\nu$ (>220 nm); 0.5 MPa; 0.5-10 h	677
C_3F_7I	O_2; $h\nu$ (>220 nm); 0.25 MPa; 1.5 h	677
CF_3CF_2CFClI	O_2; $h\nu$ (>220 nm); 0.2-0.5 MPa; 0.5 h	677



The oxidation of halogenated methanes by SO_3 is particularly worthy of mention. By choice of the halogen substituents, each of the more common carbonyl dihalides, both symmetrical and asymmetrical, can be prepared by a convenient laboratory method. For the synthesis of carbonyl difluoride, the reagents CF_2Cl_2 or CF_2Br_2 may be used. The addition of CF_2Br_2 (0.5 mol) to SO_3 (2.5 mol) at 35–44 °C over 2 h resulted in a yield (based on CF_2Br_2) of COF_2 of 63 %, according to [1875]:

$$CF_2Br_2 + SO_3 \longrightarrow COF_2 + SO_2 + Br_2$$

Inadvertent generation of small quantities of carbonyl difluoride may thus arise from the scrubbing of the commercially produced CF_2Cl_2 (CFC–12) with strong sulfuric acid.

Pentafluorosulfur hypofluorite, F_5SOF, combines with CCl_4 to give COF_2, Cl_2 and F_5SOSF_5 according to [2193]:

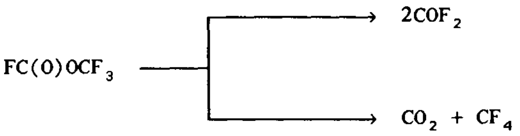
$$CCl_4 + SF_5OF \longrightarrow COF_2 + 2Cl_2 + F_5SOSF_5$$

The carbon–chlorine bond of CCl_4 required activation by u.v. light over 30 h, before any liberation of Cl_2 was observed.

13.7.11 Preparation of COF_2 by decomposition reactions of oxygenates

COF_2 is generated in a wide variety of thermal and photochemical decomposition reactions, which are conveniently considered together here; there is inevitable overlap with the material presented in Section 13.7.8.

Trifluoromethyl fluoroformate decomposes on strong heating in a quartz vessel to produce carbonyl difluoride, carbon dioxide and tetrafluoromethane [94]. The reaction may proceed by two separate pathways, as indicated below:



Gaseous tetrafluoroethene oxide, C_2F_4O, undergoes unimolecular decomposition at 115–140 °C to give COF_2, $F_2C{=}CF_2$ and perfluorocyclopropane {at lower temperatures, isomerisation of the C_2F_4O occurs to form $CF_3C(O)F$}. The high temperature reactions can be accounted for by the following reaction scheme [1230]:

$$C_2F_4O \longrightarrow COF_2 + :CF_2$$

$$:CF_2 + :CF_2 \longrightarrow F_2C{=}CF_2$$

$$:CF_2 + F_2C{=}CF_2 \longrightarrow C_3F_6$$

The reversible thermal decomposition of CF_3OF into COF_2 and F_2 has been studied over the temperature range 327–467 °C [1648] and 367–467 °C [1649]. From the equilibrium constants, ΔH for reaction (13.9) has been calculated to be 116±6 kJ mol^{-1} at 427 °C;

$$CF_3OF \longrightarrow COF_2 + F_2 \qquad (13.9)$$

113 kJ mol^{-1} at 25 °C. At temperatures between about 250 and 300 °C, the following reaction takes place:

$$COF_2 + CF_3OF \longrightarrow CF_3OOCF_3 \qquad (13.10)$$

Passage of CF_3OF over a cold-glow electrical discharge (from a vacuum "leak tester" of the Tesla-coil variety) immersed in a metallic vessel caused decomposition into COF_2 (0.38 mol per mol of CF_3OF), F_2, CF_4, CO_2, O_2 and fluorocarbons [1649].

Ultraviolet photolysis (230–400 nm) of trifluoromethyl hypofluorite in dilute argon matrices at 8 K gave carbonyl difluoride as the only product observable by infrared spectroscopy, equation (13.9), and with no evidence for the formation of the peroxide CF_3OOCF_3. The subsequent photodissociation of the molecular fluorine produced results in the production of fluorine atoms, which are sufficiently mobile to escape the argon matrix cage [1902].

The hypochlorite analogue, CF_3OCl, also decomposes both thermally and photochemically to give COF_2 [1790b]. Thus, CF_3OCl photodissociates at wavelengths below 280 nm, under similar conditions to CF_3OF, to give both COF_2 and CF_3OOCF_3, along with smaller amounts of CF_3OF, ClF, and COClF. The following processes are considered to be important [1902]:

$$CF_3OCl \xrightarrow{h\nu} COF_2 + FCl$$

$$FCl \xrightarrow{h\nu} F\cdot + Cl\cdot$$

$$(CF_3OCl)_2 \xrightarrow{h\nu} CF_3OOCF_3 + Cl_2$$

The decomposition of trifluoroethanoyl hypofluorite between 30 and 80 °C is catalysed by a copper surface to give mainly CO_2 and CF_4, with some COF_2, C_2F_6 and C_3F_8 [1956].

Photochemical decomposition of $CF_2(OF)_2$ at low conversion between −20 and 30 °C obeys the stoicheiometry [427]:

$$CF_2(OF)_2 \longrightarrow COF_2 + F_2 + \tfrac{1}{2}O_2$$

with a quantum efficiency of 0.65 ± 0.3 molecules per quantum, independent of other conditions. When a large concentration of COF_2 is added to the reactants the reaction mechanism is changed and CF_3OOCF_3 is formed amongst the products [427]. In the presence of CO, the reaction stoicheiometry is

$$CF_2(OF)_2 + 2CO \longrightarrow 2COF_2 + CO_2$$

for which $\Phi = 1.0 \pm 0.1$ molecules per quantum [427].

The hydroperoxide, $(CF_3)_3COOH$, decomposes at 120 °C to form carbonyl difluoride and hexafluoropropanone according to [2240]:

$$(CF_3)_3COOH \longrightarrow COF_2 + HF + (CF_3)_2CO$$

Photolysis (300–400 nm) of CF_3OOF in an argon matrix at 8 K resulted in trace quantities of COF_2 according to [1901]:

$$CF_3OOF \xrightarrow{h\nu} COF_2 + OF_2$$

CF_3OOCF_3 was noted to start to decompose to COF_2 and other (unidentified) products at about 225 °C, decomposition being complete at 325 °C [1649]. The kinetics of the thermal decomposition of reaction (13.11), which is the reverse of reaction (13.10), have

$$CF_3OOCF_3 \longrightarrow CF_3OF + COF_2 \qquad (13.11)$$

been measured in the temperature range of 177–307 K and the results interpreted in terms of the mechanism [1084]:

$$CF_3OOCF_3 \rightleftharpoons 2[CF_3O]\cdot$$

$$[CF_3O]\cdot \rightleftharpoons COF_2 + F\cdot$$

$$[CF_3O]\cdot + F\cdot \rightleftharpoons CF_3OF$$

The disproportionation reaction:

$$2[CF_3O]\cdot \rightleftharpoons CF_3OF + COF_2$$

is considered not to play any significant role in the scheme [1084].

Vibrationally excited $[CF_3O]^-$ ions (generated from the dissociation of CF_3OOCF_3 using an electron beam pulse) were trapped whilst irradiating with infrared light from a CO_2 laser. Multiphoton dissociation results in the following reaction [1034]:

$$[CF_3O]^- \xrightarrow{nh\nu} F^- + COF_2$$

The u.v. photolysis of the trioxide CF_3OOOCF_3, at wavelengths below 300 nm in argon matrices at 8 K, gave CF_3OOF, CF_4, CF_3OCF_3, CF_3OF and COF_2 [1901]. COF_2 is formed as a result of the reaction:

$$CF_3OOOCF_3 \xrightarrow{h\nu} COF_2 + CF_3OOF$$

Passage of $(C_2F_5)_2O$ over sodium fluoride at 700 °C or 800 °C gave 3 % or 30–50 % conversion, respectively, of the ether into COF_2 [560].

The bis(trifluoromethyl) trioxide derivatives, $CF_3OOXOCF_3$ and CF_3OXOCF_3 (X = SO_2, SF_4, or CO) prepared from reacting CF_3OOOCF_3 with SO_3, SF_4, and CO, respectively, can eliminate COF_2 according to the following reactions [974]:

$$CF_3OOXOCF_3 \longrightarrow CF_3OXF + COF_2 + \tfrac{1}{2}O_2$$

$$CF_3OXOCF_3 \longrightarrow CF_3OXF + COF_2$$

Pyrolysis of $(CF_3)_2NC(O)F$ at 500–600 °C [2238], or at 490 °C over activated carbon [910], causes elimination of COF_2 and forms $CF_3N{=}CF_2$, quantitatively, according to:

$$(CF_3)_2NC(O)F \longrightarrow CF_3N{=}CF_2 + COF_2$$

At 720 °C and at low pressure, perfluoro-(3-azabut-2-enoyl) fluoride gave mainly the decarbonylation product, $CF_3N{=}CF_2$. However the formation of COF_2 (14 % yield) and trifluoroethanenitrile (13 % yield) indicated that decomposition also occurred according to the following reaction scheme [111a]:

$$CF_3\text{-}N{=}CF\text{-}COF \longrightarrow COF_2 + CF_3NC$$

$$CF_3NC \longrightarrow CF_3CN$$

Passage over potassium fluoride at 450 °C gave a clean conversion into an inseparable mixture of CF_3NC and COF_2, both materials having boiling temperatures of around 83 °C [111a].

$(CF_3)_2NOCF_3$ decomposes to COF_2, CF_4 and $CF_3N{=}CF_2$ at room temperature in a 2 kV, 10 mA glow discharge. Under the same conditions, in the presence of mercury, $CF_3N{=}CF_2$, COF_2, NF_3 and HgF_2 are formed, although in the further presence of NO the compound is stable. At −196 °C, at 4–5 kV and 15–20 mA, in the presence of NF_3, $(CF_3)_2NOCF_3$ decomposes to COF_2, CF_4, CF_3OF, N_2O, C_2F_6, and an unidentified solid [1113].

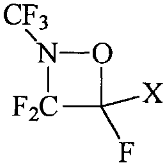
The thermal decomposition of tetrafluoroethene in shock waves is a convenient source of difluoromethylene radicals. Their oxidation with NO results in the reversible formation of CF_2NO but, above 2500 K, the reaction proceeds further to equilibrium by the following reactions [1418]:

$$2CF_2NO \longrightarrow 2COF_2 + N_2$$

$$CF_2NO \longrightarrow 2COF_2 + N_2O$$

Trifluoronitromethane, CF_3NO_2, pyrolysed at 500 °C in a platinum tube gave NOF, CO_2 and COF_2 [897].

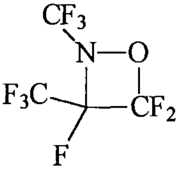
Pyrolysis [122,123] or photolysis [112] of the oxazetidine (13.5; X = F) caused almost complete decomposition into COF_2 according to the reaction:



$$\longrightarrow F_3C\text{-}N{=}CF_2 + COF_2$$

(13.5)

Irradiation of a mixture of (13.5; X = CF_3) and its isomer (13.6) gave a composition consisting of COF_2, $CF_3N{=}CFCF_3$, CF_3COF and $CF_3N{=}CF_2$ [112].



(13.6)

Decomposition of the oxaziridine (13.1) at 50 °C over KF for 24 h results in COF_2 formation along with OSF_2, CF_3NO and SF_6 [1835].

Thermal decomposition of the perfluoromethanesulfonate salt, $Nd(O_3SCF_3)_3$, at 800 °C over 4 h and under a stream of flowing N_2 gave the volatile products COF_2 and SO_2 [2022].

The photolysis of fluoral, CF_3CHO, gave mainly C_2F_6 and CHF_3 with a smaller quantity of COF_2 [907].

COF_2 is formed amongst other gaseous anodic products during the electrochemical fluorination of methanamide or ethanamide in molten $K[HF_2].HF$ [2010].

The continuous-wave CO_2 laser-induced decomposition of hexafluoropropanone, sensitized with SF_6, gave COF_2, perfluorinated hydrocarbons, carbon monoxide, and trifluoroethanoyl fluoride [1641]:

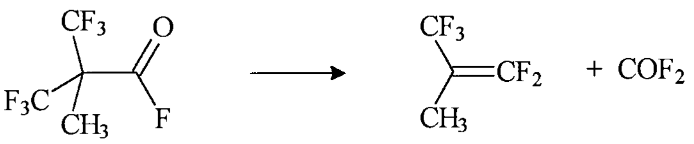
$$SF_6 \xrightarrow{nh\nu} SF_6^* \xrightarrow{(CF_3)_2CO} (CF_3)_2CO^* \longrightarrow COF_2 + 2\ {:}CF_2$$

Passage of $CF_3C(O)OH$ through a tube furnace at 950 °C and 1.9–6.7 kPa pressure gave the products CO_2, COF_2, C_2F_4, C_2F_6, and CF_4 [623]. Infrared multiphoton dissociation of $CF_3C(O)OH$ (using a pulsed CO_2 laser) also gave COF_2 as one of the photoproducts [1179b]. Barium trifluoroethanoate decomposes thermally (at 282 °C and low pressure) into trifluoroethanoyl fluoride, trifluoroethanoic anhydride and COF_2 [1884].

The dissociation of trifluoroethanoyl fluoride under pulsed CO_2 laser radiation gave COF_2, C_2F_6 and CF_4 [87a]. Traces of COF_2 were also observed by dissociation of trifluoroethanoyl chloride in a strong infrared carbon dioxide laser field [87b].

When heated to 450 °C *in vacuo*, sodium octafluorohexane-1,6-dioate, decomposed to give NaF, carbon, hexafluoro-1,3-butadiene and COF_2 [898].

The elimination of carbonyl difluoride from trifluoromethylated acyl fluorides is catalysed by amides. For example, dmf induced the following transformation at 130 °C [1545]:



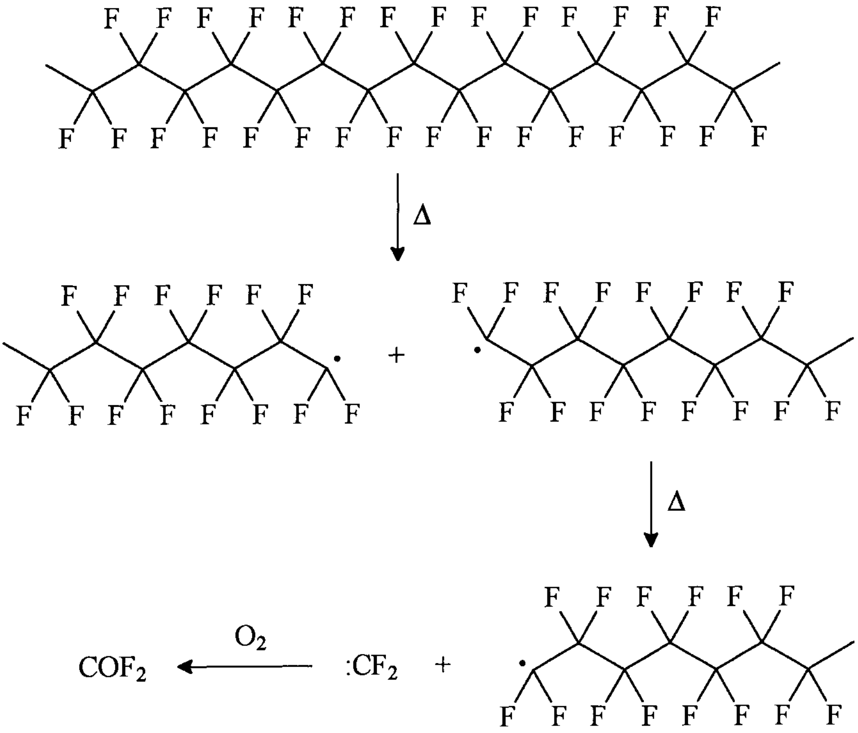
13.7.12 Formation of COF_2 by the thermal and oxidative decomposition of polymers

The thermal decomposition of poly(carbon monofluoride), $\{(CF)_n\}$, in air results in the formation of COF_2 [2235].

The potential hazards associated with the liberation of COF_2 from fluoropolymers has been described in Section 13.1.6. In particular, the thermal decomposition of poly(tetrafluoroethene) (PTFE), and of other fluorinated polymers, can give rise to a condition known as polymer fume fever. Fortunately, toxic products of PTFE (used commonly as a coating for non-stick cooking utensils) are only significant at temperatures in excess of those achieved in ordinary cooking procedures (< 200 °C) [1217]. The general nature of the hazard was recently highlighted in a considered note on chemical safety by Christe [376a]:

whilst the combustion of Teflon, $(CF_2)_n$, in dioxygen is highly exothermic (ΔH = −619 kJ mol^{-1}), the activation energies for such reactions are so high that, under normal operating conditions, it is difficult to initiate combustion [376a].

COF_2 is generated from PTFE in air, both by pyrolysis [1166,1247,1285,1382,1794, 2149,2167], and by exposure to ionizing radiation [647,790]. A possible scheme for the formation of COF_2 by PTFE pyrolysis is indicated below, involving homolytic fission of the polymer chain, fragmentation to eliminate difluorocarbene, and its subsequent oxidation to COF_2 [1382,2149]:



In addition several other products are generated by the thermal decomposition of PTFE in air. Below 275 °C, no hazards are apparent; between 300–360 °C, HF and $F_2C{=}CF_2$ are formed; above 380 °C the toxic gases, hexafluoropropene and octafluoroisobutene (see Section 13.1.7) can be generated [1553]. COF_2 is formed at temperatures above 400 °C. COF_2 is the principal volatile product generated from the thermal decomposition of PTFE between 500–650 °C, although at temperatures above 650 °C (the ignition temperature for PTFE in air is 575 °C) the dominant products were CO_2 and CF_4 [430,1217,1581]. The yield of COF_2 as a function of temperature from the decomposition of PTFE is recorded in Table 13.6 [403].

TABLE 13.6

OXIDATIVE DECOMPOSITION OF PTFE [403]

Temp/ °C	COF_2 yield (g COF_2/g PTFE)
500	0.57
600	0.63
700	0.24
800	0.14
900	0.20

When air is heated to between 2000–6000 K and passed over a PTFE surface, carbonyl difluoride is detected by its emission infrared spectrum in the PTFE/air boundary layer [2239]. COF_2 has also been detected in an ablating flat plate air–PTFE laminar boundary layer [820,821] {generated with a subsonic free stream of air (1 atm, 3000–6000 K) produced by an arc jet}: CO, CO_2, and NO were also observed in this experiment.

Primary or secondary fluorocarbon radicals formed from exposure of PTFE to an ionizing radiation source react with dioxygen to form perfluoroalkylperoxy radicals. These give rise to perfluoroalkoxy radicals which can then decompose as indicated below [790]:

$$\sim\sim\sim CF_2CF_2O\cdot \longrightarrow \sim\sim\sim CF_2\cdot + COF_2$$

Commercial samples of PTFE react with ozone, in the dark and at room temperature, to generate carbonyl difluoride, amongst other products. The rate of reaction is proportional to the surface area of the PTFE sample and to the concentration of O_3 [454a]. The mechanism appears to involve the reaction between O_3 and a terminal alkene bond at or near the surface of the polymer (see Fig. 13.1).

COF_2 was also formed by the decomposition of a PTFE-lined vessel containing SF_6 and exposed to a high current (9.2 kV; 30 kA) arc [966].

Poly(fluoroethenepropene) (PFEP) film was pyrolysed in air at 350–430 °C to produce COF_2 amongst the gaseous products, which also included trifluoroethanoyl fluoride, $F_2C{=}CF_2$ and hexafluoropropene [75]:

$$\{CF_2CF_2\sim\sim\sim CF(CF_3)CF_2\sim\sim\sim\}_n \longrightarrow \begin{array}{l} CF_2: + CF_3CF: + COF_2 + CF_3C(O)F + \\ CF_2{=}CF_2 + CF_3CF{=}CF_2 \end{array}$$

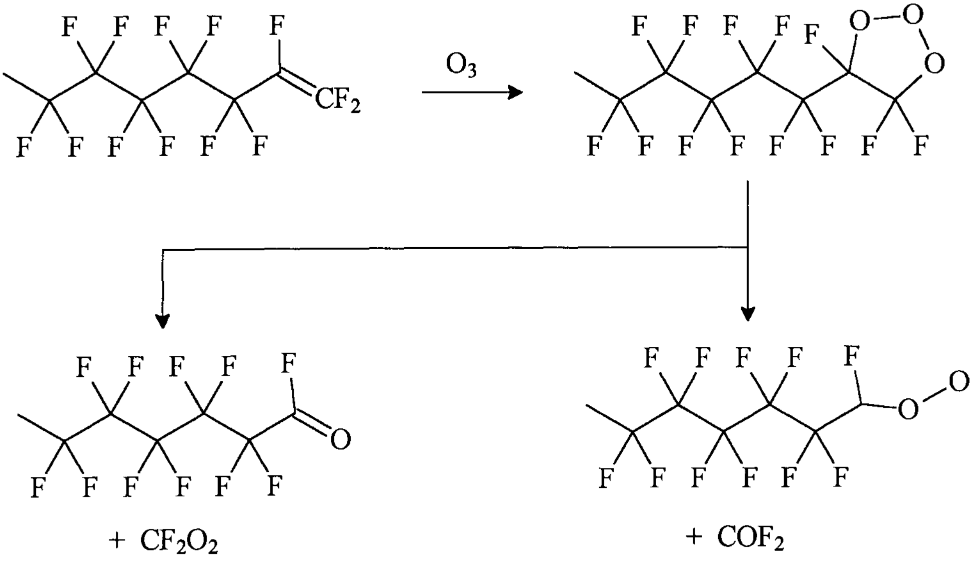


Fig. 13.1 **A possible mechanism for the decomposition of PTFE by ozone [454a].**

Fluorination of high molecular weight polyethers with elemental fluorine (diluted with helium) at room temperature gave fluorinated polyethers, which were depolymerized by further treatment with flowing F_2–He at 55–210 °C to produce carbonyl difluoride, amongst the decomposition products [1197c]. COF_2 is also formed in the oxidative thermal degradation of polyethers derived from hexafluoropropene oxide [1582]. Polymeric $C_2F_4O_2$ decomposes, at an unspecified temperature, into carbonyl difluoride [760]. The presence of hydrogen-terminated chains in commercial perfluoroalkyl ethers, such as $C_3F_7O\{CF(CF_3)CF_2O\}_xC_2F_5$, results in a lowering of the thermal oxidative stability. Thus, at *ca.* 350 °C, in a dioxygen atmosphere, $C_3F_7O\{CF(CF_3)CF_2O\}_xCF(CF_3)H$ degrades to give COF_2 and $CF_3C(O)F$ as the primary products [1580a].

COF_2 has been detected as a primary decomposition product of high stability, non-flammable, carboxynitroso rubber [1122]. The use of carboxynitroso rubber as a fire-resistant furnishing material in enclosed habitable spaces that are subject to restricted ventilation (*e.g.* aircraft) is thus to be strongly discouraged.

When heated at 270–400 °C *in vacuo*, the colourless oil believed to be the polymer $\{CF_2CF_2N(CF_3)O\}_x$ (obtained from the reaction of CF_3NO and C_2F_4 at temperatures below room temperature) gives $CF_3N{=}CF_2$ and COF_2 [122]. Indeed, reaction generally between CF_3NO and $CF_2{=}CXY$ ($CF_2{=}CFCl$, $CF_2{=}CCl_2$, or $CF_2{=}CFCF_3$) yields either an oxazetidine or a viscous or elastomeric 1:1 copolymer $\{N(CF_3)OCF_2CXY\}_n$. At 550 °C, the copolymer decomposed into COF_2 and $CF_3N{=}CXY$ [123]. Decomposition by γ-irradiation or by u.v. light (wavelength 253.7 nm) gave similar products, in addition to a small quantity of

$(CF_3)_2NC(O)F$ (in the case of the γ-irradiation) or CF_3NCO (in the case of the u.v. irradiation) [1868].

13.7.13 Miscellaneous sources of COF_2

The conditions prevalent during operation of an ArF laser give rise to a variety of small stable molecules including COF_2 [811].

13.7.14 Synthesis of labelled COF_2

13.7.14.1 $^{13}COF_2$

Irradiation of a gaseous mixture of unlabelled CF_2Cl_2 (0.03–0.7 kPa) and O_2 (0.7 kPa) by a pulsed, focused CO_2 laser beam at 1050–1075 cm^{-1} gave COF_2 enriched in carbon-13 [1502,1503,1517]:

$$^{13}CF_2Cl_2 + \tfrac{1}{2}O_2 \xrightarrow{h\nu} {}^{13}COF_2 + Cl_2$$

13.7.14.2 $^{14}COF_2$

COF_2 labelled with carbon-14 has been prepared by the following reaction sequence, from $^{14}CO_2$ [103c]:

$$^{14}CO_2 \xrightarrow[653\ K]{Zn} {}^{14}CO \xrightarrow[253\ K]{ClF} {}^{14}COClF \xrightarrow[293\ K]{NaF} {}^{14}COF_2$$

13.7.14.3 $CO^{18}F_2$

COF_2 labelled with fluorine-18 ($t_{\frac{1}{2}}$ = 109.7 min) was prepared by the interaction of $^{18}F_2$ with COF_2 [339].

13.7.14.4 $C^{18}OF_2$

$C^{18}OF_2$ has been prepared by combining $C^{18}O$ with a slight excess of elemental fluorine at room temperature. An essentially complete conversion to the labelled carbonyl halide was obtained [1901].

13.8 THERMODYNAMIC AND PHYSICAL PROPERTIES

At room temperature and atmospheric pressure, carbonyl difluoride is a colourless gas which is condensable to give a colourless liquid (boiling at −84.6 °C at normal atmospheric pressure [1580]) or a white solid (melting at −111.3 °C [1580]). It has a pungent odour and, unlike phosgene, is rapidly hydrolysed even in ambient air. The relative molecular mass of COF_2 is 66.0072, and the density of the gas is estimated to be 2.744 g dm^{-3} [1764]. The gas is heavier than air, with a specific gravity of 2.34 at 21 °C and atmospheric pressure

[277]. The specific volume of COF_2 at 21 °C and atmospheric pressure is calculated to be 365.7 cm^3 g^{-1} [1764]. Liquid COF_2 in an enclosed vessel at ambient temperature exerts a pressure of about 5.5 MPa.

13.8.1 Thermal and thermochemical properties

13.8.1.1 Gas Phase

The standard enthalpy of formation of COF_2 has been determined by several techniques; these values are summarised in Table 13.7.

The oldest value was derived from the enthalpy for the basic hydrolysis of COF_2 [2130]:

$$COF_2(g) + 4KOH(aq) \longrightarrow 2KF(aq) + K_2[CO_3](aq) + 2H_2O; \quad \Delta H = -397 \text{ kJ mol}^{-1}$$

This enabled the enthalpy of formation, and the enthalpy of the CO/F_2 reaction, to be estimated [2130]:

$$C(\text{diamond}) + \tfrac{1}{2}O_2(g) + F_2(g) \longrightarrow COF_2(g); \quad \Delta H_f = -594 \text{ kJ mol}^{-1}$$

$$CO + F_2 \longrightarrow COF_2; \quad \Delta H = -481 \text{ kJ mol}^{-1}$$

TABLE 13.7

STANDARD ENTHALPY OF FORMATION OF CARBONYL DIFLUORIDE

Year	Experimental Method	$\Delta H^\circ_{f,298}(g)$/kJ mol^{-1}	Ref.
1949	Calorimetry[a]	-629.1 ± 2.1	2131
1958	Calorimetry[b]	-647.7	108
1963	Calculation[c]	-628.4	2189b
1968	Calculation[d]	-627.18	1948a
1969	Calculation[e]	-638.1 ± 13.8	1973
1971	Calculation[f]	-638.9 ± 1.7	1972
1971	Equilibria[g]	-640.6 ± 5.9	44
1994	Computation	-607.9	1804b

[a] From COF_2 hydrolysis. [b] From the enthalpy of combustion of CH_4 in O_2-F_2 mixtures. [c] From heat capacity data. [d] Based on the data of [1078c]. [e] Based on the data of [1755]. [f] Based on the data of [2131]. [g] Based on the reaction $2COF_2(g) \rightleftharpoons CF_4(g) + CO_2(g)$.

However, much more reliable data were obtained from the calorimetric measurement of the enthalpy of hydrolysis of COF_2 [2131]:

$$COF_2(g) + H_2O(l) \longrightarrow CO_2(g) + 2HF(aq); \qquad \Delta H_r = -111.8 \pm 0.8 \text{ kJ mol}^{-1}$$

and combining this result with the enthalpies of formation of HF(aq) and CO_2, the standard enthalpy of formation of COF_2 was estimated to be −629.1 ± 2.1 kJ mol^{-1} [2131]. Based on this hydrolysis measurement, but using more recent values for HF and CO_2, Stull and Prophet obtained the value −638.9 ± 1.7 kJ mol^{-1} [1972]. From a re-evaluation of the measured [1755] equilibrium constants for the reaction:

$$2COF_2(g) \rightleftharpoons CO_2(g) + CF_4(g); \qquad \Delta H_r = 50.2 \pm 12.6 \text{ kJ mol}^{-1}$$

combined with free energy functions, the value of $\Delta H^\circ_{f,298}$ for $COF_2(g)$ was calculated to be −638.1 ± 13.8 kJ mol^{-1} [1973].

The weighted average of the most recent determinations gives the value, recommended by Stull *et al.* [1973], of −640.2 kJ mol^{-1} for $\Delta H^\circ_{f,298}$ for $COF_2(g)$. The inaccurate value of −697.1 kJ mol^{-1}, based on the original equilibrium data for $CO_2(g) + CF_4(g) \rightleftharpoons 2COF_2$ [1245] is admittedly approximate [575], but is also considered to be derived from an invalid interpretation of the equilibrium data [44].

The entropy, S°, of carbonyl difluoride gas at the normal boiling temperature was found from experimental data to be 238.9 ± 0.6 J mol^{-1} K^{-1} [1580]. The spectroscopic entropy of 239.5 J mol^{-1} K^{-1} was calculated by statistical methods from the moments of inertia and the fundamental vibrational frequency assignments [1580]. The spectroscopic entropy at 188.58 K is made up of the following contributions [1580]:

Translational: S_t = 151.5 J mol^{-1} K^{-1}
Rotational: S_r = 86.8 J mol^{-1} K^{-1}
Vibrational: S_v = 1.15 J mol^{-1} K^{-1}

The agreement between the calorimetric and spectroscopic entropy signifies the absence of any residual entropy of randomness in the solid.

The standard entropy of formation, $\Delta S^\circ_{f,298}(g)$, for $COF_2(g)$ for the equation:

$$C(graphite) + \tfrac{1}{2}O_2(g) + F_2(g) \longrightarrow COF_2(g)$$

has been calculated as −87.32 J mol^{-1} K^{-1} [1948a].

From the values for $\Delta H^\circ_{f,298}$ and the standard entropy of formation of COF_2, C(graphite), $\tfrac{1}{2}O_2$, and F_2, $\Delta G^\circ_{f,298}$ for $COF_2(g)$ is calculated as −623.36 kJ mol^{-1} [1972], leading to the value for $\ln(K_f)$ of 251.465.

TABLE 13.8

SOME CALCULATED STANDARD VALUES FOR COF_2, IDEAL GAS CONDITIONS

C_p° [a]	S° [a]	$H_{298}^\circ - H_0^\circ$ [b]	Ref.
47.254	258.78	11.117	1972
47.256	258.79	11.119	1360c
47.24	259.0	0.8	1078d
47.24	258.65		1280
46.82	258.49	11.054	2137a

[a] Units of J mol^{-1} K^{-1}. [b] Units of kJ mol^{-1}.

The expressions:

$$\Delta G_f^\circ/\text{kJ mol}^{-1} = -629.23 + 0.0922T \qquad (298.15\text{–}1500 \text{ K})$$

$$\Delta G_f^\circ/\text{kJ mol}^{-1} = -627.35 + 0.07355T + 0.0055647\log_{10}(T) \qquad (298.15\text{–}2000 \text{ K})$$

calculated by Steinmetz and Roth [1948a] are based on the value for $\Delta H_{f,298}^\circ$ of −627.18 kJ mol^{-1}, which is now considered as probably too low [780].

The standard values for COF_2 (ideal gas state, atmospheric pressure, 25 °C) have been calculated from molecular data. The data reported by various authors are recorded in Table 13.8.

The calculated standard thermodynamic functions for carbonyl difluoride, C_p°, S°, $-(G^\circ - H_{298}^\circ)/T$, $(H^\circ - H_{298}^\circ)$, ΔH_f°, ΔG_f° and $\log_{10}(K_f)$, are listed in Table 13.9 for the extended temperature range 0–6000 K in the ideal gas state [359aa], and are illustrated over the more normal working temperature range [359aa] in Fig. 13.2. Earlier values for these thermodynamic properties have now been superseded [1171,1280,1360c,1587,1972,1973].

The heat capacity of COF_2 in the ideal gas state can be fitted to the following equations [1078c,2189b]:

Between 500 and 2500 K [2189b]:

$$C_p^\circ\ /\text{J mol}^{-1}\ \text{K}^{-1} = 78.1872 + 1.89412 \times 10^{-3}T - 5.42941 \times 10^{6}T^{-2}$$

Between 2500 and 5000 K [2189b]:

$$C_p^\circ\ /\text{J mol}^{-1}\ \text{K}^{-1} = 83.0934 + 5.25234 \times 10^{-6}T - 1.01853 \times 10^{7}T^{-2}$$

TABLE 13.9

THERMODYNAMIC PROPERTIES OF COF_2 IN THE IDEAL GAS STATE [359aa]

T/K	C_p° [a]	S° [a]	$-(G^\circ-H^\circ_{298})/T$[a]	$(H^\circ-H^\circ_{298})$[b]	ΔH_f° [b]	ΔG_f° [b]	$\log_{10}(K_f)$
0	0.000	0.000	∞	-11.119	-635.798	-635.798	∞
100	33.489	217.322	295.224	-7.790	-636.888	-632.823	330.553
200	38.897	241.797	262.939	-4.228	-638.038	-628.302	164.096
250	43.168	250.931	259.642	-2.178	-638.514	-625.811	130.756
298.15	47.255	258.887	258.887	0.000	-638.897	-623.329	109.205
300	47.407	259.180	258.888	0.088	-638.910	-623.232	108.514
350	51.305	266.786	259.480	2.557	-639.239	-620.592	92.618
400	54.778	273.868	260.841	5.211	-639.514	-617.909	80.691
450	57.831	280.500	262.661	8.028	-639.751	-615.194	71.410
500	60.502	286.735	264.759	10.988	-639.959	-612.454	63.983
600	64.875	298.170	269.393	17.266	-640.312	-606.198	52.837
700	68.225	308.434	274.250	23.929	-640.602	-601.329	44.872
800	70.811	317.720	279.112	30.886	-640.843	-595.701	38.895
900	72.827	326.181	283.879	38.072	-641.049	-590.046	34.245
1000	74.417	333.940	288.503	45.437	-641.228	-584.369	30.524
1100	75.686	341.094	292.963	52.945	-641.388	-578.676	27.479
1200	76.709	347.725	297.253	60.566	-641.538	-572.968	24.941
1300	77.544	353.899	301.376	68.280	-641.684	-567.247	22.792
1400	78.231	359.672	305.336	76.070	-641.831	-561.516	20.950
1500	78.804	365.089	309.141	83.923	-641.984	-555.774	19.354
2000	80.595	388.038	326.123	123.830	-642.925	-520.905	13.761
2500	81.478	406.128	340.379	164.371	-644.146	-497.762	10.400
3000	81.974	421.031	352.616	205.245	-645.376	-468.367	8.155
3500	82.278	433.692	363.316	246.314	-646.317	-438.786	6.549
4000	82.478	444.693	372.816	287.506	-646.804	-409.099	5.342
4500	82.616	454.415	381.353	328.782	-646.811	-379.381	4.404
5000	82.716	463.125	389.102	370.116	-646.402	-349.685	3.653
5500	82.789	471.013	396.196	411.493	-645.691	-320.047	3.040
6000	82.846	478.219	402.735	452.903	-644.822	-290.480	2.529

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[a] Units of J mol^{-1} K^{-1}. [b] Units of kJ mol^{-1}.

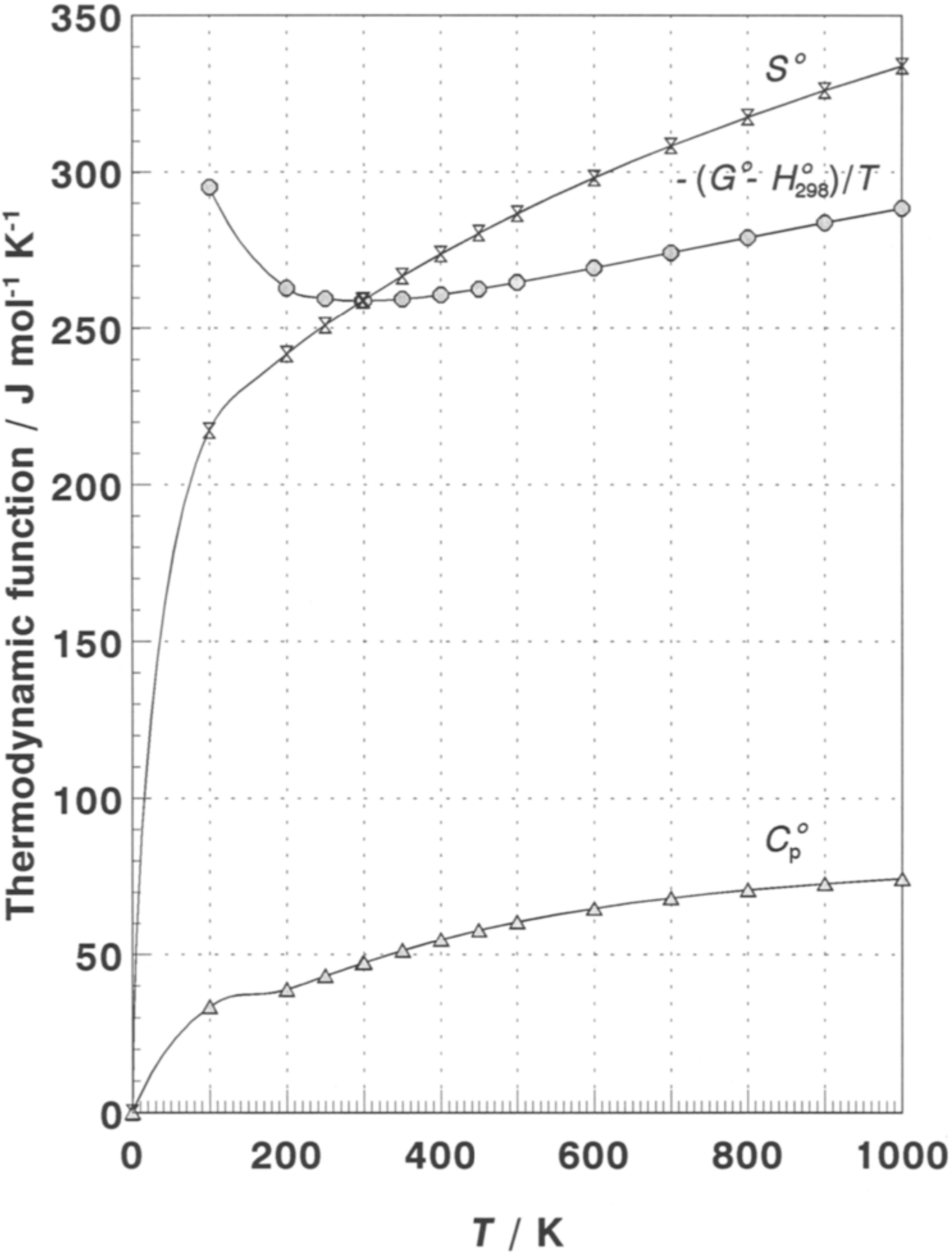
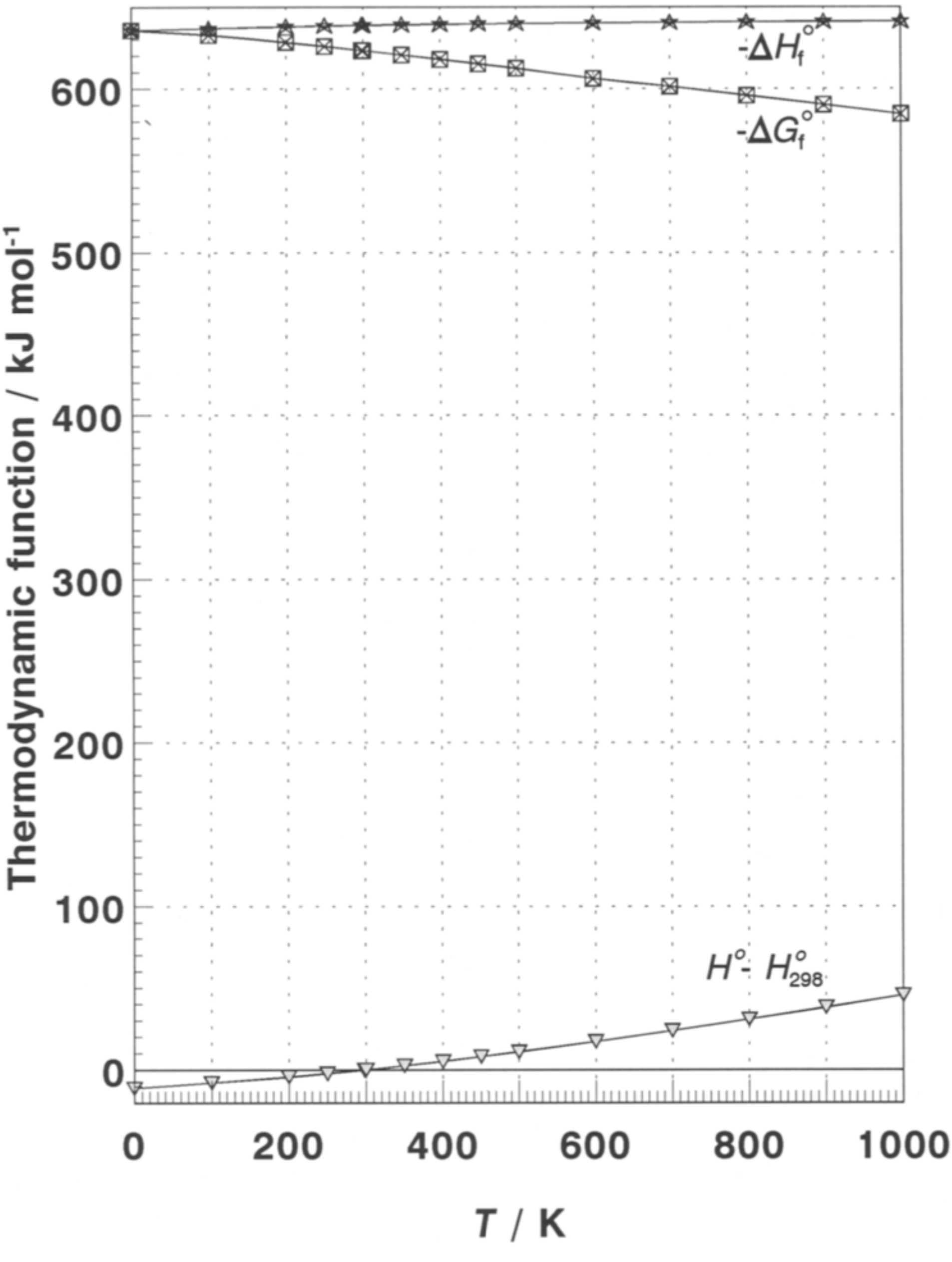


Fig. 13.2 Calculated thermodynamic properties (C_p°, S° and $-(G^\circ - H_{298}^\circ)/T$ on this page; $H^\circ - H_{298}^\circ$, $-\Delta H_f^\circ$, and $-\Delta G_f^\circ$ on facing page) of carbonyl difluoride (ideal gas) in the temperature range of 0–1000 K [359aa].


-ΔH°f
-ΔG°f
H°- H°298
Thermodynamic function / kJ mol-1
600
500
400
300
200
100
0
0
200
400
600
800
1000
T / K

Between 298 and 1500 K [1078c]:

$$C_p^\circ \text{ /J mol}^{-1}\text{ K}^{-1} = 57.78 + 1.715 \times 10^{-2}T - 1.389 \times 10^{6}T^{-2}$$

More recently, the data presented by Stull *et al.* [1972,1973] have been fitted to a cubic expression, over a wider temperature range (298–1000 K) [1842ac]:

$$C_p \text{ /J mol}^{-1}\text{ K}^{-1} = 13.5255 + 0.147778T - 1.28586 \times 10^{-4}T^2 + 0.417394 \times 10^{-7}T^3$$

Coefficients for equations which express the dependence of heat capacity, enthalpy, and entropy on temperature, in the range 150–6000 K have also been computed [801] for the purpose of obtaining equilibrium compositions and theoretical rocket performance of propellants: the form of the equations are given below (the actual coefficients are too dated to be worth quoting):

$$C_p^\circ \text{ /R} = \text{A} + \text{B}T + \text{C}T^2 + \text{D}T^3$$

$$\Delta H^\circ = \text{A} + \text{B}T/2 + \text{C}T^2/3 + \text{D}T^3/4 + \text{E}/T$$

$$S^\circ/\text{R} = \text{A}\ln(T) + \text{B}T + \text{C}T^2/2 + \text{D}T^3/3 + \text{F}$$

13.8.1.2 Liquid phase

The normal boiling temperature for COF_2, by interpolation of vapour pressure measurements, is 188.58 K (−84.57 °C) [1580]. Earlier estimations gave 189.9 ±0.5 K (−83.3 °C) [1756] and 190.05 K (−83.10 °C) [1192]. The molar enthalpy of vaporization of COF_2 at 188.58 K was determined to be 18.28 ± 0.03 kJ mol^{-1} [1580], although earlier workers reported a much lower value of 16.07 kJ mol^{-1} from vapour pressure measurements [1756]. These values correspond to a Trouton's constant of 96.94 and 85.2 J mol^{-1} K^{-1}, respectively, using the most recent value of the boiling temperature. The molar entropy of vaporization (Trouton's constant) for COF_2 (the difference between the entropy of the gas and the entropy of the liquid) has also been calculated as 100.40 J mol^{-1} K^{-1} [1683]. The calorimetrically determined values of the molar heat capacity for liquid COF_2 between the triple point and the normal boiling point are recorded in Table 13.10 [1580]. These specific heat data have been fitted to a polynomial [2241]:

$$C_p \text{ /J g}^{-1}\text{ K}^{-1} = -0.13355 + 0.022837T - 7.1109 \times 10^{-5}T^2$$

Selected thermodynamic properties of liquid COF_2 have been estimated [1683]. These calculated values for the Helmholtz free energy function ($-G/RT$), liquid entropy (S), and heat capacity at constant volume (C_v) are recorded in Table 13.11.

TABLE 13.10

MOLAR HEAT CAPACITY OF LIQUID CARBONYL DIFLUORIDE (162–189 K) [1580]

T/K	C_p/J mol^{-1} K^{-1}
161.89	Triple point
165	112.1
170	111.8
175	111.3
180	110.5
185	109.5
188.58	T_b

TABLE 13.11

SELECTED CALCULATED THERMODYNAMIC PROPERTIES OF LIQUID COF$_2$ [1683]

T/K	$-G/RT$	S/J mol^{-1} K^{-1}	C_V/J mol^{-1} K^{-1}
161.89	26.1275	124.39 (124.39)[a]	62.64
163.6	26.0429	125.78	63.01
169	25.6969	129.73	62.77
174.94	25.3595	133.50	65.49
182.9	24.6913	136.24	67.88
188.58	24.7097	139.26 (141.32)[a]	69.36

[a] Experimental value

The vapour pressure of liquid COF$_2$ from the triple point to the normal boiling temperature is given by Equation (13.12) [1580]: the experimental data from which this

$$\log_{10}(p/\mathrm{Pa}) = 33.211809 - 1682.1748/T - 8.4754322\log_{10}(T) \tag{13.12}$$

TABLE 13.12

EXPERIMENTAL VAPOUR PRESSURE OF LIQUID CARBONYL DIFLUORIDE [1580,1756]

T / K	p/kPa	
	[1580]	[1756]
161.89	12.52	
161.90		17.43
163.60	14.61	
166.90		24.70
169.00	23.81	
172.60		36.38
174.94	38.65	
175.70		44.60
179.44	54.21	
182.90	69.35	
184.90		77.50
185.73	84.16	
188.20	99.00	
189.17	105.16	

expression was derived are given in Table 13.12 [1580]. These experimental data [1580] have also been fitted to the Antoine equation, Equation (13.13) [1542], where T is in K, and the

$$\log_{10}(p/\mathrm{Pa}) = \mathrm{A} - \mathrm{B}/(T + \mathrm{C}) \qquad (13.13)$$

Antoine constants are A = 8.995902, B = 572.866, and C = −45.021 [1542]. As can be seen in Fig. 13.3, both Equations (13.12) and (13.13) fit the experimental data extremely well, and the two curves are essentially indistinguishable. The earlier vapour pressure data of Ruff and Miltschitzky [1756] are almost certainly in error (see again Fig. 13.3).

13.8.1.3 Solid phase

The melting temperature of carbonyl difluoride is 161.89 ± 0.01 K (−111.3 °C) [1580], although an earlier estimation [1756] gave 159.2 ± 0.3 K (−114.0 °C). The molar enthalpy of fusion was found to be 6.708 ± 0.01 kJ mol^{-1} at the solid–liquid–vapour equilibrium

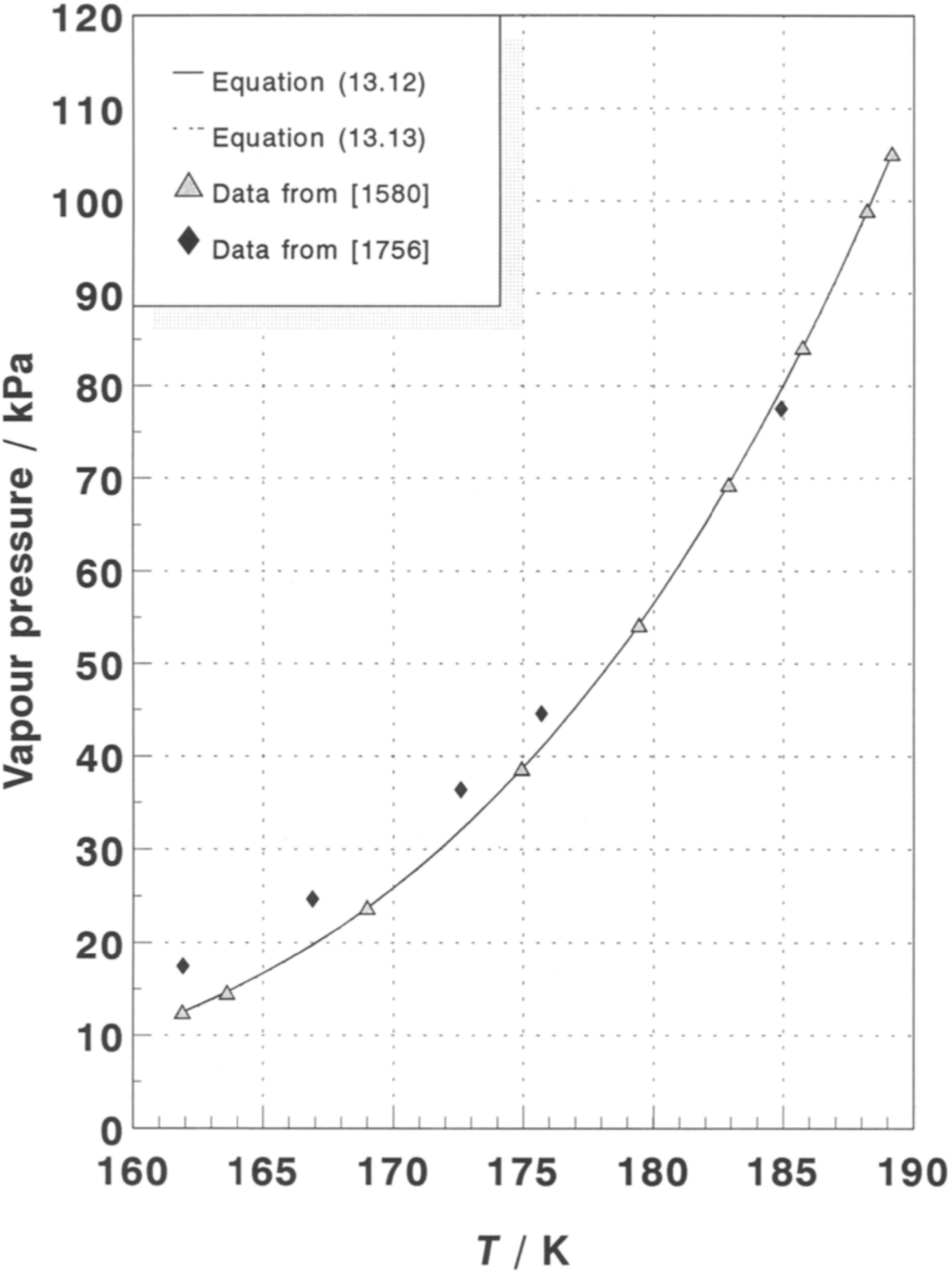


Fig. 13.3 The vapour pressure of liquid COF_2 as a function of temperature, according to Equations (13.12) and (13.13); extant experimental data are also included.

temperature of 161.89 °C [1580]. The entropy of fusion of COF_2 was determined as 41.43 ± 0.17 J mol^{-1} K^{-1} [1580], the large value indicating that no free rotation may be assumed in the solid state [1683]. The closeness of the calorimetric and spectroscopic entropies, S°, indicates that there is no disorder in the solid at the lowest experimentally determined temperature of 12 K [1580]. The experimentally determined values of the molar heat capacity for solid COF_2 between 13 K and 160 K are recorded in Table 13.13 [1580], and illustrated in Fig. 13.4.

The vapour pressure of the solid in the temperature range of 130 K to the triple point of 161.89 K is represented by Equation (13.14) [1580]. The experimental data from which

$$\log_{10}(p/\text{Pa}) = 83.071452 - 3017.1338/T - 27.311382\log_{10}(T) \qquad (13.14)$$

this expression was derived [1580] are detailed in Table 13.14, and illustrated in Fig. 13.5.

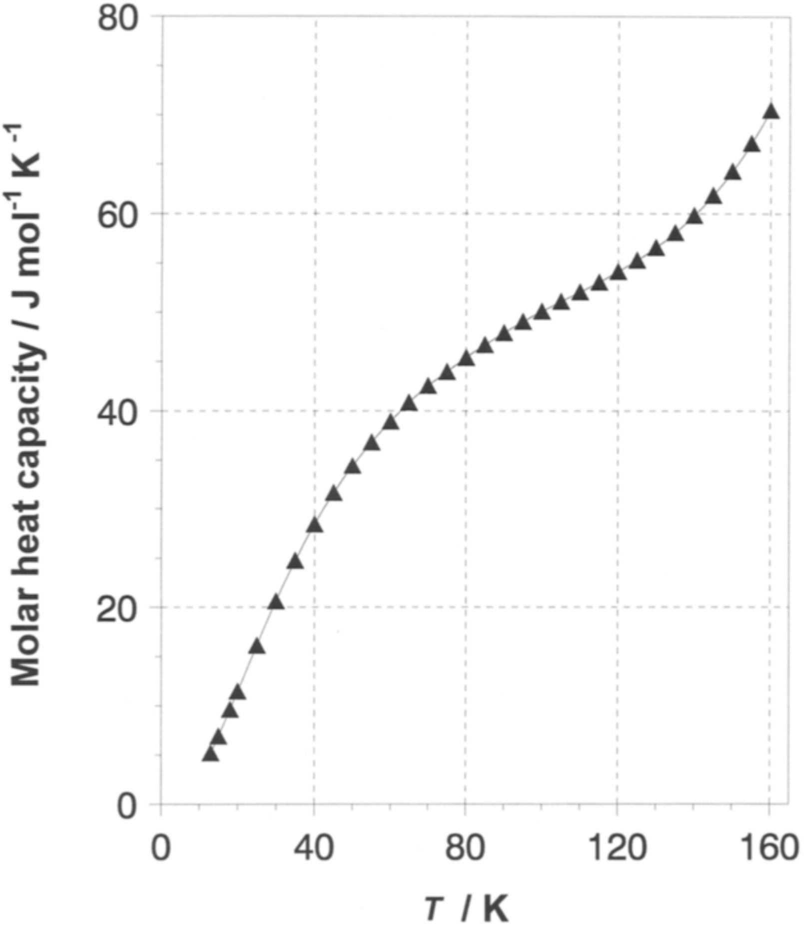


Fig. 13.4 The molar heat capacity of solid carbonyl difluoride [1580].

TABLE 13.13

MOLAR HEAT CAPACITY OF SOLID CARBONYL DIFLUORIDE (13–160 K) [1580]

T / K	C_p / J mol^{-1} K^{-1}
13	5.197
15	6.891
18	9.586
20	11.45
25	16.12
30	20.61
35	24.72
40	28.39
45	31.59
50	34.36
55	36.79
60	38.93
65	40.85
70	42.55
75	43.97
80	45.40
85	46.69
90	47.91
95	49.04
100	50.08
105	51.09
110	52.05
115	53.05
120	54.14
125	55.27
130	56.57
135	58.07
140	59.83
145	61.88
150	64.31
155	67.15
160	70.54
161.89	Triple point

TABLE 13.14

VAPOUR PRESSURE OF SOLID CARBONYL DIFLUORIDE [1580]

T / K	p / kPa
130.21	0.21
140.63	0.83
150.05	3.39
157.72	8.21
161.89	12.52

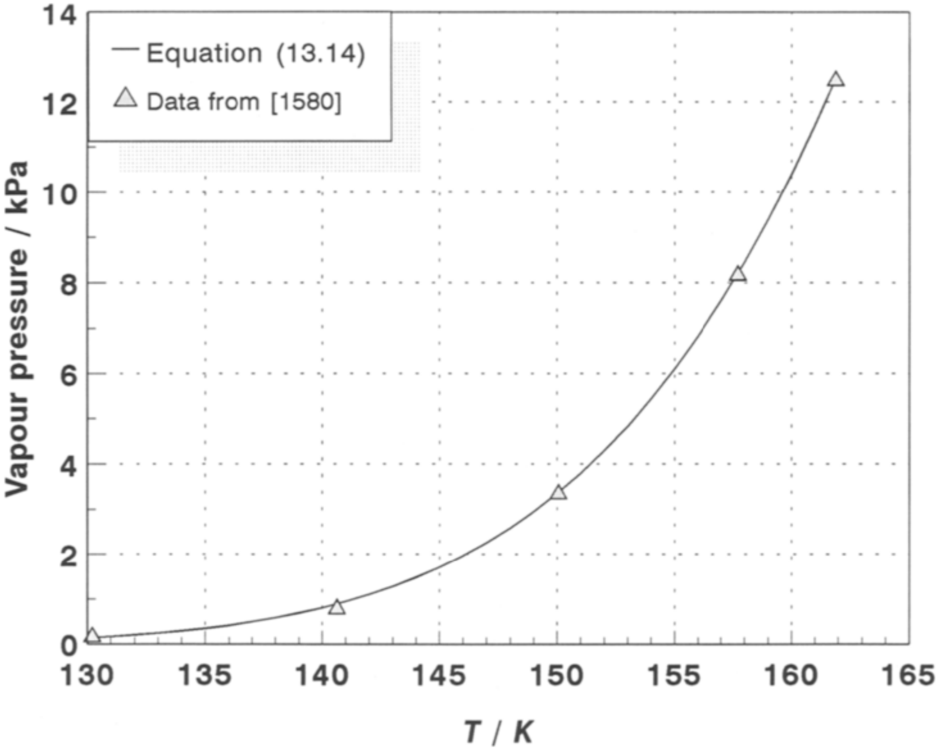


Fig. 13.5 The vapour pressure of solid COF_2 as a function of temperature, according to Equations (13.14); extant experimental data are also included [1580].

13.8.1.4 Critical properties

The critical temperature for COF_2 is reported to be 14.7 °C [1196a,1199,1751]. The critical pressure of COF_2 appears not to have been measured, but has been estimated to be 7.18 MPa [174a].

13.8.1.5 Bond dissociation energies

Values for the bond dissociation energies of COF_2 have been calculated. The results are recorded in Table 13.15.

From a study of the equilibrium reaction:

$$CF_3OOCF_3 \rightleftharpoons CF_3OF + COF_2$$

and by combining the values for the enthalpy of formation of COF_2 and of atomic fluorine, the π-bond energy in carbonyl difluoride was estimated as 402 ± 42 kJ mol^{-1} compared to

TABLE 13.15

BOND DISSOCIATION ENERGIES[a]

Bond Type	Method	D/kJ mol^{-1}	Ref.
F-CFO	Estimation[b]	481	1286
F-CFO	**Empirical/calculation[c]**	**436.4**	**716**
F-CFO	Electron collision experiments	530.9[d]	1292
F-CFO	Enthalpy measurement[e]	384.6	1420
F-CFO	Calculation	517 ± 84	2105c
F-CFO	Empirical calculation[f]	483.7	777
$O-CF_2$	Calculation	749.8	2105c
$O-CF_2$	Empirical calculations[e]	780.3	777
$\pi(O{=}CF_2)$	Enthalpy measurement[g]	402 ± 42	138
$\pi(O{=}CF_2)$	Calculation	444	138

---

[a] The highlighted value is possibly the most reliable. [b] By comparison with other fluorine-containing compounds. [c] From summation of ΔH°(FCO), ΔH°(COF_2), and ΔH°(F). [d] Upper limit of value. [e] Based on the reaction: $COF_2 \longrightarrow CO + 2F$ (ΔH = 671.5 kJ mol^{-1}); see also Section 13.15.6.2. [f] Based on the empirical relationships between dissociation energies and internuclear distances. [g] Based on the equilibrium $CF_3OOCF_3 \rightleftharpoons CF_3OF + COF_2$.

TABLE 13.16

CALCULATED MECHANICAL PROPERTIES OF LIQUID COF_2 [1683]

T / K	Molar Volume/cm^3 mol^{-1}		α/10^{-3} K^{-1}		β/10^{-6} kPa^{-1}
	Calculated	Observed ^{a}	Calculated	Observed ^{a}	Calculated
161.89	58.46	58.46	3.2269	3.7198	1.592
163.6	58.89	58.836	2.9995	3.7403	1.543
169	60.187	60.05	2.9105	3.8123	1.683
174.94	61.373	61.443	3.1232	3.914	1.984
182.9	61.697	63.419	2.9657	4.1479	1.944
188.58	62.669	64.91	3.1843	4.2779	2.235

[a] The source of the observed data is not defined in the paper.

the calculated value of 444 kJ mol^{-1} [138]. The high value of $D(COF_2)$ is consistent with the carbonyl absorptions of both the ultraviolet absorption spectrum and the infrared spectrum.

The energy of atomization of COF_2 has been calculated (Hückel calculations) to be 1718 kJ mol^{-1} [1441]: force constant calculations give a value of 1460–1650 kJ mol^{-1} [2034].

13.8.2 Mechanical properties

The density of liquid COF_2 (in each case at the saturated vapour pressure), determined pyknometrically, is given by Equation (13.15) [1756]. At the normal boiling temperature of COF_2, this equation corresponds to a density value of 1.017 g cm^{-3}, compared to the approximate value of 1.17 estimated from molecular data [174a]. At the melting point, the density of the liquid corresponds to 1.129 g cm^{-3} [1756]: this corresponds to a molar volume, at the melting point, of 58.46 cm^3 mol^{-1}. The density of solid COF_2 at the temperature of boiling liquid air was determined to be 1.388 g cm^{-3} [1756].

$$\rho_l/\mathrm{g\ cm^{-3}} = 1.809 - 0.00420\ T \qquad (13.15)$$

Lennard-Jones potential parameters (σ = 0.445 nm, ϵ/k = 224 K) have been estimated for COF_2 [1588].

Selected mechanical properties of liquid COF_2 have been estimated from molecular data [1683]. The calculated values for the molar volume, thermal expansion coefficient (α), and isothermal compressibility (β), are recorded as a function of temperature in Table 13.16.

13.8.3 Electrical and magnetic properties

From a calculated value of the mean molecular polarizability (33.03×10^{-25} cm^3), the mass diamagnetic susceptibility, χ_m, was estimated as -0.255×10^{-6} cm^3 g^{-1} (-3.21×10^{-9} m^3 kg^{-1}), the molar diamagnetic susceptibility, χ_M, being -16.9×10^{-6} cm^3 mol^{-1} (-2.12×10^{-10} m^3 mol^{-1}) [374]; no experimental values have been measured. A more recent value for the molecular polarizability of COF_2 has been calculated as 28.04×10^{-25} cm^3 [1258].

The experimental dipole moment of COF_2, as measured from the Stark effect upon the microwave spectrum, is 0.951 D (3.17×10^{-30} C m) [1215]. Many theoretical dipole moments for COF_2 have been reported [463,472,486,513,673,921,1414,1532,2037,2234], and the range of values is commensurate with the range of techniques used to calculate them.

13.9 STRUCTURAL DETERMINATIONS

All the structural information for carbonyl difluoride relates to the gas phase; there are no solid state studies. Carbonyl difluoride exhibits C_{2v} symmetry; its characteristic structural parameters have been established from electron diffraction and microwave spectroscopic data, and are summarized in Table 13.17. Of these data, those of Nakata *et al.* [1480] are the most precise.

In addition to the aforementioned empirical studies, the equilibrium $\measuredangle$FCF angles in COF_2 have been computed using the CNDO/2 formalism: with fixed r(C=O) and r(C–F) bond lengths of 0.117 and 0.132 nm respectively, the equilibrium $\measuredangle$FCF angle was calculated to be 110° [2037]. Even *ab initio* geometry optimization with a 6–31G* basis set only gives an approximately correct structure, with all the bond distances significantly underestimated [2176a]. An attempt has been made to relate the bond lengths in COF_2 with the group electronegativity concept [175].

The microwave spectrum of COF_2 yielded the ground state rotational constants, A = 11813.550, B = 11753.049, and C = 5880.896 MHz, along with centrifugal distortion constants [1413]. Rotational constants and centrifugal distortion constants for the following isotopomers of carbonyl difluoride – $^{12}C^{16}OF_2$, $^{13}C^{16}OF_2$, $^{12}C^{18}OF_2$, $^{13}C^{18}OF_2$ – have also been obtained from a detailed study of their microwave spectra [331]. Several other reliable, but less extensive, microwave investigations of COF_2 have also been reported [1214,1215,1906]. The effect of pressure upon linewidth has also been studied [1935]. The presence of strong Coriolis coupling was noted [1214]. Revised values (improved upon those recorded in [1906]) for the moments of inertia of COF_2 have been recorded [1360c] as $I_a = 7.10284 \times 10^{-46}$, $I_b = 7.13977 \times 10^{-46}$, and $I_c = 1.42677 \times 10^{-45}$ kg m^2. The mean dipole derivatives

TABLE 13.17

STRUCTURAL PARAMETERS FOR GASEOUS COF$_2$^{a}

Technique	r(CO)/nm	r(CF)/nm	∢FCF/°	∢FCO/°	Ref.
m.w	0.1174	0.1312	108.0	126.0	1215
m.w.	0.11700	0.13166	107.60	126.20	331
e.d.	0.117	0.132	112.5	123.75	279
e.d.	0.1172	0.1317			1480
e.d./m.w.	**0.11717**	**0.13157**	**107.71**	**126.145**	**1478,1480**

^{a} Emboldened data are recognized as the best set.

[290,1655,1657,2098] and anisotropies [290] have been calculated.

The microwave spectrum of vibrationally excited COF$_2$ has been obtained [1435]; the rotational constants and inertial defects obtained were used to resolve the ambiguity in the absolute assignment of its ν_3 and ν_5 bending modes (*vide infra*).

13.10 SPECTROSCOPY

13.10.1 Vibrational spectroscopy

The symmetry and activity of the six fundamental vibrational modes of carbonyl fluoride (all of which are both infrared and Raman active) are the same as those illustrated in Fig. 7.2 for phosgene.

Experimental infrared and Raman vibrational frequencies for COF$_2$ have been reported by many workers, and the most important data sets are included in Tables 13.18 and 13.19, resepctively. Other studies have been reported [169,1507,2209] and, in addition, the infrared spectrum of gaseous COF$_2$ has been included in a catalogue of common molecules [1462a].

In the original work of Nielsen *et al.* [1508], the assignments of ν_3 and ν_5 were reversed. This was corrected by Overend and Scherer [1578], reversed again by Hopper *et al.* [981], and finally corrected by Laurie and Pence [1214] and Mallinson *et al.* [1310]. Although there was clearly confusion over the correct assignment of the ν_3 and ν_5 bands, the assignments presented in Tables 13.18 and 13.19 are now universally accepted as unequivocal [*e.g.* 425a].

The peak at 1943.8 cm^{-1} involves Fermi resonance between ν_1 and $2\nu_2$. The splitting of the i.r. bands of COF$_2$ in an argon matrix has been ascribed to different sites within the matrix [1022].

TABLE 13.18

INFRARED DATA (units of cm^{-1}) FOR COF$_2$^{a}

	Medium	$\nu_1(a_1)$ ν(CO)	$\nu_2(a_1)$ ν_s(CF)	$\nu_3(a_1)$ δ_s(OCF)	$\nu_4(b_1)$ ν_{as}(CF)	$\nu_5(b_1)$ δ_{as}(OCF)	$\nu_6(b_2)$ π(COF$_2$)	$2\nu_2$	Ref.
COF_2	gas	1941	965	584	1249	626	775		2209
COF_2	**gas**	**1928**^{b}	**965**	**584**^{c}	**1249**	**626**^{c}	**774**	**1907**	**1575**
COF_2	gas	1943.8	961.9	581.5	1242.2	619.2	774.0	1909.7	1310
COF_2	CO; 14 K	1941		585		619.5		1913	1401
COF_2	Ar; 20 K	1929.9^{b}	956.6	582.9	1243.7	619.9	767.4		1310
COF_2	Ar; 14 K	1915, 1910	967, 962	585	1239, 1234	620, 618	770	1943, 1938	1022
$^{12}C^{18}OF_2$	gas	1909.7	947.3	576.5	1242.3	604.9	770.0		425a
$^{12}C^{18}OF_2$	Ar; 20 K	1894.1^{b}	950.2	577.9	1243.7	605.9	763.6		1310
$^{12}C^{18}OF_2$	Ar; 14 K	1881, 1876	951, 947	579	1238, 1233	606, 604	766	1909, 1904	1022
$^{13}C^{16}OF_2$	Ar; 20 K	1880.5^{b}	962.5	581.3	1208.2	619.9	743.2		1310
$^{13}C^{16}OF_2$	Ar; 14 K	1879, 1875	963, 959	583	1204, 1198	619	746	1926, 1919	1022
$^{13}C^{18}OF_2$	Ar; 20 K	1843.5^{b}	948.0	576.3	1208.2	604.6	739.3		1310
$^{13}C^{18}OF_2$	Ar; 14 K	1841, 1839			1203, 1198				1022

[a] Emboldened data are recognized as the best set. [b] This frequency is corrected for Fermi resonance with $2\nu_2$: the observed band is at *ca.* 1942 cm^{-1} for $^{12}C^{16}OF_2$. [c] Reassignment of the bands originally assigned incorrectly [981,1508].

As can be inferred from Table 13.18, the frequencies of ν_1, ν_4 and ν_6 are temperature dependent (*n.b.* an error in [169] has resulted in ν_2 rather than ν_6 being reported as a temperature dependent fundamental band). The temperature dependence of the 1943 cm^{-1} band intensity has been investigated between 300 and 600 K: the total integrated intensity was found to be temperature independent [6]. With the notable exception of ν_5, the fundamentals all exhibit well defined P, Q and R branches. A detailed analysis of the rotational structure associated with the ν_6 band of COF$_2$ established the band centre to be at 774.40 cm^{-1} and B'' to have a value of 0.3925 cm^{-1} [1507].

TABLE 13.19

RAMAN DATA (units of cm^{-1}) FOR COF$_2$^{a}

	Medium	$\nu_1(a_1)$	$\nu_2(a_1)$	$\nu_3(a_1)$	$\nu_4(b_1)$	$\nu_5(b_1)$	$\nu_6(b_2)$	$2\nu_2$	Ref.
		$\nu(CO)$	$\nu_s(CX)$	$\delta_s(OCX)$	$\nu_{as}(CX)$	$\delta_{as}(OCX)$	$\pi(COX_2)$		
COF$_2$	**Liquid**	**1944**	**965**	**571^{b}**	**1238**	**620^{b}**	**771**	**1909**	**1508, 2209**
COF$_2$	Liquid	1945	968	587	1261	624	771	1902	365
COF$_2$	Solid		980	587	1253	626	767	1906	365

^{a} Emboldened data are recognized as the best set. ^{b} Reassignment [1575] of the bands originally assigned incorrectly [1508].

The region of the i.r. spectrum of COF$_2$ between 3800 and 4000 cm^{-1} has been examined for triple resonances: three bands were observed, and assigned at 3873.6 (ν_1+2ν_2), 3832.4 (2ν_1) and 3791.1 cm^{-1} (4ν_2) [2252].

As is to be expected for a light tetra-atomic molecule of relative simplicity, COF$_2$ has been the subject of many force constant, Coriolis coefficient (and inertia defect) and bond asymmetry parameter calculations [30,152,169,330,581,1028,1165,1277,1310,1312,1413,1448,1449, 1466,1549,1550,1575-1578,1587,1618,1671,1673,1682,1858,1931,1961,2021,2073,2096,2108-2111,2167a], as well as the determination of atomic potential energy distribution for ν_1, ν_2 and ν_3 [1674].

Integrated i.r. intensity data have been used to calculate bond moments and their derivatives [453]: the calculated dipole moment was −0.93 D (3.10 x 10^{-30} C m), compared with an experimental value (Stark effect upon the microwave spectrum) of −0.95 D (3.17 x 10^{-30} C m) [1215]. The original vibrational intensity data for COF$_2$ [981] has now been corrected [1363], and the CNDO/2 calculations [1827] of the dipole moment derivatives have been revised [289,292,1363,1417]; many of the bond moment derivatives (the squares of which are approximately proportional to band intensities) were shown to be transferable [1675]. Bond dipole moments have also been calculated by *ab initio* methods (with a STO 5-31G basis set) [1941]. In addition, the dipole moment derivatives have been calculated under the MINDO/3 formalisms [1586], but little reliance can be placed on the results obtained.

The ν_2 band has been examined by high-resolution microwave and i.r. spectroscopy, and nearly 4000 rotational transitions were observed and assigned: the frequencies of the far infrared laser lines were calculated to estimated uncertainties of 10^{-5} and 10^{-6} cm^{-1} [400a,1243a]. Similar analyses of ν_4 [327b] and ν_6 [793a,2018b] have also been reported.

Semi-empirical methods (including CNDO, MNDO, AM1 and PM3) have been shown to be rather ineffectual at calculating vibrational frequencies, when applied to COF_2 [411a,1680,1681]. More recently, polar tensors and effective charges have been calculated [135,1516], and the sums of the gas phase infrared intensities for the molecules $C(E)X_2$ (E = O or S; X = Cl or F) were shown to be interrelated [135]. Other attempts at infrared intensity analysis have been reported [1473]; infrared band intensity ratios appear to poorly suited to the prediction of the ∢FCF bond angle [1904].

The vibrational excitation of COF_2 by collision with argon atoms (1000–3000 K) has been treated: bending modes were found to be more easily excited than stretching modes [2233]. The vibrational relaxation of COF_2 {both vibrational ⟶ (rotational, translational) and vibrational ⟶ vibrational} has also been studied [1066a], as has the dynamics of vibrational energy transfer between COF_2 and NO [1973a]. The absolute intensities of the four dominant emission bands from COF_2 (shock heated to 1300–2400 K), at 3745 ($2\nu_1$), 2817 ($\nu_1+\nu_2$), 2232 ($\nu_2+\nu_4$) and 1869 (ν_1) cm^{-1}, have been measured [1421].

13.10.2 Mass spectrometry

The mass spectrum (electron energy not specified) of COF_2 was recorded *via* an unreactive "Kel-F" inlet system (see Table 13.20) [1000].

Ionization cross sections for the molecular ion and the fragment ion $[COF]^+$ have been determined as a function of ionization energy (up to 125 eV) [1646a]; the appearance potentials were measured as 14.2 and 18.5 eV, respectively [1646a].

TABLE 13.20

MASS SPECTRAL DATA (70 eV) FOR COF_2

m/z	Relative Intensity			Assignment
	[1000]	[1071]	[2035]	
66	100	73	35	M^+
50	3	2	2	CF_2^+
47	89	100	100	CFO^+
31	5	5	5	CF^+
28	24	30	15	CO^+

13.10.3 Nuclear magnetic resonance spectroscopy

The n.m.r. spectra of COF_2 are discussed in Section 7.3. The ^{19}F n.m.r. frequency, and hence the shielding, of COF_2 has been studied in the gas phase at 300 K [1026], and as a function of density and temperature [1027]; the results were rationalized in terms of mean bond displacement variations [1028]. Chemical shift tensors have been calculated [659a]. The use of CNDO/2 [2046], INDO [2046] and MINDO/3 [1585] calculations to predict ^1J(CF) and ^2J(FF) is demonstrably ineffectual [2046].

13.10.4 High resolution microwave spectroscopy

Examination of the high resolution microwave spectrum of COF_2 enabled the ^{19}F spin–rotation constants along the principal inertial axes (M_{aa} = −19 kHz; M_{bb} = −13 kHz; M_{cc} = −5 kHz) to be measured, and the ^{19}F paramagnetic shielding in COF_2 ($\sigma^p = -324 \times 10^{-6}$) to be calculated [1263]. This was combined with n.m.r. data (see Section 7.3) to give the ^{19}F diamagnetic shielding as $\sigma^d = +560 \times 10^{-6}$ [1263] (*n.b.* the diamagnetic shielding of the atoms within COF_2 has been independently estimated [1688]). The first-order Zeeman effect was observed for COF_2, allowing a paramagnetic susceptibility of $\chi^p = +127 \times 10^{-6}$ erg G^{-2} mol^{-1} to be estimated [1263] from the diagonal molecular *g* tensor [1263]. Later observation of the second-order Zeeman effect allowed a more accurate set of *g* values to be determined (g_{aa} = −0.0568, g_{bb} = −0.0747, g_{cc} = −0.0328), along with the magnetic susceptibility anisotropies, molecular quadrupole moments (Q_{xx} = −3.7, Q_{yy} = −0.2, $Q_{zz} = +3.9 \times 10^{-26}$ esu cm^2), and the second moments of the electronic charge distribution [205]. These parameters have also been calculated by IGLO [659a], SCC [1303] and CNDO/2D [207] methods. Ground state polarizabilities have been estimated by a second-order perturbation method coupled with a CNDO/S CI calculation [1321].

More recently, improved resolution (between 5 and 20 times better) was obtained by examining several of the rotational transitions in a molecular beam maser spectrometer [2145]. This gave more precise values of the ^{19}F spin-rotation constants along the principal inertial axes (M_{aa} = −19.77 kHz; M_{bb} = −13.46 kHz; M_{cc} = −7.80 kHz) [2145], and the ^{19}F paramagnetic shielding in COF_2 was recalculated as $\sigma^p = -358.1 \times 10^{-6}$, and the diamagnetic shielding as $\sigma^d = +586.1 \times 10^{-6}$ [2145]. The absolute average magnetic shielding value was calculated as 226 ± 15 p.p.m. [2145], comparing well with the experimental value of 219 p.p.m. [1263].

13.11 THERMAL DECOMPOSITION

From equilibrium calculation studies of the $C-O_2-F_2$ system (Figure 13.6), no solid phases are present. At low temperatures, CF_4 and CO_2 coexist and, at about 1500 K, COF_2 is the predominant thermodynamic species. Above 2000 K, atomic fluorine and CO compete [537].

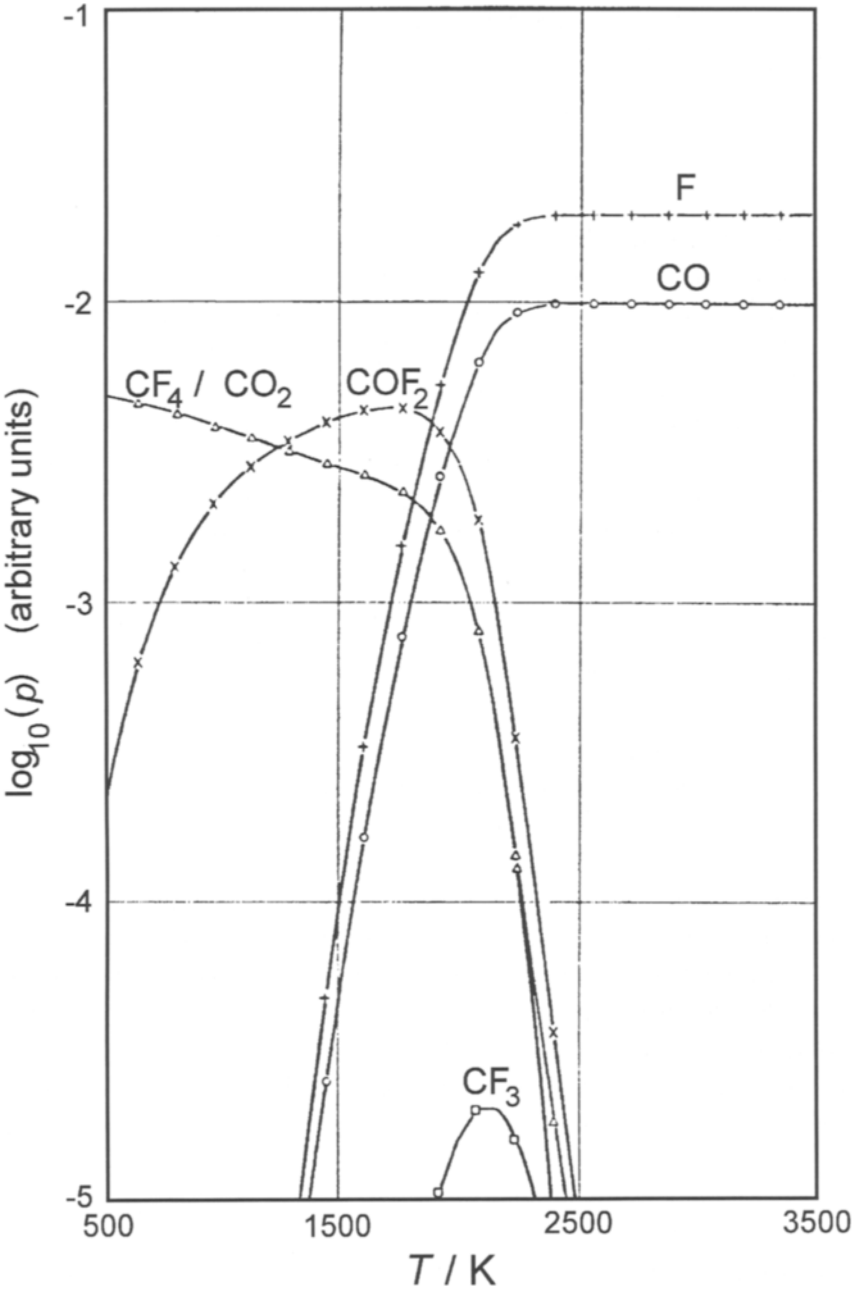


Fig. 13.6 Partial pressures in the equilibrium system $C-O_2-F_2$ [537].

Under equilibrium conditions, COF_2 will experience the following dissociative equilibrium:

$$COF_2 \rightleftharpoons CO + F_2 \qquad (13.16)$$

This process is the reverse of the reaction between carbon monoxide and difluorine, which has been discussed in some detail in Sections 13.7.3.1 and 13.12. Pyrolysis studies, in a fused silica reactor, between 600 and 700 K, showed the reaction to be heterogeneous, with concomitant production of CO_2 and SiF_4 occurring [1353]: no CF_4, CO or F_2 was detected, suggesting that these results have very little practical use [1353].

Under the non-equilibrium conditions found in a shock tube, the decomposition of COF_2 is rather more complex. The kinetics of the decomposition of COF_2 in both argon and dinitrogen diluents have been measured in the temperature range 2200–3600 K [1419,1420]: the proposed mechanism is as follows:

$$\begin{aligned}
COF_2 &\xrightarrow{Ar} [COF]\cdot + F\cdot \\
[COF]\cdot &\xrightarrow{Ar} CO + F\cdot \\
COF_2 + F\cdot &\rightleftharpoons [COF]\cdot + F_2 \\
[COF]\cdot + F\cdot &\longrightarrow CO + F_2 \\
[COF]\cdot + [COF]\cdot &\rightleftharpoons COF_2 + CO \\
F_2 + Ar &\rightleftharpoons F\cdot + F\cdot + Ar
\end{aligned}$$

No evidence was found for any reaction forming CO_2 (including the disproportionation reaction), nor for any reaction generating difluorocarbene, $:CF_2$ [1419,1420]. These findings were later confirmed independently, although there was a suggestion that the earlier results may have produced slightly high decomposition rates, owing to the presence of trace amounts of water [2170]. The first workers have now refined their data, and shown that the reaction between COF_2 and CO was found to play an insignificant *rôle* in the overall process [716,1354].

13.12 PHOTOCHEMICAL DECOMPOSITION

Prolonged photolysis (Hg) of COF_2 in a CO matrix produces $[COF]\cdot$, which was characterized by i.r. spectroscopy [1401]:

$$COF_2 \xrightarrow{h\nu} [COF]\cdot + F\cdot$$

A tentative prediction that COF_2 may be photodissociated into difluorocarbene and an oxygen atom with light of λ ≈ 170 nm has been made [273]; it was proposed that this reaction may well be important in the upper stratosphere [273]. The preliminary photodissociation step has been examined by *ab initio* methods [677a].

13.13 REACTIONS WITH INORGANIC COMPOUNDS

In an analogous manner to phosgene, carbonyl difluoride will disproportionate upon heating, a very slow reaction catalysed by nickel (300–650 °C) or platinum metal (1000–1200 °C) [44,1245,1274a,1755,1756]:

$$2COF_2 \rightleftharpoons CO_2 + CF_4 \qquad (13.17)$$

The thermodynamics of this process is discussed in some detail in Section 13.8.1.1.

COF_2 reacts with phosgene in a comproportionation reaction to give COClF in a 30% conversion [1018]:

$$COCl_2 + COF_2 \longrightarrow 2COClF \qquad (13.18)$$

However, if phosgene and COF_2 are heated together under pressure between 250 and 700 °C [899,900,902]:

$$COCl_2 + COF_2 \longrightarrow CCl_2F_2 + CO_2$$

a number of side products are formed from the following reactions [899,900,902]:

$$COCl_2 + COF_2 \longrightarrow 2COClF$$

$$COF_2 + COClF \longrightarrow CClF_3 + CO_2$$

$$COClF + COCl_2 \longrightarrow CCl_3F + CO_2$$

$$2COF_2 \longrightarrow CF_4 + CO_2$$

In analogous autoclave reactions, COF_2 will react with $COBr_2$ or COXF (X = Cl or Br) to produce CBr_2F_2, $CClF_3$ or $CBrClF_2$, respectively [902,905], but none of them cleanly.

I.c.r. experiments demonstrate that COF_2 is an excellent proton acceptor (*cf.* Section 13.13.6.1 and 13.13.6.2) [545]:

$$COF_2(g) + H^+(g) \longrightarrow COF_2.H^+(g); \qquad \Delta H^\circ = -664.4 \text{ kJ mol}^{-1}$$

13.13.1 Reactions with halides and oxide halides

The reaction between COF_2 and gaseous F^- has been studied by i.c.r. techniques [1212]:

$$H_2O.F^-(g) + COF_2(g) \longrightarrow [COF_3]^-(g) + H_2O(g);$$

$$\Delta G^\circ = -66.1 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = -80.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ = -48.5 \text{ J mol}^{-1} \text{ K}^{-1}$$

Hence [1212]:

$$F^-(g) + COF_2(g) \longrightarrow [COF_3]^-(g);$$

$$\Delta H^\circ = -178.3 \text{ kJ mol}^{-1}$$

Thus, COF_2 is a very powerful fluoride acceptor (for comparisons with other fluoride acceptors, see [1212a]), and this tendency dominates many of its reactions with metal fluorides.

13.13.1.1 Group 1

The rates of fluorine exchange have been measured for the following reactions of the Group 1 fluorides [683]:

$$A^{18}F(s) + COF_2(g) \longrightarrow AF(s) + CO^{18}F^{19}F(g)$$

At 150 °C, the order of reactivity was that expected from size and catalytic activity [683]:

$$Cs > Rb \gg K > Na,\ Li$$

At 50 °C, the order was [683]:

$$Cs > Rb \gg K,\ Na,\ Li$$

The rate of fluoride exchange is considerably enhanced in the presence of polar solvents {*e.g.* MeCN or bis(2-methoxyethyl)ether}, but not by benzene or diethyl ether; the rates in MeCN at 25 °C were comparable with the gas-solid reactions at 150 °C [683]. Similarly, rapid exchange was noted between gaseous $CO^{18}F_2$ and solid MF_3 (M = La or Tl), HgF_2, Hg_2F_2 or TlF at 150 °C; under similar conditions, AgF was largely unreactive [682]. It is of interest to note that the pattern of reactivity towards fluoride exchange does not parallel the catalytic effect of the metal fluorides upon the reaction between COF_2 and F_2 (see Section 13.7.3).

The reaction between COF_2 and AF (A = K, Rb or Cs) in MeCN at 20 °C produces $A[COF_3]$ (which is isoelectronic with $A[BF_4]$) in good yields [1692]:

$$COF_2 + AF \longrightarrow A[COF_3]$$

These complexes, although stable white crystalline solids at room temperature, all decompose at 80 °C, according to [1692]:

$$A[COF_3] \longrightarrow AF + COF_2$$

The order of thermal stability of these salts is:

$$Cs > Rb > K$$

Salts of lithium, sodium, barium or thallium(I) could not be prepared by the above route [1692].

The thermal decomposition of $Cs[COF_3]$ (*vide supra*) at 393 K *in vacuo* leads to the formation of activated CsF, with a high surface area [539a]; the kinetics of the reaction between this activated CsF and $COF^{18}F$ or $^{14}COF_2$ have been studied, and a mechanism involving surface-adsorbed COF_2 proposed [539a].

Both KF and CsF are activated by support on γ-Al_2O_3, becoming rather more Lewis basic [103b,103c]: thus $[OCF_3]^-$ was detected by i.r. spectroscopy when these supported fluorides are exposed to COF_2 at room temperature [103b,103c].

The reaction between $CF_2(OF)_2$, $Cs[OCF_3]$ and COF_2, in the presence of CsF, yields a mixture of CF_3OF and $F_3COOC(O)F$ [511a]. This reaction was believed to occur as follows [511a]:

$$CF_2(OF)_2 + Cs[OCF_3] \longrightarrow CF_3OF + Cs[OOCF_3]$$

$$Cs[OOCF_3] + 2COF_2 \longrightarrow F_3COOC(O)F + Cs[OCF_3]$$

COF_2 reacts with hot solid potassium iodide to liberate iodine vapour [1756].

13.13.1.2 Group 13

COF_2 reacts with BBr_3 to give $COBr_2$ [911], but with aluminium(III) bromide disproportionates to yield CO_2 and CF_4 [911].

13.13.1.3 Group 14

13.13.1.3.1 Simple reactions

In a remarkable and interesting patent, Ager [13] claims that COF_2 will react with CCl_4 (or C_2Cl_6) at 300 °C in an autoclave to give a mixture of fluorocarbons and chlorofluorocarbons, in the presence of tungsten(VI) chloride, niobium(V) chloride, tantalum(V) chloride, or aluminium(III) chloride catalysts. In the absence of the catalyst, the conversion of COF_2 is low (<30%), and the products include CCl_3F (major product), $COCl_2$, and COClF. In the presence of 'preconditioned' aluminium(III) chloride (approximating to $AlCl_2F$), there is 100% conversion of COF_2, giving CF_4 and $CClF_3$ (combined yield of 85%), CCl_2F_2 (12%) and CCl_3F (3%) [13]. By careful selection of catalyst, the yields of each CCl_nF_{4-n} from CCl_4 can be optimized [13].

Carbonyl fluoride has been shown to quench the ^3A_u excited state of ethane-1,2-dioyl difluoride, $(COF)_2$, with a room temperature rate constant of 1.1 x 10^7 l mol^{-1} s^{-1} [1069].

13.13.1.3.2 Polymerization reactions and COF_2 polymers

Unlike $COCl_2$ (see Section 9.1.3.1), carbonyl difluoride can be dimerized to trifluoromethyl fluoroformate, $FC(O)OCF_3$, and trimerized to bis(trifluoromethyl)carbonate, $O{=}C(OCF_3)_2$, by means of a base-catalysed reaction conducted at -50 to -110 °C in the presence of activated charcoal [45b]. The dimer is formed in 45-60% conversion, whereas the trimer is only formed in about 1% yield [45b].

Carbonyl difluoride is difficult to homopolymerize, but small amounts of polymers can be obtained under the influence of high-dose radiation [1997]. The structure of the homopolymer may be very similar to that of polyformaldehyde and may be formulated as:

$$-CF_2-O-CF_2-O-CF_2-O-$$

The infrared spectrum of the homopolymer shows a strong broad band, centred on about 1080 cm^{-1}, completely distinct from the monomer [1997].

Compounds most commonly known as poly(oxyfluoromethylene) are linear polyethers with the general formulae (where n = 1-6):

$$CF_3O-(CF_2O)_n-COF \quad \text{or} \quad CF_3O-(CF_2O)_n-CF_2-C(O)F$$

(Type A) **(Type B)**

corresponding to oligomers or polymers of carbonyl difluoride [1872]. Their preparation consists of reacting a perfluorinated alkene, such as $CF_2{=}CF-CF_3$, with dioxygen at between 350 and 700 °C in a flow system in a tubular copper, Pyrex, or stainless steel reactor. The products leaving the reactor are trapped in low temperature refrigerants and separated by fractional distillation and preparative chromatography, to give a range of COF_2 polymers or homologues (see Table 13.21; obtained at 350 °C).

Higher molecular weight (4000-8000 g mol^{-1}) liquid polymers of carbonyl difluoride are reported to be formed in a yield of 15-19 % at 15-23 °C (over 20-23 h period) from the reaction of tetrafluoroethene with trioxygen-containing molecular dioxygen (about 2 mol %) in a perhalogenated organic liquid such as fluorocarbon-113, $CF_2ClCFCl_2$, or perfluoromethylcyclohexane [1426].

TABLE 13.21

COF$_2$ POLYMERS AND HOMOLOGUES PREPARED BY OXIDATION OF C_3F_6 [1872]

Product	n		b.pt./°C	Composition/%
	Type A	Type B		
COF_2	1			40
$CF_3C(O)F$		1	-58	37.4
$CF_3OC(O)F$	2		-34	7.3
$CF_3OCF_2C(O)F$		2	-9.7	3.3
$CF_3OCF_2OC(O)F$	3		+7	2.7
$CF_3OCF_2OCF_2C(O)F$		3	+30	0.8
$CF_3O(CF_2O)_2C(O)F$	4		+45	1.3
$CF_3O(CF_2O)_2CF_2C(O)F$		4	+13[a]	0.5
$CF_3O(CF_2O)_3C(O)F$	5		+27-29[a]	0.5
$CF_3O(CF_2O)_3CF_2C(O)F$		5	+35[b]	0.8
$CF_3O(CF_2O)_4C(O)F$	6		+47-49[b]	0.7
$CF_3O(CF_2O)_4CF_2C(O)F$		6	+55	0.4

[a] At 250 torr (33.33 kPa). [b] At 150 torr (20 kPa).

Copolymers of COF_2 with $CH_2{=}CH_2$, $CH_2{=}CHMe$, $CH_2{=}CHCN$, $CF_2{=}CH_2$, $CF_2{=}CHF$, $CF_2{=}CF_2$, $CF_2{=}CFCl$, $CF_2{=}CFCF_3$ or $CH_2{=}CMe_2$ are formed by radiation induction [958,1997]. The copolymers, formed *via* a radical mechanism, are randomly distributed, as indicated by the distinct differences between the infrared spectrum of the COF_2 homopolymer and the resulting copolymer [1997].

The structure of the copolymer between ethene and COF_2 depends upon the polymerisation temperature and the concentration of the components in the monomer/solvent mixture. In addition, the rate of copolymerization of $CH_2{=}CH_2$ and COF_2, at 0 or 25 °C, decreases as the COF_2 concentration in the monomer mixture increases [1997].

13.13.1.4 Group 15

COF_2 reacts with PCl_5 in an autoclave between 100 and 400 °C, according to [899,900,903,905]:

$$COF_2 + PCl_5 \longrightarrow CCl_2F_2 + POCl_3$$

This reaction is much less efficient than the analogous phosgene reaction (see Section 9.1.4.2), owing to the occurrence of the following side reactions [899,900]:

$$COF_2 + PCl_5 \longrightarrow COClF,\ COCl_2,\ PF_3Cl_2,\ \textit{etc.}$$

$$COCl_2 + PCl_5 \longrightarrow CCl_4 + POCl_3$$

$$CCl_2F_2 + COF_2 \longrightarrow CF_3Cl + COClF$$

$$2CCl_2F_2 \rightleftharpoons CCl_3F + CClF_3$$

With mixed phosphorus(V) halides, similar reactions occur [900,903]:

$$COF_2 + PCl_2F_3 \longrightarrow CCl_2F_2 + POF_3$$

$$COF_2 + PBr_2F_3 \longrightarrow CBr_2F_2 + POF_3$$

The reaction of COF_2 with SbF_5 has been examined in SO_2ClF by ^{19}F n.m.r. spectroscopy at −100 °C: the resolved spectra were interpreted in terms of the presence of an *O*-bonded 1:1 adduct, $SbF_5.O{=}CF_2$: at 25 °C, rapid exchange occurs, indicating that the adduct is largely dissociated at room temperature [99]. With AsF_5 under similar conditions, there was evidence for weak complex formation (with rapid exchange) at −100 °C, but complete dissociation occurs at room temperature [99]. These results were later confirmed by a Raman spectroscopic study, the results of which are summarized in Table 13.22, in which the solid adducts were isolated at low temperatures (−162 °C) [365].

TABLE 13.22

RAMAN DATA (units of cm^{-1}) FOR $EF_5.COF_2$[a]

E	Medium	$\nu_1(a_1)$ $\nu(CO)$	$\nu_2(a_1)$ $\nu_s(CX)$	$\nu_3(a_1)$ $\delta_s(OCX)$	$\nu_4(b_1)$ $\nu_{as}(CX)$	$\nu_5(b_1)$ $\delta_{as}(OCX)$	$\nu_6(b_2)$ $\pi(COX_2)$	Ref.
Sb	Liquid[a]	1803	1057, 1043		1430	-[b]	777	365
Sb	Solid[c]	1770	1050	606	1436	-[b]	774	365
As	Liquid[d]	1835	1016	626	1394			365
As	Solid[c]	1788	1037	606	1402	673	792	365

[a] −1 °C. [b] Possibly hidden under SbF_5 bands. [c] −162 °C. [d] −50 °C.

The shifts in ν(CO) in $EF_5.COF_2$ compared with free COF_2 (see Table 13.22) confirm the conclusion of the n.m.r. study that the complexes are *O*-bonded.

13.13.1.5 Group 16

The labelled trioxides; $(CF_3O)_2O$, $(CF_3O)_2{}^{18}O$, $(CF_3{}^{18}O)_2O$, and $(CF_3{}^{18}O)_2{}^{18}O$ were prepared from COF_2/OF_2, $COF_2/{}^{18}OF_2$, $C^{18}OF_2/OF_2$, and $C^{18}OF_2/{}^{18}OF_2$ mixtures, respectively [1901].

In the presence of CsF, COF_2 reacts with OF_2 at room temperature to give bis(trifluoromethyl)trioxide, a surprisingly stable compound [47,140aa,1866]:

$$2COF_2 + OF_2 \longrightarrow F_3COOOCF_3$$

The proposed mechanism for this reaction is [47]:

$$COF_2 + CsF \longrightarrow Cs[OCF_3]$$

$$OF_2 + Cs[OCF_3] \longrightarrow CF_3OOF + CsF$$

$$CF_3OOF + Cs[OCF_3] \longrightarrow F_3COOOCF_3 + CsF$$

$$CF_3OOF + COF_2 \longrightarrow F_3COOOCF_3$$

The mechanism of this reaction was confirmed by using ^{17}O tracer techniques and ^{17}O n.m.r. spectroscopy [1920–1922]. The intermediate, CF_3OOF, was isolated by treating $Cs[OCF_3]$ with OF_2 at room temperature [1921,1922].

In contrast, the analogous reaction between COF_2 and OCl_2 (in the presence of CsF at −20 °C) yields CF_3OCl [807a].

Peroxydisulfuryl difluoride, $S_2O_6F_2$, reacts with COF_2, in the presence of potassium fluoride, at room temperature according to [1754a]:

$$COF_2 + S_2O_6F_2 + KF \longrightarrow CF_3OOSO_2F + Cs[SO_3F]$$

The reaction between NSF_3, COF_2 and anhydrous hydrogen fluoride or hydrogen chloride, in the presence of sodium fluoride, yields F_5SNCO [567]. However, an equimolar mixture of NSF_3, COF_2 and anhydrous hydrogen fluoride at −50 °C reacts, in the ***absence*** of sodium fluoride, to give $F_5SNHC(O)F$ in high yield [2033]. The intermediate in both reactions is F_5SNH_2 [567,2033].

COF_2 reacts with $F_4S{=}NF$ at 23 °C, in the presence of solid KF, to give $F_5SNFC(O)F$ in high yield, according to [1534]:

$$F_4S{=}NF + KF \longrightarrow K[F_5S{-}NF]$$

$$K[F_5S{-}NF] + COF_2 \longrightarrow F_5S{-}NF{-}C(O)F + KF$$

13.13.1.6 Group 17

COF_2 reacts with ClF in the presence of CsF (or FNO [2237]) at -20 °C to give CF_3OCl (a precursor, *via* reaction with HCl, of CF_3OH [1128]) in quantitative yield, a reaction discovered independently by two different groups [807a,895a,1790b,2236]. The same reaction occurs between COF_2 and ClF adsorbed on γ-Al_2O_3 [2113,2115]. With ClF_3 adsorbed on γ-Al_2O_3, the following reaction occurs [2115], which has been studied by i.r. spectroscopy in a specially designed cell [2114]:

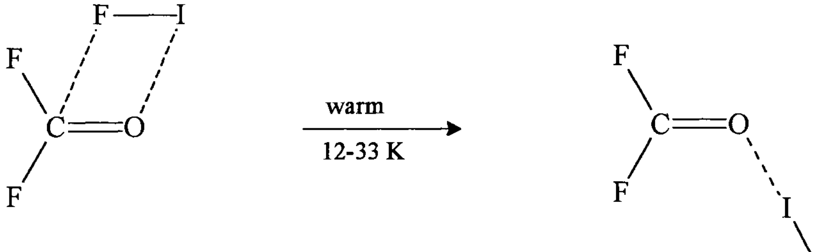
$$2(ClF_3)_{ads} + 2COF_2 \longrightarrow 2CF_4 + ClO_2F + ClF$$

However, in the presence of $K[HF_2]$ (or binary Group 1 or Group 2 fluorides) in an autoclave at 250 °C, the principal fluorocarbon product of the reaction between ClF_3 and COF_2 was bis(trifluoromethyl)peroxide, F_3COOCF_3 (92.3%), with only a small amount of by-product CF_4 (1.5%) being formed [587]:

$$2COF_2 + ClF_3 \longrightarrow F_3COOCF_3 + ClF$$

$$6COF_2 + 2ClF_3 \longrightarrow 3F_3COOCF_3 + Cl_2$$

In a fascinating matrix study, codeposition of CF_3I and ozone in an argon matrix (17 K) generated a $CF_3I...O_3$ molecular complex, which dissociated upon irradiation at 470–1000 nm to yield monomeric isolated CF_3IO. Photolysis of this iodoso species at 240–420 nm produces two different isomers of a $F_2C{=}O...IF$ adduct, one converting into the other upon slight warming [50b]:



In an independent study, the same pair of isomers were also generated in the photooxidation of CF_3I by O_2 in an argon matrix at 4.2 K [395a].

13.13.1.7 Pseudohalides and their derivatives

COF_2 reacts with liquid HCN in the presence of NaF to give CO(CN)F [2068a,2070]. The reaction between COF_2 and FCN (at -78 °C in the presence of CsF) is rather more complex, giving a mixture of products: $CF_3N(CN)_2$ (13.8%), CF_3NCO (8.8%), $CF_3OC(O)F$ (5.8%), $(FCN)_3$ (4%), $(CF_3)_2NCN$ (3.6%), $(CF_3)_2NC(O)F$ (2.3%) and a polymeric residue

[1790]. A reaction scheme to account for this distribution of products was proposed [1790].

COF_2 reacts with K[NCO] in a LiCl–KCl eutectic mixture at 400 °C to give either $CO(NCO)_2$ or CO(NCO)F, according to conditions [1018,2111a]:

$$COF_2 + 2K[NCO] \longrightarrow CO(NCO)_2 + 2KF$$

$$COF_2 + K[NCO] \longrightarrow CO(NCO)F + KF$$

Analogous reactions occur with K[NCS], yielding $CO(NCS)_2$ and CO(NCS)F [1018], and with K[CN] to produce only a small yield of $CO(CN)_2$ [2111a]. COF_2 will also react with an equimolar Na[SCN]–K[SCN] ionic liquid at 140 °C to give low yields of CO(NCS)F [2111a].

A mixture of carbonyl difluoride and carbonyl diisocyanate will undergo a comproportionation reaction at 180 °C, to give a 100% yield of the mixed product [1018]:

$$COF_2 + CO(NCO)_2 \longrightarrow 2CO(NCO)F$$

A similar comproportionation reaction occurs between COF_2 and $CO(NCS)_2$ at 50 °C in an autoclave, producing CO(NCS)F in 64% yield [1018].

13.13.2 Reactions with oxides

As for phosgene (see Section 9.4), the thermodynamic driving force for the following reactions is the elimination of carbon dioxide:

$$COF_2(g) + O^{2-} \longrightarrow CO_2(g) + 2F^-$$

It is rather sad to contrast the detailed study of the chloride system with the relatively sparse study of the potentially much more interesting fluoride systems. If it was not for two excellent recent papers by Shreeve and coworkers [1309a,1866a], this Section would have made rather dull reading.

13.13.2.1 Main group oxides

The reaction between Cs_2O and COF_2 in MeCN was originally [1337] reported to give $Cs_2[CO_2F_2]$, but reinvestigation [1216] showed the solid products to be a mixture of $Cs[OCF_3]$ and $Cs_2[CO_3]$ (with traces of $Cs[HF_2]$); CO_2 was evolved. The products formed could be rationalized, however, in terms of $Cs_2[CO_2F_2]$ being formed as a reactive intermediate [1216]:

$$Cs_2O + COF_2 \longrightarrow Cs_2[CO_2F_2]$$

$$Cs_2[CO_2F_2] \longrightarrow 2CsF + CO_2$$

$$CsF + COF_2 \longrightarrow Cs[OCF_3]$$

$$Cs_2O + CO_2 \longrightarrow Cs_2[CO_3]$$

In a subsequent study to the above investigations, an attempt was made to prepare $[CO_2F_2]^{2-}$ by codepositing COF_2 with Tl_2O in an argon matrix [459]: the principal product was $Tl[CO_2F]$, but there was some evidence that $Tl_2[CO_2F_2]$ had been formed, and that this readily eliminated TlF upon warming (14–35 K) to give the more stable $Tl[CO_2F]$ [459].

Carbonyl difluoride is completely absorbed by CaO, with evolution of heat [1756].

Carbonyl difluoride will react with B_2O_3 at 150 °C to give essentially quantitative conversion to BF_3 [1309a]. Treatment of γ–Al_2O_3 with COF_2 promotes the Brønsted acidity of the surface (probably due to HF generation at surface hydroxyl sites), but not its Lewis acidity [2032c]; the treated γ–alumina is an active catalyst for halogen exchange with halohydrocarbons [2032d].

Carbonyl difluoride will react with partially oxidized charcoals to produce graphite fluorides, containing up to 10% fluoride [ICI29]. Treatment of carbonyl difluoride with carbon monoxide at temperatures in excess of 350 °C and elevated pressures, and in the presence of a catalyst (*e.g.* Fe or CuF_2), is reported to generate tetrafluoroethene [842]:

$$2COF_2 + 2CO \longrightarrow C_2F_4 + 2CO_2$$

This is surprising, in view of the unfavourable energetics of this reaction (ΔG_r = +185 kJ mol^{-1} at 700 K). Moreover, under the non–equilibrium conditions in a shock tube, addition of CO to COF_2 has little observable effect upon the overall kinetics of thermal decomposition (2400–3000 K) of COF_2 (*cf.* Section 13.11) [716,1354].

Carbonyl difluoride slowly attacks SiO_2 at room temperature [1756], and immediately attacks glass (particularly in the presence of moisture) to give SiF_4 and CO_2 [1756]; Pyrex is attacked more rapidly than silica [1480]. Quantitative conversion of SiO_2 to SiF_4 is achieved at 160 °C [1309a]. GeO_2 is also converted to GeF_4 under mild conditions [1309a], but SnO_2 requires the presence of catalytic amounts of CsF and a temperature of 220 °C in order to achieve significant conversion to SnF_4 [1309a]. Under similar conditions, PbO_2 does not react with COF_2 [1309a,1866a].

Carbonyl difluoride reacts with lithium nitrate (in the presence of CsF, to absorb liberated HF), at 45–90 °C, according to [1790a]:

$$Li[NO_3] + COF_2 \longrightarrow FNO_2 + CO_2 + LiF$$

FNO_2 was isolated in a quantitative yield; in the analogous reaction with $Na[NO_3]$, the yield was 85%, and with $Cs[NO_3]$, no reaction was observed [1790a].

Treatment of phosphorus(V) oxide with COF_2 at 180 °C produces a mixture of PF_5 and POF_3 [1309a]. Under similar conditions, Bi_2O_3 is converted to BiF_3, but Sb_2O_3 is unreactive [1866a].

Reports on the reaction between SO_2 and COF_2 are contradictory, rather surprising considering that the reports are recent, and that both originate within the same research group. In the earlier report, it is stated that "SO_2 did not react with COF_2 at 200 °C even in the presence of CsF and with longer reaction time (86 h)" [1309a]. In contrast, in the later report, it is stated that "Sulfur dioxide or SOF_2 reacted with COF_2 in the presence of a trace of CsF to give quantitative conversion to SF_4" [1866a]. *L'embarras des richesses* (Abbé d'Allainaval, 1726). Thermodynamic calculations for the reaction:

$$SO_2(g) + 2COF_2(g) \longrightarrow SF_4(g) + 2CO_2(g)$$

indicate that the reaction is unfavourable ($\Delta G_{500} \simeq 85$ kJ mol^{-1}) [1764].

The reaction between COF_2 and SO_3 is complex: the products (of reaction at 100 °C in a pressurized glass vessel) are CO_2, FSO_2OSO_2F and $FSO_2OSO_2OSO_2F$ (and traces of SO_2F_2, SiF_4 and $FSO_2(OSO_2)_nF$, where $n > 2$) [1167]. The reaction is believed to proceed *via* an intermediate fluorocarbonyl fluorosulfate, which reacts readily with SO_3 [1167]:

$$\begin{tikzcd}
SO_3 \arrow[r, "COF_2"] & FC(O)OSO_2F \arrow[r, "SO_3"] & \begin{array}{c} FSO_2OC(O)OSO_2F \\ \text{or} \\ FC(O)OSO_2OSO_2F \end{array} \arrow[r] \arrow[d, "SO_3"] & FSO_2OSO_2F + CO_2 \\
 & & FSO_2OSO_2OSO_2F + CO_2 &
\end{tikzcd}$$

No reaction is observed between SO_3 and COF_2 at room temperature, however, even after several days [2069]. In contrast, at higher temperatures, SF_6 is formed in high yield [1866a].

The reaction between SeO_2 and COF_2 at 200 °C is reported to yield either $SeOF_2$ [1309a] or SeF_4 [1866a], whereas TeO_2 reacts at 160 °C to indisputably form TeF_4 [1309a,1866a].

Carbonyl difluoride reacts with $Na[ClO_3]$ at 85 °C, in the presence of CsF, according to [1790a]:

$$Na[ClO_3] + COF_2 \longrightarrow FClO_2 + CO_2 + NaCl$$

Attempts to prepare $FClO_3$ by treating $Li[ClO_4]$ with COF_2 were unsuccessful [1790a]. However, I_2O_5 reacts at 160 °C to produce IF_5 in *ca.* 60% yield [1309a].

13.13.2.2 Transition metal oxides

Titanium(IV) oxide, with a high surface area, has been used to remove COF_2 from waste gases [581a]. Vanadium(V) oxide reacts with COF_2 at 210 °C to give VOF_3 in quantitative yield [1309a], whereas niobium(V) oxide and tantalum(V) oxide give their respective pentafluorides, under similar conditions, also in quantitative yield [1309a].

Chromium(VI) oxide and COF_2 were heated at 185 °C in a sealed vessel to give a quantitative yield of $[CrO_2F_2]$ [718b,818]:

$$CrO_3 + COF_2 \longrightarrow [CrO_2F_2] + CO_2$$

A fluoroformate intermediate was postulated [818], but further reaction of CrO_2F_2 with an excess of COF_2 could not be observed [1309a]. The heavier oxides, MoO_3 and WO_3, reacted with COF_2 at 180–190 °C, and gave quantitative yields of $MoOF_4$ and WOF_4, respectively, but "commercial" WO_3 was unreactive [1309a].

Given all the above observations, it is rather surprising to note that, over the temperature range 150 to 200 °C, none of the following oxides showed any reactivity with COF_2: MnO_2, OsO_4, Co_2O_3, NiO or HgO (red or yellow) [1309a].

13.13.2.3 Actinide oxides

Uranium(VI) oxide has been converted almost quantitatively into uranium(VI) fluoride, in a CO_2 flow system, at 1023 K [1498]:

$$UO_3 + 3COF_2 \longrightarrow [UF_6] + 3CO_2$$

This process was calculated to be thermodynamically more favourable than either of the following competing reactions over the range 200–1200 K [1498]:

$$UO_3 + COF_2 \longrightarrow UO_2F_2 + CO_2$$
$$UO_3 + 2COF_2 \longrightarrow UF_4 + 2CO_2 + \tfrac{1}{2}O_2$$

Similar conversions were observed in a static system at 180 °C [1866a]; under similar conditions, ThO_2 gave ThF_4 in *ca.* 80% yield [1866a]. The presence of a small amount of CsF promotes the quantitative formation of UO_2F_2 [1309a].

13.13.3 Reactions with elements

13.13.3.1 Reactions with main group elements

The reaction between COF_2 and H_2 has been studied under shock tube conditions, between 1900 and 2700 K [716,1354]. The overall reaction was:

$$COF_2 + H_2 \longrightarrow CO + 2HF$$

The observed kinetics were explained in terms of the following mechanism [716,1354]:

$$\begin{aligned} COF_2 + M &\longrightarrow [COF]\cdot + F\cdot + M \\ [COF]\cdot + M &\longrightarrow CO + F\cdot + M \\ H_2 + M &\longrightarrow H\cdot + H\cdot + M \\ F\cdot + H_2 &\longrightarrow HF + H\cdot \\ H\cdot + COF_2 &\longrightarrow [COF]\cdot + HF \\ H\cdot + [COF]\cdot &\longrightarrow CO + HF \end{aligned}$$

Sodium appears to burn in COF_2, to give sodium fluoride, sodium carbonate and carbon [1756].

Magnesium, aluminium and zinc react with COF_2 at red heat to give their respective fluorides and carbon monoxide [1756].

In a carbon arc, COF_2 is thought to react with carbon according to:

$$COF_2 + C \longrightarrow :CF_2 + CO$$

Calculations suggest [ICI33] that $\Delta G^{\bullet}_{2500}$ is −184 kJ mol^{-1}. Quenching the reaction mixture from >1500 °C to <400 °C in less than 1 s produced C_2F_4 as the principal product (35 mol %), along with CF_4 (20 mol %) and C_2F_6 (10 mol %): 35 % of the COF_2 was recovered [570,621]. Addition of an elemental halogen (X_2 = Cl_2 or Br_2) to the COF_2 passing through the carbon arc at >1500 °C generates mixtures of CX_2F_2 and CXF_2CXF_2, along with CF_4 and C_2F_4 and other minor products [395].

Carbonyl difluoride has been used as a plasma etchant for silicon, and was found to etch the surface rapidly [397]. A CF_4–O_2 plasma etchant has also been used; COF_2 is formed as a primary oxidation product [153]. An excess of O_2 in the plasma causes loss of COF_2 by reaction with singlet oxygen (*vide infra*), with a concomitant drop in the formation of SiF_4 [153]. COF_2 will also thermally (625 °C) etch Si(111) surfaces, and photochemically (CO_2 laser) etch SiO_2 on Si(111), both processes occurring *via* SiF_4 formation [974a]. Fluorine atoms (generated by ArF laser photolysis of COF_2) also form a very effective etchant for polycrystalline silica deposited on SiO_2 [1273a]. Finally, COF_2 and fluorine atoms are both generated in a CF_4–NO plasma [1775].

The reaction between COF_2 and $O(^1D)$ has been studied, and is about ten times slower than the analogous reactions with $CCl_{4-n}F_n$ [88]. This quenching has also been studied by time-resolved resonance fluorescence spectroscopy, and proceeds by two parallel pathways [2199]:

$$COF_2 + O(^1D_2) \xrightarrow{k_1} CO_2 + F_2$$

$$COF_2 + O(^1D_2) \xrightarrow{k_2} COF_2 + O(^3P_J)$$

The rate constants for these competing reactions are of a similar order of magnitude (k_1 = 2.1 x 10^{-11} cm^3 molecule^{-1} s^{-1}; k_2 = 5.3 x 10^{-11} cm^3 molecule^{-1} s^{-1}), and these values [2199] are to be preferred to earlier determinations [88,660,1038]; the measurements reported by Fletcher and Husain [660] are significantly in error. The following analogous thermal reaction has also been proposed as part of a complex series of reactions associated with the oxidation of $CBrF_3$ [68]:

$$2COF_2 + O_2 \longrightarrow 2CO_2 + 2F_2$$

Although there is no detectable thermal reaction between COF_2 and F_2 at room temperature [93], reaction occurs under UV irradiation at 35 °C to give CF_3OF (one of the few thermally stable compounds containing an oxygen–fluorine bond) in 80% yield [93]:

$$COF_2 + F_2 \xrightarrow{h\nu} CF_3OF$$

The reaction also produced small amounts of F_3COOCF_3, CO_2 and SiF_4, and traces of CF_4 [93]. The following simple mechanism was proposed to account for these reactions [93]:

$$F_2 + h\nu \longrightarrow 2F\cdot$$

$$F\cdot + COF_2 \longrightarrow F_3CO\cdot$$

$$F_3CO\cdot + F_2 \longrightarrow F_3COF + F\cdot$$

$$2F_3CO\cdot \longrightarrow F_3COOCF_3$$

A more recent, and more detailed, study of this reaction proposed that the key propagating radical was $[CF_2OF]\cdot$ rather than $[CF_3O]\cdot$, on the grounds that very little F_3COOCF_3 is formed: the mechanism proposed was much more elaborate, involving eight reactions and the intermediacy of $(CF_2OF)_2$ [1274].

At high temperatures, CF_3OF can be decomposed back into COF_2 and F_2 [1649]:

$$CF_3OF \rightleftharpoons COF_2 + F_2$$

From equilibrium constant measurements between 367 and 467 °C, ΔH° for this reaction was calculated as 116 ± 6 kJ mol^{-1} at 700 K, and 112.5 kJ mol^{-1} at 298 K; ΔG°_{298} is 77.8 kJ mol^{-1}, and ΔS°_{298} is 117 J mol^{-1} K^{-1} [1649].

AF (A = Na, K, Rb, Cs or $[NH_4]$), AF_2 (A = Mg, Ca, Sr or Ba) and LaF_3 act as catalysts for the fluorination of carbonyl difluoride at −78 °C to produce excellent yields of CF_3OF [319,1082,1083,1287a,1754b,2159a]:

$$COF_2 + F_2 \longrightarrow CF_3OF$$

Gaseous FNO also catalyses this reaction, at −20 °C, to give almost quantitative yields of CF_3OF [2237]. $Cs[HF_2]$, $K[AgF_4]$ and ThF_4 are much less active, but will catalyse the reaction at 25 °C. In the presence of LiF or NiF_2 (at 25–125 °C), as well as the formation of CF_3OF, the following process is also observed [1082,1083]:

$$2COF_2 + F_2 \longrightarrow F_3COOCF_3$$

The chemistry of bis(perfluoroalkyl)peroxides has been reviewed elsewhere [502,1866]. It is possible that F_3COOCF_3 can also be generated directly from the reaction between COF_2 and CF_3OF [1649,2159a]. Mixtures of COF_2 and F_3COOCF_3 were also generated (100–150 °C) in the presence of a wide range of metal fluorides, MF_2 (M = Be, Cu, Zn or Cd), MF_3 (M = Al, In, Mn, Fe, Co, Pr or Nd), ZrF_4 or UO_2F_2, and F_3COOCF_3 was generated (100–150 °C) in high yield in the presence of $M'F_2$ (M' = Pb or Hg), $M'F_3$ (M' = Bi, Tb, Y, Gd or Au) or $M'F_4$ (M' = Sn, Pb or Ce) [1082,1083]. In the presence of AgF, AgF_2 or TlF_3, very high yields (>95%) of F_3COOCF_3 are generated at 25 °C [319,1082,1083,2159a]. Mechanisms for these reactions were proposed, but there was little supportive evidence [1083]. The reaction between COF_2 (generated *in situ* from the reaction between methanol and AgF_2) and F_2 in the presence of AgF_2 at 160 °C, however, apparently produces only CF_3OF [1078e].

Electrochemical fluorination of COF_2 in anhydrous liquid hydrogen fluoride (in the presence of NaF) produces (in 74% overall yield) CF_3OF (73%), CF_4 (10%), and CF_3OOCF_3 (17%), along with OF_2 [1470,1471]. Predictions of the reaction between COF_2 and the pseudohalogen cyanogen, N≡C–C≡N, have been made [ICI33,ICI34]:

$$COF_2 + C_2N_2 \longrightarrow 2CF_2 + 2CO + N_2 \qquad (13.19)$$

$$2COF_2 + C_2N_2 \longrightarrow CF_4 + 2N_2 + 2CO + 3C \qquad (13.20)$$

Reaction (13.19) should be favoured at high temperatures (1500 K), reaction (13.20) being favoured at lower temperatures.

COF_2 forms a weakly-bound van der Waals complex with argon, which has been studied by microwave spectroscopy. It is non-planar, with a C_s equilibrium geometry, r(Ar...C) = 0.3402 nm and ∡ArCO = 100.3° (see Fig. 13.7) [1850]. The depth of the potential well for the complex is 178 cm^{-1} (2.13 kJ mol^{-1}) [1850].

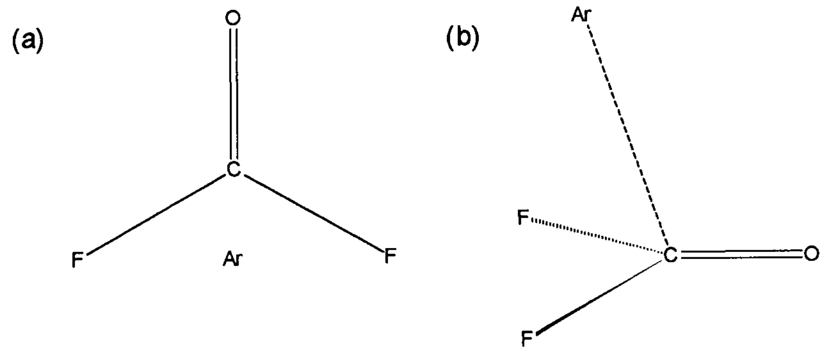


Fig. 13.7 The (a) plan and (b) elevation of Ar...COF_2 [1850].

13.13.3.2 Reactions with transition elements

There is believed to be a significant reaction between platinum metal and COF_2 at high temperatures [44,1755], but this is not well documented.

There is no perceptible reaction between either mercury or silver and COF_2 [1756].

13.13.4 Organometallics

The lithium reagent $LiN{=}C(CF_3)_2$ reacts with carbonyl difluoride to give the unexpected product $(CF_3)_2C{=}NC(CF_3)_2NCO$, along with traces of $(CF_3)_2C(F)NCO$ [1985].

Triethylsilyl radicals react with COF_2 in cyclopropane solution to give a siloxy derivative, which was characterized by e.p.r. spectroscopy [1175]:

$$COF_2 + [SiEt_3]\cdot \longrightarrow [C(OSiEt_3)F_2]\cdot$$

Trimethylsilyl isothiocyanate reacts with COF_2 at 50 °C in an autoclave to produce CO(NCS)F in quantitative yield [2111a]:

$$Me_3SiNCS + COF_2 \longrightarrow Me_3SiF + CO(NCS)F$$

An analogous reaction with Me_3SiCN at room temperature produces CO(CN)F in 26% yield [2111a].

13.13.5 Reactions with hydride derivatives

13.13.5.1 Reactions with Group 15 hydrides

COF_2 reacts with ammonia to give urea, guanidine, isocyanuric acid, and hydrogen fluoride (*cf*. Section 9.10.2.1) [1756].

13.13.5.2 Reactions with Group 16 and Group 17 hydrides

Carbonyl difluoride is more easily hydrolysed than phosgene (see Section 9.10.3.1). Indeed, in the presence of alkali metal carbonates or hydrogencarbonates (to remove HF), COF_2 has been suggested as a drying agent for organic solvents [1457].

Carbonyl difluoride reacts vigorously with water, to produce carbon dioxide and hydrogen fluoride [1756]. A similar reaction is observed with concentrated sulfuric acid, and it is completely absorbed by sodium hydroxide solution [1756]. Indeed, the reaction between COF_2 and D_2O at ≥50 °C has been used to prepare DF in purities >99.5% and yields of 90% [1554]. A recent *ab initio* study [677aa] of the mechanism and energetics of the gas-phase reaction of carbonyl difluoride with water indicates that the reaction proceeds through two transient intermediates - $CF_2(OH)_2$ and FC(O)OH. The former dissociates to the latter and HF, and the FC(O)OH then dissociates into CO_2 and HF, consistent with the overall stoicheiometry:

$$COF_2 + H_2O \longrightarrow CO_2 + 2HF$$

The loss of COF_2 at the surface of solid ice has been measured; it was concluded that the loss of COF_2 at the surface of stratospheric ice particles was insignificant for processes that occur on timescales of a year [879a].

There is no perceptible reaction between either H_2S or HCl and COF_2 [1756].

13.13.6 Miscellaneous reactions

13.13.6.1 "Gedanken" experiments

Del Bene and her coworkers [481-486] (and also Karpas and coworkers [1073a,1950b]) have performed a series of *ab initio* calculations in which they investigated the reactivity of carbonyl difluoride with Lewis acids. In particular, the interactions with water, H^+, and Li^+ have been studied, and the calculated planar equilibrium structures of the 1:1 adducts are illustrated in Fig. 13.8. Calculations were also performed upon similar adducts of C(O)RR' {R,R' = H,F; H_2; $(OH)_2$; H,Me; Me_2; H,NH_2; or $(NH_2)_2$}: in all cases, the COF_2 adducts were predicted to be the least stable. The strength of the intermolecular interaction was calculated as 10.97 kJ mol^{-1} for $COF_2.H_2O$ [481], 574.5 kJ mol^{-1} for $COF_2.H^+$ [485], and 105 kJ mol^{-1} for $COF_2.Li^+$ [483].

The $n \longrightarrow \pi^*$ transition in the adducts is predicted to be shifted to higher energy by *ca.* 1000 cm^{-1} for $COF_2.H_2O$ [481] and *ca.* 7800 cm^{-1} for $COF_2.Li^+$ [483]: these shifts are a reflection of the strength of the intermolecular interaction. Protonation is predicted to cause a lengthening of the C=O bond, and a differential shortening of the C-F bonds {see Fig. 13.8(c)} [484]; the effect is much less pronounced for $COF_2.Li^+$ {see Fig. 13.8(d)} [482].

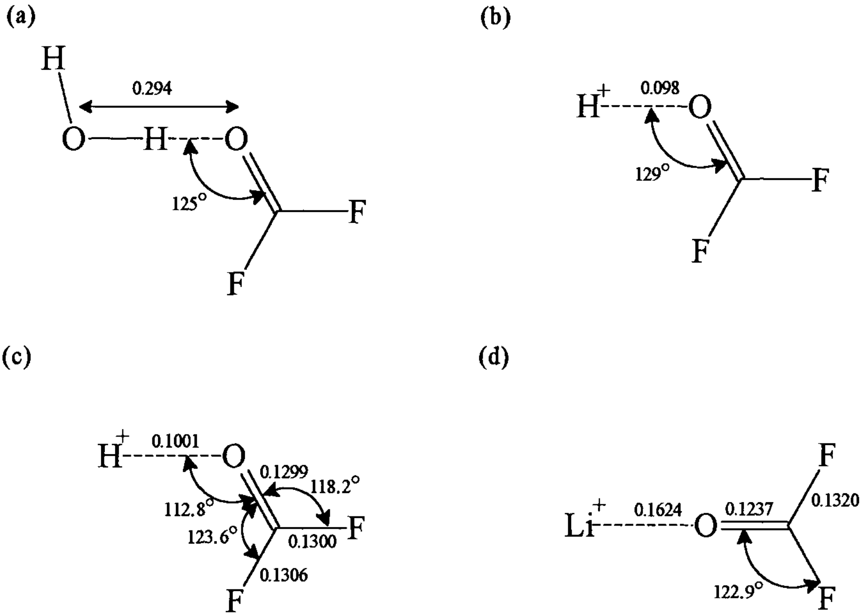


Fig. 13.8 The calculated structures for (a) $COF_2.H_2O$ (STO-3G) [481], (b) $COF_2.H^+$ (4-31G) [485], (c) $COF_2.H^+$ (STO-3G) [484], and (d) $COF_2.Li^+$ (STO-3G) [482]. Bond lengths are given in units of nm.

In a similar manner, the interaction between COF_2 and NH_3 has been investigated, using both 3-21G and 6-31G* basis sets [2226aa]. The structure of the transition state is given in Fig. 13.9 [2226aa]. It will come as little surprise that the nucleophilic nitrogen atom on the ammonia has attacked the electrophilic carbon on the COF_2, and that the transition state is stabilized by a hydrogen bond between a hydrogen atom on the ammonia and the oxygen atom on the COF_2 (but see Section 17.6).

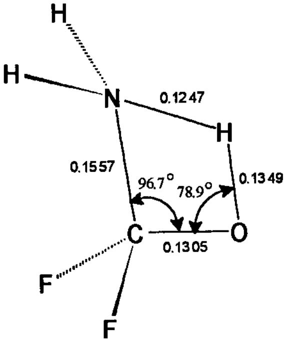


Fig. 13.9 The calculated structure for $COF_2.NH_3$ (STO 3-21G) [2226aa].

13.13.6.2 Electron and ion cyclotron resonance studies

As seen for phosgene (see Section 9.12.1.2), ion cyclotron resonance spectrometry is becoming a valuable tool for studying the gas phase reactions of COF_2 with a wide range of ions.

At 30–70 eV, three primary ions are formed by electron impact [886,1071,1292,2035]:

$$COF_2 + e^- \longrightarrow F^- + [COF]\cdot \qquad \Delta H = 200\ \text{kJ mol}^{-1}$$

$$COF_2 + e^- \longrightarrow [F_2]^- + CO \qquad \Delta H = 250\ \text{kJ mol}^{-1}$$

$$COF_2 + e^- \longrightarrow [COF]^- + F\cdot \qquad \Delta H = 270\ \text{kJ mol}^{-1}$$

The most abundant ion (at 70 eV) is F^- (91.7%), followed by $[F_2]^-$ (7.3%) and then $[COF]^-$ (<1%) [1071]. In phosgene, these ions are formed at near thermal energies (<1 eV); for COF_2, the resonance maxima occur between 2.7 and 3.3 eV [1071].

The secondary negative ion, $[COF_3]^-$, is formed in two parallel processes, the former being just over ten times faster than the latter [1071]:

$$COF_2 + [COF]^- \longrightarrow [COF_3]^- + CO$$

$$COF_2 + [F_2]^- \longrightarrow [COF_3]^- + F\cdot$$

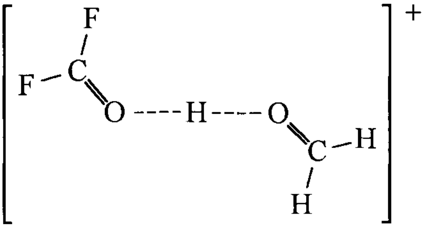
The i.c.r. experiments suggest upper limits on the enthalpy of formation for $[COF]^-$ of −435 kJ mol^{-1} and for $[COF_3]^-$ of −962 kJ mol^{-1} [1071].

Protonation of carbonyl difluoride has been observed in COF_2–formaldehyde mixtures [1072]:

$$COF_2 + [H_2CO]^+ \longrightarrow [F_2COH]^+ + HCO$$

$$COF_2 + [HCO]^+ \longrightarrow [F_2COH]^+ + CO$$

The data yield a calculated upper limit for the enthalpy of formation of $[F_2COH]^+$ as +305 kJ mol^{-1} [1072]. This gives COF_2 a proton affinity of 590 kJ mol^{-1} [1072]; more recent data suggest a value of 664 kJ mol^{-1} [545]. Evidence for the formation of the protonated dinuclear species $[F_2C{=}O\cdots H\cdots O{=}CH_2]^+$ was also obtained [863], although $[F_2C{=}O\cdots H\cdots O{=}CF_2]^+$ could not be observed [863]. *Ab initio* geometry optimization using a 4–31G basis set indicates the following gas-phase structure, containing a linear $O\cdots H\cdots O$ hydrogen bond:



Methyl nitrite is an efficient source of gaseous methoxide ion, which reacts with COF_2 to efficiently produce fluoroformate [1366]:

$$COF_2 + [CH_3O]^- \longrightarrow [FCO_2]^- + CH_3F$$

The following side reactions were also observed [1366]:

$$[CH_3O]^- + CH_3ONO \longrightarrow CH_3OH + [CH_2ONO]^-$$
$$[CH_2ONO]^- + COF_2 \longrightarrow [CHFONO]^- + HF + CO$$
$$[FCO_2]^- + COF_2 \longrightarrow [F_3CO]^- + CO_2$$

The gas-phase allyl anion, $[C_3H_5]^-$, is readily generated from a mixture of propene and N_2O in an i.c.r. mass spectrometer, and its reactions with a mixture of N_2O and COF_2 have been studied [468]. The principal reaction observed is [468]:

$$[CH_2{=}CH{-}CH_2]^- + F_2C{=}O \longrightarrow [CH_2{=}CH{-}C{\equiv}C{-}O]^- + 2HF$$

The following side reactions were also observed [468]:

$$[OH]^- + COF_2 \longrightarrow HF + [FCO_2]^-$$
$$[NO]^- + COF_2 \longrightarrow NO + [COF_2]^-$$

The reaction with hydroxide parallels the reaction observed (*vide supra*) with methoxide.

13.13.6.3 Salmagundi

The complexes $[Ni(dppm)X_2]$ (X = Cl, Br or I) are oxidatively fluorinated by COF_2 under mild conditions (25 °C; either in CH_2Cl_2 solution or in the solid state) to give $Ph_2PF_2CH_2PF_2Ph_2$, carbon monoxide and NiX_2 [849a], whereas $[Ni(dppe)X_2]$ and $[Ni(dppp)X_2]$ are unreactive under the same conditions [849a]. The complex $[Ni(dppe)_2]X_2$ reacts with COF_2 to give $[Ni(dppe)X_2]$, CO and $Ph_2PF_2CH_2CH_2PF_2Ph_2$; $[Ni(dppp)_2]X_2$ similarly yields $[Ni(dppp)X_2]$ and $Ph_2PF_2CH_2CH_2CH_2PF_2Ph_2$ [849a]. Both $[Ni(dppe)_2]$ and $[Ni(dppp)_2]$ are oxidized by carbonyl difluoride to give NiF_2 and $Ph_2PF_2CH_2CH_2PF_2Ph_2$ or $Ph_2PF_2CH_2CH_2CH_2PF_2Ph_2$, respectively [849a].

$CF_2{=}NF$ reacts with caesium fluoride to generate $Cs[CF_3NF]$, which attacks COF_2 to form $CF_3NFC(O)F$ in 93% yield [354].

$FC(O)\{CF(CF_3)OCF_2\}_nCF_2I$ (n = 1 or 2), in the presence of a Zn–Cu couple, reacts with COF_2 to give $FC(O)\{CF(CF_3)OCF_2\}_nCF_2C(O)F$ [2222].

13.14 REACTIONS WITH ORGANIC COMPOUNDS

Carbonyl difluoride is a particularly versatile fluorinating agent, and an important material for the synthesis of organofluorine compounds [1079]. Its reactions with perfluoroalkenes gives perfluoroacyl fluorides in the presence of a fluoride ion source, and its facile reaction with amines or alcohols results in the formation of carbamoyl fluorides or fluoroformates, respectively. The fluorination of carbonyl compounds, such as aldehydes and ketones, with COF_2 can give *gem*-difluorides by replacement of the carbonyl oxygen atom with two atoms of fluorine:

e.g.:

$$R_2C{=}O + COF_2 \longrightarrow R_2CF_2 + CO_2$$

This simple transformation plays an important *rôle* in the synthetic organic chemist's ability to selectivity place fluorine atoms into organic molecules. Carbonyl difluoride can be compared with sulfur(IV) fluoride for its effectiveness to replace oxygen. COF_2 is said to be more effective than SF_4 in its ability to difluorodeoxygenate amides, but it is considerably less reactive towards carboxylic acids (to form the CF_3 group). On the other hand, the co-product of sulfur(IV) fluoride reactions with carbonyl-containing compounds is SOF_2, whereas with COF_2, the co-product is the innoxious and fluorine-free CO_2.

Unlike phosgene, however, the use of carbonyl difluoride as a carbonylating agent is limited, since there is little point in preparing carbonates, ureas or simple isocyanates from COF_2, when $COCl_2$ will function just as well at a fraction of the cost. Fluoroformates, on the other hand, are a unique class of material which find uses as intermediates for pharmaceuticals, agricultural chemicals and dyestuffs, as peptide reagents and as plant protective reagents. Their preparation by the halide exchange of chlorine for fluorine {see Equation (13.21)} is applicable only to a limited number of compounds since the exchange

$$ROC(O)Cl + MF \longrightarrow ROC(O)F + MCl \qquad (13.21)$$

reaction generally requires elevated temperatures, under which conditions many chloroformates, particularly aliphatic ones, are unstable. Where the exchange reaction can be performed at low or ambient temperatures, the times required can be excessively long.

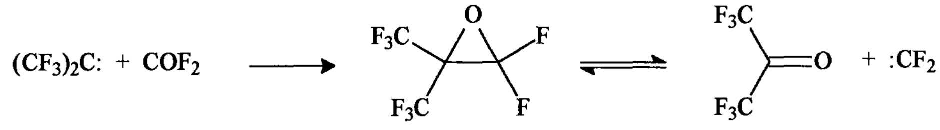
Alkyl fluoroformates can be decarboxylated, for example by heating in the presence of pyridine or BF_3, to give the corresponding fluoride [380,382], or they can be further treated with SF_4 to produce $ROCF_3$ [1856b,1856c]:

$$ROC(O)F + SF_4 \longrightarrow ROCF_3 + SOF_2$$

Aryl fluoroformates can be decarboxylated into aromatic fluorides by gas-phase decomposition at 600–800 °C [380,382], or at around 300 °C by passing the vaporized aromatic fluoroformate over an alumina catalyst [86].

13.14.1 Reactions with carbenes

Bis(trifluoromethyl)carbene, from bis(trifluoromethyl)diazirine, reacts with carbonyl difluoride at 180 °C over 4 h in a sealed tube, to give a yield (40%) of the adduct, perfluoroisobutene oxide, along with hexafluoropropanone (10%) [1300]:

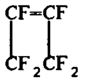
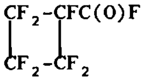


13.14.2 Reactions with alkenes

The reaction of carbonyl difluoride with fluoroalkenes generally proceeds to give perfluoroacyl fluorides by addition of F and C(O)F units across the double bond, Table 13.23.

TABLE 13.23

REACTION OF COF_2 WITH PERFLUOROALKENES

Perfluoroalkene	Product	Conversion/%	Ref.
$CF_2{=}CF_2$	$CF_3CF_2C(O)F$	13	628,632
$CF_3CF{=}CF_2$	$(CF_3)_2CFC(O)F$	80	628,632
$CF_3CF{=}CFCF_3$	$CF_3CF_2CF(CF_3)C(O)F$	62	628,632
$CF_2{=}CFC(O)F$	$CF_3CF\{C(O)F\}_2$	-	592
$CF_2{=}CFCN$	$CF_3CF(CN)C(O)F$	93	593
$CF_2{=}C(CF_3)C(OF)$	$CF_3C(CF_3)\{C(O)F\}_2$	-	592
$CH_3OCF{=}CF_2$	$CH_3OCF_2CF_2C(O)F$	62	628,632
$SF_5CF{=}CF_2$	$SF_5CF(CF_3)C(O)F$	45	473
		54	628,632

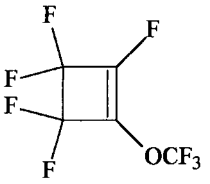
The reactions take place readily in a pressure vessel, at 100–150 °C, using an excess of COF_2 in the presence of a fluoride ion source in an aprotic solvent, such as KF, $K[HF_2]$, CsF or $[NEt_4]F$ in CH_3CN [632]. Under similar conditions, COF_2 reacts with two molar equivalents of hexafluoropropene to give the perfluoroketone according to [628,1908]:

$$(CF_3)_2CFC(O)F + CF_2{=}CF{-}CF_3 \longrightarrow (CF_3)_2CFC(O)CF(CF_3)_2$$

The reaction mechanism for this metal fluoride catalysed addition is presumed to involve the addition of fluoride ion to the fluoroalkene to form an intermediate fluorocarbanion, which then reacts with COF_2 [473,632]:

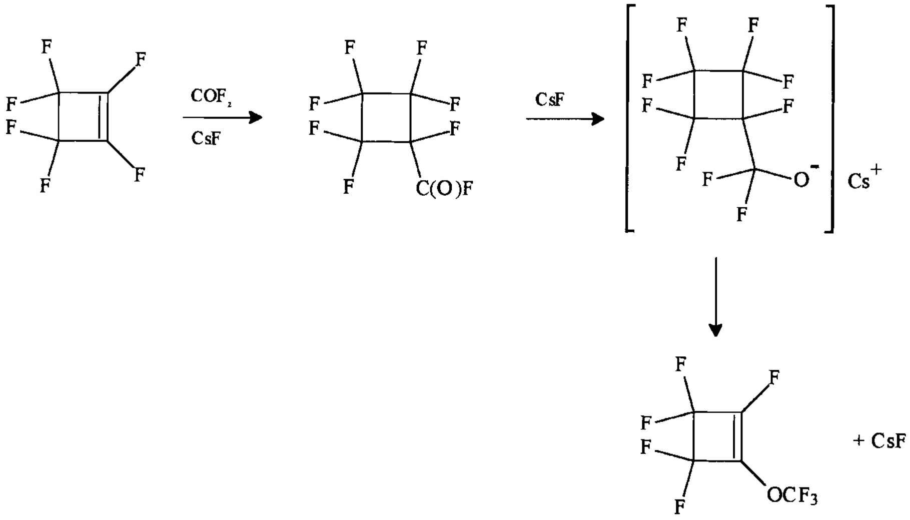
$$F^- + CF_2{=}CFCF_3 \longrightarrow [CF_3CFCF_3]^- \xrightarrow{COF_2} (CF_3)_2CFC(O)F + F^-$$

The reaction of an excess of COF_2 with perfluorocyclobutene in the presence of CsF in CH_3CN at 95 °C for 64 h is claimed to result in the production of (13.7) [48].



(13.7)

This reaction may be considered to occur as a result of the further reaction of the perfluoroacid fluoride with CsF, as illustrated below:



As with phosgene (Section 10.1.3), "ene" reactions with carbonyl difluoride are unknown [972].

13.14.3 Reactions with dienes

The reaction of 1,4-perfluoropentadiene with an excess of carbonyl difluoride, in the presence of CsF and CH_3CN at 180 °C over 12 h, results in the production of a mixture of mono- and di-acid fluorides [628].

13.14.4 Reactions with aromatic hydrocarbons

Triphenylmethane is fluorinated by COF_2 at room temperature, over 12 h in the presence of a stoicheiometric quantity of NEt_3 in CH_2Cl_2, as illustrated in Equation (13.22): the yield of Ph_3CF is 60% [850,2193a].

$$Ph_3CH + COF_2 + NEt_3 \longrightarrow Ph_3CF + CO + [NHEt_3]F \qquad (13.22)$$

Although, at the time of writing, this is the only example of the reaction of COF_2 with a hydrocarbon, it is believed that the reaction is extendible to other systems [850,2193a].

13.14.5 Reactions with nitrogen compounds

13.14.5.1 Primary amines

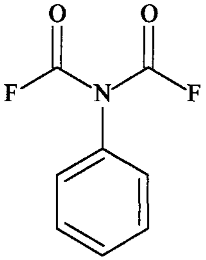
When COF_2 is passed into a solution of methylamine in benzene at room temperature, MeNHC(O)F and HF are formed [589]. Similarly, aniline reacts with carbonyl difluoride to form the corresponding carbamyl fluoride [589]:

$$2PhNH_2 + COF_2 \longrightarrow PhNHC(O)F + [NPhH_3]F$$

Where an excess of aniline is used, the reaction continues to produce diphenylurea, consistent with the overall stoicheiometry:

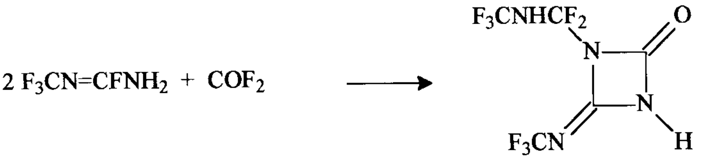
$$4PhNH_2 + COF_2 \longrightarrow (PhNH)_2C{=}O + 2[NPhH_3]F$$

However, treatment of aniline with COF_2 at 150 °C, in a pressure vessel in the presence of sodium fluoride (to absorb the HF), results in the production of the bis-fluoroformyl derivative (13.8) [632]. This compound may arise as a result of the formation of phenyl isocyanate from the dehydrofluorination of PhNHCOF, followed by subsequent addition of COF_2 (see Section 13.14.5.5) [632].



(13.8)

The cyclization of the amine-ketimine, $F_3CN{=}CFNH_2$, with COF_2 occurs through the amine groups, according to Equation (13.23) [1131].



(13.23)

13.14.5.2 Secondary amines

The secondary amines, diethylamine and methylaniline, were amongst the first materials to be studied in combination with COF_2. The reactions, using an excess of COF_2, take place readily at room temperature, according to [589]:

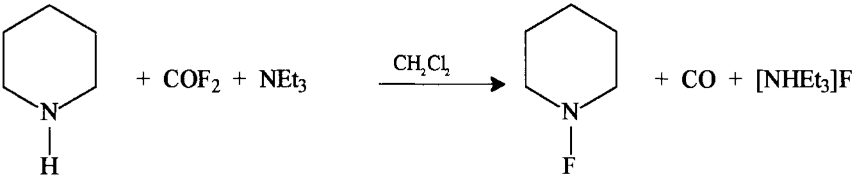
$$R_1R_2NH + COF_2 \longrightarrow R_1R_2NC(O)F + HF$$
$$(R_1 = R_2 = Et;\ R_1,R_2 = Ph,Me)$$

Diphenylamine ($R_1 = R_2 = Ph$) reacts in a similar fashion [95], but bis(trifluoromethyl)amine ($R_1 = R_2 = CF_3$) apparently required high temperatures (up to 300 °C) and extended reaction times (>12 h), in addition to the use of a caesium fluoride catalyst, to give the expected carbamoyl fluoride product [632].

N-Fluoro derivatives have been prepared from the reactions of carbonyl difluoride with secondary amines [850,2193a]. When mixed according to the stoicheiometry indicated in Equation (13.24), dimethylamine reacts at 25 °C to form *N*-fluorodimethylamine with a yield of 45% [850,2193a].

$$NHMe_2 + COF_2 + NEt_3 \longrightarrow NFMe_2 + CO + [NHEt_3]F \qquad (13.24)$$

Piperidine also reacts with COF_2 under similar conditions, to form the *N*-fluoro derivative, Equation (13.25) [850,2193a].



(13.25)

13.14.5.3 Carboxamides

13.14.5.3.1 Primary amides

Primary amides, such as ethanamide or benzamide, react readily with COF_2, at 25–50 °C under autogenous pressure, to give a mixture of products which include acyl fluorides, acyl isocyanates, carbonitriles, *N*-fluoroformyl amides and 1,1-difluoroisocyanates. High yields of any single product were not obtained under the conditions investigated.

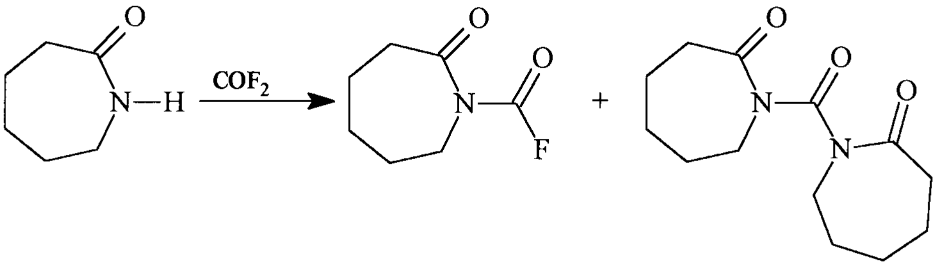
13.14.5.3.2 Secondary amides

Amides having only one nitrogen substituent can react with carbonyl difluoride in three ways: by *N*-acylation, by cleavage, or by displacement of oxygen with fluorine [632]. Reactions involving *N*-acylation and oxygen displacement are illustrated by the examples given in Table 13.24. The three reaction types are all illustrated by the transformations of caprolactam [632]. At 75 °C, using equimolar amounts of COF_2 and caprolactam, the *N*-fluoroformylcaprolactam (**13.9**) is formed (30% conversion), with a slightly smaller amount (25% conversion) of the ureide carbonyl (**13.10**). At 75–125 °C, using a larger quantity of COF_2 in the presence of sodium fluoride, the reaction results both in difluorodeoxygenation to

TABLE 13.24

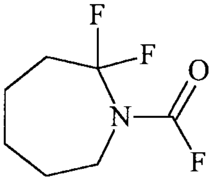
REACTIONS OF CARBONYL DIFLUORIDE WITH *N*-MONOSUBSTITUTED AMIDES [571,632]

Amide	Reaction conditions		Product	Conversion/%
	T / °C	time / h		
HC(O)NHMe	75	2	HC(O)NMeC(O)F	34
			$HCF_2NMeC(O)F$	6
MeC(O)NHMe	125	2	MeC(O)NMeC(O)F	42
			$MeCF_2NMeC(O)F$	20
$(CH_2)_3C(O)NH$	50	2	$[(CH_2)_3C(O)N]_2C{=}O$	15
			$(CH_2)_3C(O)NC(O)F$	47
	125	1	$(CH_2)_3C(O)NC(O)F$	23
			$(CH_2)_3CF_2NC(O)F$	17



(13.9) (13.10)

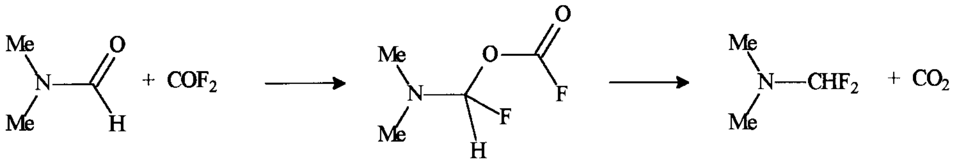
give the *N*-fluoroformyl-2,2-difluoro derivative (**13.11**) with 19% conversion, and in cleavage of (**13.9**) to give the fluoroformylpentyl isocyanate, $OCN(CH_2)_5C(O)F$ with 34% conversion [632].



(13.11)

13.14.5.3.3 Tertiary amides

Carbonyl difluoride reacts with *N*,*N*-dimethylmethanamide (dmf) at room temperature to give a *gem*-difluoride accompanied by the elimination of carbon dioxide [571,632]. Although no fluoroformate intermediate could be isolated from this reaction (see Section 13.14.6), labelling of the dmf with carbon-14 at the carbonyl group showed that this carbon was retained in the difluorotrimethylamine product. The following mechanism was indicated [632]:



A similar reaction occurs between COF_2 and *N*,*N*-dimethylbenzamide to give the analogous difluoro derivative [571,632]. A more complex reaction occurs between COF_2 and *N*,*N*-dimethylethanamide (dma). At room temperature, and in the presence of caesium fluoride, the reaction proceeds as illustrated in Figure 13.10 [632]. The final product, (conversion of 19% based on the amide) is presumably formed as a result of the successive

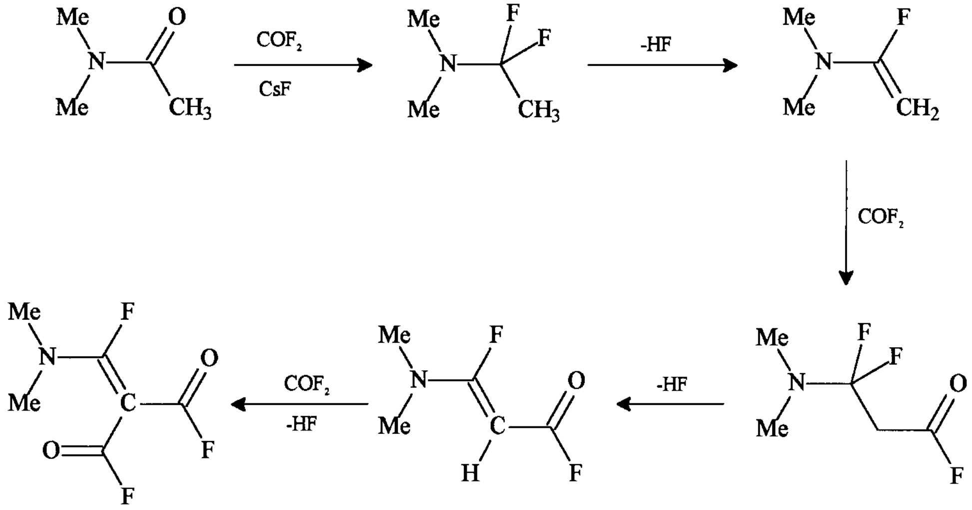
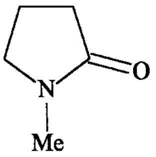


Fig. 13.10 The reaction of COF_2 with *N,N*-dimethylethanamide [632].

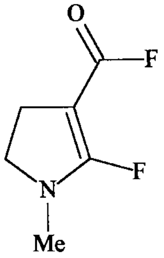
eliminations of HF and additions of COF_2 as illustrated. In combination with HF, reaction of *N,N*-dimethylethanamide with COF_2 resulted in cleavage [632]:

$$Me_2NC(O)CH_3 + COF_2 \longrightarrow Me_2NC(O)F + CH_3C(O)F$$

Treatment of *N*-methyl-2-pyrrolidone (13.12) with COF_2, in the presence of CsF, gave the analogous reaction to that given by dma: however, only a small conversion to the product (13.13) was obtained [632].

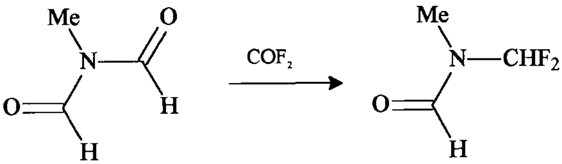


(13.12)



(13.13)

In the presence of pyridine, between 25 and 55 °C, *N*-methyldimethanamide (13.14) reacts with a six-fold excess of COF_2 to give predominantly (13.15). Trace amounts of $MeN(CHF_2)_2$ and $MeNHCHF_2$ were also obtained.



(13.14) (13.15)

13.14.5.4 Imines

COF_2 reacts readily with $Ph_2C{=}NH$ to give $Ph_2C{=}NC(O)F$, which is tautomeric [1770]:

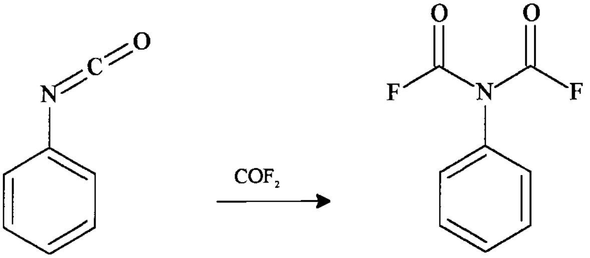
$$Ph_2C{=}NC(O)F \rightleftharpoons Ph_2CF(NCO)$$

and such tautomerism has been put to advantage in the preparation of other isocyanates. Thus, the compounds $CF_3CFR(NCO)$ (R = CF_3 or $CClF_2$) were prepared by treating $CF_3CR{=}NH$ with COF_2 in the presence of KF in CH_3CN, at room temperature [188].

The perfluorinated imine, $CF_3N{=}CF_2$, reacts with COF_2 and caesium fluoride catalyst in CH_3CN at 150 °C to give the corresponding carbamoyl fluoride, $(CF_3)_2NC(O)F$, with a conversion of 56% [632].

13.14.5.5 Isocyanates

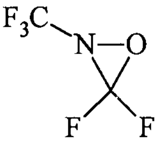
Phenyl isocyanate adds on COF_2 in the presence of CsF, upon heating in a pressure vessel, to give high yields of the bis(fluoroformyl) derivative according to [632]:



The same compound was obtained when phenyl isocyanate dimer was treated with COF_2 under similar conditions.

13.14.5.6 Oxaziridines

In the presence of CsF, carbonyl difluoride combines with the oxaziridine (**13.16**) to form a high yield of $CF_3N(OCF_3)C(O)F$ [1834]. The result indicates that the $[CF_3O]^-$ nucleophile, generated from the reaction of CsF with COF_2, attacks the nitrogen atom, and this is confirmed, in a separate experiment, in which the salt $Cs[OCF_3]$ was employed in the reaction.



(13.16)

13.14.5.7 Nitriles and isonitriles

The simplest nitrile, HCN, reacts with COF_2 and HF at room temperature, *via* the intermediate isocyanate, according to [632]:

$$HC{\equiv}N + COF_2 \longrightarrow [HCF{=}NC(O)F] \longrightarrow [HCF_2N{=}C{=}O] \xrightarrow{HF} HCF_2NHC(O)F$$

$MeCF_2NCO$ was prepared by treating MeCN with COF_2 in anhydrous HF at room temperature [396], but only small yields were obtained unless very long reaction times were employed. Propanenitrile reacts with COF_2 more readily than ethanenitrile, to give the 1,1-difluoroalkyl isocyanate [396a]. The perfluorinated nitrile, $CF_3C{\equiv}N$, reacts with COF_2 only under more forcing conditions (200–300 °C) according to [632]:

$$CF_3C{\equiv}N + COF_2 \longrightarrow CF_3CF_2N{=}C{=}O$$

TABLE 13.25

REACTIONS OF NITRILES WITH COF_2 OVER MERCURY CATALYSTS [1524]

Nitrile	Product	Reaction Conditions	Yield/%
CH_3CN	CH_3CF_2NCO	100 °C, 15 h	29
CH_3CH_2CN	$CH_3CH_2CF_2NCO$	90 °C, 2 h	67
$CH_3CH_2CH_2CN$	$CH_3CH_2CH_2CF_2NCO$	120 °C, 10 h	61
Me_2CHCN	$Me_2CHCFNCO$	120 °C, 10 h	58
PhCN	$PhCF_2NCO$	180 °C, 10 h	-
CCl_3CN	CCl_3CF_2NCO	130 °C, 12 h	88
CF_3CN	CF_3CF_2NCO	140 °C, 10 h	79
$ClCH_2CN$	$ClCH_2CF_2NCO$	120 °C, 13 h	50
$CH_2CF_2CF_2CH(CN)$	$CH_2CF_2CF_2CH(CF_2NCO)$	140 °C, 12 h	59

Only small yields of product are formed and, again, the isocyanate is presumably formed *via* the intermediate, $\mathrm{CF_3CF{=}NC(O)F}$. However, the reaction between RCN and $\mathrm{COF_2}$ can be catalysed over HgO (or $\mathrm{HgF_2}$) catalysts at 50–130 °C to give $\mathrm{RCF_2NCO}$ [1524] in good yields, Table 13.25.

Cyanamide, $\mathrm{H_2NC{\equiv}N}$, with $\mathrm{COF_2}$ gives a mixture of $\mathrm{F_3CN{=}C{=}O}$ and cyanuric acid [396a], whilst the disubstituted nitrile, $\mathrm{N{\equiv}C(CH_2)_4C{\equiv}N}$, with $\mathrm{COF_2}$ gave the expected compound, $\mathrm{O{=}C{=}NCF_2(CH_2)_4CF_2N{=}C{=}O}$, together with $\mathrm{O{=}C{=}NCF_2(CH_2)_4C{\equiv}N}$ [396a]. Carbonyl difluoride adds to aryl nitriles $\mathrm{PhC{\equiv}N}$, $\mathrm{3\text{-}MeC_6H_4C{\equiv}N}$, $\mathrm{4\text{-}MeC_6H_4C{\equiv}N}$, $\mathrm{4\text{-}CF_3C_6H_4C{\equiv}N}$ in the presence of anhydrous HF and alkali metal fluorides to produce the corresponding aryldifluoromethyl isocyanate, $\mathrm{ArCF_2N{=}C{=}O}$ [2032]. Further reaction of the isocyanate can occur with two additional moles of the aryl nitrile, to produce $\mathrm{ArCF_3}$ and 2-hydroxy-4,6-diaryl-1,3,5-triazines. This reaction is considered to proceed *via* the formation of an anionic intermediate, generated from the interaction of the aryl nitrile with $\mathrm{[HF_2]^-}$ (resulting from interaction of the alkali metal fluoride with HF):

$$\begin{tikzcd}
\mathrm{ArCN + [HF_2]^-} \arrow[r] & \mathrm{[ArC(F){=}N]^- + HF} \arrow[r, "\mathrm{COF_2}"] & \mathrm{ArC(F){=}NC(O)F + F^-} \arrow[d, "\mathrm{HF}"] \\
 & \mathrm{ArCF_2NCO + HF} & \mathrm{ArCF_2NHC(O)F} \arrow[l]
\end{tikzcd}$$

The reaction of $\mathrm{4\text{-}NO_2C_6H_4C{\equiv}N}$ with $\mathrm{COF_2}$ resulted in the formation of the carbamoyl fluoride, $\mathrm{4\text{-}NO_2C_6H_4CF{=}N{-}C(O)F}$, rather than the isocyanate [2032].

The radical anion generated from propanenitrile (by abstraction of the two 1-hydrogen atoms of the nitrile with $\mathrm{[O]^{\cdot-}}$) reacts slowly with $\mathrm{COF_2}$ to eliminate HF [469], but provided no definite conclusion regarding the structure of $\mathrm{[C_2H_3CN]^{\cdot-}}$.

$$\mathrm{[C_2H_3CN]^{\cdot-} + COF_2 \longrightarrow C_4H_2FNO + HF}$$

When a mixture of $\mathrm{CF_3N{\equiv}C}$ (55% v/v) and $\mathrm{COF_2}$ (45% v/v) is passed through a platinum tube at 700 °C, isomerization of the isonitrile occurs to give $\mathrm{CF_3C{\equiv}N}$, whilst the $\mathrm{COF_2}$ remains unchanged [111a]. When the above reactants in the same molar ratio were stored at room temperature over 48 h in a Pyrex ampoule, the inner surface of the glass became coated with a film of pale yellow solid polymer, which analysed as $\mathrm{\{C({=}NCF_3){-}C({=}NCF_3)\}}_n$: $\mathrm{COF_2}$ was again recovered unchanged [111a].

13.14.5.8 Ureas

Tetramethyl urea, when heated at 150 °C for 2 h with COF_2 and CsF, gave the *gem*-difluoro derivative in low (10%) yield according to [632]:

$$Me_2NC(O)NMe_2 + COF_2 \longrightarrow Me_2NCF_2NMe_2 + CO_2$$

The tetramethyl thiourea gave a much higher yield of the difluorodiamine upon reaction with COF_2 [632].

13.14.6 Reactions with Oxygen Compounds

13.14.6.1 Alcohols, phenols and their derivatives

Alcohols react with carbonyl difluoride in a similar way to that described for phosgene (see Section 10.3.1). The first stage of the reaction is the formation of the fluoroformate,

$$ROH + COF_2 \longrightarrow ROC(O)F + HF$$

(R = Me or CMe_3 [1118]; Et or Ph [589]; CF_3CH_2 [ICI115]; $MeOC(O)CH_2$ [2219]; cyclohexyl [1118]; $ClCH_2CH_2$, $BrCH_2CH_2$, CCl_3CH_2, $CClF_2CH_2$, $CHF_2CF_2CH_2$, or $H(CF_2)_4CH_2$ [24a], 2-O_2N-C_6H_4, 4-O_2N-C_6H_4, 4-BrC_6H_4, or 2,4-$Br2C_6H_4$ [1856b]) which can react with a further molecule of ROH to form the carbonate, ROC(O)OR. Whilst the preparation of the fluoroformates from COF_2 is an important and efficient synthetic method, the preparation of carbonates *via* COF_2 is of much less interest, since these compounds can be synthesized effectively and cheaply from phosgene. Although high yields of fluoroformates can be obtained by the acylation of alcohols with COF_2, the method is not regarded as economical (on a small industrial scale) owing to the prohibitive cost of commercial COF_2 and its preparative inaccessibility in most laboratories [441].

In the reaction of ethanol with COF_2, the reaction is catalysed by pyridine [589]. Ethane-1,2-diol, however, is reported to react with an excess of COF_2 at −80 °C to give a 79% yield of the bis(fluoroformate) in the presence of sodium fluoride (which acts as a base to absorb the HF by-product) [24a]. No reaction occurs when carbonyl difluoride is passed into a solution of phenol in diethyl ether, and passage of COF_2 into a mixture of phenol, pyridine and benzene results in the production of a quantitative yield of diphenyl carbonate. Phenyl fluoroformate was prepared by heating a mixture of COF_2, PhOH and benzene at 100 °C, however, in an autoclave [589].

A similar catalytic method has been employed for the synthesis of the series of compounds, $XC(NO_2)_2CH_2OC(O)F$ (X = NO_2, F, Me or CH_2OCF_3), prepared from COF_2 and the precursor alcohol, Equation (13.26), at room temperature [1608]. Reaction of

$$XC(NO_2)_2CH_2OH + COF_2 \longrightarrow XC(NO_2)_2CH_2OC(O)F + HF \qquad (13.26)$$

2,2,2-trinitroethanol with COF_2 using pyridine as the base resulted in formation of the corresponding carbonate; by using NaF as the base, fluoroformate was formed with a yield of 77%. More detailed results are recorded in Table 13.26 [1608].

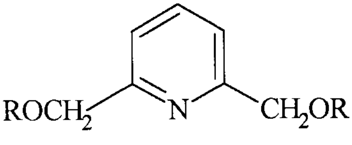
TABLE 13.26

PREPARATION OF $XC(NO_2)_2CH_2OCOF$ [1608]

X	Molar Ratio		Time / h	Yield/%
	COF_2/ROH	NaF/ROH		
NO_2	7.7	1.0	72	77
F	9.0	1.0	64	71
CH_3	13.0	1.0	64	70
CH_2OCOF	9.4	2.0	84	91

Isobutene (2-methylpropene) has also been employed as an acid acceptor [1118] during the reaction of COF_2 (or COF_2/COFCl mixtures) with aliphatic or cycloaliphatic alcohols.

The dicarbamate derivatives (13.17; R = C(O)NHMe or C(O)NHEt) have been prepared by treatment of (13.17; R=H) with COF_2, followed by treatment with RNH_2 [1010], see also Chapter 16.



(13.17)

As with other acyl fluorides, COF_2 combines with the potassium salt of $[(CF_3)_3CO]^-$ to form the corresponding fluoroformate [2142,2240]:

$$COF_2 + [(CF_3)_3CO]K \longrightarrow (CF_3)_3COC(O)F + KF$$

An excess of the carbonyl halide is required in order to obtain an appreciable yield of the mono-substituted derivative. At 22 °C, over 24 h, and using a molar ratio of about 5:1

COF_2:$[(CF_3)_3CO]K$, the yields of fluoroformate and of carbonate, $\{(CF_3)_3CO\}_2O$, were 50% and 22%, respectively [2142]. Similarly, the reaction of $Cs[(CF_3)_2CFO]$ with COF_2 at low temperature gives the expected perfluoro ester, $FC(O)OCF(CF_3)_2$ [501].

In a related system, the reaction of $[C_6F_5O]K$ with an 8:1 excess of COF_2 at 23 °C, but using much shorter reaction times (8 min), results in the formation (29% yield) of the corresponding perfluorinated aromatic fluoroformate, $C_6F_5OC(O)F$. When an excess of COF_2 was not employed, the carbonate, $(C_6F_5O)_2CO$, was formed [610].

At temperatures between about 250 and 300 °C, trifluoromethyl hypofluorite combines with COF_2 according to Equation (13.27), although at higher temperatures, the CF_3OF can

$$CF_3OF + COF_2 \rightleftharpoons CF_3OOCF_3 \qquad (13.27)$$

decompose reversibly into COF_2 and F_2 [1649]. The kinetics of reaction (13.27) have been studied in an aluminium reactor at 223 and 233 °C [444]. The rate of formation of the peroxide, formed as the only product, was found to be proportional to the CF_3OF concentration and independent of the concentration of COF_2, if a sufficient quantity of the carbonyl fluoride was present. The rate of formation of CF_3OOCF_3 could thus be described by the expression:

$$\frac{d[CF_3OOCF_3]}{dt} = k_1[CF_3OF]$$

in which $k_1/s^{-1} = 2.12 \times 10^{-14} \exp[(-21790 \pm 250)/T]$

The formation of the bis(trifluoromethyl peroxide) proceeds according to the following mechanism [444]:

$$CF_3OF \longrightarrow [CF_3O]\cdot + F\cdot$$

$$COF_2 + F\cdot \longrightarrow [CF_3O]\cdot$$

$$2[CF_3O]\cdot \longrightarrow CF_3OOCF_3$$

The sulfonyl fluoride derivative, $(CF_3)_3COOSO_2F$, combines with an excess of carbonyl difluoride, over activated KF at room temperature over 23 h, to give an average yield of 30% of the peroxyfluoroformate $(CF_3)_3COOC(O)F$. The reaction is proposed to proceed *via* the reaction of COF_2 with the peroxyanion, $[(CF_3)_3COO]^-$, as illustrated in the following scheme [2240]:

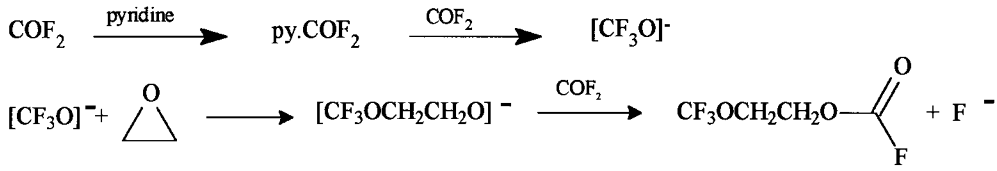
$$(CF_3)_3COOSO_2F + KF \longrightarrow K[(CF_3)_3COO] + SO_2F_2$$

$$K[(CF_3)_3COO] + COF_2 \longrightarrow (CF_3)_3COOC(O)F + KF$$

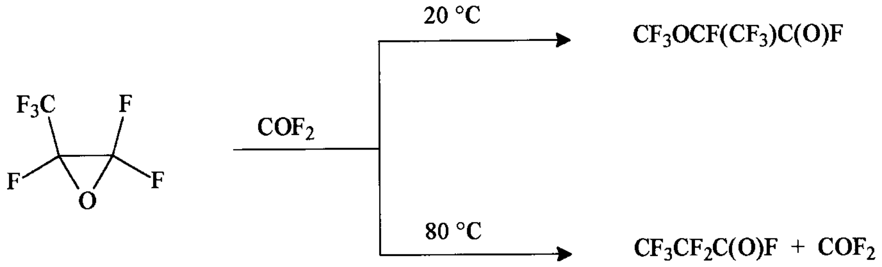
At longer reaction times (50 h), using the same molar ratio of 5:1 COF_2:$(CF_3)_3COOSO_2F$, $(CF_3)_3COOC(O)OCF_3$ is formed as a result of the combination of $K[OCF_3]$ (from KF and COF_2) with the peroxyfluoroformate [2240].

13.14.6.2 Cyclic ethers

Cyclic ethers would be expected to undergo ring-opening reactions with carbonyl difluoride as with phosgene. Epoxyethane reacts with two moles of COF_2, in the presence of pyridine, according to the following equations [24a]:



Perfluorinated 1,2-epoxypropane reacts with COF_2, in the presence of cyanide or thiocyanate ions, to give two different products depending upon the temperature conditions [2116]:



However, in the presence of COF_2 and caesium fluoride in a polar solvent at 50 °C over 6 h, this fluoroepoxy compound is polymerized to give $CF_3\{OCF(CF_3)CF_2\}_nOCF(CF_3)C(O)F$, in which n = 1–6 [1429].

13.14.6.3 Carbonyl compounds

The reaction of carbonyl difluoride with carbonyl compounds follows the general pattern of addition of the F and C(O)F units across the unsaturated C=O entity. However, the resulting fluoroformate can be frequently readily decarboxylated to the corresponding *gem*-difluoro compound. The reactions of COF_2 with simple carbonyl compounds can thus be regarded as potential new routes to the many industrially-important fluorocarbons or halofluorocarbons [ICI1] from many readily available starting materials.

13.14.6.3.1 Aldehydes

When a 1:3 mixture of α-polyoxymethylene and COF_2 is heated sequentially at 100 °C for 2 h, 200 °C for 2 h, and 250 °C for 10 h, a liquid reaction product is obtained; distillation of this from NaF yields a colourless liquid which consists of CH_2FOCH_2F and $CH_2FOC(O)F$ [571].

In a recent study [1762,ICI85], it was shown that gaseous methanal combines with carbonyl difluoride, over a charcoal catalyst impregnated with caesium fluoride, to form the commercially important low-temperature refrigerant difluoromethane, HFC-32, according to:

$$CH_2O + COF_2 \longrightarrow CH_2F_2 + CO_2$$

At about 275 °C, and with a superficial contact time of sixteen seconds, a yield of 86% of CH_2F_2 was obtained based upon a conversion of COF_2 of 61% [1762,ICI85]. This reaction is similar to the charcoal-catalysed reaction of methanal with phosgene (see Section 10.3.3.1), although the reaction is not so rapid and requires the presence of fluoride ions on the catalyst. By analogy, it is suggested [ICI85] that the reaction proceeds via the formation and subsequent decarboxylation of the fluoromethyl fluoroformate into CH_2F_2 and CO_2:

$$CH_2O + COF_2 \longrightarrow CH_2FOC(O)F \longrightarrow CH_2F_2 + CO_2$$

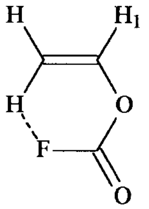
At higher temperatures (>400 °C), carbon monoxide and hydrogen fluoride are formed predominantly, with only small proportions of CH_2F_2, consistent with the direct reaction:

$$COF_2 + CH_2O \longrightarrow 2CO + 2HF$$

In contrast to the methanal reactions, vaporized ethanal combines with COF_2 over CsF/charcoal, in the temperature range of about 100–160 °C, to form a mixture of 1-fluoroethyl fluoroformate and vinyl fluoroformate [ICI116]:

$$COF_2 + CH_3CHO \longrightarrow CH_3CHFOC(O)F \longrightarrow CH_2{=}CHOC(O)F + HF$$

It is curious that the three fluoroformates – $CH_2FOC(O)F$, $CH_3CHFOC(O)F$ and $CF_3CH_2OC(O)F$ – behave so differently. $CH_2FOC(O)F$, presumed to be formed *in situ* from methanal and COF_2, must undergo rapid decarboxylation at temperatures >200 °C in order to escape detection [ICI85]. On the other hand, $CF_3CH_2OC(O)F$, prepared from trifluoroethanol and COF_2, is stable to decarboxylation except at much higher temperatures [ICI115], and $CH_3CHFOC(O)F$ is unstable at relatively low temperatures with respect to dehydrofluorination [ICI116]. The relative thermal stability of $CH_3CHFOC(O)F$ towards decarboxylation, but its instability towards dehydrofluorination, may possibly be accounted for by the structure of the vinyl fluoroformate product. The ^{19}F n.m.r. spectrum of the material indicates that no coupling interaction exists between the H_1 atom and the F atom, and that the most likely conformation is as shown below:



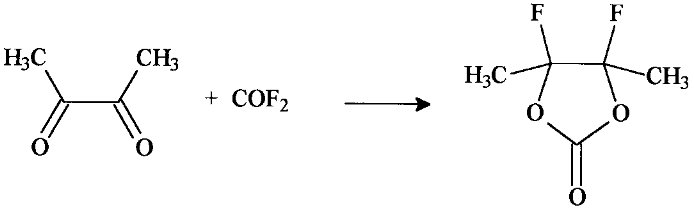
Benzaldehyde is converted by COF_2 at 250 °C in a pressure vessel into the *gem*-difluoride with a conversion of 58% [632]:

$$C_6H_5CHO + COF_2 \longrightarrow C_6H_5CHF_2 + CO_2$$

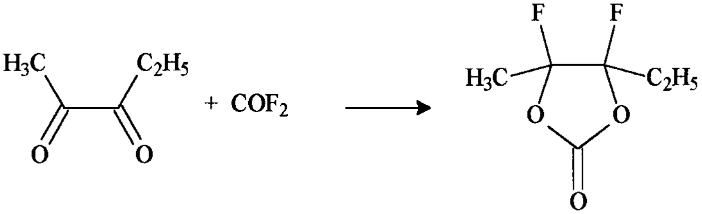
In the presence of pyridine, comparable conversions were obtained at the lower temperature of 150 °C, whilst with dmf as catalyst, the aldehyde conversion was 80% [632]. The compound 4-Me_2N-$C_6H_4CHF_2$ was similarly prepared from 4-Me_2N-C_6H_4CHO and COF_2 [571] and a small yield of 4-MeO-$C_6H_4CHF_2$ was obtained from treatment of 4-MeO-C_6H_4CHO with COF_2 at 50-75 °C over 8 h [571].

13.14.6.3.2 Ketones

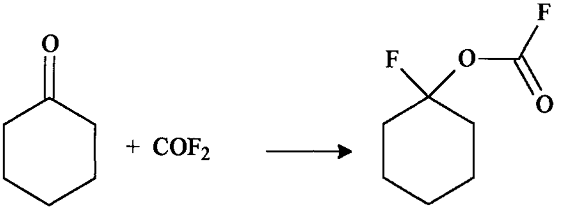
Treatment of diacetyl (butanedione) with an excess of COF_2 in the presence of pyridine at the maximum temperature of 100 °C for 10 h resulted in the formation of the fluorinated carbonate (50% conversion) [632]:



When similarly treated, 2,3-pentanedione gave a mixture of the *cis*- and *trans*- isomers of 1,2-difluoro-1-ethyl-2-methyl ethylene carbonate [632]:

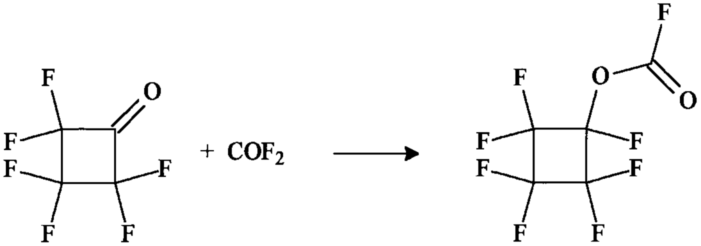


Cyclohexanone and carbonyl difluoride, when combined in a pressure vessel at 50 °C for 12 h in the presence of a catalytic amount of dmf or pyridine, gave the fluoroformate adduct in a conversion corresponding to 64% [571,632]:

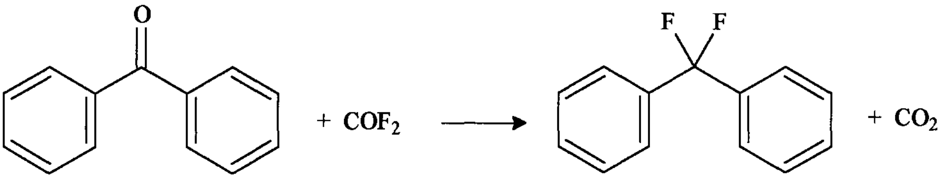


Elimination of carbon dioxide occurs at 45–70 °C upon treatment of the fluoroformate with BF_3–etherate to give 1,1-difluorocyclohexane [571,632].

Similarly, treatment of hexafluorocyclobutane with COF_2 and CsF gave heptafluorocyclobutyl fluoroformate [632]:



Benzophenone, when heated at 250 °C for 10 h with COF_2 and CsF, gave difluorodiphenylmethane with a conversion of 40%, according to [632]:



By using pyridine in place of the CsF catalyst, the conversion was increased to 62% [632]. Without the use of a catalyst, the conversion for this reaction was only 3% [571,632].

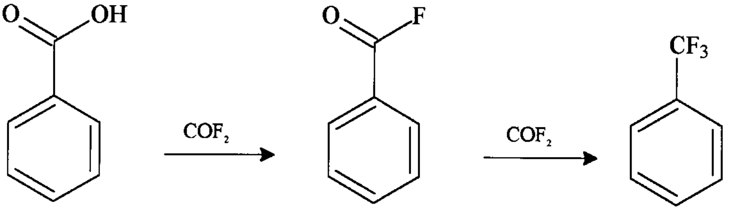
13.14.6.3.3 Carboxylic acids

Carbonyl difluoride reacts with carboxylic acids to give the corresponding acid fluoride. Reaction of trifluoroethanoic acid with COF_2 at 150 °C over 6 h results in the formation (56% yield) of trifluoroethanoyl fluoride, $CF_3C(O)F$ [571,632]. In a similar manner, perfluorobutanoic acid reacts with COF_2 to give perfluorobutanoyl fluoride (78% yield) [571,632] and $CHF_2CF_2CF_2CF_2C(O)OH$ with COF_2 gave $CHF_2CF_2CF_2CF_2C(O)F$ with a conversion of 67% [1908]. $CF_3(CF_2)_6C(O)OH$ gave $CF_3(CF_2)_6C(O)F$ [571]. At 175 °C, over 11–12 h and under autogenous pressure, the perfluorinated dicarboxylic acids, tetrafluorobutane-1,4-dioic acid or hexafluoropentane-1,5-dioic acid, react with COF_2 to form the diacid fluoride according to:

$$HO(O)C(CF_2)_nC(O)OH + 2COF_2 \longrightarrow F(O)C(CF_2)_nC(O)F + 2CO_2 + 2HF$$
$(n = 2 \text{ or } 3)$

Alkali metal salts of carboxylic acids can also be used in the preparation of acid fluorides [844]. Reaction with COF_2 at 110–180 °C, with continuous removal of the volatile products, results in increased yields to 91–98%. Typically, $[CF_3CF_2CF_2C(O)O]Na$ was converted into the corresponding acid fluoride (91% yield) and CO_2 at 180 °C, over 1 h using a 20% molar excess of COF_2 [844].

A mixture of benzoic acid, HF, and COF_2, when heated in a pressure vessel at 350 °C for 10 h, gave predominantly benzoyl fluoride with small yields 1,1,1-trifluorotoluene, consistent with the following transformations [571,632]:



A higher (62%) yield of benzoyl fluoride was obtained from the reaction of benzoic acid and COF_2 in the presence of sodium fluoride, by heating the charged vessel at 175 °C for 10 h. The presence of the highly electronegative fluorine atom in benzoyl fluoride clearly deactivates the carbonyl group for further reaction with carbonyl difluoride.

13.14.6.3.4 Carboxylic acid anhydrides

Phthalic anhydride reacts with an excess of COF_2, in the presence of pyridine at between 100 and 350 °C over 8 h, to yield a mixture of $2\text{-}CF_3\text{-}C_6H_4C(O)F$ and $C_6H_4\text{-}1,2\text{-}(COF)_2$ [571].

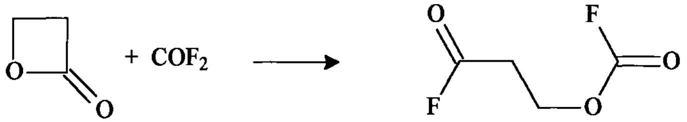
13.14.6.3.5 Esters and salts

Methyl benzoate reacts with COF_2 in the presence of dmf at 200–300 °C, over 10 h, to produce benzoyl fluoride [632]. Further reaction of the acid fluoride with COF_2 in the presence of BF_3 at 350 °C over 10 h gave the benzotrifluoride $C_6H_5CF_3$ [571].

Methyltriethylammonium (or tetramethylammonium) 3-cyanotetrafluoropropanoate, $[NEt_3Me][N{\equiv}CCF_2CF_2CO_2]$, reacts with COF_2 to give the corresponding salt of $[N{\equiv}CCF_2CF_2CF_2O]^-$ [1166a]. Similarly, the azido salt, $[NEt_3Me][N_3CF_2CF_2CO_2]$, gave the azido alkene, $N_3CF_2CF_2CF_2OCF_2CF{=}CF_2$ upon treatment with COF_2, followed by the fluorosulfate, $CF_2{=}CFCF_2OSO_2F$ [1166a].

13.14.6.3.6 Lactones

As with phosgene, the lactone 3-propanolide is ring-opened upon treatment with COF_2 (100 °C over 8 h in the presence of pyridine) to give the fluoroformate derivative (as opposed to the decarboxylated product), according to [632]:



13.14.7 *Reactions with organosilicon compounds*

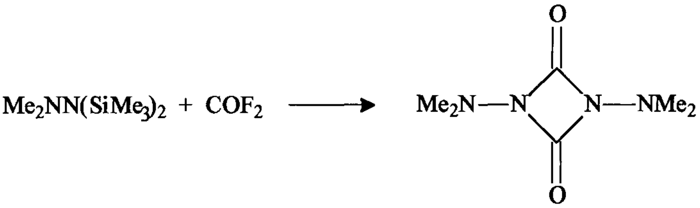
13.14.7.1 Trifluoromethylsilyl compounds

COF_2 will react with three equivalents of Me_3SiCF_3 in MeCN, in the presence of KF; upon work up, followed by acidification with concentrated sulfuric acid, $(CF_3)_3COH$ is isolated in *ca.* 75% yield [1159aa]. The reaction is believed to proceed by the mechanism illustrated in Fig. 13.11, involving a five-coordinate silicon intermediate, $[Me_3SiF(CF_3)]^-$.

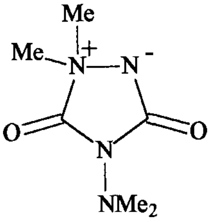
13.14.7.2 *N*-Silyl-substituted compounds

13.14.7.2.1 Silylamines

Protection of Me_2NNH_2 with a silyl group before exposing to COF_2 (or $COCl_2$, see Section 10.4.2.1) results in the formation of the dimethylaminoisocyanate dimer, according to [772a]:



This compound, or the related (**13.18**), is similarly formed from the reaction of $Me_2NN(SiMe_3)_2$ with COF_2 [772a,1409], but the yield is less than that obtained with phosgene.



(**13.18**)

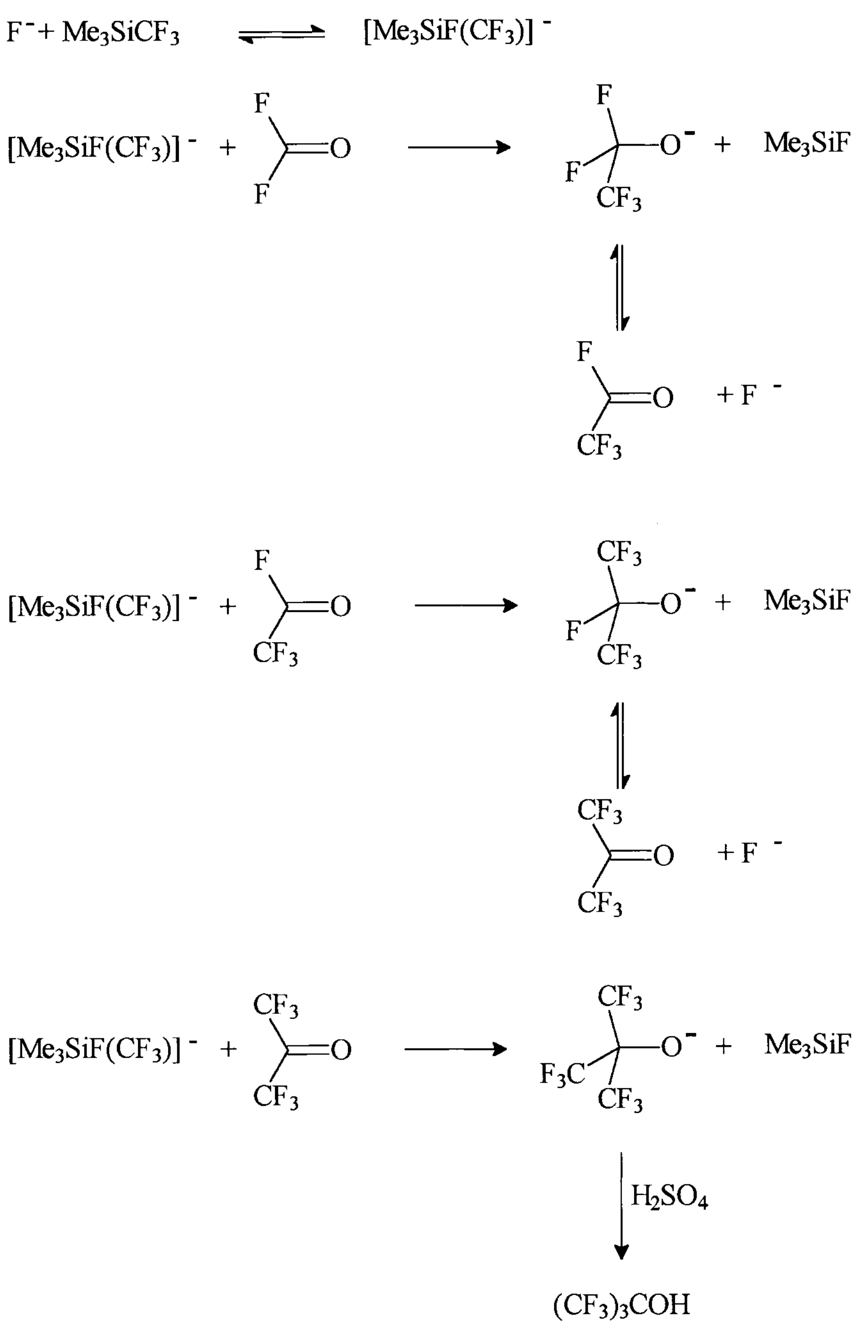


Fig. 13.11 Reaction scheme for the synthesis of $(CF_3)_3COH$ [1159aa].

13.14.7.2.2 Isocyanatosilanes

The interaction of $Si(NCO)_4$ or $Me_3Si(NCO)$ with COF_2 occurs in an autoclave at 200–285 °C; the NCO group is substituted and fluorocarbonyl isocyanates are formed according to [771a]:

$$Si(NCO)_4 + 4COF_2 \longrightarrow 4FC(O)(NCO) + SiF_4$$

$$Me_3Si(NCO) + COF_2 \longrightarrow FC(O)(NCO) + Me_3SiF$$

13.14.7.3 *O*-Silyl-substituted compounds

13.14.7.3.1 Silanols

Carbonyl difluoride reacts with silanols and silanediols between 0–20 °C, in the absence of an HF acceptor, to replace the hydroxyl groups for fluorine [1452]. For example, with R_3SiOH (R = Me or Ph):

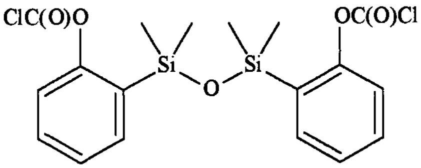
$$2R_3SiOH + COF_2 \longrightarrow 2R_3SiF + CO_2 + H_2O$$

and with $Ph_2Si(OH)_2$:

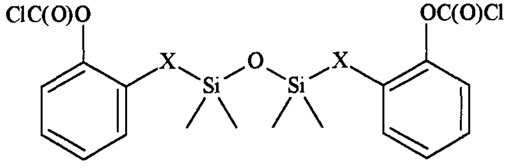
$$2Ph_2Si(OH)_2 + COF_2 \longrightarrow 2Ph_2SiF_2 + CO_2 + H_2O$$

13.14.7.3.2 Siloxanes and silyl ethers

The siloxane linkage in hexamethyldisiloxane, $Me_3SiOSiMe_3$, or trimethylphenoxysilane, Me_3SiOPh, is not cleaved under normal pressure conditions between 0 and 20 °C [1452]. Similarly, the disiloxane fragments in (13.19) and (13.20) are resistant to attack by COF_2.



(13.19)



(13.20; X = $(CH_2)_3$ or OCH_2)

Alkoxysilanes, however, react with COF_2 (at 0–20%) in a similar way to that described for $COCl_2$ to give silyl fluoride and alkyl fluoroformate derivatives [1452] in high yields:

$$Me_3SiOMe + COF_2 \longrightarrow Me_3SiF + MeOC(O)F$$

$$Me_2Si(OEt)_2 + 2COF_2 \longrightarrow Me_2SiF_2 + 2EtOC(O)F$$

$$Me_3SiO(CH_2)_nMe + COF_2 \longrightarrow Me_3SiF + Me(CH_2)_nOC(O)F$$
(n = 2 or 3)

$$Me_3SiOCH_2CF_2CF_2H + COF_2 \longrightarrow Me_3SiF + HCF_2CF_2CH_2OC(O)F$$

Where a deficiency of COF_2 is employed in these reactions, the yield of fluoroformate tends to fall owing to the formation of carbonates.

13.14.7.4 *F*–Silyl-substituted compounds

COF_2 reacts with $[(Me_2N)_3S]^+[Me_3SiF_2]^-$ in MeCN at 0 °C to form $[(Me_2N)_3S]^+[F_3CO]^-$ with a yield of 97%. This compound reacts with $PhCH_2Br$ to give a good yield of $PhCH_2OCF_3$ [624b].

13.14.8 Reactions with organophosphorus and organoarsenic compounds

Oxidative addition occurs between COF_2 and organophosphine compounds at room temperature over 12 h, to give the difluoro derivatives shown in Equations (13.28) and (13.29) [850,2193a].

$$R_3P + COF_2 \longrightarrow R_3PF_2 + CO \qquad (13.28)$$

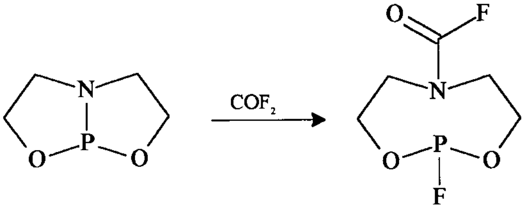
$$(R = Me,\ Me(CH_2)_3,\ Me_3C \text{ or } Ph)$$

$$Ph_2PCH_2CH_2PPh_2 + 2COF_2 \longrightarrow Ph_2PF_2CH_2CH_2PF_2Ph_2 + 2CO \qquad (13.29)$$

No oxidative addition was found to occur at arsenic, as exemplified in Equation (13.30):

$$Ph_2PCH_2CH_2AsPh_2 + COF_2 \longrightarrow Ph_2PF_2CH_2CH_2AsPh_2 + CO \qquad (13.30)$$

In contrast, the bicyclo compound **(13.21)** reacts with COF_2 at 25 °C to add the F and C(O)F fragments to the phosphorus and nitrogen, respectively [850,2193a].



(13.21)

Under similar conditions, organophosphites can also undergo oxidative addition {see Equation (13.31)} [850,2193a].

$$(RO)_3P + COF_2 \longrightarrow (RO)_3PF_2 + CO \qquad (13.31)$$

$$(R = EtO \text{ or } Me(CH_2)_3O)$$

Abstraction of hydrogen and replacement by fluorine occurs when dialkylphosphonates combine with COF_2 at room temperature, in the presence of triethylamine [850,2193a]:

$$(RO)_2P(O)H + COF_2 + NEt_3 \longrightarrow (RO)_2P(O)F + [NEt_3H]F + CO$$
$$\{R = Et \text{ or } Me(CH_2)_3\}$$

13.14.9 Organosulfur Compounds

Carbonyl difluoride was found to cleave C=S linkages between 50–85 °C, over 1 h, to replace thiono sulfur by fluorine [632]. Thus, *N,N*-dimethyl thiocarbamoyl fluoride reacts with COF_2 according to the following stoicheiometry:

$$Me_2NC(S)F + COF_2 \longrightarrow Me_2NCF_3 + COS \qquad (13.32)$$

This reaction contrasts markedly to the difficult conversion of the $-C(O)F$ group to $-CF_3$ using COF_2; the reaction of benzoyl fluoride or benzoic acid to give 1,1,1-trifluorotoluene (Section 13.14.6.3.3), for example, requiring particularly forcing conditions.

In a similar fashion, tetramethylthiuram disulfide gave both the *N,N*-dimethylcarbamoyl fluoride and 1,1,1-trifluorodimethylamine; but in view of Equation (13.32), this last reaction should be capable of forming two molar equivalents of the trifluorodimethylamine under suitable conditions [632].

$$Me_2NC(S)SSC(S)NMe_2 \xrightarrow{COF_2} Me_2NC(S)F + Me_2NCF_3$$

Carbonyl difluoride reacts with two molar equivalents of dimethylsulfoxide, in a sealed tube at room temperature, according to the following reaction [1204b]:

$$CH_3S(O)CH_3 + COF_2 \longrightarrow CH_3SCH_2F + HF + CO_2$$

The sulfide is formed with a yield of 70%, the reaction mechanism is presumably analogous to that described for the reaction of phosgene with dmso (Section 10.6.5.1). When an excess of COF_2 is used, $CH_2FOC(O)F$ is formed in a yield of 38% [1204b].

In the presence of potassium fluoride at −25 °C, trifluoromethyldisulfane, CF_3SSH, reacts with COF_2 to produce $CF_3SSC(O)F$ and $CF_3SSC(O)SSCF_3$ in yields of 55% and 5%, respectively [311].

$$CF_3SSH + COF_2 + MF \longrightarrow CF_3SSC(O)F + M[HF_2]$$

Further reaction can then occur at the C(O)F group. The metal fluoride enhances the formation of the strong nucleophile, $[CF_3SS]^-$, which attacks at the carbonyl group of the COF_2, the carbon atom of which is particularly susceptible to nucleophilic attack owing to the relatively large positive charge (resulting from the electronegative fluorine atoms).

14 CARBONYL DIBROMIDE

The most remarkable feature of the chemistry of carbonyl dibromide is how little of it has been studied. Indeed, in a compendium of the uses and applications of chemicals published (perhaps significantly) in 1944, the only use of $COBr_2$ to be listed (apart from the preparation of crystal violet, Section 14.7) was "as a poison gas (similar in effects to phosgene)" [826]. The only previous review to have been published [783] was in German.

Carbonyl dibromide is the least studied (and the least stable with respect to dissociation) of the three isolated symmetrical carbonyl dihalides. However, as it is the only one which is liquid at room temperature, it is the most easily handled: it may be detected using a phosgene Dräger tube [1223a]. Examination of the last two Sections of this chapter reveals that $COBr_2$ has great promise as a general laboratory reagent, both in inorganic and organic chemistry, and it is hoped that this Chapter will stimulate interest in its wider use.

14.1 BIOLOGICAL ACTIVITY

The physiological effects were judged (as a result of some rather amateur experiments on white mice) similar to those of phosgene [1822], but clearly a modern detailed evaluation is required if $COBr_2$ is to be used more widely. Liver microsomes from phenobarbital pre-treated rats catalysed the conversion of tribromomethane into $COBr_2$ [1636], a process believed to be at least partially responsible for the hepatotoxicity of $CHBr_3$. The observation of a marked deuterium isotope effect ($CDBr_3$ is less hepatotoxic than $CHBr_3$ and is less efficiently converted, by a factor of 1.6, to $COBr_2$ [1636]) lends some support to this theory (*cf*. Section 2.5.4). More recently, the metabolization of $CHBr_3$ to CO by hepatic microsomal function oxidases has been shown to be stimulated by sulfhydryl compounds, particularly glutathione, and the intermediacy of $COBr_2$ demonstrated (by ^{13}C-labelled studies of its reaction with cysteine to form 2-oxothiazolidine-4-carboxylic acid, analogous to the reaction with phosgene, Section 2.5.4) [1951].

14.2 ENVIRONMENTAL HAZARDS

The environmental problems associated with $COBr_2$ are minimal when compared with phosgene, but there is a report that it may be a by-product from tribromomethane oxidation in waste water treatment [1702], and it has been identified as a minor impurity in commercial bromine produced by the electrolysis of brine [865], and a possible minor impurity in silicon(IV) bromide [1679]. It is also formed when bromomethane or bromoethane (which have been both used as refrigerants) are passed through an oil or wood flame, or come in contact with a hot iron surface [1529].

14.3 FORMATION

The first claim to have prepared $COBr_2$ was that of Schiel, in 1863, by the exposure of a mixture of CO and bromine vapour to sunlight (see also Section 14.4) [1795a]. Emmerling, in 1880, attempted to oxidize $CHBr_3$ with a mixture of potassium dichromate(VI) and concentrated sulfuric acid, and obtained a highly impure product (b.pt. 12–30 °C) [589a]. Later studies of the same reaction [2126] obtained trace amounts of a colourless liquid (b.pt. 60–68 °C), identified as $COBr_2$ by its reaction with *N,N*-dimethylaniline (see Section 10.2.1.4).

Early attempts by Besson to prepare $COBr_2$ by the reaction between CO and Br_2, by oxidation of $CHBr_3$ or CCl_2Br_2 with ozone, and by treating phosgene with aluminium(III) bromide were unsuccessful [184], but $COBr_2$ was claimed to be formed in the reaction between $COCl_2$ and BBr_3 at 100–150 °C (see also Section 9.1.2.3) [184] and between phosgene and hydrogen bromide (but in extremely small yield) [184a]. The product was described as a pale yellow liquid (b.pt. 63–66 °C) with a density of 2.48 g cm^{-3} at 0 °C, which reacted slowly with cold water, more rapidly with mercury, and had an irritating and suffocating vapour [184]. These findings were soon contested by Brochet [277d] and von Bartal [2126], who found problems with the procedure as originally described. However, there can be no doubt that Besson had produced the first reasonably pure sample of $COBr_2$, albeit contaminated and in low yield. More recently, the formation of $COBr_2$ has been noted in the reaction between CO and Br_2 in sealed tubes ($\geqslant$600 °C), in the presence of flint glass [2121a].

The detailed study of von Bartal [2126] demonstrated that bromination of COS (by dibromine, $SbBr_3$ or CBr_4) failed to produce $COBr_2$, but that it was formed in small quantities by the reaction of carbon monoxide and dibromine either in the presence of aluminium(III) bromide or under the action of a dark electric discharge. However, $COBr_2$ can be prepared in 50–60% yield by the oxidation of CBr_4 with concentrated sulfuric acid at 150–170 °C [2126], although oleum is too vigorous a reagent, oxidizing the CBr_4 through to CO_2 and Br_2 [2126]:

$$CBr_4 + H_2SO_4 \longrightarrow COBr_2 + 2HBr + SO_3$$

$$2HBr + SO_3 \longrightarrow SO_2 + H_2O + Br_2$$

By the nature of the synthetic routes to $COBr_2$, it is always produced contaminated with bromine. Von Bartal [2126] has proposed a two-step purification technique. Crude $COBr_2$ is initially shaken with mercury at 0 °C, and then distilled, collecting the 62–65 °C fraction. This distillate is then treated with powdered antimony, and redistilled to yield colourless $COBr_2$. If the first stage of the reaction with mercury is omitted, the reaction with antimony is too vigorous, and some $COBr_2$ is lost through decomposition. Slight modifications of this procedure were later published by Schumacher and Lenher [1822], and this has become the most commonly used procedure [1575]. A convenient laboratory procedure is given in Appendix A5.

A process for the commercial co-production of BrCN and $COBr_2$ has been patented: when tribromomethane and NO_2 are heated at 250–350 °C in the presence of activated charcoal, BrCN is the predominant product; higher temperatures favour the formation of $COBr_2$ [2161].

Labelled $COBr_2$, $^{13}COBr_2$ and $C^{18}OBr_2$, has been prepared by treating the appropriately labelled CO with difluorine to give labelled COF_2. This was then treated with BBr_3 to give labelled $COBr_2$ [911].

Although not a convenient synthesis, it is worth noting that $COBr_2$ is formed in the photochemical reaction between CBr_4 and O_2 [1136a]:

$$2CBr_4 + O_2 \longrightarrow 2COBr_2 + 2Br_2$$

It has also been noted that $COBr_2$ can only be made in very low yields by heating ethane-1,2-dioyl dibromide *in vacuo* in a sealed tube at 150 °C, since $COBr_2$ is less thermally stable than the starting material [1937a]:

$$(COBr)_2 \longrightarrow COBr_2 + CO$$

Finally, there is a report that heating tribromonitromethane with concentrated sulfuric acid produces carbonyl dibromide [1380a]:

$$CBr_3NO_2 \longrightarrow COBr_2 + NOBr$$

$COBr_2$ cannot be prepared by treating the bromides of the platinum group metals with carbon monoxide [1313], or by treating paraformaldehyde with bromine [2037a].

14.4 THERMODYNAMIC AND PHYSICAL PROPERTIES

Carbonyl dibromide is a dense, colourless, mobile liquid, fuming in moist air due to hydrolysis, with an odour similar to that of phosgene [2126]. Its relative molecular mass is 187.8184. It is much less stable to dissociation than phosgene: even distillation at atmospheric pressure results in a slight yellow colouration due to liberated bromine.

$COBr_2$ has a boiling point of 64–65 °C [2126] or 64.5 °C [65], and a specific gravity of 2.45 [2126] or 2.52 [1822] at 15 °C. It is reported to melt below -80 °C [1937a].

Carbonyl dibromide is much less stable than phosgene, being almost completely decomposed at 'weak red heat' [2126]:

$$COBr_2 \longrightarrow CO + Br_2$$

Although thermodynamically unstable with respect to dissociation, pure $COBr_2$ is apparently kinetically stable up to 200 °C, but impurities (especially organic molecules) can rapidly catalyse its decomposition [1822]. It is also unstable with respect to photodecomposition [232,2126], the onset of absorption being at 31250 cm^{-1} (320 nm) [1821], and must be stored in the dark [569]. In the absorption region, $COBr_2$ is dissociated by light into CO and Br_2 with a quantum efficiency of unity [1821]. The reaction is zero order, and the simple mechanism proposed was [1821]:

$$COBr_2 + h\nu \longrightarrow [COBr]\cdot + Br\cdot$$

$$[COBr]\cdot \longrightarrow CO + Br\cdot$$

The vapour pressure of $COBr_2$ has been measured between −50 and +25 °C (see Fig. 14.1), and these studies yielded a value of ΔH_{vap} of 30.1 kJ mol^{-1}, and of the Trouton

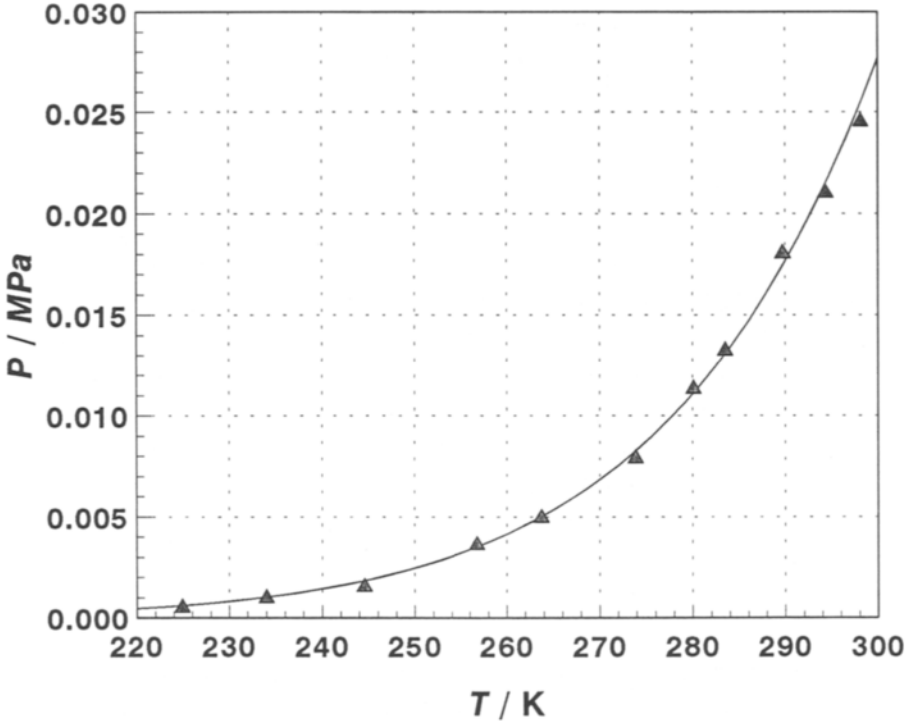


Fig. 14.1 The dependence of the vapour pressure of $COBr_2$ upon temperature [1822].

constant (the molar entropy of vaporization) of 90 J K^{-1} mol^{-1} [1822]. The molar enthalpy of hydrolysis of $COBr_2$ was measured to be −205.3±0.7 kJ mol^{-1}, yielding a value for the standard molar enthalpy of formation of liquid $COBr_2$ of −145.2±0.9 kJ mol^{-1} [65].

The statistical thermodynamic functions for $COBr_2$ have been calculated from spectroscopic data, and the standard values are those of Overend and Evans (Table 14.1; Fig. 14.2) [1575]. More recent values have been calculated [1587], but these differ from the standard values by less than 0.2%, and have not therefore been detailed here.

TABLE 14.1

ESTIMATED THERMODYNAMIC FUNCTIONS (IN J mol^{-1} K^{-1}) FOR $COBr_2$ [1575]

T/K	C_p°	S°	$(H^\circ-H_0^\circ)/T$	$(G^\circ-H_0^\circ)/T$
298.15	61.84	308.86	46.86	262.00
400	66.90	327.77	51.38	276.40
500	70.25	343.09	54.85	288.24
600	72.68	356.14	57.61	298.53
700	74.52	367.48	59.91	307.57
800	75.98	377.52	61.84	315.72
900	77.11	387.02	63.47	323.55
1000	78.03	394.72	64.89	329.87

Use of the standard statistical thermodynamic functions for $COBr_2$ (Table 14.1) [1575] enabled the following data for gaseous $COBr_2$ to be calculated: $\Delta H^\circ_{f,298}$ = −114 kJ mol^{-1}, $\Delta G^\circ_{f,298}$ = −129 kJ mol^{-1}, and $\Delta S^\circ_{f,298}$ = 48.4 J K^{-1} mol^{-1} [65]. Slightly less exothermic (and probably less accurate) values of $\Delta H^\circ_{f,298}$ of −102 kJ mol^{-1} [537] and −96 kJ mol^{-1} [2137a] have been calculated [537], S°_{298} for gaseous $COBr_2$ has been variously estimated as 306 J mol^{-1} K^{-1} [1078d] and 322 J mol^{-1} K^{-1} [537], and $C^\circ_{p,298}$ was evaluated as 64 J mol^{-1} K^{-1} [537] {*cf.* Table 14.1}.

There have been a number of studies of the following reaction:

$$CO(g) + Br_2(g) \rightleftharpoons COBr_2(g)$$

The results of the most recent study [569] clearly indicate that the earlier reports [1626a,1693, 1821,2048a] should be disregarded, as the system had failed to come to equilibrium. The reaction between CO and Br_2 is slow to come to equilibrium in the dark at room temperature

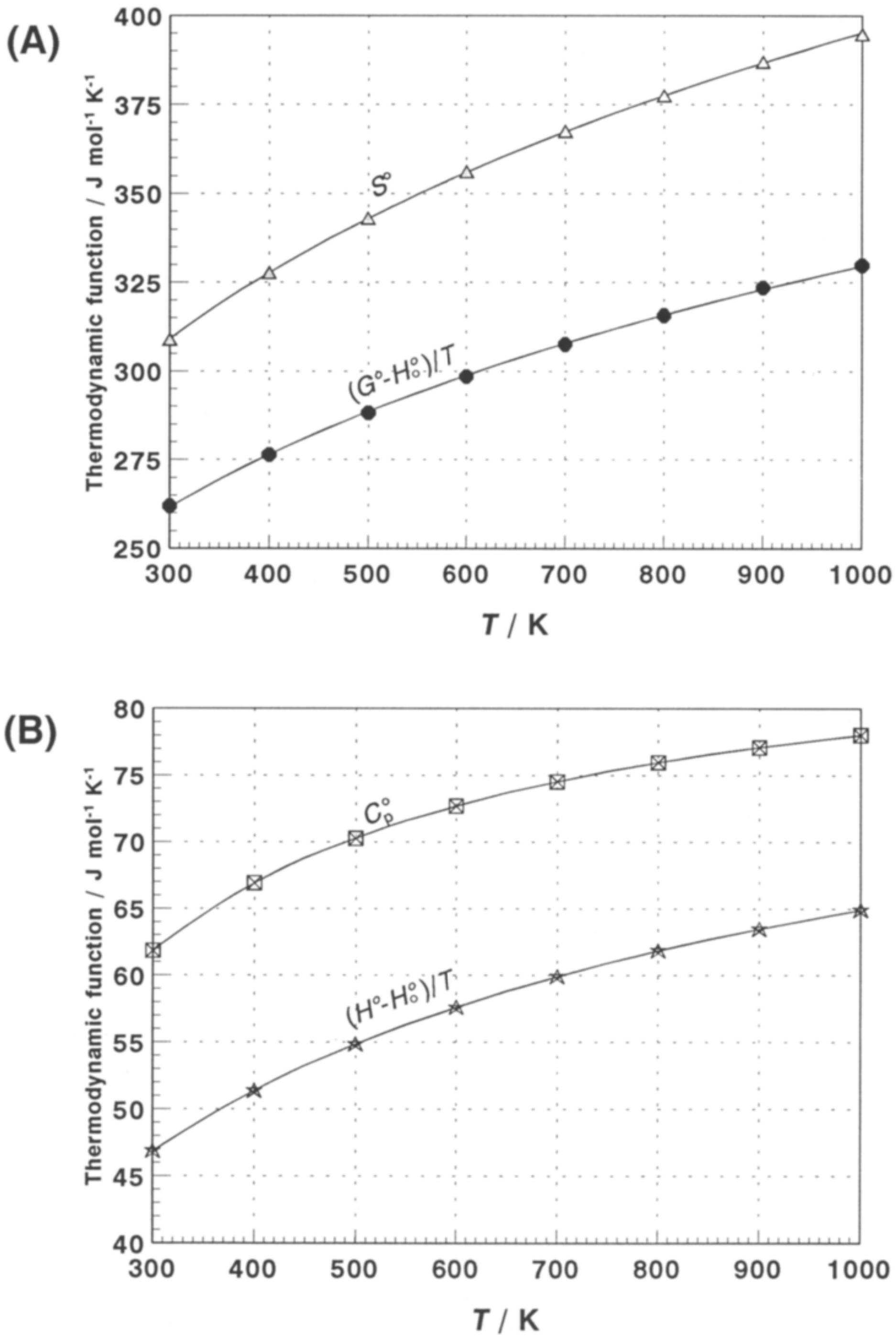


Fig. 14.2 The temperature dependence of the estimated thermodynamic functions for $COBr_2$: (A) S° and $(G^\circ-H^\circ_0)/T$, and (B) C°_p and $(H^\circ-H^\circ_0)/T$ [1575,1587].

[1227]. Although it has been reported that the approach to equilibrium is accelerated in the light [1227], the thermal decomposition of $COBr_2$ is a wall-catalysed reaction [1227,1822], and the reaction is not now believed to be photocatalyzed[†] [1821]. In the modern study [569], equilibrium was established by heating either $COBr_2$ or CO/Br_2 mixtures at 150–200 °C for between 20 and 4 days under the full illumination of a 150 W tungsten lamp, and product analysis (which also established the stoicheiometry of the decomposition of $COBr_2$) was performed by gas chromatography:

$$CO(g) + Br_2(g) \longrightarrow COBr_2(g);$$

$$\Delta H^\circ_{298} = -33.9 \pm 0.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298} = -134.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta G^\circ_{298} = +6.08 \text{ kJ mol}^{-1}$$

The above value of ΔH°_{298}, calculated from the third law of thermodynamics using data from Overend and Evans [1575], was in good agreement with the less precise value obtained from a van't Hoff plot (−33.9 ± 8.8 kJ mol^{-1}) [569], thus convincingly demonstrating that equilibrium had been achieved. These data, based on equilibrium studies, give a value of $\Delta H^\circ_f = -113.5 \pm 0.5$ kJ mol^{-1}, in excellent agreement with the value calculated from calorimetric data (*vide supra*).

The enthalpy of atomization has been calculated, from force constant data, to be 1160–1240 kJ mol^{-1} (*cf.* the experimental value of 1284 kJ mol^{-1}) [2034].

The diamagnetic susceptibility of carbonyl dibromide has never been measured. It has been estimated, however, from the computed value of the mean molecular polarizability (89.24×10^{-25} cm^3): the mass diamagnetic susceptibility, χ_m, was estimated as -0.318×10^{-6} cm^3 g^{-1} (-3.99×10^{-9} m^3 kg^{-1}), the molar diamagnetic susceptibility, χ_M, being -59.7×10^{-6} cm^3 mol^{-1} (-7.50×10^{-10} m^3 mol^{-1}) [374]. An earlier calculated value of the polarizability of $COBr_2$ was 86.26×10^{-25} cm^3 [1258].

14.5 STRUCTURAL AND SPECTROSCOPIC PROPERTIES

The structure of $COBr_2$ in the gas phase has been investigated by both microwave spectroscopy [333] and electron diffraction [1477]. The combined results of these studies (ignoring an early electron diffraction study [549]) give the following parameters for the average structure: r(CO) = 0.1173(9) nm, r(CBr) = 0.1918(4) nm, and ∡BrCBr = 112.3(4)°. The carbonyl bond length is similar to that for $COCl_2$ (Table 7.1) and COF_2 (Table 13.17), but shorter than that of methanal; the carbon–bromine bond length is shorter than those in dibromomethane and tribromomethane.

[†] Probably because of the expected very low thermal stability of the [COBr]· radical, much lower than for [COCl]· {*cf.* Section 6.1.4}.

The infrared spectra of matrix isolated $COBr_2$ (argon; 12 K), $^{13}COBr_2$ and $C^{18}OBr_2$ have been recorded (see Table 14.2), and the force constants were calculated [911]; Raman data are detailed in Table 14.3. Other calculations of force constants, mean amplitudes of vibration, bond asymmetry parameters, and Coriolis coefficients and inertia defects have also been reported [152,333,581,1220–1222,1448–1550,1575–1578,1587,1671,1931,1961,2021,2109,2111, 2167a], as well as the determination of atomic potential energy distributions for ν_1, ν_2 and ν_3 [1674].

TABLE 14.2

INFRARED DATA (units of cm^{-1}) FOR $COBr_2$[a]

	Medium	$\nu_1(a_1)$	$\nu_2(a_1)$	$\nu_3(a_1)$	$\nu_4(b_1)$	$\nu_5(b_1)$	$\nu_6(b_2)$	$\nu_2+\nu_5$	Ref.
		$\nu(CO)$	$\nu_s(CX)$	$\delta_s(OCX)$	$\nu_{as}(CX)$	$\delta_{as}(OCX)$	$\pi(COX_2)$		
$COBr_2$	Gas	1826							168a
$COBr_2$	**Gas**	**1828**	**425**		**757**[b]	**350**	**512**	785	1575
$COBr_2$	Liquid	1826.6	425.6		743.3		511.1	779	1804
$COBr_2$	Ar;12 K	1816.0	424.5		734.4	347.8	511.5	778.6	911
$^{13}COBr_2$	Ar;12 K	1775.2	419.1		711.9		494.7	769.8	911
$C^{18}OBr_2$	Ar;12 K	1774.2	413.8		725.5		507.5	759.8	911

[a] Enboldened data are recognized as the best set. [b] This frequency is corrected for Fermi resonance with ($\nu_2+\nu_5$): the observed band is at 747 cm^{-1}.

TABLE 14.3

RAMAN DATA (units of cm^{-1}) FOR $COBr_2$[a]

	Medium	$\nu_1(a_1)$	$\nu_2(a_1)$	$\nu_3(a_1)$	$\nu_4(b_1)$	$\nu_5(b_1)$	$\nu_6(b_2)$	$\nu_2+\nu_5$	Ref.
		$\nu(CO)$	$\nu_s(CX)$	$\delta_s(OCX)$	$\nu_{as}(CX)$	$\delta_{as}(OCX)$	$\pi(COX_2)$		
$COBr_2$	Liquid	1806	434	181	735	353			1804
$COBr_2$	**Liquid**		**429**	**181**		**350**			1575

[a] Enboldened data are recognized as the best set.

The dipole moment of $COBr_2$ has not been measured, but has been crudely estimated as 1.38 ± 0.27 D {(4.6 ± 0.9) x 10^{-30} C m} [981], close to a previous estimate of 1.25 D (4.17 x 10^{-30} C m) [168a]. The mean dipole moment derivatives [290,1655,1657,2098] and anisotropies [290] have been calculated. The signs of these dipole moment derivatives for $COBr_2$ reported by Bruns and Nair [292] have been re-evaluated [1656] from the empirical integrated infrared intensities [981], giving a set of parameters concordant with those for COF_2 (Chapter 13) and $COCl_2$ (Section 7.2). The re-evaluated signs of these parameters have since been confirmed by polar tensor [136] and CNDO [291] calculations, and effective charges have also been calculated [136]. There have also been other attempts at infrared band intensity analysis [1473]; infrared band intensity ratios appear to be poorly suited to the prediction of the ∡BrCBr bond angle [1904].

The vibrational excitation of $COBr_2$ by collision with argon atoms (1000–3000 K) has been studied: bending modes are found to be more easily excited than stretching modes [2233].

The ^{13}C and ^{17}O n.m.r. spectra of $COBr_2$ are discussed in Section 7.3; the mass spectrum of $COBr_2$ [1b] is detailed in Table 14.4. The photoelectron spectra, electronic absorption spectra, and electronic structure of $COBr_2$ are discussed in Chapter 17.

TABLE 14.4

MASS SPECTRAL DATA FOR $COBr_2$ [1b]

m/z	Relative Intensity	Assignment
190,188,186	-	M^+
162,160,158	37	$[Br_2]^+$
109,107	100	$[COBr]^+$
93,91	12	$[CBr]^+$
81,79	86	Br^+
28	4	$[CO]^+$

14.6 REACTIONS WITH INORGANIC COMPOUNDS

14.6.1 Reactions of carbonyl dibromide with other carbonyl halides

Carbonyl dibromide reacts with the other carbonyl halides, upon heating in an autoclave, according to [902,905]:

$$COBr_2 + COF_2 \longrightarrow CBr_2F_2 + CO_2$$

$$COBr_2 + COCl_2 \longrightarrow CBr_2Cl_2 + CO_2$$

$$COBr_2 + COClF \longrightarrow CBr_2ClF + CO_2$$

14.6.2 Reactions of carbonyl dibromide with water

$COBr_2$ reacts slowly with water at room temperature, according to [1626a,2126]:

$$COBr_2 + H_2O \longrightarrow CO_2 + 2HBr$$

This reaction appears slower than that of phosgene [1822], with a half-life of *ca.* 10 min at ambient temperature [65]. In basic solution, the reaction is rapid [1822]:

$$COBr_2 + 4[OH]^- \longrightarrow [CO_3]^{2-} + 2Br^- + 2H_2O$$

Even at its boiling point, there is no significant reaction between $COBr_2$ and mercury [2126].

14.6.3 Reactions of carbonyl dibromide with halides or pseudohalides

Unpublished results of Anthoney *et al.* [65; ref. 3] suggest that $COBr_2$ is catalytically decomposed to CO and Br_2 in the presence of aluminium(III) bromide. A similar reaction has been reported with aluminium(III) chloride [1937a], but results from our own laboratory suggest that the reaction which occurs is very complex: phosgene and COBrCl are also formed, and ^{27}Al n.m.r. spectroscopy detected the presence of three new aluminium-containing species [1589b]. There are no apparent reactions detectable between $COBr_2$ and BBr_3 or SnX_4 (X = Cl or Br), at room temperature or at −90 °C [1589b].

The reaction between $COBr_2$ and PCl_5 is postulated to proceed according to [900,903]:

$$PCl_5 + COBr_2 \longrightarrow CCl_2Br_2 + POCl_3$$

However, whether this reaction was in fact attempted is not explicit.

$COBr_2$ (or a mixture of CO and Br_2) reacts with HgF_2 and AlF_3 at 500 °C in an autoclave to produce a mixture of CF_4 (55%), $CBrF_3$ (40%), C_3F_8 (<1%), CHF_3 (1%) and C_2F_6 (trace) [1454].

The reaction between $COBr_2$ and ammonium thiocyanate can be performed in liquid sulfur(IV) oxide at −22 °C, to give $CO(NCS)_2$ in 78% yield {*cf.* Section 9.1.7} [300].

$$2[NH_4][SCN] + COBr_2 \longrightarrow CO(NCS)_2 + 2[NH_4]Br$$

14.6.4 Reactions of carbonyl dibromide with oxides

Prigent [1663b] reports that heating UO_3 with $COBr_2$ in a sealed tube for 2 h at 126 °C produces uranium(V) bromide. In our hands [1589b] and the hands of others [1288a], however, these observations were unrepeatable. Indeed, as uranium(V) bromide decomposes above 80 °C, it would have been a very surprising result. Instead, the reaction produces the much more stable uranium(V) oxide tribromide, $UOBr_3$ [1589b].

Further investigation revealed that carbonyl dibromide reacts with a wide selection of *d*- and *f*- block transition metal oxides to form either the metal bromide or metal oxide bromide; the reactions are driven by the elimination of carbon dioxide [1589b,1764a]. In a typical reaction, the metal oxide was treated with an eight-fold excess of $COBr_2$ in a sealed Carius tube at 125 °C for ten days (to ensure complete reaction of the metal oxide). As $COBr_2$ and the reaction by-products {CO_2, CO and Br_2; see, for example, Equations (14.1) and (14.2)} are all volatile, the desired products were obtained in essentially quantitative yield and a high degree of purity. Under these conditions, V_2O_5, MoO_2, Re_2O_7, Sm_2O_3 and UO_3 were converted into $VOBr_2$, MoO_2Br_2, $ReOBr_4$, $SmBr_3$ and $UOBr_3$, respectively, and in all cases this method should now represent the synthetic method of choice [1589b,1764a]. This route offers great potential for the preparation of many known bromide derivatives of the transition metals, lanthanides and actinides, in a very convenient manner, and for the synthesis of new materials.

$$V_2O_5 + 3COBr_2 \longrightarrow 2VOBr_2 + 3CO_2 + Br_2 \tag{14.1}$$

$$COBr_2 \rightleftharpoons CO + Br_2 \tag{14.2}$$

However, at 70–80 °C, carbonyl dibromide does not react with sulfur(IV) oxide (although it does dissolve in it) [918a].

14.7 REACTIONS WITH ORGANIC COMPOUNDS

Rubber, upon exposure to $COBr_2$ vapour, swells, becoming hard and brittle [2126].

$COBr_2$ has been investigated as a potential catalytic acylating agent with 1,4-dimethylbenzene in the presence of aluminium(III) chloride, but (perhaps not too surprisingly) free bromine liberated from dissociated $COBr_2$ led to the formation of by-products such as $Me\text{-}4\text{-}C_6H_4CH_2Br$ [312].

Like $COCl_2$ (Section 10.2.1.4), $COBr_2$ reacts with *N,N*-dimethylaniline {in the presence of either zinc bromide or aluminium(III) bromide} to give a "crystal violet" dye:

$$3C_6H_5NMe_2 + 2COBr_2 \longrightarrow [\{Me_2N\text{-}4\text{-}C_6H_4\}_3C]Br + 3HBr + CO_2$$

However, in the absence of a Friedel-Crafts catalyst, the reactions of $COCl_2$ and $COBr_2$ proceed differently. Whereas $COCl_2$ produces $(Me_2N\text{-}4\text{-}C_6H_4)_2CO$, $COBr_2$ yields

4-bromo-*N*,*N*-dimethylaniline [2126]:

$$C_6H_5NMe_2 + COBr_2 \longrightarrow Br\text{-}4\text{-}C_6H_4NMe_2 + CO + HBr$$

Similarly, the reaction with aniline itself proceeds differently. With phosgene, aniline gives the simple disubstituted urea (see Section 10.2.1.1), whereas it reacts with carbonyl dibromide in diethyl ether to yield a disubstituted urea, but with the phenyl rings 4-brominated [1937a]:

$$2C_6H_5NH_2 + 2COBr_2 \longrightarrow (Br\text{-}4\text{-}C_6H_4NH)_2CO + CO + 2HBr$$

In a related reaction, $COBr_2$ reacts with the ethyl ester of glycine [1423]:

$$2H_2NCH_2C(O)OEt + COBr_2 \longrightarrow \{EtOC(O)CH_2NH\}_2CO + 2HBr$$

The effect of carbonyl bromide upon the polypeptide hormone, insulin, has also been examined [1423]: it was assumed that the $COBr_2$ reacted preferentially with the amino groups of the insulin, and that either inter- or intra-molecular linkages were created [1423]:

$$2(Ins)NH_2 + COBr_2 \longrightarrow (Ins)NHC(O)NH(Ins) + 2HBr$$

$COBr_2$ has also been proposed as a substitute for $COCl_2$ in the conversion of primary amines to organic isocyanates [31], thus eliminating HBr instead of HCl.

There is an early report [156] that $COBr_2$ reacts with ethanol, in the presence of quinoline in diethyl ether, to form the expected ethyl bromoformate, $BrC(O)OC_2H_5$. Bis(bromoformates) are claimed to be produced from the reactions of $COBr_2$ with the long-chain diols $HOCH_2CH_2OCH_2CH_2OH$, $HO(CH_2CH_2O)_2CH_2CH_2OH$, $(CH_3CHOHCH_2)_2O$ and $HO(CH_2CH_2O)_3CH_2CH_2OH$, but no synthetic or characterization details were given [1625].

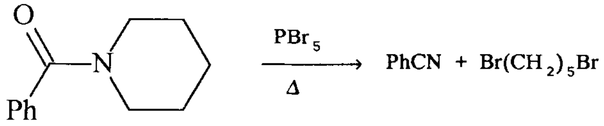
Treatment of pyridinium benzoate with carbonyl dibromide in toluene gives benzoyl bromide [1919]:

$$[pyH][O_2CPh] + COBr_2 \longrightarrow PhC(O)Br + [pyH]Br + CO_2$$

$COBr_2$ is reported to be a catalyst for the α-bromination of saturated carboxylic acids, in a modified Hell-Volhard-Zelinsky reaction [*e.g.* 1320b]. Thus, treatment of octadecanoic acid with bromine in the presence of catalytic amounts of $COBr_2$ gave a 99.5% yield of 2-bromooctadecanoic acid [2029].

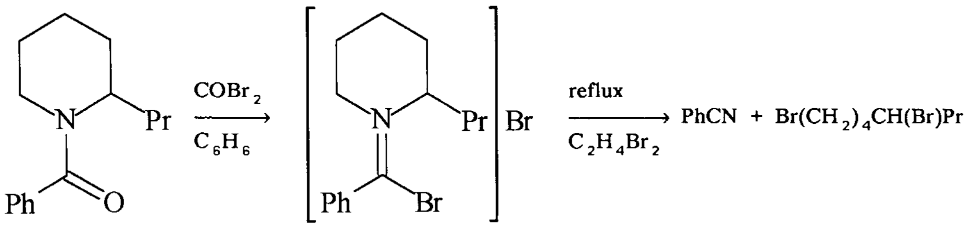
The normal reagent used in the von Braun reaction [*e.g.* 1320b] with heterocyclic benzamides is PBr_5:

e.g.



The harsh conditions of this reaction have limited its general utility for degradative studies, despite its obvious advantages over the Hofmann degradation. It has now been demonstrated that $COBr_2$ is a much milder reagent for this reaction, and this has resulted in the isolation of the iminium bromide (or tribromide, $[Br_3]^-$) intermediate [662,1612]:

e.g.



Thus, $COBr_2$ does appear to have a future as a reagent for organic synthesis, but it has been largely ignored to date. The only detailed study reported is that of Phillips, being the substance of his doctoral dissertation [1611a].

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15 CARBONYL DIIODIDE

Carbonyl diiodide has never been synthesized, and the only report of its observation is as a possible (but improbable) component of the essential oil of a Hawaiian seaweed. The properties reported in this Chapter for carbonyl diiodide are therefore only estimated values, but they do give some insight into the reason for its non-existence.

15.1 EVIDENCE FOR THE PRESENCE OF CARBONYL DIIODIDE IN THE ESSENTIAL OIL OF *Asparagopsis taxiformis*

Limu kohu (*Asparagopsis taxiformis*) is an edible red seaweed which is highly appreciated, for both its taste and smell, in the American state of Hawaii. This alga, whose Hawaiian name means "supreme seaweed", contains a wealth of halogenated compounds in its essential oil, many of which (such as $BrCH_2CH_2Br$, $ClCH_2CH_2OH$, $Cl_3CC(O)CCl_3$, $CH_2{=}CHCl$, CBr_2Cl_2 and $CHBr_3$) are normally regarded as acutely or chronically toxic. Indeed, it is curious that no cases of illness have been reported as a result of the consumption of this delicacy.

In addition to the compounds mentioned above, the volatile oil of *A. taxiformis* (obtained by condensing onto a −78 °C condenser finger *in vacuo*) contains iodine compounds. Separation of the oil using chromatography (on silica gel at 5 °C) and analysis by g.c.–m.s. reveals a trace of material (<0.1%) whose mass spectrum is not inconsistent with that expected for carbonyl diiodide (see Table 15.1) [310].

TABLE 15.1

THE MASS SPECTRUM REPORTED FOR CARBONYL DIIODIDE [310]

m/z	Ion	Relative Intensity/%
282	$[COI_2]^+$	35
155	$[COI]^+$	100
127	I^+	20

By analogy with the aerial decomposition of $CHCl_3$ to $COCl_2$, carbonyl diiodide has been postulated as an intermediate during thermal oxidation [310] or photooxidation [1627a] of triiodomethane:

$$CHI_3 + \tfrac{1}{2}O_2 \longrightarrow (COI_2) + HI$$

Free iodine results from the further decomposition of the COI_2:

$$(COI_2) \longrightarrow CO + I_2$$

Although CHI_3, and several other iodinated compounds, were readily identified by both n.m.r. and m.s. analysis of the crude oil obtained from *A. taxiformis*, many of the original iodine-containing compounds were found not to survive the chromatographic separation. Carbonyl diiodide was therefore postulated as an artefact that results from the decomposition of CHI_3 during the chromatographic process. Clearly, further work is required to substantiate or refute the possible formation of this compound, as this remains the only claim of its existence in the literature.

15.2 ATTEMPTED SYNTHESES OF CARBONYL DIIODIDE

Attempts to prepare COI_2 from phosgene and either hydrogen iodide [184a] or aluminium(III) iodide [2037a] were unsuccessful, yielding only CO and iodine. The reaction between sodium iodide and phosgene in propanone at room temperature {equation (15.1)} quantitatively produces iodine, and has been proposed as an analytical method for the determination of phosgene, iodometrically {*cf.* Section 3.2.1.2} [1778,1937a].

$$2NaI + COCl_2 \longrightarrow 2NaCl + CO + I_2 \qquad (15.1)$$

Similarly, the reactions between solid sodium iodide and either phosgene or carbonyl dibromide at −78 °C produced only CO, I_2 and NaX (X = Cl or Br) [1589b], and a reaction between tetrabutylammonium iodide and phosgene in dichloromethane at −78 °C yielded only CO, I_2 and $[NBu_4]Cl$ [1589b]. These results, particularly those obtained at low temperature, clearly point to COI_2, even if it was formed as a transient intermediate, being extremely unstable.

In a related reaction, the action of HI on ethanedioyl dichloride, $(COCl)_2$, resulted in the formation of only CO and I_2, rather than $(COI)_2$, even at −80 °C. Carbonyl diiodide was presumed to be an intermediate in the decomposition process {equation (15.2)}, itself being decomposed at low temperature [1937a]:

$$(COI)_2 \longrightarrow (COI_2) + CO \longrightarrow 2CO + I_2 \qquad (15.2)$$

15.3 ESTIMATED PHYSICAL AND THERMODYNAMIC PROPERTIES FOR CARBONYL DIIODIDE

The thermodynamic properties for the formation of COI_2 have been calculated for the ideal gas state at 25 °C (Table 15.2). Using Benson's group contribution method [1973], Horvath [985] has recently estimated a more complete range of thermodynamic properties than hitherto reported: his value estimated for the theoretical entropy of $COI_2(g)$ is in reasonable agreement with that given by Kelley and King [1078d], whilst the value of $\Delta H^\circ_{f,298}$ for COI_2 reported by Dittmer and Niemann [537] disagrees with Horvath's [985] by more than 50 kJ mol^{-1}, and is endothermic rather than exothermic.

TABLE 15.2

ESTIMATED THERMODYNAMIC PROPERTIES FOR $COI_2(g)$

$\Delta H^\circ_{f,298}$ /kJ mol^{-1}	$\Delta G^\circ_{f,298}$ /kJ mol^{-1}	$\Delta S^\circ_{f,298}$ /J mol^{-1} K^{-1}	S°_{298} /J mol^{-1} K^{-1}	$C^\circ_{p,298}$ /J mol^{-1} K^{-1}	Ref.
-14.64	-49.62	117.4	341.7	55.6	985
40	-	-	360	69	537
-	-	-	321.3	-	1078d

On the basis of the most recent and most complete data set [985], the thermodynamics of the dissociation reaction {equation (15.3)} strongly favour the right-hand side of the equation [1764]. The thermodynamic trends in dissociation of the carbonyl dihalide series of symmetrical compounds are shown in Table 15.3.

$$COI_2(g) \rightleftharpoons CO(g) + I_2(g) \qquad (15.3)$$

$$COX_2(g) \rightleftharpoons CO(g) + X_2(g) \qquad (15.4)$$

These thermodynamic calculations would seem to rule out the possibility of preparing COI_2 by the simple combination of carbon monoxide and diiodine. However, if the oxidative decomposition of CHI_3 does proceed *via* the formation of COI_2 as a primary product, then the kinetics of the dissociation of COI_2 becomes an important consideration in the question of the material's instability.

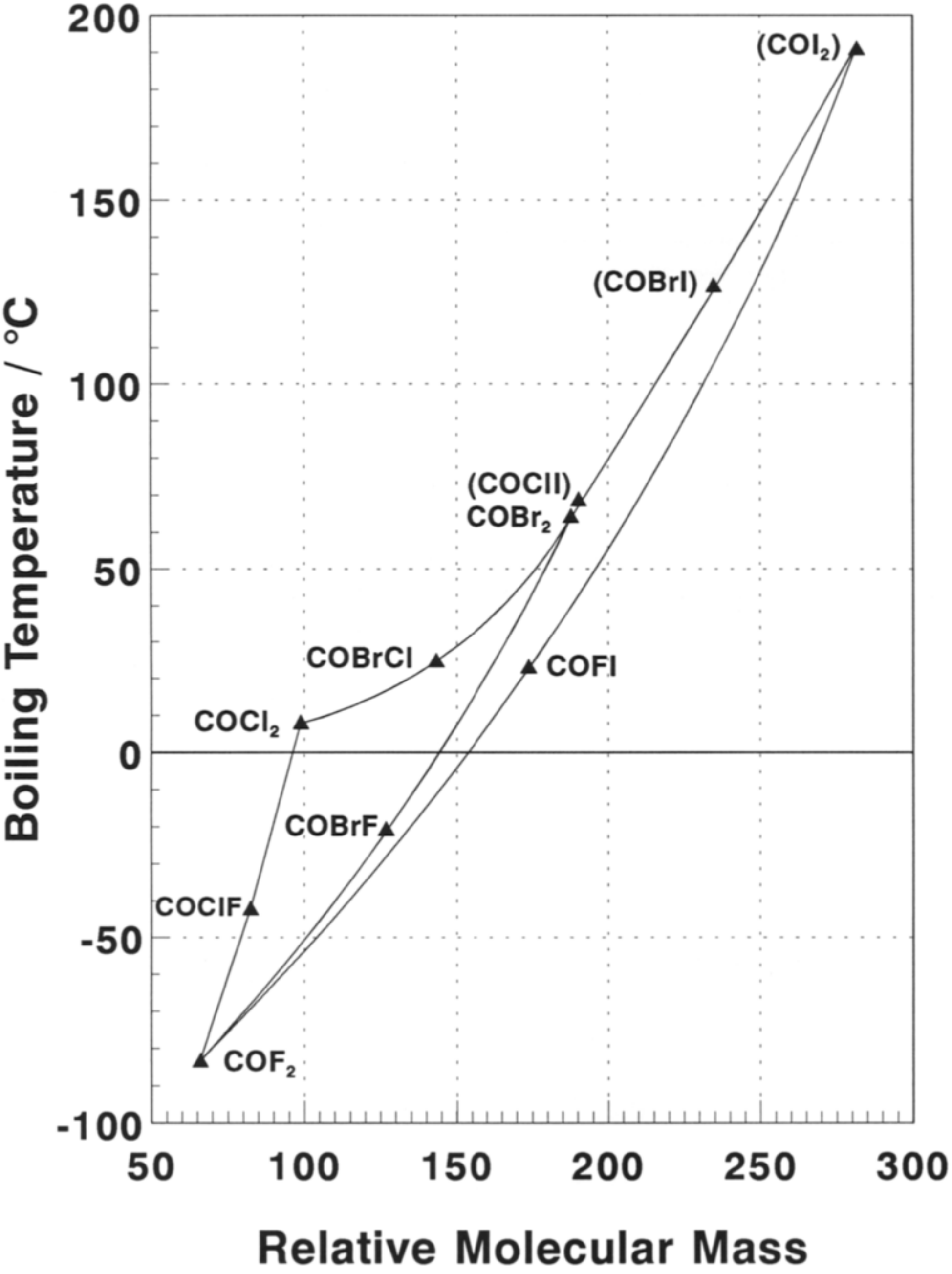


Fig. 15.1 Boiling temperature estimations for COXI (X = Cl, Br or I) [985].

TABLE 15.3

THERMODYNAMICS OF DISSOCIATION FOR COX_2 (X = F, Cl, Br or I) [1764]

COX_2	ΔG°_{298}/kJ mol^{-1} [a]	K_p	Comments
COF_2	+487.3	4.3×10^{-86}	Undissociated
$COCl_2$	+ 68.7	9.1×10^{-13}	Substantially undissociated
$COBr_2$	- 6.1	1.2×10^{1}	Partially dissociated
COI_2	- 68.3	9.2×10^{11}	Substantially dissociated

[a] For equation (15.4).

Since authentic carbonyl diiodide has never been prepared, no data exist concerning the measurement of its physical properties. However, the boiling temperature of COI_2 has been estimated as 191 °C by Horvath [985], based on the similarity principle (see Fig. 15.1), and taking into account its molecular mass of 281.82 g mol^{-1}.

The critical properties of carbonyl diiodide have also been estimated by Horvath [985], based on the Lydersen method:

$$T_c = 740.4 \text{ K}$$
$$P_c = 5.43 \text{ MPa}$$
$$V_c = 290 \text{ cm}^3 \text{ mol}^{-1}$$

No doubt, if other values for COI_2 are determined in the future, they are more likely to be a result of estimation than of measurement.

16 ASYMMETRIC CARBONYL HALIDES

The commercial dominance of phosgene, relative to the related carbonyl halides, stems from its use, mainly, as a carbonylating agent. There would be no commercial advantage in using any of the other carbonyl halides for this type of transformation. In contrast, the potential utility of carbonyl difluoride lies in its capacity as a fluorinating agent and, likewise, the potentially useful chemistry of carbonyl dibromide lies in its ability to act as a brominating agent. Logically, the synthetic utility of the thermodynamically stable mixed carbonyl halides, COXY, would be expected to be their inherent capacity to introduce the halogens, X and Y, into the substrate molecule. For example, under appropriate conditions, the reaction of an aldehyde with an asymmetric carbonyl halide would proceed according to:

$$\mathrm{RC(O)H + COXY \longrightarrow RCHXY + CO_2}$$
$$(\mathrm{X = F,\ Y = Cl\ or\ Br})$$

In addition, perhaps, owing to their lower symmetry (C_s), the mixed carbonyl halides, COXY, may have enhanced reactivity compared to the symmetrical parent compounds, COX_2 and COY_2. Moreover, the compounds COXI have the added interest that COI_2 is unknown. Compared to phosgene and carbonyl difluoride, much less work has been published on the asymmetric carbonyl halides. However, carbonyl chloride fluoride, COClF, is commercially (although not consistently) available, from specialist suppliers, typically in 50 g or 100 g batches, and the reaction of phosgene with fluorspar offers an economically attractive method for its manufacture on a large scale. The reaction of COClF with phenol, in particular, offers the potential to displace the established Balz–Schiemann process for the generic manufacture of fluoroarenes by the synthesis and decomposition of aryl fluoroformates. Indeed, detailed calculations have anticipated that both capital and variable costs are lower for COClF–based routes. Despite their molecular simplicity, the remaining thermodynamically stable compounds, COBrF, COBrCl, and COFI, are grossly neglected compounds. Their present lack of any industrial relevance partly explains why these materials are not available from the usual commercial sources, and yet it is this lack of ready availability which impedes the exploitation of these fascinating materials at the research and small industrial scale.

Much of the early work in this area was reviewed by Rüdorff [1751] and Fischer [656a] in the FIAT Review of German Science; these contain extremely important, otherwise unpublished, experimental data based upon the observations of Kwasnik.

16.1 CARBONYL CHLORIDE FLUORIDE

Although the discovery of phosgene was published as early as 1812 [46], it was not until 1946 that the preparation of authentic carbonyl chloride fluoride (COClF) was first described [1885]. It is probable, however, that COClF was generated in a reaction, reported in 1919, between phosgene and elemental fluorine over granulated calcium fluoride at 200 °C [992]. The product from this reaction was reported to have a boiling point of −42 °C, and to be accompanied by the generation of dichlorine. Although the material was then considered to be a mixture of dichlorine and carbonyl difluoride, it is likely to have been the then unknown carbonyl chloride fluoride.

Under normal conditions of temperature and pressure, COClF is a gas. It is colourless in both the gaseous and condensed states, and has an odour similar to, but distinguishable from, phosgene. It is non-flammable.

Unlike phosgene, COClF fumes in moist air and is readily hydrolysed. It shows no tendency, when dry, to react with glass. It is generally regarded as being much more reactive than either phosgene or carbonyl difluoride and, unlike COF_2, it is readily separated, by distillation, from hydrogen chloride (which is frequently a by-product of its reactions) [1194,1195]. Some contamination by $COCl_2$ or COF_2 can often be tolerated, owing to the generally greater reactivity of COClF. COClF should be stored in either quartz ampoules at −196 °C or in pressurized stainless steel cylinders [1194]. Contact with glass causes a cloudy film to appear over a period of weeks; quartz reacts more slowly [1194].

Very few toxicological data have been recorded for COClF. The available LC_{50} data for six animal species are recorded in Table 16.1. Although there is no commercially available detector tube for the monitoring of COClF, *per se*, it has been noted in our own laboratories that the material may be detected using a Dräger tube designed for phosgene determination.

The synonyms of carbonyl chloride fluoride are carbonic chloride fluoride (currently used in *Chemical Abstracts*), carbonyl chlorofluoride, and monofluorophosgene. The *Chemical Abstracts* Registry No. is [353-49-1]. COClF is included in the European inventory of existing chemical substances (EINECS) [602a], since it was included in the core inventory [602]: its EINECS number is 206-533-7. No full-scale commercial synthesis of COClF has ever been operated.

16.1.1 Biological activity of carbonyl chloride fluoride

There are no recorded cases of humans being poisoned with COClF. Consequently, the only information available is from animal experiments, most of this work having been performed during the Second World War, when looking for alternatives to the existing war gases.

16.1.1.1 Animal experiments

The known dose-response relationships are summarised in Table 16.1. As can be seen, for most animal species, carbonyl chloride fluoride is only slightly less toxic than phosgene, and in mice there appears to be a particular susceptibility to this poison.

TABLE 16.1

COClF DOSE-RESPONSE RELATIONSHIPS IN ANIMALS [411b,1432a]

Species	LC_{50}/p.p.m. min
Mouse	350
Rat	395
Cat	520
Guinea pig	790
Dog	1750
Rabbit	2040

16.1.1.2 Symptoms

There are few signs of irritation upon exposure to COClF, except at high doses. Some rabbits showed signs of eye irritation and some dogs had increased salivation [411b]. After exposure to the gas, most animals appeared normal until one to six hours before death. The delayed symptoms of respiratory distress are similar to those seen after phosgene poisoning, *i.e.* breathing becomes increasingly laboured, and is often accompanied by expiratory noises [411b,1432a].

16.1.1.3 Pathophysiology of carbonyl chloride fluoride poisoning

There seems to be no discernible difference at the cellular level between COClF and phosgene damage [1432a]. COClF has little effect on the upper respiratory passages, but shows increasing effects, such as desquamation, in the finer bronchioles. Damage to the blood-air barrier is similar to that for phosgene, and results in pulmonary œdema. The causes of death in the experimental animals are variously recorded as asphyxia from pulmonary œdema, bronchopneumonia and/or associated disorders. The right side of the heart and the pulmonary vessels were also found to be greatly enlarged with blood [411b].

16.1.2 Analytical methods

A Dräger tube, specific for the detection and determination of phosgene (see

Section 3.2.3.1.2) can be employed for the detection of carbonyl chloride fluoride.

For quantitative analysis, and particularly in the presence of other carbonyl dihalides, gas chromatographic methods are recommended. A good working system employs a thermal conductivity detector and a Porapak P column using helium carrier gas (see Section 13.3.3) [84a].

16.1.3 Environmental considerations

COClF has been detected (by i.r. matrix isolation) in the stratosphere in several flights over Northern Europe, but not in the troposphere (*cf.* phosgene, Section 3.7.2) [932a,932b].

Although there are no industrial sources of COClF emissions, natural emissions of COClF from volcanoes have been predicted by equilibrium thermodynamic models [1990a]. COClF may also be generated environmentally from the photochemical decomposition of CCl_3F (CFC-11). Subsequent removal can be assumed to be effected by its reaction with $O(^1D)$ [1994], and by further photolysis (the preliminary photodissociation step has been examined by *ab initio* methods [677a]). Using calculated production and removal rates, an altitude profile for COClF was calculated: maximum COClF formation was noted to occur at an altitude of about 25 km [1994].

16.1.4 Synthesis and formation

16.1.4.1 From the reactions of phosgene with fluorides of the main group elements

COClF has been reported to be preparatively inaccessible in the standard laboratory [441], and yet this material has been prepared, or at least its formation noted, from the reactions of phosgene with the fluorides of Groups 1, 2, 14, 15 and 16. Fluorides of the Group 13 elements have not been examined under conditions that might favour the production of COClF, although there appears to be no fundamental reason why these should not function just as well as the fluorides of elements in other groups. Although the lattice energies of AlF_3, GaF_3, InF_3 and TlF_3 are large (*e.g.* $U(AlF_3) \approx -6150$ kJ mol^{-1}), this in itself cannot preclude the reaction of these materials with phosgene. The lattice energy of aluminium(III) bromide (*ca.* 5245 kJ mol^{-1}) is also large, and yet it reacts with $COCl_2$ to form COBrCl (see Section 9.1.2.6).

The reactions of phosgene with transition metal fluorides appear not to have been studied in this connection.

16.1.4.1.1 Hydrogen fluoride and the fluorides of Group 1 elements

In 1946, carbonyl chloride fluoride, COClF, was reported in the open literature for the first time [1885] (although a US Defense report appeared in 1942 [1883a]): it was prepared (*ca.* 25% yield) by the reaction between phosgene and anhydrous hydrogen fluoride in a copper bomb at 80 °C and 1.93 MPa, in the presence of a trace of antimony(V) chloride: as well as hydrogen chloride, some by-product COF_2 was also formed [1885]:

$$COCl_2 + HF \longrightarrow COClF + HF$$

Traces of antimony(V) chloride were found to catalyse this reaction, and yields of COClF were found to vary between 25% and 50% [1885]. At 7 °C and atmospheric pressure, only a small degree of reaction was detected [1470], but electrolysis of a solution of phosgene in liquid anhydrous hydrogen fluoride (in the presence or absence of NaF) performed at 0 °C produces COClF (90.7%), $COCl_2$ (5.7%) and COF_2 (3.6%) [2132]. A mixture of phosgene and anhydrous hydrogen fluoride, when passed over activated charcoal at 775–850 °C in a graphite tube gives only small quantities of COClF; the major product is tetrafluoromethane (in 20% yield), along with smaller amounts of CF_3Cl and COF_2 [399]. Larger amounts of COClF can be formed from the combination of HF and $COCl_2$, where the HF:$COCl_2$ molar ratio is substantially less than 2:1 [2069]. Moreover, in the presence of activated charcoal or activated α-Al_2O_3 at 200 °C, yields approaching 60% of COClF have been obtained [ICI36].

A trace of carbonyl chloride fluoride is reported to be formed during the preparation of carbonyl difluoride from the reaction of phosgene with excess of sodium fluoride slurried in ethanenitrile at 30–45 °C [632]. Carbonyl difluoride is formed, free of any COClF, when phosgene is condensed onto an excess of sodium fluoride in ethanenitrile and the reaction mixture maintained at 20 °C for 24 h in a sealed tube. COClF, however, is reported to be formed in a small amount when a lower ratio of NaF to $COCl_2$ is employed [1692]. In contrast, heating phosgene with solid anhydrous sodium fluoride in an autoclave at 100 °C gives a 25% yield of COClF, along with 75% unreacted phosgene and no significant levels of COF_2 [631]. In a flow system, small amounts (<20% at 525 °C) of COClF were also formed [ICI26]. With solid potassium fluoride, the yields of COClF were even lower, but at short reaction times (*i.e.* high effective fluoride ion concentrations), large amounts of COF_2 were initially formed [ICI26]. In molten LiF–NaF–KF at 550 °C, phosgene gives only trace amounts of COClF (see Section 9.1.1) [1979].

The reaction of $[NH_4][HF_2]$ with phosgene is discussed in Section 16.1.4.1.5.

16.1.4.1.2 Fluorides of Group 2 elements

Although it was not identified as such at the time, the first report of a material which could have been carbonyl chloride fluoride appeared in 1919 [992]. The reaction (oft explosive) between phosgene and difluorine at 200 °C, in the presence of calcium fluoride, produced a liquid which boiled at *ca.* −42 °C [992]. The product was thought, at the time [992], to be a mixture of COF_2 and dichlorine, but the proximity if its boiling point to that of COClF is too close for coincidence.

A mixture of calcium fluoride ("fluorspar"; 0.08 mol), potassium chloride (0.1 mol) and phosgene (0.14 mol), maintained at 500 °C and about 3.4 MPa over a period of 63 h, gave a mixture consisting of COClF, COF_2 and unconverted $COCl_2$. The solid residue consisted of a $CaCl_2$.KCl phase; no CaF_2.$CaCl_2$ was detected, and 79% of the CaF_2 was converted. Under similar conditions, maintained over 24 h, 67% of the CaF_2 was converted and, after 4 h, 42% of the CaF_2 was said to be converted [1561]; similar results were obtained in a flow system, but with single-pass yields of COClF only approaching 10% [ICI27,ICI28]. In the presence of iron metal and dichlorine promoters, very high conversions (84%) were achieved [1561]. In the absence of potassium chloride, when subjected to the above conditions over 63 h, only 35% of the CaF_2 was converted and the solid residues were composed of $CaF_2.CaCl_2$ (which is said to tie-up the inorganic fluoride and prevent its further reaction). The product gases were shown to contain COF_2, COClF and unreacted phosgene. The heating of a mixture of CaF_2 (0.08 mol), KCl (0.1 mol), $COCl_2$ (0.14 mol), iron powder (0.5 mol) and Cl_2 (0.02 mol) at 500 °C and 3.4 MPa for 64 h gave a mixture composed of 66% COClF, 2.8% COF_2 and 31.2% $COCl_2$. The solid residue was found to be substantially all $CaCl_2.KCl$, with no $CaCl_2.CaF_2$ detected. Analysis indicated the conversion of about 84% of the CaF_2 charged [1561].

The passage of gaseous phosgene (1.4 l h^{-1}) through a tubular reactor containing CaF_2 (0.3 mol) and KCl (0.7 mol) at atmospheric pressure, and at an estimated residence time greater than about one minute, gave the results listed in Table 16.2 [1561].

TABLE 16.2

THE REACTION OF PHOSGENE WITH CaF_2/KCl IN A FLOW-SYSTEM [1561]

Reactor Temperature/°C	Exit Gas Composition/% v/v		
	$COCl_2$	COClF	COF_2
110	97.6	2.4	-
145	96.3	3.7	-
175	92.7	7.3	-
200	86.2	13.8	trace
230	79.0	20.7	0.3
280	67.7	31.3	1.0
350	55.0	42.5	2.5

COClF has been prepared in a convenient manner by passage of gaseous phosgene (*ca.* 10 l h^{-1}) over dried calcium fluoride (*ca.* 2 Kg) in a flow system at *ca.* 450 °C. The volatile reaction products were passed into a bed of activated charcoal held at about 200 °C (to recombine the carbon monoxide and dichlorine formed as a result of the thermal dissociation of phosgene) and then condensed in a dry-ice trap. The COClF was separated from unreacted phosgene by distillation in a low-temperature fractionating column and collected at about −45 °C [86].

The reaction of phosgene with an inorganic binary fluoride at temperatures above 450 °C is reported to result in the formation of fluorine-containing perhalomethanes, CCl_nF_{4-n} (n = 0–4). At lower temperatures, it is said that (if the reaction proceeds at all) chlorofluoromethanes are not produced, but solely carbonyl difluoride and/or carbonyl chloride fluoride [1454]: however, conditions may be optimized to give COClF with a selectivity in excess of 90% [ICI25]. The heating of a mixture of phosgene (0.5 mol), calcium fluoride (0.58 mol) and antimony(V) chloride (5 g) in a steel bomb at 500 °C for 3 h under autogenous pressure gave a reaction product consisting of carbonyl difluoride (3%), phosgene (10%), carbon dioxide (10%), carbon tetrachloride (0.5%), $CClF_3$ (10%), CCl_2F_2 (3%), HCl (3%) and a small amount of COClF: the remainder of the mixture was dichlorine and adventitious air [1454].

16.1.4.1.3 Fluorides of Group 13 elements

The reactions of phosgene with fluorides of the Group 13 elements to give COClF have not been reported, although it is interesting to note the existence of the boron(III) fluoride-phosgene adducts; $BF_3.COCl_2$ and $BF_3.2COCl_2$ (see Section 9.1.2.1), formed from the combination of phosgene with BF_3 at low temperature [1329].

It is also interesting to note that the mixed carbonyl halide, COBrCl, has been prepared by the reaction of phosgene with aluminium(III) bromide (see Section 9.1.2.6) [2127]:

$$3COCl_2 + AlBr_3 \longrightarrow AlCl_3 + 3COBrCl$$

16.1.4.1.4 Fluorides of Group 14 elements

COClF is reported to be prepared by the redistribution reaction of COF_2 with $COCl_2$ (although earlier workers [1275] had been unable to bring about the reaction) [1018]:

$$COF_2 + COCl_2 \rightleftharpoons 2COClF$$

A yield of 30% of COClF is claimed by using equimolar mixtures of phosgene and carbonyl difluoride, but no further experimental details are provided [1018]. The passage of an equimolar mixture of $COCl_2$ and COF_2, diluted with dinitrogen, through a platinum-lined vessel packed with activated carbon pellets between 250 and 450 °C, resulted in the formation of some COClF along with traces of CF_4, CO_2, CF_2Cl_2 and CF_3Cl. The off-gases consisted largely of unchanged reactants. A mixture containing 10–20% COClF was formed by passing $COCl_2$ and COF_2 (molar ratio 3:1) over activated carbon at 665 °C. Alternatively, a gaseous product comprising 25% COClF was generated from the heating of a mixture of COF_2

(0.36 mol), $COCl_2$ (0.42 mol) and activated carbon (35 g) in a stainless steel autoclave at 435 °C for 14.5 h [900,905].

The passage of an equimolar gas mixture of $COCl_2$ and SiF_4 into a quartz tube, packed with quartz granules, at about 400 °C is reported to produce COClF with a selectivity of 100% (neglecting the dissociation of $COCl_2$ into carbon monoxide and dichlorine). COF_2 is said not to be formed, and conversions of phosgene may be as high as 40% per pass. The results of this experiment are recorded in Table 16.3 [377]. Silicon(IV) fluoride is a waste product of fertilizer manufacture.

TABLE 16.3

THE REACTION OF PHOSGENE WITH SILICON(IV) FLUORIDE [a]

Temp / °C	Conversion / % [b]	Dissociation / % [b,c]
360	3.7	0
420	42.4	0
500	37.5	0.15
600	15.4	1.4
700	11.1	35.3

[a] Performed using a contact time of 15 s. [b] Based on phosgene. [c] The yields of COClF estimated did not take into account the dissociation of $COCl_2$ since, it is said, quite rightly, that CO and Cl_2 can be easily recombined to give phosgene.

16.1.4.1.5 Fluorides of Group 15 elements

Phosgene and nitrogen(III) fluoride react at 310 °C, in a nickel tube, to form a mixture composed of COClF (65%), COF_2 (35%) and dichlorine, according to [771]:

$$3COCl_2 + 2NF_3 \longrightarrow 3COF_2 + 3Cl_2 + N_2$$

$$6COCl_2 + 2NF_3 \longrightarrow 6COClF + 3Cl_2 + N_2$$

Raising the temperature to 400 °C lowers the yield of COClF to zero [771].

When phosgene was added, over 50 min, to $[NH_4][HF_2]$ in ethanenitrile and the mixture heated for an hour at 70 °C, a product consisting of COF_2 (89.8%) and COClF (7.6%) was formed [1248].

An excess of phosgene reacts with arsenic(III) fluoride in the presence of a catalytic amount of $SbCl_5$, at 130 °C over 10 h in a stainless steel lecture bottle (5.5 MPa), to give a 67% yield of COClF based upon the quantity of phosgene charged [378]. Similarly, antimony(III) fluoride reacts with four molar equivalents of $COCl_2$ in the presence of a small quantity of antimony(V) chloride at 135 °C over one hour in a copper autoclave to give a yield of COClF, based upon phosgene charged, of about 53% (see Section 9.1.4.4) [589]. A small quantity of COF_2 was also generated, the yield of which increased upon increasing the molar ratio of SbF_3 [589].

16.1.4.1.6 Fluorides of Group 16 elements

A 4:1 mixture of gaseous SOF_2 and $COCl_2$, when passed through a column consisting of iron(III) chloride on an iron packing at 400 °C, and at a contact time of 10 min, resulted in the formation of carbonyl difluoride, accompanied by minor quantities of COClF and CCl_2F_2 [704]. The reaction which forms COClF may be represented by the equation:

$$SOF_2 + COCl_2 \longrightarrow SOClF + COClF$$

16.1.4.2 From the reactions of carbon monoxide

In the same year as the first open literature report of COClF (1946), the FIAT review of German science (1939–1945) was published, and included a report of an alternative synthesis of COClF [1194]:

$$ClF + CO \longrightarrow COClF$$

COClF may be prepared by the passage of a gas stream of chlorine(I) fluoride and an excess of carbon monoxide at −18 °C into an iron reaction vessel, with the exclusion of air and moisture. The gaseous reaction product is then condensed into a quartz vessel and the crude product distilled through, and from, antimony powder. The yield was found to vary between 85 and 90% (based upon ClF), and was greater if the reaction was performed more slowly: the main contaminants were COF_2 and $COCl_2$ [1194]. Only a ten percent yield of COClF was obtained by reaction of ClF_3 and CO (diluted with dinitrogen) at −180 °C over activated charcoal [1196a].

The heating of a mixture of calcium fluoride (0.5 mol) and dichlorine (0.5 mol) in a steel bomb, pressurized to 80 MPa with an excess of carbon monoxide at 450 °C for 6 h, is reported to produce a yield of about 2% of COClF, contaminated with $COCl_2$, COF_2, $CClF_3$, CCl_2F_2 and HCl [28]. Similarly, the passage of a mixture of carbon monoxide and dichlorine through a bed consisting of CaF_2 and KCl (molar ratio ≈ 1:2) is said to generate COClF at temperatures above 200 °C [1561].

SF_5Cl combines with carbon monoxide (five molar equivalents), when irradiated with ultraviolet light over 5 h, to give COClF as the major product. Small amounts of COF_2,

$COCl_2$ and COS are also generated [1345].

16.1.4.3 From the reactions of carbonyl difluoride or formyl fluoride

COClF was obtained as one of the by-products from the reaction of carbonyl difluoride with a small excess of PCl_5 at 265 °C over 16 h in an autoclave. The reaction of COF_2 with PCl_2F_3 (molar ratio ~ 1:2) at 300 °C for 12 h in an autoclave is also reported to generate COClF, accompanied by $COCl_2$, CCl_2F_2, CO_2, CCl_4 and $POCl_3$ (see Section 13.13.1.4) [900,905].

The photochemical reaction of HC(O)F with a small excess of dichlorine has been used to prepare a synthetic sample of COClF [656]. The reaction is considered to take place as shown in the following scheme:

$$\begin{aligned}
Cl_2 &\xrightarrow{h\nu} 2Cl\cdot \\
Cl\cdot + HCOF &\longrightarrow HCl + [COF]\cdot \\
[COF]\cdot + Cl_2 &\longrightarrow COClF + Cl\cdot
\end{aligned}$$

$$HCOF + Cl_2 \xrightarrow{h\nu} COClF + HCl$$

Hydrogen chloride and dichlorine impurities were removed by fractional distillation and treatment with mercury, respectively.

16.1.4.4 From the reactions of ethane-1,2-dioyl dichloride

Ethane-1,2-dioyl dichloride {oxalyl chloride; $(COCl)_2$} reacts with antimony(V) fluoride above −35 °C to form COClF (identified by *in situ* infrared analysis) and SbF_3. The reaction was accompanied by the generation of a small quantity of CO, and possibly COF_2. Examination of the infrared spectrum during the progress of the reaction when cooled to −50 °C revealed the formation of an intermediate oxocarbonium salt. The reaction was interpreted in the following terms [7]:

$$\begin{aligned}
(COCl)_2 + 2SbF_5 &\longrightarrow [(CO)_2]^{2+}[SbF_5Cl]_2^- \\
[(CO)_2]^{2+} &\longrightarrow 2[CO]^+ \\
[(CO)_2]^{2+}[SbF_5Cl]_2^- &\longrightarrow 2COClF + SbF_3.SbF_5 \\
2[CO]^+[SbF_5Cl]^- &\longrightarrow 2COClF + SbF_3.SbF_5
\end{aligned}$$

The initially formed dication $[(CO)_2]^{2+}$ is stable below −50 °C, but decomposes with cleavage of the carbon-carbon bond into the radical ions $[CO]^{\dot{+}}$, and COClF is formed *via* a redox reaction with the associated anion.

16.1.4.5 From the reactions of metal carbonyls

Reaction of $[Fe(CO)_5]$ with SF_5Cl at room temperature resulted in the formation of predominantly carbon monoxide; smaller amounts of COClF, COF_2 and COS were also formed [1345].

16.1.4.6 From the reactions of fluorinated hydrocarbons and related species

16.1.4.6.1 Oxidation and oxygenation

The oxo-dechlorination of CCl_3F (CFC-11) using SO_3 constitutes the most convenient laboratory preparation of COClF, and analogous reactions may be employed for the preparations of the other mixed and symmetrical carbonyl halides, such as COBrF - from CBr_3F and SO_3, and $COBr_2$ - from CBr_4 and SO_3 [1874,1875]. SO_3 and CCl_3F combine in the presence of $HgSO_4$ and Hg_2SO_4 or sulfuric acid as follows:

$$CCl_3F + nSO_3 \longrightarrow COClF + ClSO_2(SO_3)_{n-1}Cl$$

Since SO_2Cl_2, or polysulfuric chlorides, are known to be rapidly hydrolysed by water to generate SO_3, the above process could, in principle, be operated on a continuous basis, represented by the following equation, corresponding to the action of water on CFC-11, with SO_3 acting only as a catalyst [1764]:

$$CCl_3F + H_2O \xrightarrow{SO_3} COClF + 2HCl$$

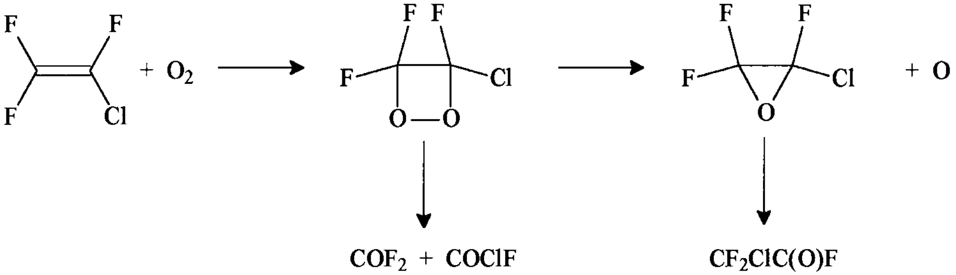
The full details of the preparation are described in Appendix A5 [1874].

The chlorine-initiated reaction of $CF_2{=}CFCl$ with dioxygen in a flow system, in the dark at room temperature, gives predominantly $CF_2ClC(O)F$, COF_2, and COClF [1197]. The following reactions are indicated:

$$2CF_2{=}CFCl + O_2 \longrightarrow 2CF_2ClC(O)F$$

$$CF_2{=}CFCl + O_2 \longrightarrow COF_2 + COClF$$

and the reaction mechanisms are believed to be as follows [1197]:



The same reaction products are observed when $CF_2{=}CFCl$ is photolysed in the presence of O_2 by a TEA–CO_2 laser at 1050.44 cm^{-1}. Under these conditions, the products may be accounted for as follows:

$$CF_2{=}CFCl \xrightarrow{nh\nu_{ir}} [CF_2]{:} + [CClF]{:}$$

$$[CF_2]{:} + O_2 \longrightarrow COF_2 + O{:}$$

$$[CClF]{:} + O_2 \longrightarrow COClF + O{:}$$

$$O{:} + CF_2{=}CFCl \longrightarrow CF_2ClC(O)F$$

Alternatively, COF_2 may be formed subsequent to the formation of the $CF_2ClC(O)F$:

$$O{:} + CF_2{=}CFCl \longrightarrow [CClF]{:} + COF_2$$

Air–oxidized $CF_2{=}CFCl$ results in the formation of these compounds and is noted to be more toxic than pure $CF_2{=}CFCl$ [43]. When used to saturate a dinitrogen stream containing equal volumes of dioxygen and difluorine at 25 °C, $CF_2{=}CFCl$ gave a mixture of $CF_2ClC(O)F$, $CF_2{=}CFCl$, $COClF$, COF_2 and CF_3COF [1397].

The carbonyl halides, $COClF$, $COCl_2$ and COF_2, were co–produced in small quantities during the air–oxidation of CCl_2FCClF_2 (CFC–113) [1325]. The concentrations of each of these products increases from about 600–650 °C, and reach a maximum ($COClF$ 2600, $COCl_2$ 1300, COF_2 800 p.p.m.) at around 700 – 800 °C. Thereafter, the concentrations of each of these components decrease as the pyrolysis temperature increases further (the thermal stability decreasing with fluorine content). The concentration of $COClF$ diminishes to zero at about 1000 °C. The stoicheiometry of the oxidation reactions in which $COClF$ is formed is as follows [1325]:

$$CCl_2FCClF_2 + O_2 \longrightarrow COClF + COF_2 + Cl_2$$

$$CCl_2FCClF_2 + O_2 \longrightarrow COClF + COCl_2 + F_2$$

16.1.4.6.2 Photo–oxidation

The chlorine–sensitive, photochemical (436 nm) oxidation of $CHCl_2F$ (HCFC–21) with a molar equivalent of dioxygen, below 100 °C, results in the formation of a high yield (95%) of $COClF$, with 5% of the $CHCl_2F$ converted into CCl_3F. The reaction is proposed to occur by the following steps [1820]:

$$Cl_2 \xrightarrow{h\nu} 2Cl\cdot$$

$$Cl\cdot + CHCl_2F \longrightarrow [CFCl_2]\cdot + HCl$$

$$[CFCl_2]\cdot + O_2 \longrightarrow [Cl_2FCOO]\cdot$$

$$[Cl_2FCOO]\cdot + CHCl_2F \longrightarrow 2COClF + HCl + Cl\cdot$$

Thus, the nett reaction corresponds to Equation (16.1):

$$2CHCl_2F + O_2 \longrightarrow 2COClF + 2HCl \qquad (16.1)$$

The formation of CCl_3F is represented by Equation (16.2):

$$CHCl_2F + Cl_2 \longrightarrow CCl_3F + HCl \qquad (16.2)$$

The rate of the reaction is expressed by the equation:

$$\frac{d[COClF]}{dt} = \frac{I_{abs}\, k_1\, [CHCl_2F]}{([CHCl_2F] + k_2)}$$

where k_1 and k_2 represent the rate constants for reactions (16.1) and (16.2).

The chain length for the formation of COClF is of the order of 100 molecules per quantum at 80 °C (partial pressure of $CHCl_2F \approx 13.2$ kPa), and the temperature coefficient for the rate of formation of COClF is 1.4 per 10 °C [1820]. The laser–sensitized chlorination and oxidation of $CHCl_2F$ gives [CClF]: as an intermediate which reacts with Cl_2 to give CCl_3F, and with dioxygen to give COClF and COF_2 [1857a]. The steady–state photolysis of a mixture of Cl_2–$CHCl_2F$–O_2–NO–NO_2–N_2 at room temperature and atmospheric pressure gave COClF amongst the reaction products [765a].

The photolysis of CCl_3F at 213.9 nm and 25 °C in the presence of dioxygen [1037,1325a] or ozone gives COClF and dichlorine as the products, with quantum yields corresponding to $\Phi(COClF) = 0.90$ and $\Phi(Cl_2) = 0.50$–0.63 [1037]. COClF was also found to be the photooxidation product of CCl_3F at 184.9 nm, with a quantum yield near to unity ($\Phi \approx 0.96$) [88]. A similar reaction occurs when $O(^1D)$ atoms combined with CCl_3F [88], the overall reaction being represented by [1624]:

$$CCl_3F + O(^1D) \longrightarrow COClF + Cl_2$$

Stratospheric photodissociation is regarded as the only significant removal process for CCl_3F in the atmosphere (see Section 16.1.3) [366]:

$$CCl_3F \xrightarrow{h\nu} [CCl_2F]\cdot + Cl\cdot$$

The chlorine atoms react with many ozone molecules before being removed as HCl. The $[CCl_2F]\cdot$ radicals are consumed by dioxygen to give [ClO]· and COClF [366], which is then dissociated into CO, and F· and Cl· atoms.

COClF is said to form in ambient air when CCl_3F vapour is exposed to an intensive source of u.v. emission, such as a welding arc [1130c].

16.1.4.6.3 Photolysis

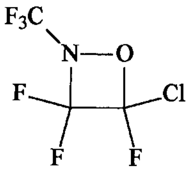
The photolysis of CF_3OCl at wavelengths below 280 nm, in a dilute argon matrix at 8 K, produces COF_2 and CF_3OOCF_3, with lesser amounts of CF_3OF, ClF and COClF. The appearance of COClF may be attributed to a secondary photolytic decomposition of CF_3OCl, induced by wavelengths below 230 nm [1902]:

$$\begin{aligned} CF_3OCl &\xrightarrow{h\nu} COF_2 + FCl \quad (\lambda < 280\ \text{nm}) \\ FCl &\xrightarrow{h\nu} F\cdot + Cl\cdot \\ COF_2 &\xrightarrow{h\nu} [FCO]\cdot + F\cdot \quad (\lambda < 230\ \text{nm}) \\ [FCO]\cdot + Cl\cdot &\longrightarrow COClF \end{aligned}$$

The photolysis of $CF_2ClC(O)F$ in ultraviolet light results in the formation of CF_2ClCF_2Cl, CF_2Cl_2, COF_2 and COClF [908].

16.1.4.6.4 Pyrolysis

Pyrolysis of oxazetidine (16.1; formed from the reaction of CF_3NO with $CF_2{=}CFCl$) at 550 °C results in the production of COClF and $CF_3N{=}CF_2$ [123], in almost quantitative yield.



(16.1)

This reaction can be used as a method for structure determination of oxazetidines [112].

16.1.5 Thermodynamic and physical properties

Carbonyl chloride fluoride (relative molecular mass: 82.46) is a colourless gas, with an odour similar to, but distinguishable from, phosgene [1194,1885]. It is stable at room temperature, both as a gas and as a liquid under pressure [1194]. It has a melting point of −138 °C [843,1885] (replacing an earlier value of −148 °C [1196a]), and a boiling point of −46 °C [656] (replacing −47.2 °C [1196a] and −42 °C [1885]). Some of the physical properties of carbonyl chloride fluoride have been previously compiled [42,782,1079].

16.1.5.1 Thermal and thermochemical properties

16.1.5.1.1 Gas phase

The enthalpy of formation, ΔH_f°, free energy of formation, ΔG_f°, and the corresponding equilibrium constant, K_p, have not been determined experimentally for gaseous COClF. The value of ΔH_f° of −427 ± 33 kJ mol^{-1} was estimated from the mean of the enthalpies of $COCl_2$ and COF_2 [1972]. Other estimates of ΔH_f° at −426.1 [1360c] or −445.6 kJ mol^{-1} [2189b] have been reported, and a calculated (MNDO) value of −387 kJ mol^{-1} exists [514].

The standard Gibbs free energy of formation, ΔG_f°, for gaseous COClF was calculated to be −412.6 kJ mol^{-1}, from the relation:

$$\Delta G^{\circ}[\mathrm{Cl{-}CO{-}F}] \sim \tfrac{1}{2}(\Delta G^{\circ}[\mathrm{Cl{-}CO{-}Cl}] + \Delta G^{\circ}[\mathrm{F{-}CO{-}F}])$$

The calculated values for this method are said to agree with experimental values, where available, to within 1% [124].

The standard values of the enthalpy, H°, entropy, S°, and specific heat capacity, C_p°, for COClF (ideal gas state, atmospheric pressure, 25 °C) have been calculated from molecular data. The data reported by various authors are recorded in Table 16.4.

TABLE 16.4

CALCULATED THERMODYNAMIC PROPERTIES FOR COClF IN THE IDEAL GAS STATE

C_p° a	S° a	$H_{298}^{\circ} - H_0^{\circ}$ b	Ref.
52.396	276.914	11.067	1972
52.396	276.760	11.904	1360c
52.426	276.897	11.903	1280
52.426	276.981	-	1078d

[a] Units of J mol^{-1} K^{-1}. [b] Units of kJ mol^{-1}.

The calculated standard thermodynamic functions for carbonyl chloride fluoride, C_p°, S°, $-(G^{\circ} - H_{298}^{\circ})/T$, $(H^{\circ} - H_{298}^{\circ})$, ΔH_f°, ΔG_f° and $\log_{10}(K_f)$, are listed in Table 16.5 for the extended temperature range 0–6000 K in the ideal gas state [359aa], and are illustrated over the more normal working temperature range [359aa] in Fig. 16.1. Earlier values [1280,1360c,1972] for these thermodynamic properties have now been superseded.

The specific heat capacity, C_p°, from 400 to 1100 K may be represented by the equation [2189b]:

$$C_p^{\circ}\ /\mathrm{J\ mol^{-1}K^{-1}} = 68.9770 + 0.942851 \times 10^{-2}T - 2.30251 \times 10^{6}T^{-2}$$

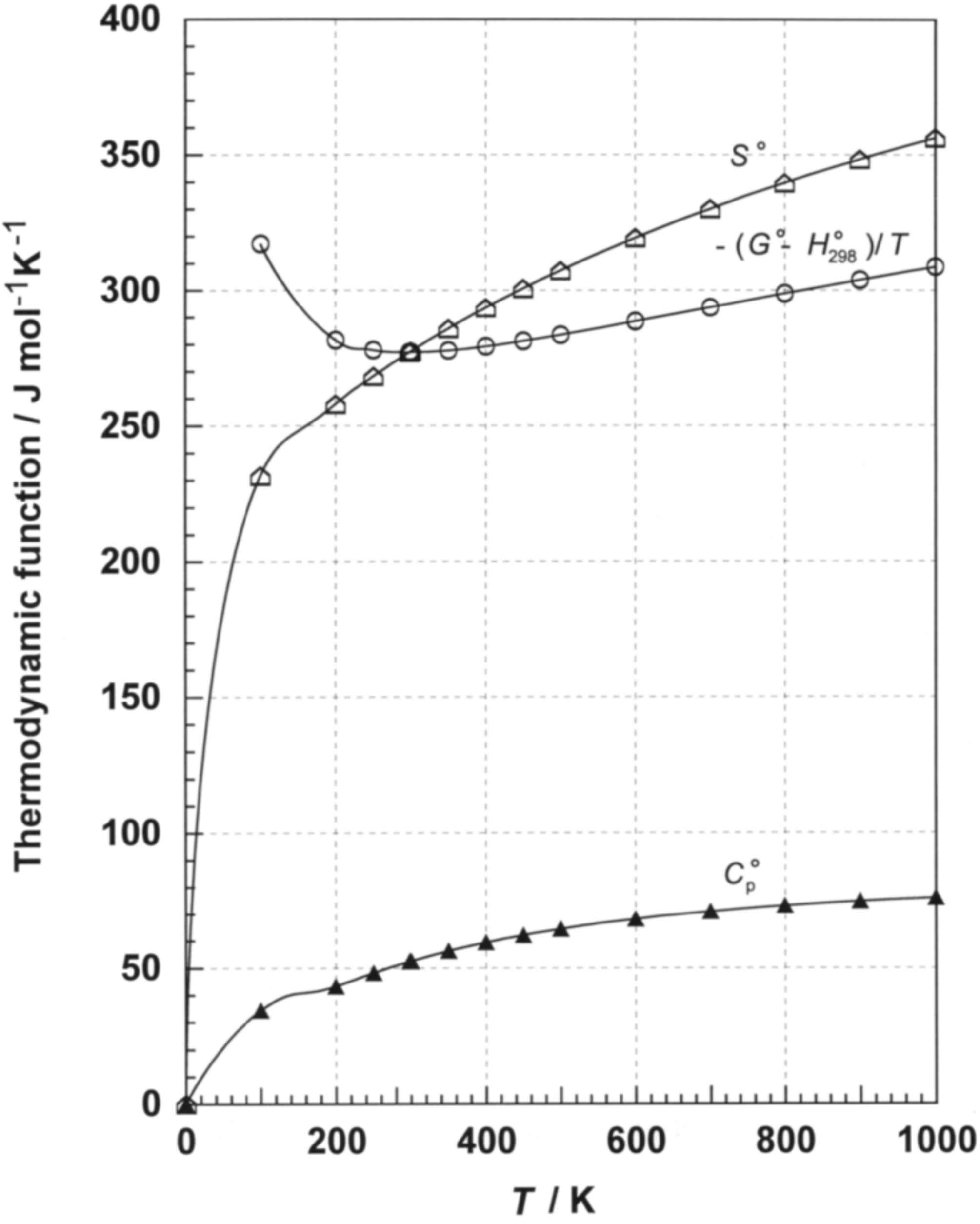


Fig. 16.1 Calculated thermodynamic properties (C_p°, S° and $-(G^\circ - H_{298}^\circ)/T$ on this page; $H^\circ - H_{298}^\circ$, $-\Delta H_f^\circ$, and $-\Delta G_f^\circ$ on facing page) of carbonyl chloride fluoride (ideal gas) in the temperature range of 0–1000 K [359aa].

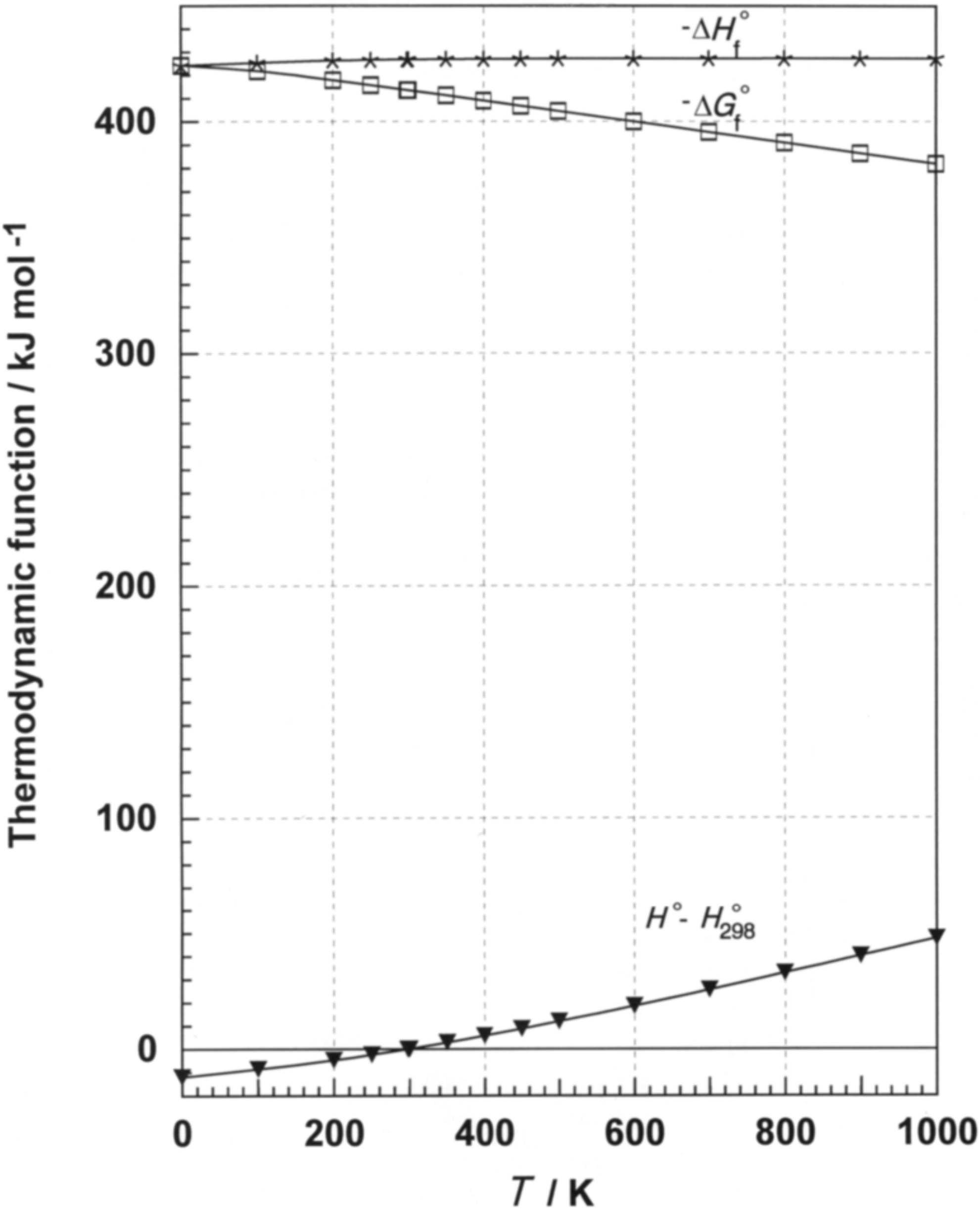

$-\Delta H_f^\circ$
$-\Delta G_f^\circ$
$H^\circ - H^\circ_{298}$
Thermodynamic function / kJ mol -1
0
100
200
300
400
0
200
400
600
800
1000
T / K

TABLE 16.5

THERMODYNAMIC PROPERTIES OF COClF IN THE IDEAL GAS STATE [359aa]

T/K	C_p° [a]	S° [a]	$-(G^\circ-H^\circ_{298})/T$ [a]	$(H^\circ-H^\circ_{298})$ [b]	ΔH_f° [b]	ΔG_f° [b]	$\log_{10}(K_f)$
0	0.000	0.000	∞	-11.904	-424.276	-424.276	∞
100	34.405	231.656	317.256	-8.560	-425.354	-421.790	220.320
200	43.300	257.957	281.526	-4.714	-426.273	-417.838	109.128
250	48.207	268.154	277.852	-2.424	-426.569	-415.693	86.854
298.15	52.396	277.012	277.012	0.000	-426.768	-413.579	72.457
300	52.545	277.337	277.013	0.097	-426.774	-413.497	71.996
350	56.256	285.723	277.667	2.820	-426.915	-411.272	61.379
400	59.407	293.446	279.163	5.713	-427.011	-409.031	53.414
450	62.091	300.602	281.152	8.753	-427.080	-406.779	47.218
500	64.390	307.266	283.434	11.916	-427.133	-404.520	42.260
600	68.086	319.349	288.434	18.549	-427.211	-399.990	34.822
700	70.879	330.064	293.631	25.503	-427.268	-395.448	29.509
800	73.020	339.674	298.796	32.703	-427.313	-390.899	25.523
900	74.684	348.375	303.829	40.091	-427.349	-386.345	22.423
1000	75.993	356.314	308.686	47.628	-427.380	-381.788	19.943
1100	77.036	363.608	313.352	55.281	-427.410	-377.227	17.913
1200	77.876	370.348	317.825	63.028	-427.442	-372.664	16.222
1300	78.561	376.610	322.109	70.851	-427.481	-368.097	14.790
1400	79.124	382.453	326.213	78.736	-427.528	-363.528	13.563
1500	79.593	387.928	330.146	86.673	-427.587	-358.954	12.500
2000	81.060	411.054	347.612	126.884	-428.126	-336.008	8.776
2500	81.783	429.228	362.183	167.613	-429.136	-312.871	6.537
3000	82.188	444.178	374.640	208.615	-430.576	-289.489	5.040
3500	82.437	456.867	385.503	249.776	-432.320	-265.841	3.967
4000	82.600	467.887	395.127	291.038	-434.203	-241.930	3.159
4500	82.713	477.623	403.763	332.368	-436.058	-217.783	2.528
5000	82.794	486.342	411.593	373.745	-437.763	-193.437	2.021
5500	82.854	494.236	418.752	415.158	-439.262	-168.931	1.604
6000	82.900	501.447	425.347	456.597	-440.575	-144.296	1.256

[a] Units of J mol^{-1} K^{-1}. [b] Units of kJ mol^{-1}.

and from 1100 to 4500 K [2189b]:

$$C_p^\circ \text{ /J mol}^{-1}\text{K}^{-1} = 82.7390 + 0.830708 \times 10^{-4}T - 0.731359 \times 10^{7}T^{-2}$$

Between 400 and 1500 K, the values of the specific heat capacity have also been represented by [1078c]:

$$C_p^\circ \text{ /J mol}^{-1}\text{K}^{-1} = 16.93 + 1.247 \times 10^{-2}T - 1.356 \times 10^{6}T^{-2}$$

and between 298 and 1500 K, the standard molar enthalpy increment, $H^\circ - H^\circ_{298}$, has been represented by [2105c]:

$$H^\circ - H^\circ_{298} \text{ /J mol}^{-1} = 63.93T + 6.234 \times 10^{-3}T^2 + 1.356 \times 10^{6}T^{-1} - 24163$$

16.1.5.1.2 Liquid phase

The normal boiling point of COClF has been recorded as −47.2 °C [1196a], although the earliest workers measured −42 °C [1885]. When calculated from the vapour pressure equation, a value of −44.8 °C was obtained [589]. The most recently obtained value is −46 °C [656], but our own measurements [1764] agree with the value of −42 °C.

The vapour pressure of COClF, as a function of temperature, has been represented by [1885]:

$$\log_{10}(p/\text{Pa}) = 10.055 - 1165T^{-1}$$

and, according to [589], by:

$$\log_{10}(p/\text{Pa}) = 10.0484 - 1151.51T^{-1}$$

between −116.5 and −46.3 °C. The most recent estimation of the vapour pressure curve (between −108.9 and −62.4 °C) gives [656]:

$$\log_{10}(p/\text{Pa}) = 10.2298 - 1187.2T^{-1} \qquad (16.3)$$

The experimental curve for these data (Table 16.6) is presented in Fig. 16.2, and yields values of ΔH_{vap} of (22.7±0.8) kJ mol^{-1}, the entropy of vaporization of (100 ± 3) J mol^{-1} K, and a boiling point of −(46±1) °C [656]. From the law of weighted means, using input data from $COCl_2$ and COF_2, these values had been calculated as ΔH_{vap} = 20.3 kJ mol^{-1}, Trouton's constant as 86 J mol^{-1} K^{-1}, and a boiling point of −38 °C [656]. Early data gave the vapour pressures of COClF at −88, −70, −57 and −47.2 °C as 11.92, 32.22, 66.21 and 101.3 kPa, respectively [1196a].

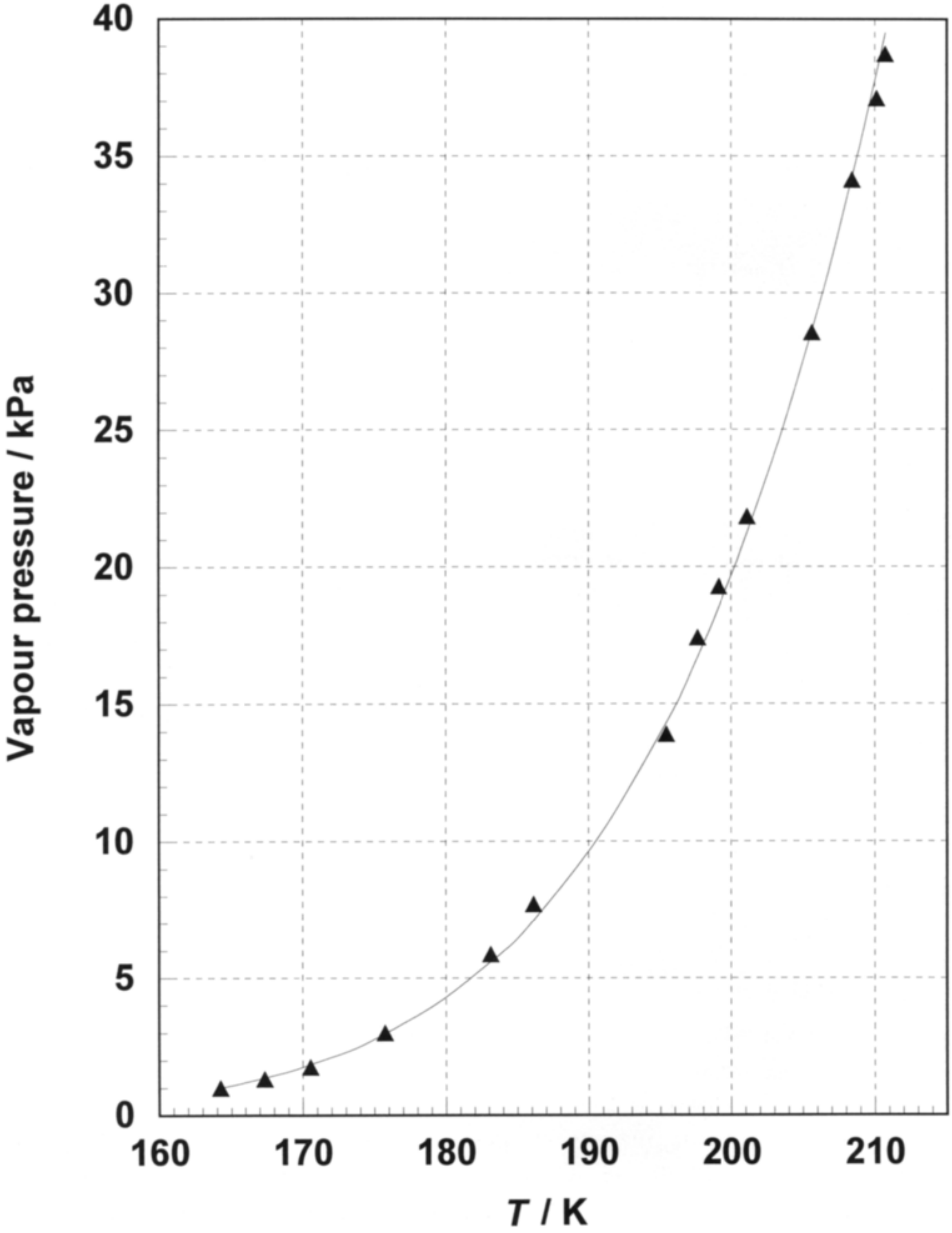


Fig. 16.2 The vapour pressure of liquid COClF as a function of temperature [656]; the experimental points are linked by Equation (16.3).

TABLE 16.6

EXPERIMENTAL VAPOUR PRESSURE OF LIQUID COClF [656]

T / K	p/kPa
164.25	0.986582
167.35	1.319887
170.55	1.759850
175.75	2.999745
183.15	5.866168
186.15	7.706011
195.45	13.89215
197.65	17.41185
199.15	19.27836
201.15	21.83814
205.65	28.54424
208.45	34.13043
210.15	37.10351
210.75	38.71670

16.1.5.1.3 Solid phase

The melting point of COClF has been determined as −148 °C in 1949 [1196a], and as −138 °C in 1966 [843,1885].

16.1.5.1.4 Critical properties

The critical temperature of COClF was estimated as 85 °C [1194,1196a].

16.1.5.1.5 Bond dissociation energies

From the calculated enthalpy of formation (see Section 16.1.5.1.1), the bond dissociation energy D(F–COCl) was estimated to be 487 kJ mol^{-1}, and D(Cl–COF) was estimated to be 356 kJ mol^{-1} [2105c]. The corresponding values for CH_3COF and CH_3COCl, for comparison, are 494 and 347 kJ mol^{-1}, respectively (also see Sections 6.1.4 and 13.8.1.5 for $COCl_2$ and COF_2, respectively).

16.1.5.2 Mechanical properties

The experimental density data for liquid COClF are summarized in Table 16.7 and Fig. 16.3 [656a,1196a].

TABLE 16.7

DENSITY OF LIQUID COClF [1196a]

Temperature/°C	Density/g cm^{-3}
-78	1.506
-50	1.440
-40	1.417
-17	1.362
0	1.323
+18	1.277

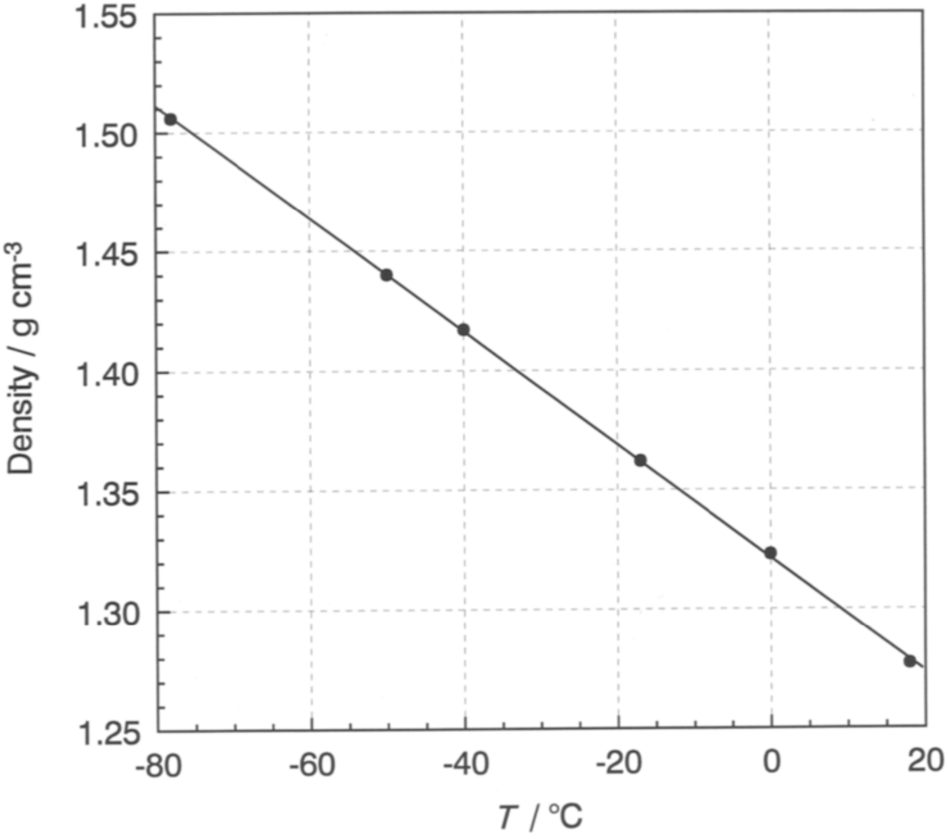


Fig. 16.3 The density of COClF as a function of temperature [656a,1196a].

16.1.5.3 Electrical and magnetic properties

The electric dipole moment of carbonyl chloride fluoride has been measured as ±1.23(1) D (4.103 x 10^{-30} C m) from the Stark effect upon the $0_0 \rightarrow 1_0$, $0 \rightarrow 1_{-1}$ and $1_{-1} \rightarrow 1_1$ rotational transitions [843]. Calculated dipole moments have been given by Oberhammer [1532]: for the molecule superimposed in the *xy* plane, with the C=O bond in the positive *x*-direction and the C-F bond in the positive *y*-direction, the following values were calculated; μ_x = −1.27 D (−4.236 x 10^{-30} C m), μ_y = −0.83 D (−2.769 x 10^{-30} C m) and $|\mu|$ = 1.52 D (5.070 x 10^{-30} C m). A value of 0.92 D (3.07 x 10^{-30} C m) was calculated by the MNDO method [514], in contrast to a very early estimate of 0.1 D (0.33 x 10^{-30} C m) [168a].

The diamagnetic susceptibility anisotropies and molecular second moments of the electronic charge distributions for COClF have been calculated by Maksić and Mikac [1303a], and these authors suggested that their calculated values showed that the experimentally derived second moments (calculated from the Zeeman effect in the Stark-modulated microwave spectrum) of Scappini and Guarnieri [1788] were in error. This indeed proved to be the case, and these values were later corrected by Scappini and Guarnieri, themselves [1789].

16.1.6 Structural determinations

Carbonyl chloride fluoride does not associate in the gas phase [1885], and possesses the expected planar C_s structure. The results of the published structural studies are summarized in Table 16.8: the most reliable determination is the result of the combined electron diffraction and microwave spectroscopic study [1531]. Remarkably, prior to these data being published, the fully optimized geometry calculated by *ab initio* molecular orbital methods [1532] was demonstrated (correctly) to be far superior to the best experimental results available (see Table 16.8). Rather unfortunately, a more recent *ab initio* study [2176a] performed rather less well, but was deemed successful as a very favourable comparison was made with the old, inaccurate experimental data!

The microwave study, using the isotopomers $CO^{35}ClF$ and $CO^{37}ClF$, yielded the ground state rotational constants for the predominant isotopomer, $CO^{35}ClF$, as: A_0 = 11830.31(5), B_0 = 5285.95(5) and C_0 = 3648.59(5) MHz [843a,1411], and for the minor isomer, $CO^{37}ClF$, as: A_0 = 11829.42(5), B_0 = 5127.73(5), and C_0 = 3572.54(5) MHz. The centrifugal distortion constants have also been determined [48a,930,1411,1412].

The principle moments of inertia for COClF, from estimated molecular parameters, are I_a = 7.480 x 10^{-46}, I_b = 1.6008 x 10^{-45} and I_c = 2.331 x 10^{-45} kg m^2 [1280]. More recent estimates [1360c] give I_a = 7.0208 x 10^{-46}, I_b = 1.6378 x 10^{-45}, and I_c = 2.3399 x 10^{-45} kg m^2. The inertia deficiency, ΔI, defined by $\Delta I = I_c - I_b - I_a$, derived from the analysis of the rotation spectrum, is 1.7 x 10^{-40} kg m^2 for $CO^{35}ClF$ and 1.8 x 10^{-40} kg m^2 for $CO^{37}ClF$ [1412]. The inertia defect for COClF (and other planar molecules) has been explained in terms of vibration-rotation interactions and the effect of out-of-plane electrons. The calculated and observed inertia defects for COClF are found to

TABLE 16.8

STRUCTURAL PARAMETERS FOR GASEOUS COClF[a]

Technique	r(CO)/nm	r(CCl)/nm	r(CF)/nm	∡OCCl/°	∡OCF/°	∡ClCF/°	Ref.
m.w.				126.8		107.1	843a
m.w.	0.1162	0.1750	0.1303	117.5	130.5	112.0	1411, 1412
m.w.	0.1172	0.1733	0.1324	126.1	124.7	109.2	930
e.d.	0.1174	0.1724	0.1335	127.2	124.0	108.8	1531
e.d./m.w.	**0.1173**	**0.1725**	**0.1334**	**127.5**	**123.7**	**108.8**	**1531**
e.d./m.w.		0.172433	0.133429				48a
ab initio	0.1175	0.1731	0.1345	126.6	123.5	109.9	1531[b]

[a] Enboldened data are recognized as the best set. [b] The results calculated in [1532] (prior to the results of the experimental study) had not fully converged.

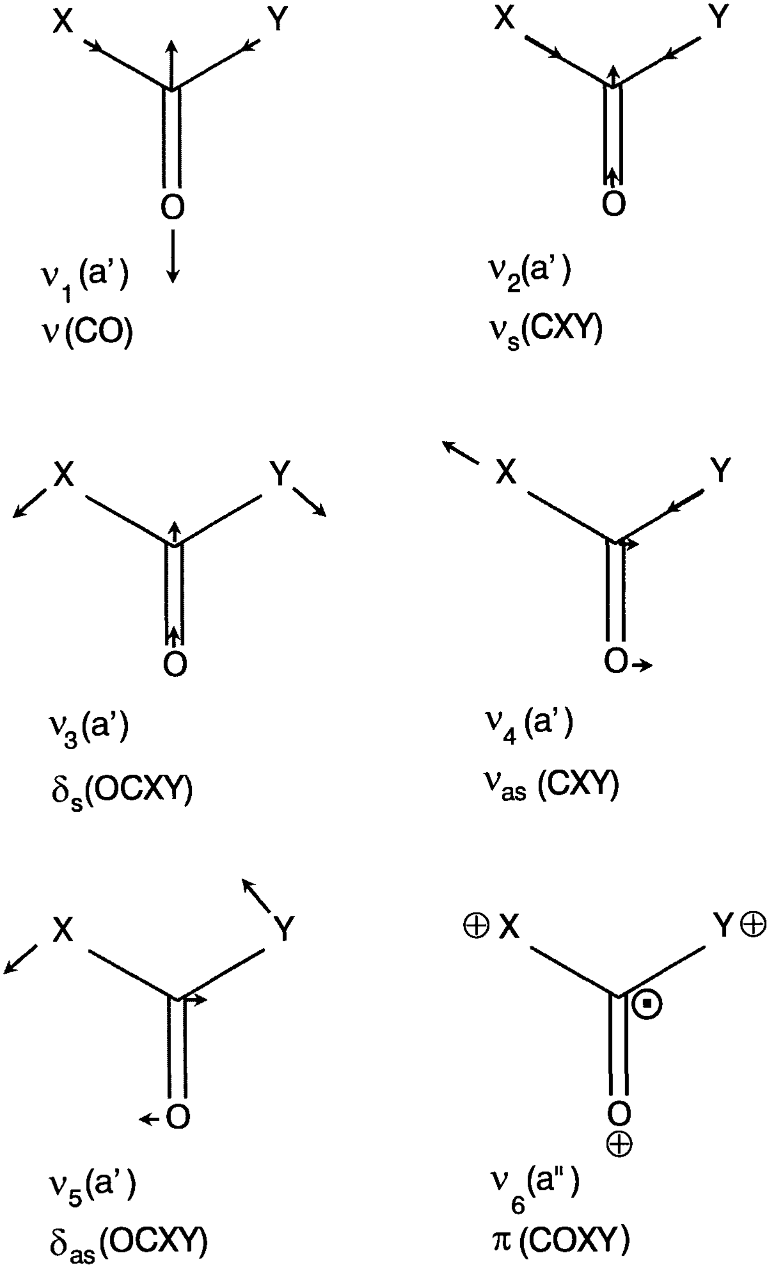
be in agreement [1549]. The nuclear quadrupole coupling constants (eqQ) of CO^{35}ClF and CO^{37}ClF were derived from the hyperfine splitting in the rotation spectrum. For CO^{35}ClF; $eq_{aa}Q$ = −73.7(5) and $eq_{bb}Q$ = 44.5(5), for CO^{37}ClF; $eq_{aa}Q$ = −58.04(50) and $eq_{bb}Q$ = 29.68(50) MHz. These values indicate a high degree of covalent bonding.

16.1.7 Molecular and spectroscopic properties

16.1.7.1 Vibrational spectroscopy

COClF possesses C_s symmetry (see Appendix A4), and the fundamental vibrational modes, their symmetry and activity are illustrated in Fig. 16.4, for a general COXY molecule. Thus, the planar COClF molecule has six normal modes of vibration, all of which are infrared and Raman active. ν_1 to ν_5 belong to the A' irreducible representation, and ν_6 belongs to A". The ν_1 mode corresponds to the carbonyl stretching frequency, ν_2 is often described as ν(CCl), and ν_4 is frequently described as ν(CF). ν_3 and ν_5 represent the in-plane bending modes, and ν_6 represents the out-of-plane bending mode [1578]. The numbering of the modes ν_1 to ν_5 is rather unconventional, but has been adopted to aid comparison with the vibrational analyses of COCl$_2$, COF$_2$ and COBr$_2$ (see Sections 7.2, 13.10.1 and 14.5). In view of the early controversy over the assignments of ν_3 and ν_5 for COF$_2$ (see Section 13.10.1), the assignments of ν_3 and ν_5 for COClF must be regarded with caution.

The infrared bands of gaseous COClF [1051,1508] are summarized in Table 16.9, along with their assignments (*n.b.* the infrared spectrum of gaseous COClF has also been included in



$\nu_1(a')$ $\nu(CO)$

$\nu_2(a')$ $\nu_s(CXY)$

$\nu_3(a')$ $\delta_s(OCXY)$

$\nu_4(a')$ $\nu_{as}(CXY)$

$\nu_5(a')$ $\delta_{as}(OCXY)$

$\nu_6(a'')$ $\pi(COXY)$

Fig. 16.4 The fundamental vibrations of a general asymmetrical carbonyl halide, COXY.

TABLE 16.9

INFRARED DATA (units of cm^{-1}) FOR COClF^a

	Medium	$\nu_1(a')$ $\nu(CO)$	$\nu_2(a')$ $\nu_s(CXY)$	$\nu_3(a')$ $\delta_s(OCXY)$	$\nu_4(a')$ $\nu_{as}(CXY)$	$\nu_5(a')$ $\delta_{as}(OCXY)$	$\nu_6(a'')$ $\pi(COX_2)$	$\nu_2+\nu_4$	Ref.
COClF	**gas**	**1868^b**	**776**	**501**	**1095**	**415**	**667**	**1847**	**1508**
COClF	gas	1867^b	776	501	1095	415	665		1051

^{a}Enboldened data are recognized as the best set. ^{b}This frequency is corrected for Fermi resonance with ($\nu_2+\nu_4$): the observed band is at 1876 cm^{-1}.

TABLE 16.10

RAMAN DATA (units of cm^{-1}) FOR COClF^a

	Medium	$\nu_1(a')$ $\nu(CO)$	$\nu_2(a')$ $\nu_s(CXY)$	$\nu_3(a')$ $\delta_s(OCXY)$	$\nu_4(a')$ $\nu_{as}(CXY)$	$\nu_5(a')$ $\delta_{as}(OCXY)$	$\nu_6(a'')$ $\pi(COX_2)$	$\nu_2+\nu_4$	Ref.
COClF	**Liquid**	**1858**	**765**	**506**	**1085**	**410**	**665**	**1832**	**1508**
COClF	Liquid	1832	765	506	1085	410	665	1856	1051

^{a}Enboldened data are recognized as the best set.

a standard catalogue of common molecules [1462a]). The ν_2, ν_4 and ν_5 bands have P, Q and R branches and the ν_3 band appears to be a doublet. The observed frequencies of liquid COClF in the Raman spectrum are recorded in Table 16.10 [1051,1508]. In addition to the fundamental vibrations, the combination band, ($\nu_1+\nu_4$) was also observed in the Raman spectrum at about 213 K.

Force constant and inertia defect calculations have been performed for COClF [604,1312,1531,1549,1550,1575–1578]. CNDO calculations have been used to calculate ν(C=O) for COClF [1680], and the fundamental frequencies for COClF have been calculated from the force constants calculated for COX_2 (X = F, Cl or Br) [1578].

16.1.7.2 Nuclear magnetic resonance spectroscopy

The n.m.r. spectra of COClF are discussed in detail in Section 7.3. The ^{13}C, ^{19}F and ^{17}O n.m.r. chemical shifts of COClF in CCl_3F have been measured as 139.9, 60.0 and 375.1 p.p.m. with respect to TMS, CCl_3F and water, respectively [797,1589b].

16.1.7.3 Mass spectrometry

The mass spectrum of COClF is detailed in Table 16.11.

TABLE 16.11

MASS SPECTRAL DATA FOR COClF [1b,1071]

m/z	Relative Intensity		Assignment
	[1b]	[1071]	
84,82	64	34	M^+
65,63	57	18	$[COCl]^+$
47	100	100	$[COF]^+$
37,35	16	17	Cl^+
28	7	21	$[CO]^+$

The gas-phase ion chemistry of COClF has been studied by ion cyclotron mass spectrometry, and the relative abundance of the primary negative ions: X^-, $[X_2]^-$ and $[XCO]^-$ (X = F or Cl) formed by electron impact was measured. The electron energy dependence of the dissociative electron attachment cross-sections for the negative ion formation was determined [1071,1073].

16.1.8 Inorganic reactions

Despite its molecular simplicity, the known inorganic chemistry of COClF is even more scant than that of phosgene. Only one coordination compound is known and, in particular, there appear to be no reports of the reactions of COClF with metal oxides, even though phosgene has been used, industrially, to prepare many anhydrous metal chlorides from the corresponding oxides.

16.1.8.1 Miscellaneous reactions

COClF is reported not to attack aluminium, brass or stainless steel. It is only slightly reactive towards nickel, ™Monel, tin, zinc and Mg–Al alloys, but reacts with iron, copper, lead, silver and mercury [1194,1751].

COClF is reported not to react with glass [1883a,1885], although Kwasnik reported that glass and quartz become cloudy, and rubber becomes hard, upon exposure to it [1751]. Our own observations are that glass is not attacked, providing that the COClF is kept dry [1589b]. COClF was noted to be hydrolysed in water within thirty minutes, and to be quickly absorbed by aqueous sodium hydroxide solution [1751], or by soda lime, $NaOH–Ca(OH)_2$ [1883a,1885]. The reaction between carbonyl chloride fluoride and aqueous base can be represented by [1197]:

$$COClF + 4[OH]^- \longrightarrow Cl^- + F^- + [CO_3]^{2-} + 2H_2O$$

and can be employed as the basis for volumetric analysis [1197].

On prolonged contact with SO_3 at −35 °C, COClF appears to react according to the stoicheiometry [ICI114]:

$$COClF + SO_3 \longrightarrow CO_2 + SO_2ClF$$

COClF is said to react with phosphorus(V) halides upon heating in an autoclave, according to [903]:

$$COClF + PCl_5 \longrightarrow CCl_3F + POCl_3$$
$$COClF + PF_3Cl_2 \longrightarrow CCl_3F + POF_3$$

These reactions are very unlikely to yield clean products, however.

The interaction between COClF and SbF_5 has been investigated in SO_2ClF by ^{19}F n.m.r. spectroscopy [99]. In dilute solution, the ^{19}F n.m.r. spectroscopic data were interpreted in terms of the formation of $SbF_5.COClF$ at −95 °C; at higher temperatures, or in more concentrated solutions, halide exchange occurs, and COF_2 and $SbF_5.COF_2$ were detected [99]. The same adduct is also formed, as a by-product, in the reaction between phosgene and SbF_5 in SO_2ClF (see Section 9.1.4.4) [1653c]: the COClF ligand is *O*-bonded.

Finally, COClF reacts with dry sodium azide to form $C(O)(N_3)F$ – an explosive material, only to be handled with proper safety precautions in millimolar quantites [1292a].

16.1.8.2 Dissociation, disproportionation, dismutation and exchange reactions

Heating COClF between 400–600 °C in an autoclave induces disproportionation, as represented by Equation (16.4) [1454]:

$$2COClF \rightleftharpoons COCl_2 + COF_2 \qquad (16.4)$$

The effect of the disproportionation reaction, Equation (16.4), is that, in reactions of phosgene which can produce both COF_2 and COClF, high temperatures favour the formation of COF_2 and low temperatures favour the formation of COClF.

A secondary dismutation reaction, Equation (16.5), may also occur [899], and the conditions for the synthesis of dichlorodifluoromethane by this route have been optimized, but the yield remains low [900,902,905]:

$$2COClF \longrightarrow CCl_2F_2 + CO_2 \tag{16.5}$$

In the presence of calcium fluoride, the products of this treatment include COF_2 (20%), COClF (35%), $COCl_2$ (10%), CO_2 (15%), CF_3Cl (5%) and CF_2Cl_2 (2%) [1454], and in the presence of iron(III) chloride at 425 °C, the product distribution was CCl_2F_2 (13%), $CClF_3$ (38%) and CF_4 (13%) [900].

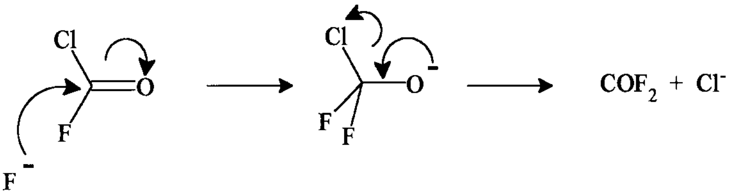
When heated to 425 °C for 19 h, in the presence of a silicate-free activated carbon catalyst impregnated with iron(III) chloride, COClF disproportionates to the extent of 13% into CCl_2F_2, 38% into $CClF_3$, and 13% into CF_4. The $CClF_3$ is believed to form from the following series of equilibria:

$$2COClF \rightleftharpoons COF_2 + COCl_2$$
$$COClF + COF_2 \rightleftharpoons CClF_3 + CO_2$$

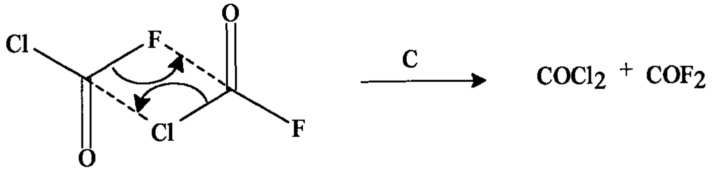
and CF_4 is thought (possibly) to arise from the disproportionation reaction:

$$2CClF_3 \rightleftharpoons CF_4 + CCl_2F_2$$

Although the disproportionation reaction, Equation (16.4), has been noted to occur at elevated temperatures (*e.g.* 500 °C under autogenous pressure for 1–2 h) [1454,2069], in the presence of a charcoal catalyst the reaction proceeds (in a flow system) even at room temperature [85a,ICI110]. The rate at which the reaction reaches the equilibrium position (about 40% at room temperature) increases with temperature. The reaction is catalysed to a far lesser degree using high surface area silica (see also Section 13.7.6), and the disproportion is noted to be strongly inhibited in the presence of a large excess of phosgene, as predicted by equilibrium calculations [1764]. The observation that this reaction, Equation (16.4), takes place at room temperature is indeed remarkable, since the C–F bond dissociation energy in CF_4, for example, is 546 kJ mol^{-1}, and the bond dissociation energy *D*(F–COCl) was estimated to be 487 kJ mol^{-1} for COClF [2105c]. It is possible that the reaction is initiated by fluoride ion adsorbed onto the charcoal:



Whilst this mechanism may explain the formation of COF_2, the formation of phosgene is more difficult to explain. It has been suggested [111aa] that COClF may be adsorbed at the charcoal surface, and that an exchange of fluoride and chloride may then occur, involving a bridged transition state without formally breaking the C–F bond:



In analogous reactions to Equation (16.5), heating COClF with $COBr_2$, COF_2 or $COCl_2$ in an autoclave produces CBr_2ClF, $CClF_3$ or CCl_3F, respectively [902,905].

$$COClF + COBr_2 \longrightarrow CBr_2ClF + CO_2$$

$$COClF + COF_2 \longrightarrow CClF_3 + CO_2$$

$$COClF + COCl_2 \longrightarrow CCl_3F + CO_2$$

16.1.8.3 Photo–oxidation

Phosgene derivatives have been found to be major products from the photo–oxidation of chlorofluorohydrocarbons, and the production of COClF from $CHCl_2F$ and from CCl_3F has been noted in Section 4.3.2. The collisional quenching of atomic oxygen (2 $^1D_2$) by COClF was measured spectroscopically, and found to have a second–order rate constant of 3.7(4) x 10^{-10} cm^3 molecule^{-1} s^{-1} at 300 K. This value is lower than the corresponding rate constants observed for phosgene, 7.1(9) x 10^{-10} cm^3 molecule^{-1} s^{-1}, or for carbonyl difluoride, 4.6(4)x 10^{-10} cm^3 molecule^{-1} s^{-1}) [660]. Doubt has been cast [2199] upon Fletcher and Husain's observation [660] that COClF reacts with electronically excited oxygen atoms O($^1D_2$) more slowly than does COF_2, given the relatively facile nature of the chlorine abstraction reaction: it is most probable that it is their COF_2 data that is in error (see Section 13.13.3.1). Earlier workers had determined COClF to be 2.34 times more effective at quenching O($^1D_2$) than COF_2 [1038]. According to another source [1808], the recommended rate constant value for the reaction between COClF and O (2$^1D_2$) at 298 K is 3.4(7) x 10^{-10} cm^3 molecule^{-1} s^{-1}.

Some reaction is found to occur between O(^{1}D) atoms (produced from the photolysis of ozone at 253.7 nm and 25 °C) and COClF, as indicated by the high value of the quantum yield for ozone removal. However, no products were found (although analysis was not made for CO_2 which could be the major product), unlike the $COCl_2$ – O(^{1}D) reaction, in which evidence was obtained for the formation of both CO and chlorine oxides [1038]. The rate constant for the reaction of COClF with O(^{1}D) atoms was estimated to be 2.8 times the value obtained for the reaction of O(^{1}D) with N_2O [88]. The quantity of stratospheric HF derived from COClF has been calculated from the rate of photolysis. The ratio of HF:HCl at between 20 and 30 km is found to depend upon the prevailing hydroxyl ion concentration [1994].

16.1.8.4 "Gedanken" experiments

The protonation of COClF has been studied by *ab initio* techniques, using a 4-31G basis set [1073a,1950b]; a proton affinity of 640 kJ mol^{-1} was calculated [1950b].

16.1.8.5 Electron and ion cyclotron resonance studies

As seen for phosgene (see Section 9.12.1.2), ion cyclotron resonance spectrometry is becoming a valuable tool for studying the gas phase reactions of COClF with a wide range of ions.

At 30–70 eV, five primary ions are formed by electron impact [1071]:

$$\mathrm{COClF} + e^- \longrightarrow \mathrm{Cl}^- + [\mathrm{COF}]\cdot$$

$$\mathrm{COClF} + e^- \longrightarrow \mathrm{F}^- + [\mathrm{COCl}]\cdot$$

$$\mathrm{COClF} + e^- \longrightarrow [\mathrm{ClF}]^- + \mathrm{CO}$$

$$\mathrm{COClF} + e^- \longrightarrow [\mathrm{COCl}]^- + \mathrm{F}\cdot$$

$$\mathrm{COClF} + e^- \longrightarrow [\mathrm{COF}]^- + \mathrm{Cl}\cdot$$

The most abundant of these ions (at 70 eV) is Cl^- (80.9%), followed by $[ClF]^-$ (14.2%), $[COCl]^-$ (2.3%), $[COF]^-$ (1.0%) and F^- (0.8%) [1071]; a small amount of $[Cl_2]^-$ is also observed. In phosgene, these ions are formed at near thermal energies (<1 eV); for COClF, the resonance maxima occur between 1.85 and 2.4 eV [1071].

The secondary negative ions, $[COClF_2]^-$ and $[COCl_2F]^-$, are formed in four parallel processes [1071]:

$$\mathrm{COClF} + [\mathrm{COF}]^- \longrightarrow [\mathrm{COClF_2}]^- + \mathrm{CO}$$

$$\mathrm{COClF} + [\mathrm{COCl}]^- \longrightarrow [\mathrm{COCl_2F}]^- + \mathrm{CO}$$

$$\mathrm{COClF} + [\mathrm{ClF}]^- \longrightarrow [\mathrm{COClF_2}]^- + \mathrm{Cl}\cdot$$

$$\mathrm{COClF} + [\mathrm{ClF}]^- \longrightarrow [\mathrm{COCl_2F}]^- + \mathrm{F}\cdot$$

The i.c.r. experiments suggest upper limits on the enthalpy of formation for $[COClF_2]^-$ of −753 kJ mol^{-1} and for $[COCl_2F]^-$ of −674 kJ mol^{-1} [1071].

16.1.9 Organic reactions

The organic chemistry of COClF has been limited to the study of its reactions with alcohols, cyclic ethers, thiophenol, dmso, and a few amines. No reactions at a carbon centre, for example, have been examined despite the multiplicity of interesting compounds that might be expected.

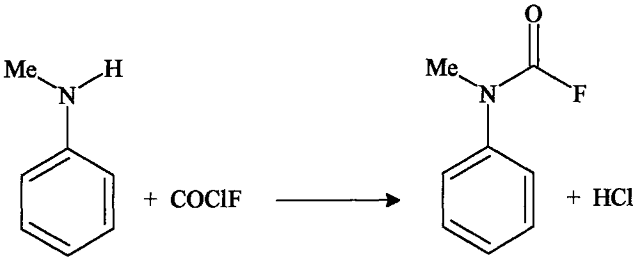
16.1.9.1 Reactions at a nitrogen centre

Although the most extensively recorded aspect of phosgene chemistry is its interaction with compounds at a nitrogen centre, only three reactions of carbonyl chloride fluoride with amines have been reported. No reports have appeared concerning the reactions of COClF with tertiary amines, amino acids, hydrazine derivatives, imino compounds or nitrogen-containing heterocycles, to name but a few unstudied reagents.

A vigorous reaction is observed between an ethereal solution of diethylamine and COClF even at −78 °C [589]. The product consisted of a mixture of diethylcarbamyl fluoride and diethylamine hydrochloride, which was separated by distillation:

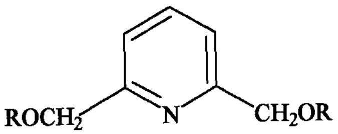
$$2Et_2NH + COClF \longrightarrow Et_2NC(O)F + [NEt_2H_2]Cl$$

N-methylaniline also was found to react at low temperature with COClF [589], to give a high yield of the corresponding carbamyl fluoride (16.2):



(16.2)

Treatment of (16.3; R = H) with COClF and R'NH$_2$ gave (16.3; R = CONHMe or CONHEt), depending upon whether R' = Me or Et [1010].



(16.3)

16.1.9.2 Reactions at an oxygen centre

Phosgene is reported to combine with a wide range of oxygenated materials, including alcohols, ethers, ketones, carboxylic acids, anhydrides, lactones, esters, carbonic acid derivatives, *etc.* Only the reactions of COClF with alcohols, phenols and cyclic ethers have been reported, resulting usually in the generation of fluoroformates. Such materials can often be usefully converted into the corresponding fluoro compound by means of decarboxylation in the presence of BF_3, Et_2O, pyridine, or other materials.

16.1.9.2.1 Aliphatic and alicyclic alcohols

Ethanol combines with COClF at low temperature to give predominantly ethyl fluoroformate: some diethyl carbonate is also produced. No base catalyst is required for the reaction [589]:

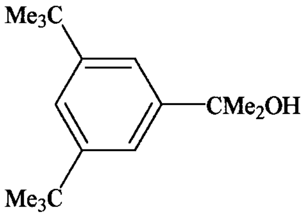
$$CH_3CH_2OH + COClF \longrightarrow CH_3CH_2OC(O)F + HCl$$

$$2CH_3CH_2OH + COClF \longrightarrow (CH_3CH_2O)_2C{=}O + HCl + HF$$

t-Butyl fluoroformate was obtained from the reaction of COClF with *t*-butanol at about −25 °C. Similar results were obtained when the reaction was carried out in a solvent (CCl_3F), or in the presence of an acid acceptor [1803,2137]:

$$(CH_3)_3COH + COClF \longrightarrow (CH_3)_3COC(O)F + HCl$$

The tertiary alcohol (**16.4**) reacts with COClF in the presence of NEt_3 to give the corresponding fluoroformate [2121].



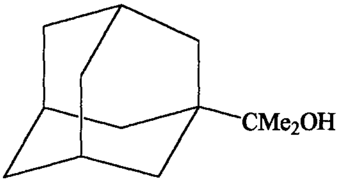
(16.4)

Reaction of a benzene solution of $HOCH_2CH_2OH$ with COClF in the presence of a tributylamine catalyst for 12 h at 20 °C gave a yield of 99% $FC(O)OCH_2CH_2OC(O)F$ and 1% of ethylene carbonate [384,379]. Treatment of this bis(fluoroformate) with $BF_3.OEt_2$ at 120 °C gave 1,2-difluoroethane in a yield of 28.6% [379]. This reaction can be extended to include other polyhydric alcohols from which polyfluoroformates may be generated [384]:

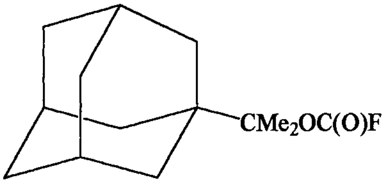
$$R\{C(OH)H\}_nR' + nCOClF \longrightarrow R\{C[OC(O)F]H\}_nR' + nHCl$$

Aliphatic or alicyclic fluoroformates may be prepared continuously from the reaction of the corresponding alcohols with a mixture of carbonyl halides (*e.g.* COF_2, COClF and $COCl_2$ at −20 to +80 °C in the presence of isobutene, which acts as a hydrogen halide acceptor). The process was illustrated using methanol, *t*-butanol and cyclohexanol as examples [1118].

1-Adamantyl fluoroformate was prepared with a yield of 91% by acylating 1-adamantanol with COClF [1436]. Adamantylisopropanol, (16.5), when treated in dichloromethane or diethyl ether with COClF in the presence of triethylamine, gave (16.6) in a yield of greater than 90% [1063,1070,2120].



(16.5)



(16.6)

16.1.9.2.2 Phenols

Simple aromatic fluorocompounds are not easily prepared in a high yield: in contrast with the direct aromatic substitution reactions of elemental chlorine or bromine, direct fluorination cannot be generally employed owing to the difficulties of handling and controlling reactions involving elemental fluorine. Halogen exchange chemistry, often applied to the preparation of aliphatic fluorides, cannot be used in the preparation of aromatic fluorides unless the aromatic substrate is suitably activated by strongly electron-withdrawing groups, such as $-NO_2$. The traditional methods of synthesis employ the Balz–Schiemann reaction [109b], involving the decomposition of diazonium tetrafluoroborates [1980a]:

$$[ArN_2][BF_4] \xrightarrow{\Delta} ArF + BF_3 + N_2$$

or a modification of conventional diazotization using a large excess of anhydrous hydrogen fluoride [1573aa]. Although these processes are frequently employed in large-scale industrial syntheses, they suffer from the disadvantage that the yields are often mediocre and the reaction mixtures are excessively corrosive.

Dinitrogen and carbon dioxide are considered to be similar leaving groups [144a], and the evolution of CO_2 from a carboxylium salt, such as $[ArOC(O)]^+F^-$, should provide a large exothermic driving force, similar to that obtained by the elimination of N_2 from the diazonium salt, $[ArN_2]^+F^-$. Indeed, the catalytic decarboxylation of alkyl fluoroformates to the corresponding alkyl fluorides has been achieved by using pyridine or boron(III) fluoride etherate as the catalyst [378]. Aryl fluoroformates, however, are much more resistant to decarboxylation, and the use of tertiary amines and of BF_3 or $BF_3.OEt_2$ catalysts has been shown to be ineffective [380].

The thermal decomposition of aryl fluoroformates was examined by Christe and Pavlath (using a platinum gauze catalyst) [380–383], who found that temperatures typically in the range of 700–800 °C were required in order to produce the most favourable yields of the corresponding fluorides. These temperatures, however, are considered to be beyond the scope of common industrial practice. More recently, the decarboxylation of phenyl fluoroformate, for example, has been achieved in a flow system, employing alumina catalysts, at temperatures of around 300 °C [86,87].

COClF combines with phenol or sodium phenolate (toluene solutions) under a variety of conditions, and preferably in the presence of a tertiary amine catalyst:

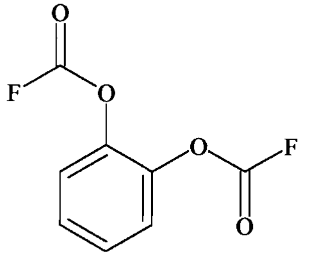
$$COClF + C_6H_5OH \longrightarrow C_6H_5OC(O)F + HCl$$

By using a three molar equivalent of COClF at 50 °C and 1.3 Mpa, over 5 h in the presence of tributylamine, a conversion of 97.2% of phenol with 99.9% yield of phenylfluoroformate was obtained [380]. Phenyl fluoroformate may be decarboxylated to give fluorobenzene:

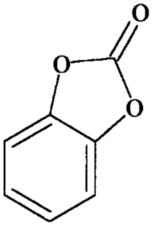
$$C_6H_5OC(O)F \longrightarrow C_6H_5F + CO_2$$

At higher pressures (1.9 MPa) and temperatures (80 °C), and using concentrated solutions over extended contact times (15 h), the yield of phenyl fluoroformate was reduced to 54.3%, accompanied by a yield of diphenyl carbonate of 45.7% [380].

Treatment of a benzene solution of catechol, C_6H_4-1,2-$(OH)_2$, with COClF at room temperature gave the bis(fluoroformate) (**16.7**) in a yield of about 50%. (**16.7**) partially decomposes to the cyclic carbonate (**16.8**), but could not be decarboxylated to the corresponding 1,2-difluorobenzene by the use of BF_3-containing catalysts [379]. Resorcinol, C_6H_4-1,3-$(OH)_2$, and hydroquinone, C_6H_4-1,4-$(OH)_2$, react with COClF, preferably in the presence of a tertiary amine, to give an almost quantitative yield of the corresponding bis(fluoroformates) [382]. Phloroglucinol, C_6H_3-1,3,5-$(OH)_3$, and COClF combine similarly to form C_6H_3-1,3,5-$(OCOF)_3$ with a yield of 65.5% [382]. The reaction of COClF with 2,4,6-tribromophloroglucinol, $C_6Br_3(OH)_3$, in the presence of tributylamine in benzene at 100 °C over 20 h, gave only an intractable oil [382].



(16.7)



(16.8)

Quantitative yields of fluoroformates are obtained from the reactions of substituted phenols (dissolved in toluene or benzene) with COClF in the presence, preferably, of a tertiary amine catalyst [381], see Table 16.12.

TABLE 16.12

SOME REACTIONS OF COClF WITH SUBSTITUTED PHENOLS [381]

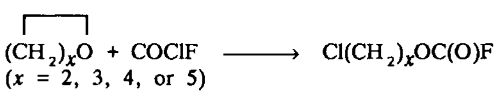
Phenol	T / °C	Reaction time / h	Conversion [a] / %	Yield [b] / %
2-Bromo	100	24	99.9	100
4-Bromo	70	12	100	99.9
2-Fluoro	60	12	100	100
4-Fluoro	60	16	100	99
4-Trifluoromethyl	70	12	99	100
4-Methoxy	60	18	100	99
1-Napthylfluoroformate	60	14	100	99
4-Methyl	60	15	100	99

[a] Based on phenol. [b] Of fluoroformate.

Thermal decarboxylation of the resulting fluoroformate derivatives at around 700–800 °C gave the corresponding substituted fluorobenzene, in yields of up to about 50% [381]. 2,4,6-Trimethylphenyl fluoroformate was prepared in quantitative yield by the slow passage of COClF into a solution of 2,4,6-trimethylphenol in toluene at about 60 °C: 4-chlorophenyl fluoroformate was prepared similarly [86,87], except that a small quantity of NEt_3 was added to the 4-chlorophenol solution.

16.1.9.2.3 Cyclic ethers

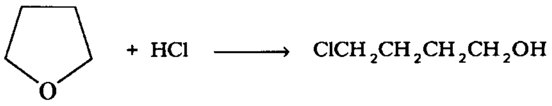
COClF is noted to have a greater reactivity towards cyclic ethers than has $COCl_2$ or COF_2. ω-Chloroalkyl fluoroformates (useful for the preparation of ω-chloroalkyl fluorides or ω-fluoroalkenes) are produced in good yields when COClF combines with ethylene oxide, trimethylene oxide, tetrahydrofuran, or tetrahydropyran [378,386].



$$(CH_2)_xO + COClF \longrightarrow Cl(CH_2)_xOC(O)F$$

$(x = 2, 3, 4, \text{ or } 5)$

Further improved yields may be obtained in the presence of a tertiary amine catalyst, which are known to complex with carbonyl halides; for the higher-membered rings, the addition of a catalytic amount of HCl is beneficial. With tetrahydrofuran, for example, the following sequence of reactions is believed to take place:



$$Cl(CH_2)_4OH + COClF \longrightarrow Cl(CH_2)_4OC(O)F + HCl$$

However, since the ω-chloroalkyl fluoroformate may also be formed in the absence of hydrogen chloride (albeit in lower yield), it may be assumed that the reaction can proceed directly, without formation of the intermediate alcohol.

The reactivity order is:

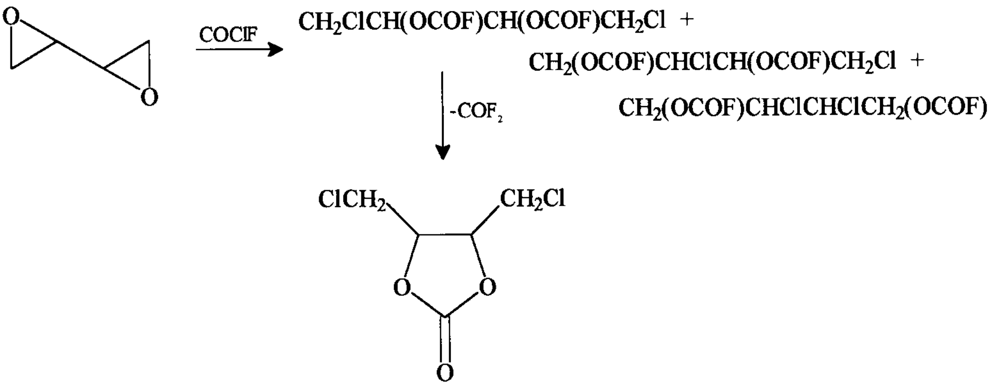
ethylene oxide > trimethylene oxide > tetrahydrofuran > tetrahydropyran

and is in accord with that expected on the basis of decreasing ring strain [378].

The substituted ethylene oxides (propylene oxides and butadiene monoxide) react with COClF in the presence of tributylamine, as illustrated below [378]:

(R = CH_3 or $CH_2{=}CH$)

With butadiene dioxide, all of the theoretically possible isomers are formed, in addition to the COF_2-elimination product [378]:



16.1.9.2.4 Aldehydes (Alkanals)

The reactions of COClF with aldehydes has been particularly examined in ICI [ICI117,ICI118].

The reaction of methanal with COClF has been examined in both the gas and liquid phase. In the liquid phase, in the presence of a catalytic amount of a tertiary amine in toluene, the novel fluoroformate $CH_2ClOC(O)F$ is produced and undergoes subsequent rapid decarboxylation over an alumina catalyst at >100 °C to give a high yield (*ca.* 95%) of CH_2ClF [ICI118].

The reaction between CH_2O and COClF is catalysed in the gas phase using an activated charcoal and alumina catalyst, held in series, at about 125 °C. Under these conditions, the major reaction product is CH_2ClF (*n.b.* this is highly toxic; OEL ≈ 10 p.p.b.), formed with a selectivity of 71.5% [ICI118]. The lower yield (compared to the two-stage reaction above) is a result of the competing disproportionation reaction, which is also catalysed by charcoal (Section 16.1.8.2) [ICI118], although careful choice of the reaction conditions enables the latter reactions to be minimized.

Depending upon the reaction conditions, ethanal can combine with phosgene to produce 1,1-dichloroethane, chloroethene, vinyl chloroformate or 1-chloroethyl chloroformate (see Section 10.3.3.1). However, under conditions which produce 1,1-dichloroethane from phosgene and ethanal (charcoal catalyst, 150 °C), carbonyl difluoride reacts (using a charcoal catalyst impregnated with caesium fluoride) to produce a mixture of the saturated 1-fluoroethyl fluoroformate and the unsaturated vinyl fluoroformate (see Section 13.14.6.3.1). Thus, the COF_2/CH_3CHO/charcoal system is unstable with respect to dehydrofluorination, whilst the $COCl_2/CH_3CHO$/charcoal system is unstable with respect to decarboxylation:

$$CH_3CHO + COCl_2 \xrightarrow[150\ ^\circ C]{C} CH_3CHCl_2 + CO_2$$

$$CH_3CHO + COF_2 \xrightarrow[150\ ^\circ C]{CsF/C} CH_2{=}CHOC(O)F + HF$$

In contrast, in the gas phase over a charcoal catalyst, COClF reacts with ethanal between 128 and 205 °C to produce 1-chloroethyl fluoroformate along with a smaller quantity of the dehydrochlorinated material, vinyl fluoroformate [ICI16A16A]:

$$CH_3CHO + COClF \longrightarrow CH_3CHClOC(O)F$$

$$CH_3CHO + COClF \longrightarrow CH_2{=}CHOC(O)F + HCl$$

The reaction is accompanied by disproportionation (see Section 16.1.8.2), and as a result both 1,1-dichloroethane and $CH_3CHClOC(O)Cl$, were detected from the further reactions of the phosgene with ethanal [ICI117]. The same reactions occur, but to a much lesser degree, when carried out in an empty tube or in the presence of a silica catalyst [ICI117].

In the liquid phase, at ambient temperature, and in the presence of triethylamine in toluene, the disproportion reaction is avoided and 1-chloroethyl fluoroformate is produced in a yield of >80% (the yield of vinyl fluoroformate is 3.8%) [ICI117].

16.1.9.3 Reactions at a sulfur centre

Treatment of a thiol or thiophenol with carbonyl chloride fluoride in the presence of a tertiary amine (in an inert solvent such as heptane) results in the formation of the corresponding thiol fluoroformate in 75–85% yield [1555a]:

$$\mathrm{RSH + COClF \longrightarrow RSC(O)F + HCl}$$

$$\mathrm{(R = Me,\ Et,\ Pr,\ Me_2CH,\ Br,\ Ph,\ 4\text{-}ClC_6H_4,\ or\ 4\text{-}FC_6H_4)}$$

In particular, in benzene solution at 50 °C and 1.3 MPa, COClF combines with thiophenol in the presence of tributylamine, over 12 h, to give a 100% yield of phenyl thiofluoroformate, with a conversion of phenol of 100% [380]:

$$\mathrm{C_6H_5SH + COClF \longrightarrow C_6H_5SC(O)F + HCl}$$

Dimethylsulfoxide reacts with COClF at room temperature, in a sealed tube, to form CH_3SCH_2Cl (*cf.* corresponding reaction with $COCl_2$, Section 10.6.5.1) and $ClCH_2OC(O)F$, the relative proportions depending upon the stoicheiometric ratio of dmso–COClF. At a molar ratio of dmso/COClF = 2:1, the formation of sulfide is favoured, whilst at 1:2 the ester is favoured [1204b].

16.2 CARBONYL BROMIDE FLUORIDE

The asymmetrical, fluorine-containing carbonyl halides, COXF (X = Cl, Br or I) were first prepared and examined by Kwasnik at I.G. Leverkusen (a part of I.G. Farbenindustrie) during World War II. This work was later disclosed by Rüdorff [1751], and by Fischer [656a] in the enemy-property confiscation reports, known as the FIAT Reviews of German Science.

Under normal conditions of temperature and pressure, carbonyl bromide fluoride is a gas. Although colourless in both the gaseous and condensed states, it has been noted to develop a red-brown appearance within a few weeks when stored at room temperature (20 °C), and storage in quartz ampoules cooled in low-boiling refrigerants (or in pressurized stainless steel cylinders) is recommended [1195]. Despite the observation of this decomposition, presumably arising as a result of the reaction illustrated in Equation (16.6), COBrF is reported to be thermally stable to at least 125 °C [1751].

$$\mathrm{2COBrF \longrightarrow COF_2 + CO + Br_2} \qquad (16.6)$$

Dibromine contamination can be removed by passing the impure carbonyl bromide fluoride over antimony powder [1555], and then COBrF can be purified by fractional distillation (removal of trace COF_2) [1195].

COBrF is described [1751] as having an odour similar to that of phosgene, and although there are no standard methods available for its detection specifically, it has been noted that the substance may be detected using a Dräger tube designed for the detection of phosgene [1764]. Unlike phosgene, COBrF fumes copiously in moist air. It is rapidly absorbed by sodium hydroxide solution and is said to be completely hydrolysed (in an excess of water) within thirty minutes [1751]. Rubber is rendered hard following its exposure to COBrF; glass and quartz are not attacked. Monel and V2A steel are resistant to COBrF, but ordinary steel becomes severely corroded when exposed to this material [1751].

No toxicological data have been recorded for COBrF, and no Occupational Exposure Limits have been recommended. Although it is undoubtedly an irritant with a lethal capacity, it is unlikely to be as poisonous as phosgene. It is unlikely to be flammable. COBrF is not a commercially available substance, and it is not included in the European inventory of existing chemical substances (EINECS) [602a].

The synonyms of carbonyl bromide fluoride include carbonic bromide fluoride (ACS nomenclature), carbonyl bromofluoride, carbon oxybromide fluoride and bromofluorophosgene. The IUPAC name is carbonyl bromide fluoride. The Chemical Abstracts Registry number for COBrF is [753-56-0].

16.2.1 Synthesis and formation

16.2.1.1 From the reactions of carbon monoxide

Carbon bromide fluoride is formed in a flow system with a yield of 30% when a mixture of dinitrogen (saturated with dibromine), molecular fluorine, and carbon monoxide are passed simultaneously through a copper tube [1751]. No further details of this preparation are available, but if it is probably consistent with the stoicheiometry shown in Equation (16.7).

$$2CO + Br_2 + F_2 \longrightarrow 2COBrF \qquad (16.7)$$

The first report of the synthesis of COBrF was in the FIAT review of German science (1939-1945) [1195,1196a,1751], and this is a more convenient reaction than that summarized in Equation (16.7). Thus, COBrF was prepared, according to Equation (16.8), by passing carbon monoxide through liquid bromine(III) fluoride at between 8 and 30 °C, in a steel vessel [1195]. The lower temperature limit for this exothermic reaction is fixed by the freezing point of BrF_3; at too high a temperature, the reaction mixture explodes [1195,1751]:

$$2CO + BrF_3 \longrightarrow COBrF + COF_2 \qquad (16.8)$$

The product (90% yield based on BrF_3) was purified by passing through antimony powder, followed by distillation (in quartz equipment) to separate it from COF_2.

In their modified preparation based upon Equation (16.8), Patty and Lagemann [1596] used a vacuum system constructed of copper vessels and tubing, with inspection traps constructed of a fluoropolymer. The system was conditioned with ClF_3 before introduction of the reactants. The carbon monoxide was slowly passed through the liquid BrF_3, which was held in the reaction vessel maintained at 60 °C.

16.2.1.2 From the oxidation of bromofluoromethanes

The reaction of tribromofluoromethane with sulfur(VI) oxide provides the most convenient laboratory method of preparation of COBrF, particularly since it avoids the use of halogen fluorides, and hence related special equipment. The detailed experimental procedure, requiring the use only of conventional glassware, is given in Appendix A5 [1874,1875]. In summary, CBr_3F is added slowly to SO_3 over 2 h at 37–43 °C. Dibromine, formed according to Equation (16.9), is removed from the gaseous product by reaction with trichloroethene under ultraviolet light. The distillation product (boiling fraction −17.5 to −10 °C) was composed of CO_2, 3%; SO_2, 29.5% and COBrF, 67.5%: this corresponds to a yield of COBrF of *ca*. 64%, relative to the quantity of CBr_3F introduced.

$$CBr_3F + SO_3 \longrightarrow COBrF + SO_2 + Br_2 \qquad (16.9)$$

COBrF has been detected, by infrared spectroscopy, as a product of the oxidation and combustion of H_2–O_2–N_2–$CBrF_3$ mixtures between 400 and 500 °C: HF, HBr and CO_2 are also produced as a result of the subsequent hydrolysis of COBrF [1225]. It would be extremely surprising if COBrF were not detectable as an oxidation/combustion product of other bromofluoroalkanes or bromochlorofluoroalkanes, such as those commonly used as fire-fighting agents.

16.2.2 Thermodynamic and physical properties

Only a few of the physical properties of COBrF have been measured. Carbonyl bromide fluoride (relative molecular mass: 126.91) is a colourless gas, with an odour similar to, but distinguishable from, phosgene [1195]. The melting point at atmospheric pressure of COBrF has been reported as −120 ± 2 °C [1196a], and the boiling point as −20.6 °C [1196a]. Its critical temperature occurs at +124 °C, and its critical pressure is *ca*. 6.18 MPa [656a,1751].

16.2.2.1 Thermal and thermochemical properties

16.2.2.1.1 Gas phase

Thermodynamic data for COBrF are even more scarce than physical property data. In particular, the enthalpies, entropies, and free energies of formation of the material have been neither measured nor calculated, and other important thermodynamic functions of COBrF, other than the thermodynamics of the phase transition described in the following paragraphs, are not recorded.

16.2.2.1.2 Liquid phase

The saturated vapour pressure of liquid carbonyl bromide fluoride is illustrated in Fig. 16.5 as a function of temperature, and is derived from the data points (Table 16.13) as measured by Kwasnik and reported by Fischer [656a].

The empirical vapour pressure data [656a] have been fitted here (Equation 16.10) by linear regression (Fig. 16.6), and are given by:

$$\log_{10}(p/\mathrm{Pa}) = 9.8636 - 1228T^{-1} \tag{16.10}$$

The boiling point of COBrF, estimated from Fig. 16.6, is −20.3 °C. The enthalpy of vaporization, derivable from these data, has not been reported and a plot of the data in a form suitable for the determination of this quantity is provided in Fig. 16.6. From the relationship given in Equation (16.11), and the slope of the line provided in Fig. 16.6, ΔH_{vap} is calculated to be 22.9 ± 0.6 kJ mol^{-1}, from which the value of the Trouton constant is estimated to be 91 ± 2 J mol^{-1} K^{-1} [656a].

$$\ln(p/\mathrm{Pa}) = \frac{-\Delta H_{\mathrm{vap}}}{\mathrm{RT}} + \mathrm{C} \tag{16.11}$$

The enthalpy and entropy of vaporization of COBrF have also been calculated from a weighted means law (based upon the values of the related symmetrical carbonyl halides) as 23.1 kJ mol^{-1} and 87.4 J mol^{-1} K^{-1}, respectively [1343]. The calculated value for ΔH_{vap} is in excellent agreement with the experimentally derived value noted above. However, a boiling temperature of −12 °C was calculated from this work [1343], compared to the value of −20.6 °C determined by experiment [1751].

16.2.2.1.3 Solid phase

The only solid state property on record for carbonyl bromide fluoride is its melting point: −120 ± 2 °C [1196a].

16.2.2.1.4 Critical properties

The critical temperature of COBrF occurs at +124 °C, and its critical pressure is *ca.* 6.18 MPa [656a,1751].

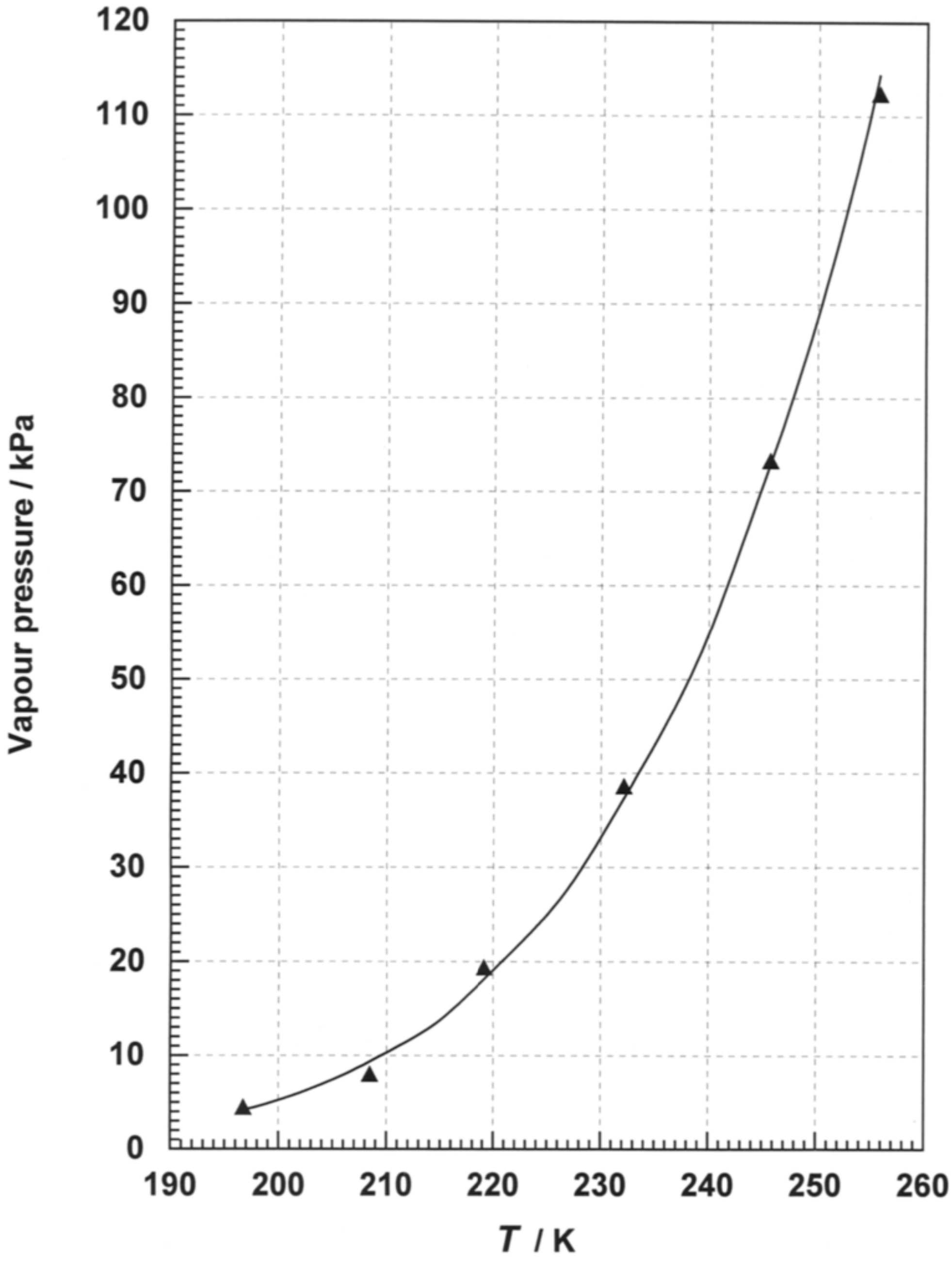


Fig. 16.5 The vapour pressure of liquid COBrF as a function of temperature [656a]; the experimental points are linked by Equation (16.10).

TABLE 16.13

EXPERIMENTAL VAPOUR PRESSURE OF LIQUID COBrF [656a]

T / K	p/kPa
-76.4	4.47
-64.7	8.00
-54.0	19.37
-41.0	38.62
-27.5	73.30
-17.5	112.39

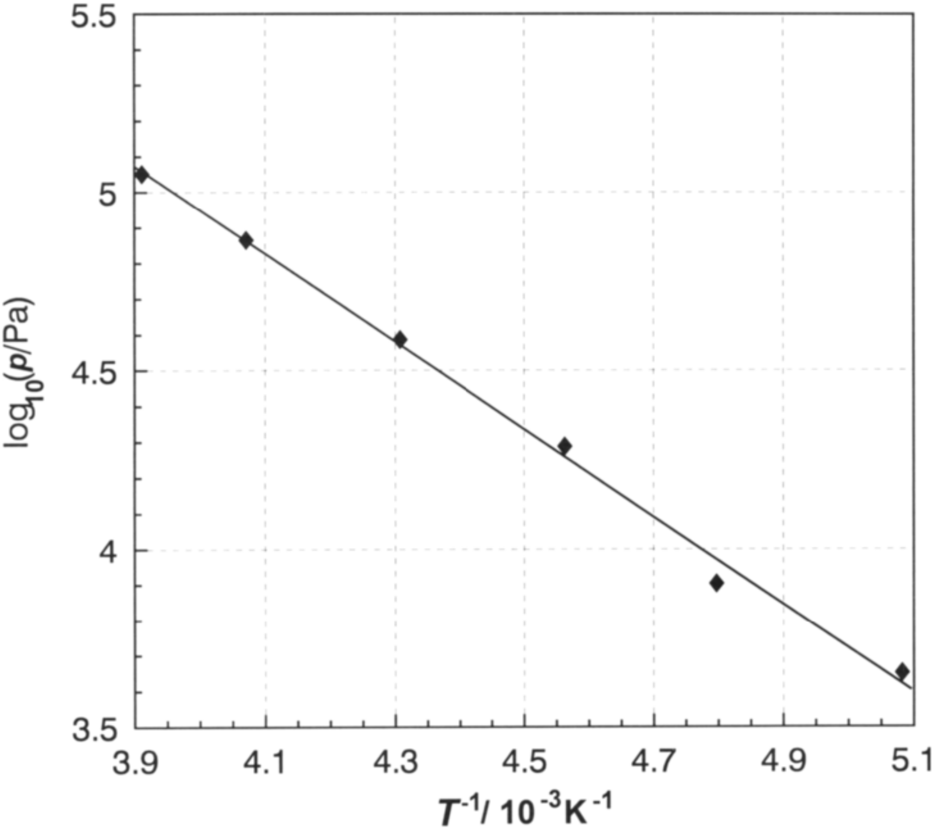


Fig. 16.6 A plot of $\log_{10}(p/\mathrm{Pa})$ *versus* T^{-1} for COBrF; the data are taken from [656a], the line represents equation (16.10).

16.2.2.2 Mechanical properties

The experimental density data for liquid COBrF in the temperature range of −71 to +23 °C are summarized in Table 16.14, and illustrated in Fig. 16.7 [1196a].

TABLE 16.14

DENSITY OF LIQUID COBrF [1196a,1751]

Temperature/°C	Density/g cm^{-3}
-71	2.197
-62	2.167
-52	2.132
-27	2.041
0	1.944
+23	1.860

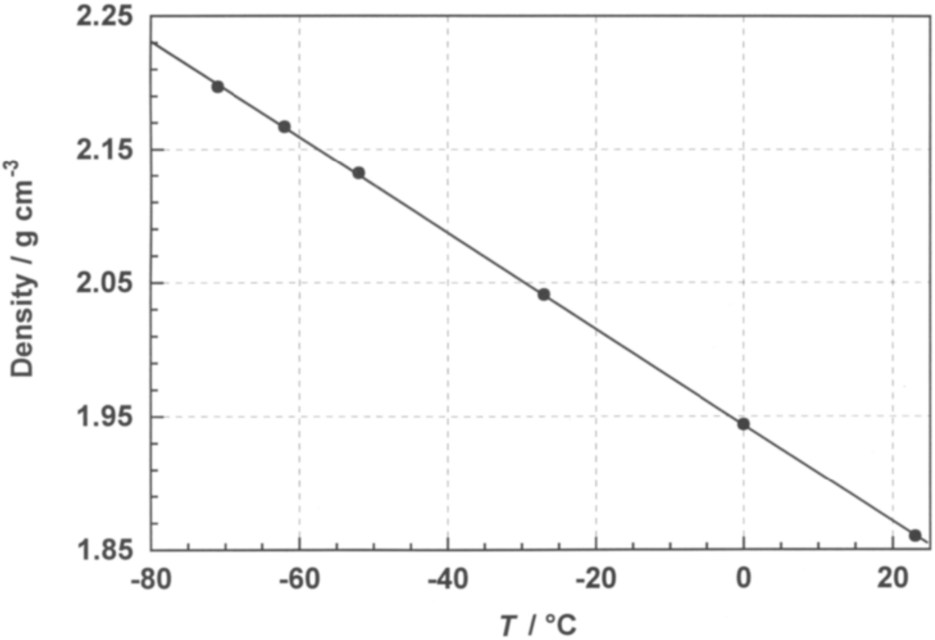


Fig. 16.7 The density of COBrF as a function of temperature [656a,1751].

16.2.2.3 Electrical and magnetic properties

Electrical measurements (such as those required for the determination of dipole moments, the dielectric constant, or the electrical conductivity) and magnetic measurements (such as required for the derivation of the magnetic susceptibility) have not been recorded for COBrF, and nothing is known of its solvent properties.

16.2.3 Structural determinations

There are no structural data known for carbonyl bromide fluoride. In particular, the microwave spectrum of COBrF has not been recorded, and no X-ray diffraction or electron diffraction studies have been performed. For this reason, the geometries of the molecule in the gas, liquid or solid phases are unknown, and calculations on COBrF that have required bond length and bond angle data have been performed using the known parameters of "closely related" molecules, or from geometry optimization calculations [2251b,2251c].

A reasonable parameter set would appear to be [2251b,2251c]:

r(CO)/nm	0.1178
r(CBr)/nm	0.1906
r(CF)/nm	0.1328
∡OCBr/°	126.0
∡OCF/°	124.8
∡BrCF/°	109.2

16.2.4 Molecular and spectroscopic properties

There are very few experimentally-recorded spectroscopic data for COBrF, and only one publication [1596] exists in which the spectroscopic properties of COBrF have been studied for their own sake. Apart from the recording of a ^{19}F n.m.r. spectrum and a mass spectrum [1163], the remaining spectroscopic studies of COBrF have been confined to the recording of its infrared spectrum [1596], and to the derivation of spectroscopic correlations with other members of the carbonyl halide series [604,864,1860].

No electronic spectra have been recorded for COBrF.

16.2.4.1 Vibrational spectroscopy

Raman spectra of COBrF have not been reported in any phase, but its infrared spectrum has been examined in the region of 263-5000 cm^{-1}, and assignments made on the basis of a planar molecule possessing C_s symmetry (see Appendix A4 and Section 16.1.7.1: the

TABLE 16.15

INFRARED DATA (units of cm^{-1}) FOR COBrF

	Medium	$\nu_1(a')$ $\nu(CO)$	$\nu_2(a')$ $\nu_s(CXY)$	$\nu_3(a')$ $\delta_s(OCXY)$	$\nu_4(a')$ $\nu_{as}(CXY)$	$\nu_5(a')$ $\delta_{as}(OCXY)$	$\nu_6(a'')$ $\pi(COX_2)$	$\nu_2+\nu_4$	Ref.
COBrF	gas	1874	721	398	1068	335	620		1596
COBrF	gas	1868	721	394	1068	-[a]	621		2251b
COBrF	liquid	1865	722		1070				1163

[a] Not observed, as below KBr cut-off [2251b]

fundamental vibrational modes, their symmetry and activity are illustrated in Fig. 16.4, for a general COXY molecule) [1596]. The observed fundamental frequencies and assignments are listed in Table 16.15. The ν_1, ν_2, ν_4 and ν_6 bands have P, Q and R branches, and the ν_3 and ν_5 bands appear to be doublets. Infrared cross-sections for ν_1, ν_2 and ν_4 have also been measured [2251b].

The fundamental frequencies for COBrF have been calculated from the force constants calculated for COX_2 (X = F, Cl or Br) [1578], and by high level *ab initio* calculations [2251b]. Other force constant and inertia defect calculations have also been performed [1550,1575-1577].

In a recent paper, the infrared multiphoton dissociation of COBrF (into COF_2, CO and Br_2, and not CO and BrF) has been studied, both experimentally and theoretically [2251c]. The primary dissociation step appears to be into Br· and [COF]· [2251c].

16.2.4.2 Nuclear magnetic resonance spectroscopy

The ^{13}C, ^{17}O and ^{19}F n.m.r. spectra of COBrF have been recorded [1163,1589b], and the chemical shift data are summarized in Table 7.4.

16.2.4.3 Mass spectrometry

The mass spectrum of COBrF (Table 16.16) has been reported [1b,1163], but the data from the two sources are rather different.

TABLE 16.16

MASS SPECTRAL DATA FOR COBrF

m/z	Relative Intensity		Assignment
	[1163]	[1b]	
128,126	46.8	37	M^+
109,107	89.4	100	$[COBr]^+$
93,91		10	$[CBr]^+$
81,79	14.9	34	Br^+
47	100.0	13	$[COF]^+$
28		4	$[CO]^+$

16.2.5 Inorganic reactions

The reported inorganic chemistry of COBrF is indeed scant. Even though the compatibility of COBrF with some metals and with glass and quartz, and the hydrolysis of COBrF, have been noted, a detailed study of these observations has not been published.

16.2.5.1 Miscellaneous reactions

Gaseous COBrF is thermally stable up to 125 °C, but liquid COBrF slowly decomposes at room temperature [1195]. It is quantitatively hydrolysed in water within half an hour, according to [1195]:

$$COBrF + H_2O \longrightarrow CO_2 + HBr + HF$$

Hydrolysis in aqueous sodium hydroxide solution is reported to occur instantly [1195]. Liquid COBrF blackens and embrittles rubber, and attacks both iron and mercury [1195].

Haszeldine and Iserson have also speculated [899,903] that various tetrahalomethanes can be prepared from the reactions of COBrF with phosphorus(V) halides, analogous to the reaction of phosgene with PCl_5 to give CCl_4 and $POCl_3$. For example:

$$COBrF + PF_3Cl_2 \longrightarrow CBrCl_2F + POF_3$$

However, no patent examples [899] or other experimental details [903] relating to COBrF were provided, and it is not clear whether these reactions were ever performed.

Treatment of bis(sulfonylamido)mercury(II) with COBrF yields fluorosulfinyl isocyanate, *via* an intermediate fluorocarbonylsulfinylamine (which was not observed) [1162,1163]:

$$\begin{tikzcd} \mathrm{Hg(NSO)_2 + 2COBrF} \arrow[r] & 2\left[\,\mathrm{C(=O)(}N\mathrm{SO)F}\,\right] \arrow[d] & \mathrm{+\ HgBr_2} \\ & \mathrm{2S(=O)(}N\mathrm{CO)F} & \end{tikzcd}$$

The carbonyl fluoride sulfinylimine intermediate undergoes rearrangement to form the product, $S(=O)(NCO)F$, containing an S–F rather than a C–F bond, and demonstrating the relatively high activity of the fluorine atom when in the vicinity of a C=O group [1162,1163].

The reaction of COBrF with trimethylsilylsulfinylimine, $(CH_3)_3SiNSO$, is reported to form the trimethylsilyl halides, $(CH_3)_3SiF$ and $(CH_3)_3SiBr$, $S(NSO)_2$, and polymer. No further details of the reaction were described [1163].

16.2.5.2 Dissociation, disproportionation, dismutation and exchange reactions

Carbonyl bromide fluoride is decomposed by passage of the vapour over activated charcoal according to Equation (16.12) [ICI112]:

$$2COBrF \longrightarrow COF_2 + CO + Br_2 \qquad (16.12)$$

Although the reaction is slower at any particular temperature than for the disproportionation of COClF (Equation 16.4), unlike that reaction, the decomposition of COBrF is not equilibrium limited owing to the further dissociation of $COBr_2$ into CO and Br_2. Thus, the reaction proceeds to the extent of 95% at above 130 °C (30 s contact time); 180 °C (13.6 s); and 255 °C (0.9 s). At 300 °C and a contact time of about 1 s, the reaction is essentially complete. The reaction is far slower over a high surface area (300 $m^2\ g^{-1}$) silica catalyst [ICI112]: in the absence of a suitable catalyst, the carbonyl halide is quite stable – only 4% of the COBrF was found to react at 503 °C despite the long contact time employed (19 s) [ICI112].

A general patented method [905] for the preparation of tetrahalomethanes has been claimed in which a carbonyl halide of general formula, COXY (X = F, Cl or Br; Y = Cl or Br) is combined with a carbonyl fluoride halide, COXF (X = F, Cl or Br) in the presence of an activated carbon catalyst (containing the halide of a transition metal) at a temperature of 250–1400 °C. Thus, heating COBrF in an autoclave is claimed to induce the following reaction [902,905]:

$$2COBrF \longrightarrow CBr_2F_2 + CO_2$$

16.2.6 Organic reactions

The only classes of organic materials with which COBrF has been treated are alcohols, thiols, and aldehydes. From alcohols, fluoroformates are formed consistent with Equation (16.13), and no bromoformates were detected [1555].

$$\text{COBrF} + \text{ROH} \longrightarrow \text{ROC(O)F} + \text{HBr} \qquad (16.13)$$

This reaction is reported to produce yields of alkyl or cycloalkyl fluoroformates which are typically 20% higher than those obtained using COClF [1555], and without the by-production of organic carbonates. By using a slight molar excess of COBrF relative to the alcohol, and warming the reaction mixture to 30–40 °C, the following yields of fluoroformates were obtained within a few minutes: R = CH_3, 72%; C_2H_5, 84%; C_3H_7, 81%; $(CH_3)_2CH$, 75%; C_4H_9, 85%; $CH_3CH_2CH(CH_3)$, 75%; C_6H_{11}, 79%.

Thiols, or thiophenols, are reported to react with COBrF to produce the corresponding thiol fluoroformate, RSC(O)F. However, no specific reaction using this reagent was discussed, preference being given to their preparation with COClF (see Section 16.1.9.3) [1555a].

The fluoroformate species, $CH_2BrOC(O)F$, is formed by an addition reaction when gaseous methanal and COBrF are combined in a toluene solution containing a small amount of triethylamine at room temperature [ICI113]:

$$\text{CH}_2\text{O} + \text{COBrF} \longrightarrow \text{CH}_2\text{BrOC(O)F}$$

Passage of this product over a high surface area alumina catalyst at about 100 °C results in the formation of bromofluoromethane in a yield of about 50 % [ICI113]:

$$\text{CH}_2\text{BrOC(O)F} \longrightarrow \text{CH}_2\text{BrF} + \text{CO}_2$$

16.3 CARBONYL BROMIDE CHLORIDE

16.3.1 Formation

The first claim to have synthesised COBrCl was published in 1895, when Besson [184] reported that the reaction between boron(III) bromide and phosgene (150 °C; 12 h) yielded a mixture of $COBr_2$ and COBrCl, which he separated by distillation (see also Sections 9.1.2.3 and 14.3). The colourless fraction claimed as COBrCl boiled between 35 and 37 °C, had a density of 1.98 g cm^{-3}, and slowly reacted with cold water [184]. The vapour "irrite les yeux et les voies respiratoires, provoquant une suffocation suivie d'oppression" [184]. Later workers [277d,2127], however, were unable to repeat this reaction, but there can be little doubt (*vide infra*) that Besson had prepared impure COBrCl.

In 1907, von Bartal [2127] demonstrated that the reaction between aluminium(III) bromide and an excess of phosgene at salt–ice temperatures, followed by warming to 15 °C, proceeded (but see also Section 9.1.2.6) according to:

$$AlBr_3 + 3COCl_2 \longrightarrow AlCl_3 + 3COBrCl$$

This reaction was optimized for the preparation of COBrCl by performing it in a Carius tube at 140–145 °C for *ca.* 8 h [2127]. After removal of by-product bromine with mercury, the COBrCl was purified by distillation. It boiled, without apparent decomposition, at 25 °C, and had a density of 1.82 g cm^{-3} at 15 °C. It was stable at 100 °C (although decomposed slowly in sunlight) and did not react with mercury: it did react with antimony, however [2127].

COBrCl has also been detected (by smell) in the aerial oxidation of CHClBrI [719a]:

$$2CHClBrI + 3[O] \longrightarrow 2COBrCl + I_2 + H_2O$$

and *may* be formed *in vivo* when $CBrCl_3$ is metabolized by rat liver microsomes [1632].

16.3.2 Thermodynamic and physical properties

Only a few properties of COBrCl (relative molecular mass: 143.37) have been measured. The data in Table 16.17 were calculated from spectroscopic data [1575].

TABLE 16.17

THERMODYNAMIC FUNCTIONS FOR COBrCl (units of J mol^{-1} K^{-1}) [1575]

T/K	C_p°	S°	$(H^\circ-H_0^\circ)/T$	$-(G^\circ-H_0^\circ)/T$
298.15	59.75	301.42	44.89	256.52
400	65.44	319.82	49.45	270.37
500	69.16	334.85	53.01	281.83
600	71.88	347.69	55.94	291.75
700	73.93	358.95	58.37	300.58
800	75.48	368.95	60.42	308.49
900	76.73	378.36	62.17	316.18
1000	77.70	386.02	63.68	322.34

From the law of weighted means, using input data from $COCl_2$ and $COBr_2$, the enthalpy and entropy of vaporization of COBrCl have been calculated as 27.2 kJ mol^{-1} and 88.7 J mol^{-1} K^{-1}, respectively [656]: a boiling point of 34 °C was similarly estimated [656].

16.3.3 Structural determinations

There are no structural data known for carbonyl bromide chloride. In particular, the microwave spectrum of COBrCl has not been recorded, and no X-ray diffraction or electron diffraction studies have been performed. The molecular dimensions of COBrCl have been assumed to be r(CO) = 0.117 nm, r(CBr) = 0.194 nm, r(CCl) = 0.175 nm, ∡BrCCl = 111° and ∡ClCO = 124.5° [1575].

16.3.4 Molecular and spectroscopic properties

There are very few experimentally-recorded spectroscopic data for COBrCl.

16.3.4.1 Vibrational spectroscopy

Both the infrared and the Raman spectra of COBrCl have been recorded; assignments were made on the basis of a planar molecule possessing C_s symmetry (see Appendix A4 and Section 16.1.7.1: the fundamental vibrational modes, their symmetry and activity are illustrated in Fig. 16.4, for a general COXY molecule) [1596]. The observed fundamental frequencies and assignments are listed in Table 16.18.

TABLE 16.18

INFRARED AND RAMAN DATA (units of cm^{-1}) FOR COBrCl

Medium	$\nu_1(a')$ $\nu(CO)$	$\nu_2(a')$ $\nu_s(CXY)$	$\nu_3(a')$ $\delta_s(OCXY)$	$\nu_4(a')$ $\nu_{as}(CXY)$	$\nu_5(a')$ $\delta_{as}(OCXY)$	$\nu_6(a'')$ $\pi(COX_2)$	$\nu_2+\nu_4$	Ref.
COBrCl^a gas	1828	517		806	374	547		1575
COBrCl^b liquid		518	240		372			1575

^{a} IR data. ^{b} Raman data.

Force constant and inertia defect calculations have also been performed [1222,1550,1575–1577]. The fundamental frequencies for COBrCl have been calculated from the force constants calculated for COX_2 (X = F, Cl or Br) [1578].

16.3.4.2 Nuclear magnetic resonance spectroscopy

The ^{13}C and ^{17}O n.m.r. spectra of COBrCl have been recorded [1163,1589b], and the chemical shift data are summarized in Table 7.4.

16.3.4.3 Mass spectrometry

The mass spectral data for COBrCl are summarized in Table 16.19 [1b].

TABLE 16.19

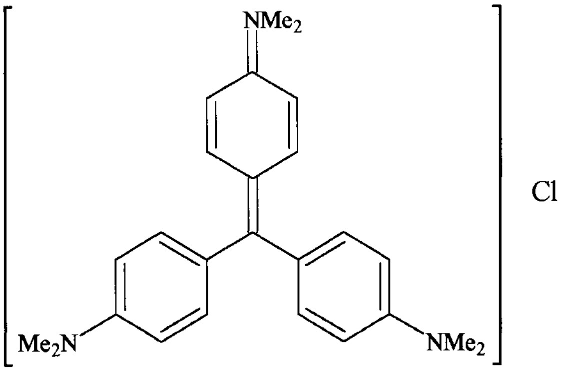
MASS SPECTRAL DATA FOR COBrCl [1b]

m/z	Relative Intensity	Assignment
146,144,142	14	M^+
109,107	92	$[COBr]^+$
93,91	18	$[CBr]^+$
81,79	90	Br^+
65,63	100	$[COCl]^+$
49,47	12	$[CCl]^+$
37,35	23	Cl^+
28	8	$[CO]^+$

16.3.5 Inorganic and organic reactions

Carbonyl bromide chloride is stable at 100 °C (although decomposed slowly in sunlight) and does not react with mercury [2127]. It does react with antimony, however [2127].

COBrCl reacts violently with *N,N*-dimethylaniline to give methyl violet (**16.9**) [2127].



(16.9)

COBrCl is also briefly reported to be a catalyst for the α-bromination of saturated carboxylic acid, in a modified Hell-Volhard-Zelinsky reaction, but is apparently less successful than either $COCl_2$ or $COBr_2$ [2029].

16.4 CARBONYL FLUORIDE IODIDE

Carbonyl fluoride iodide, COFI, is a colourless liquid close to its boiling temperature of 23.4 °C under normal conditions. Its odour is described as being similar to that of phosgene.

16.4.1 Formation

As with a number of the other unsymmetrical halides, carbonyl fluoride iodide was first reported in the FIAT review of German science (1939–1945) [1196a,1751]. The compound was prepared by Kwasnik [1196a,1751] from the reaction of iodine(V) fluoride with carbon monoxide according to:

$$IF_5 + 3CO \longrightarrow COFI + 2COF_2$$

The reaction takes place in a rotating autoclave over eight hours, and under a partial pressure of carbon monoxide of 12 MPa. After bleeding off the carbonyl difluoride co-product and the excess of carbon monoxide, the COFI was removed by distillation at about 26.7 kPa, followed by a further distillation *in vacuo* over antimony powder to give a yield of 12% for COFI (based on IF_5). The material is suitably stored in quartz vessels cooled with dry ice [1196,1751].

16.4.2 Thermodynamic and physical properties

Carbonyl fluoride iodide (relative molecular mass: 173.91) is a colourless liquid with a choking odour, similar to COBrF, and quite distinct from phosgene [1196]. It can only be stored in quartz ampoules at temperatures below −78 °C [1196]. The melting point of COFI has been reported as −90 to −91 °C [1196a,1751] and the boiling point as +23.4 °C [1196a,1751]. It should be noted that the data given in [1196] are in error, being the values appropriate for COBrF. Above −20 °C, liquid COFI decomposes visibly, with concomitant liberation of iodine [1196]: gaseous COFI decomposes at room temperature [1196].

TABLE 16.20

VAPOUR PRESSURE OF LIQUID COFI [656a]

Temp/°C	Vapour pressure/kPa
-43	4.31
-31	10.15
-20	17.53
0	42.54
18.6	85.99

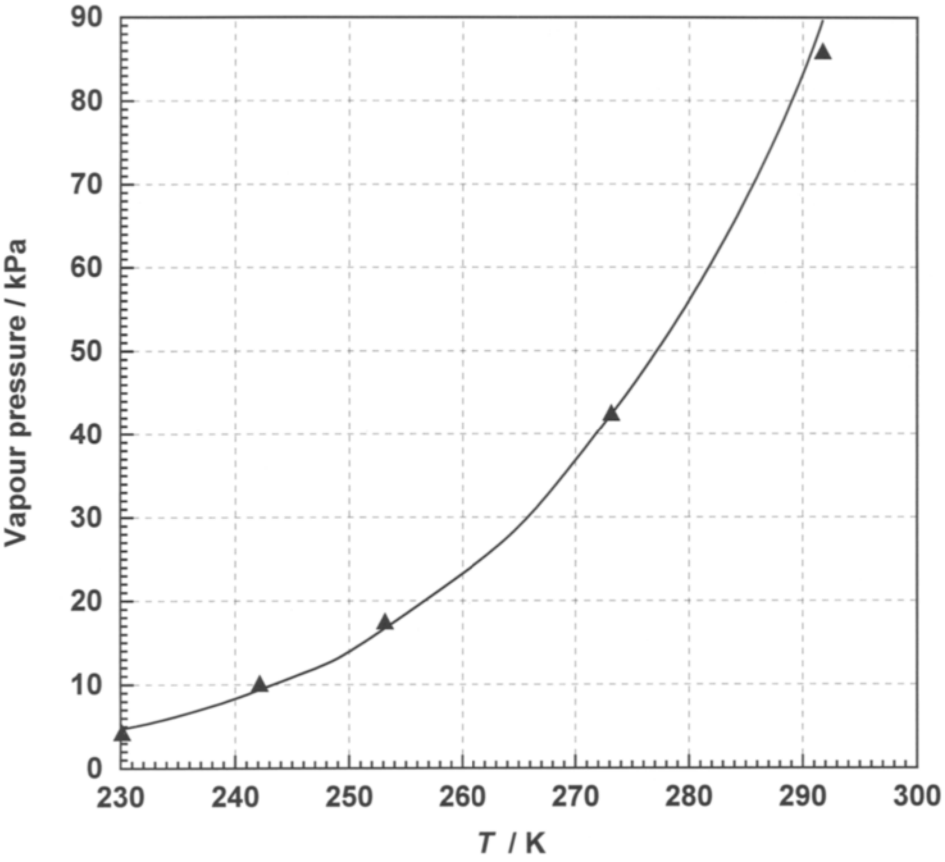


Fig. 16.8 The vapour pressure of liquid COFI as a function of temperature [656a,1751]; the experimental points are linked by Equation (16.14).

The empirical vapour pressure data [656a] for COFI (see Table 16.20) have been fitted here by linear regression (Fig. 16.8): this fit is given by Equation (16.14).

$$\log_{10}(p/\mathrm{Pa}) = 9.7372 - 1396T^{-1} \qquad (16.14)$$

Serious errors are reported in Brauer [1196], in which the data for COFI are confused with those for COBrF.

The density of liquid COFI has also been recorded as a function of temperature, and these data are summarised in Table 16.21.

TABLE 16.21

DENSITY OF LIQUID COFI [656a,1751]

Temperature/°C	Density/g cm^3
0	2.618
16	2.470
21.2	2.425

16.4.3 Inorganic reactions

Carbonyl fluoride iodide decomposes at temperatures as low as −20 °C with evolution of diiodine. It is reported to be hydrolysed by water (within thirty minutes), and is rapidly and completely absorbed by aqueous sodium hydroxide solution [1196,1751]. When exposed to liquid COFI at normal temperatures, quartz and glass are reported to become coated with a yellow substance [1196].

16.5 CARBONYL CHLORIDE IODIDE

There are no reports concerning the preparation of carbonyl chloride iodide, COClI. When exposed to moist air, however, chlorodiiodomethane, $CHClI_2$, is reported to develop a phosgene-like odour [90b]. If phosgene is formed during this process, it is probable that it arises as a result of the following reactions:

$$2CHI_2Cl + O_2 \xrightarrow{-2HI} 2COClI \longrightarrow COCl_2 + CO + I_2$$

The boiling temperature of COClI has been estimated at 69 °C from the similarity principle, taking into account the relative molecular mass of the material at 190.37 (see Fig. 15.1) [985]. The critical properties for COClI, T_c (542.O K), P_c (6.08 MPa) and V_c (244 cm^3 mol^{-1}), have been estimated by the Lydersen method [985]. In addition, the thermodynamic functions, $\Delta H^\circ_{f,298}$ (−127.9 kJ mol^{-1}), $\Delta G^\circ_{f,298}$ (−140.8 kJ mol^{-1}) and $S^\circ_{f,298}$ (321.1 J mol^{-1} K^{-1}) have been estimated for COClI in the ideal gas state at 25 °C [985]. C_p^{300} is estimated to be 57.2 J mol^{-1} K^{-1} [985].

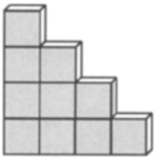
16.6 CARBONYL BROMIDE IODIDE

Carbonyl bromide iodide is predicted to be an unstable material with respect to isolation, dissociation or disproportionation reactions. Not surprisingly, no reports of its formation are extant.

In the absence of decomposition, COBrI (relative molecular mass: 234.82) is estimated to be a liquid material with a normal boiling temperature of 127 °C (see Fig. 15.1). Its critical properties have been estimated by Horvath [985] as follows: T_c = 640.1 K, P_c = 6.17 MPa, V_c = 265 cm^3 mol^{-1}, and the thermodynamic functions $\Delta H^{\circ}_{f,298}$, $\Delta G^{\circ}_{f,298}$, $S^{\circ}_{f,298}$, and C_p^{300} have been calculated to be −81.46 kJ mol^{-1}, −108.70 kJ mol^{-1}, 333.7 J mol^{-1} K^{-1} and 58.0 J mol^{-1} K^{-1}, respectively [985].

SECTION C

THEORETICAL STUDIES



17 ELECTRONIC STRUCTURE OF THE CARBONYL HALIDES

The organization of this final chapter differs from that of the earlier chapters, in that it deals with the electronic structures of *all* of the carbonyl halides. This approach has been taken in order to avoid needless repetition, and to highlight the trends that inevitably exist in a series of such closely related molecules. The first part of this chapter (Section 17.1) gives a basic treatment of the electronic structure of the carbonyl halides, and uses the simpler structure of gaseous formaldehyde to highlight the complexities caused by introducing halogen atoms. The early part of this section will undoubtedly be too basic for many readers, as it is designed for those who would normally avoid such material: we make no apologies for this, the savant may sample the later sections with a self-satisfied contentment. The remaining sections of the chapter describe the spectroscopic evidence that has led to an empirical description of the electronic structure of the carbonyl halides, against which the theoretical models can be evaluated.

17.1 THEORETICAL DESCRIPTIONS OF THE ELECTRONIC STRUCTURES OF THE CARBONYL HALIDES

17.1.1 Formaldehyde

Formaldehyde (methanal, COH_2) is an apposite starting point for a discussion of the electronic structure of the carbonyl halides, as its orbital interactions are relatively simple. Like the carbonyl halides, the ground state of COH_2 is planar with C_{2v} symmetry[†], and its molecular orbitals can be constructed from those of carbon monoxide and the 1*s* atomic orbitals of two hydrogen atoms (see Fig. 17.1). Its valence electron configuration is:

$$[\text{core}](3a_1)^2(4a_1)^2(1b_1)^2(5a_1)^2(1b_2)^2(2b_1)^2$$

resulting in an $\tilde{X}\ {}^1A_1$ ground-state classification; the 'shapes' of the valence molecular orbitals

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[†] In this case, as in all cases of molecules with C_{2v} symmetry, an arbitrary choice has to be made concerning the coordinate system, *viz.* the y axis may be in, or perpendicular to, the molecular plane. Throughout this chapter, the y axis has been chosen to be ***perpendicular*** to the molecular plane, which is consistent with the character table in Appendix A4. However, in the open literature, both coordinate systems (depending only upon individual preferences) are to be found. A comparison of the data reported here with literature reports adopting the alternative convention merely requires the interchange of b_1 and b_2 wherever they occur in this chapter (or, of course, in the literature report, but not both!). The a_i designations do NOT require changing.

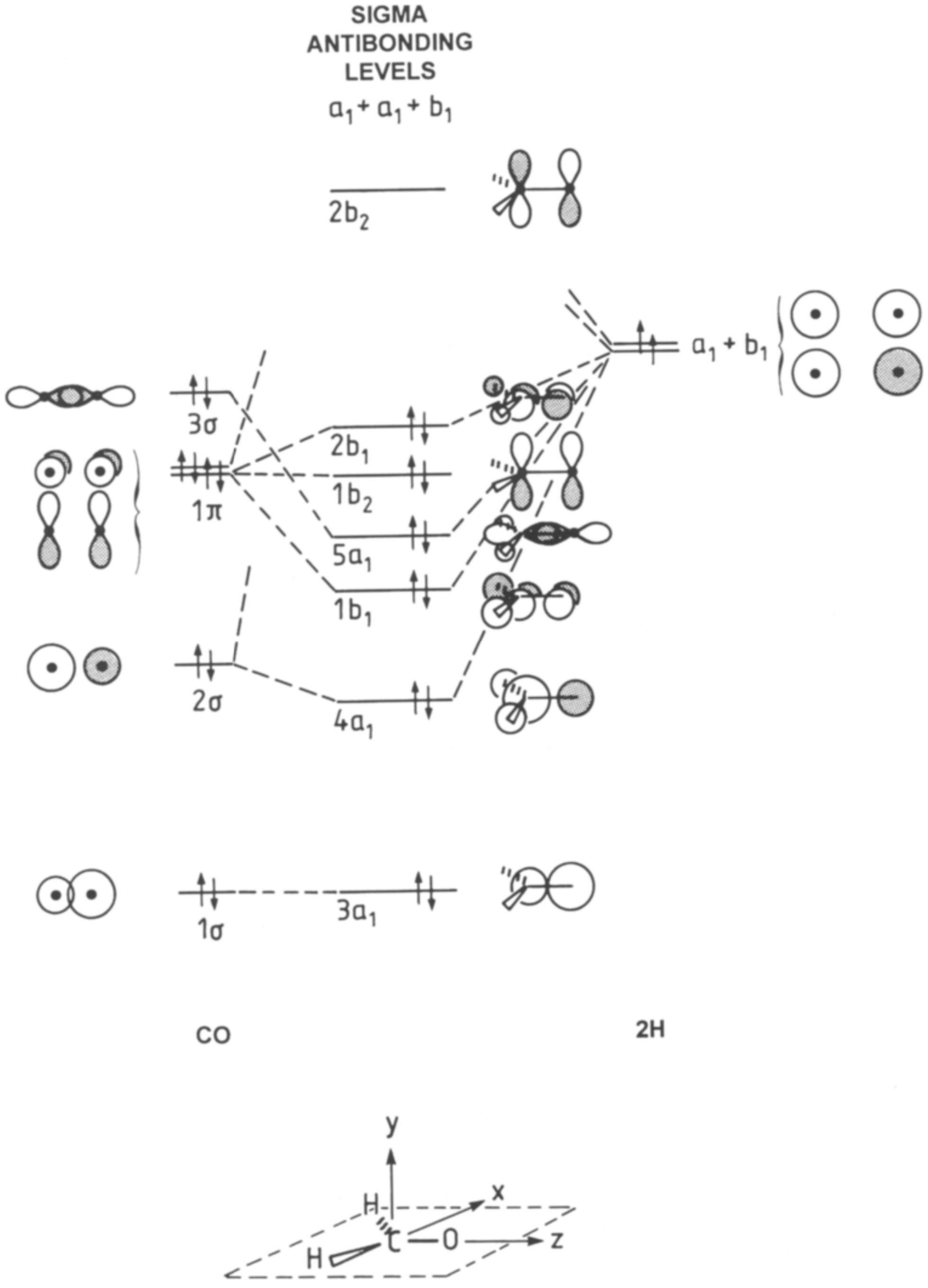
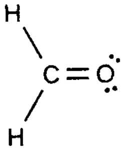


Fig. 17.1 A qualitative molecular orbital diagram for formaldehyde.

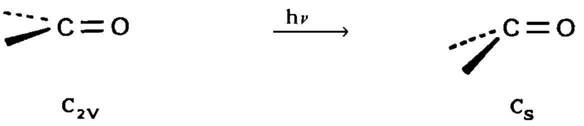
are illustrated in Fig. 17.2. It is quite helpful to consider the atomic orbital parentage (*e.g.* hydrogen, carbon or oxygen 1*s*, 2*s*, 2*p*, *etc.*) of these molecular orbitals. Thus the HOMO, of b_1 symmetry, can be seen to be derived from a $2p_x$ orbital, principally associated with the oxygen atom, and the SHOMO, the only occupied molecular orbital of b_2 symmetry, is clearly the carbonyl π-bonding molecular orbital, formed from the carbon and the oxygen $2p_y$ orbitals, without any hydrogen atomic orbital character.

The Lewis structure for formaldehyde is:



In this simple valence bond model, the bonding in formaldehyde is described by three localized σ-orbitals, one localized π-orbital, and two equivalent oxygen lone-pairs. A major difference between this description of the bonding in COH_2 and that resulting from a molecular orbital approach is the delocalization of the bonding in the latter case. Under the molecular orbital (m.o.) treatment, there is only one orbital that is unquestionably a lone-pair orbital – the $2b_1$ molecular orbital. The other 'lone-pair' orbital, of a_1 symmetry (derived from the oxygen $2p_z$ and 2*s* atomic orbitals), is at much lower energy and there is such a large degree of σ(CO) bonding interaction that it cannot meaningfully be considered as a lone-pair. Similar cautionary notes have been expressed by others, for example by Hoffmann [972aa] with regard to the 'lone-pair' orbital in pyridine. The experimental evidence (*vide infra*) is so overwhelming in its support for the molecular orbital scheme that the simple valence bond treatment will not be considered further.

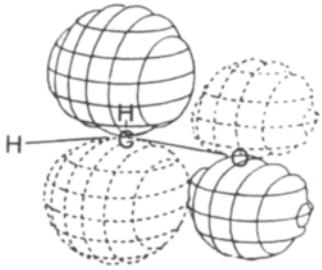
If formaldehyde is distorted away from planarity, equation (17.1), the molecular



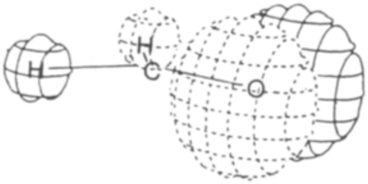
(17.1)

symmetry is reduced to C_s (see Appendix A4 for the correlation between C_{2v} and C_s), and the behaviour of the orbital energies is depicted in the Walsh diagram of Fig. 17.3. Pyramidal distortion of the molecule occurs upon electronic transition to the first excited triplet ($\tilde{a}$) or singlet ($\tilde{A}$) states, when the outer electron configuration becomes:

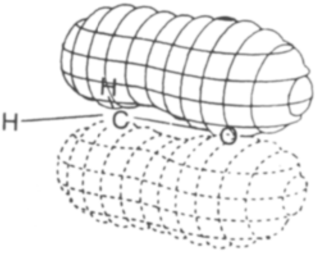
$$....(6a')^2(2a'')^1(7a')^1$$



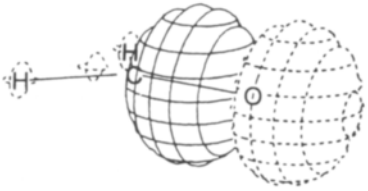
$2b_2$ - LUMO
π^*(CO)



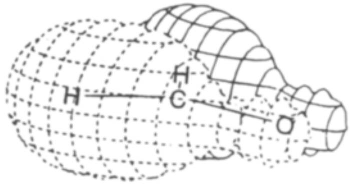
$2b_1$ - HOMO
n(O)



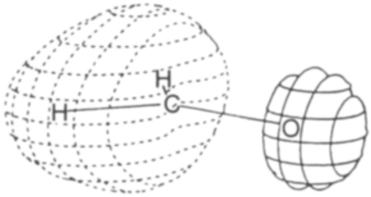
$1b_2$ - SHOMO
π(CO)



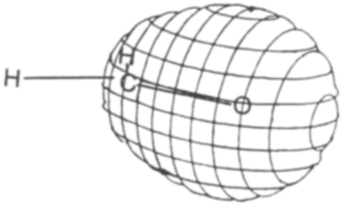
$5a_1$
n(O)/σ(CO)



$1b_1$
σ(CH$_2$)



$4a_1$
σ(CH$_2$)



$3a_1$
O(2s)

Fig. 17.2 The valence molecular orbitals of formaldehyde [1055a]. The solid and dashed lines correspond to regions of the wave functions with opposite signs. The value of the electron density represented by the contours (6.75 e nm^{-3}) has no fundamental significance, having been chosen so that the molecular orbitals can be visualized clearly.

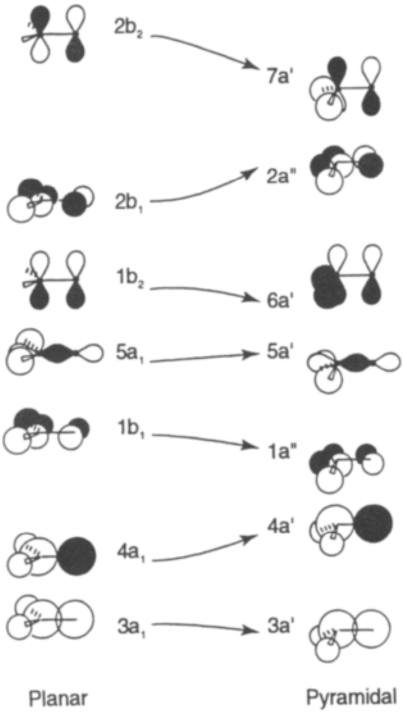
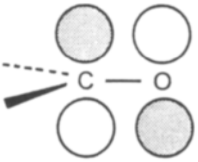


Fig. 17.3 **A Walsh diagram illustrating the correlation of the orbitals for both the planar and pyramidal configurations of formaldehyde [758a].**

Upon distortion, most of the changes in the molecular orbital energies are consistent with the changes in overlap of the constituent atomic orbitals. For example, the LUMO ($2b_2$), which



$2b_2$

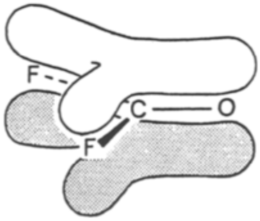
is mainly CO antibonding in character, falls sharply in energy because the symmetry-forbidden interaction between the hydrogen $1s$ atomic orbitals and the carbon $2p_y$ atomic orbitals in the planar molecule becomes an allowed bonding interaction in the non-planar molecule. Also of note are the $1b_2$ and $5a_1$ orbitals, which are similar in energy in the planar molecule and would be expected to converge: upon distortion, both become a' orbitals which mix and start to diverge.

17.1.2 *Carbonyl Halides*

Although for COH_2, the HOMO $2b_1$ orbital can be considered as an oxygen lone-pair, for the carbonyl halides there exists considerable interaction between the b_1 non-bonding orbitals on the oxygen and on the halogen atoms. For the rest of this chapter, although molecular orbitals may be described as oxygen or halogen lone-pairs, it should be borne in mind that there will be considerable orbital mixing, and that the terms oxygen or halogen lone-pair refer to the predominant orbital characteristics.

17.1.2.1 Carbonyl difluoride

Upon substitution of the hydrogen atoms of formaldehyde by halogen atoms, a far wider range of interactions is possible with the carbonyl orbitals, especially π interactions of the type illustrated:



Ab initio m.o. calculations (utilizing STO-3G, 4-31G and 6-31G [1589c,1950c], double-zeta [284,845,2104a], or double-zeta with polarization [1857aa] basis sets) have been used to establish m.o. energy level orderings for COF_2. It is clear from the calculations that there is significant mixing of the fluorine p_z {referred to as n(F) in Table 17.1} and the π(CO) orbitals. However, as the symmetric and the antisymmetric combinations are both occupied, there is no significant nett π-bonding. The orbital characteristics of the valence molecular orbitals of COF_2 are summarized in Table 17.1; the ground electronic state has $^1A_1$ symmetry. An inverted ordering of the $8a_1$ and $4b_1$ levels was predicted in some early reports (*e.g.* [1950b]), but recent work [1857aa] has shown this ordering to be particularly sensitive to small changes in geometry. The results reported in Table 17.1 are the result of *ab initio* calculations utilising double-zeta plus polarization basis sets, and the best structural information currently available. The m.o. energy level ordering for COF_2 is thus:

$$[\text{core}](6a_1)^2(3b_1)^2(1b_2)^2(7a_1)^2(1a_2)^2(8a_1)^2(4b_1)^2(2b_2)^2(5b_1)^2$$

The LUMO of COF_2 is a π(CO) antibonding orbital whilst the HOMO essentially corresponds to a non-bonding oxygen $2p_x$ orbital directed in the plane of the molecule. The SHOMO, of b_2 symmetry, is a CO π-bonding orbital, which is also antibonding with respect to fluorine. Between the $4b_1$ and $1a_2$ orbitals, which are both very 'pure' fluorine lone-pair orbitals, is the $8a_1$ orbital which is a mix of fluorine, and σ(CO) orbitals. The $7a_1$ and $1b_2$ orbitals are also of very mixed character.

An experimental value for the vertical electron affinity of COF_2 has been obtained

TABLE 17.1

ORBITAL CHARACTERISTICS OF THE MOLECULAR ORBITALS OF COF_2, IN ORDER OF INCREASING STABILITY [1857aa]

Orbital	E_n/eV	Mulliken analysis			Character[a]
		C	O	F	
$5b_1$	-15.24	5	81	14	n(O),n(F)
$2b_2$	-15.76	17	66	17	π(CO)-n(F)
$4b_1$	-19.12	1	1	98	n(F)
$8a_1$	-19.20	11	51	38	σ(CO),n(F),n(O)
$1a_2$	-19.74	1	0	99	n(F)
$7a_1$	-21.88	8	30	62	n(F),n(O),σ(CO)
$1b_2$	-22.21	19	6	75	n(F)+π(CO)
$3b_1$	-23.50	23	8	69	n(F),σ(CF),π_{xz}(CO)
$6a_1$	-26.02	22	6	72	n(F),σ(CF)

[a] + indicates a bonding interaction, and - an antibonding interaction.

using electron transmission spectroscopy [372a]; at −1.85±0.05 eV it is considerably larger than that for COH_2 (−0.86 eV).

The potential energy curve for the $^1A_1$ ground state of COF_2 has been computed (see Fig. 17.4) using *ab initio* projected-unrestricted Hartree-Fock theory with a contracted Gaussian-type basis set [273]. The potential minimum was found to occur at a CO bond length of 0.1174 nm, which is in very good agreement with the best experimental value of 0.11717 nm [1480]. The local maximum in the potential energy curve at around 0.2 nm is probably an artefact of the calculation.

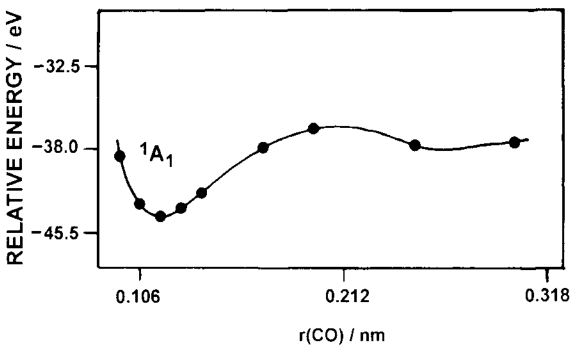


Fig. 17.4 Potential energy curve for the $^1A_1$ ground state of COF_2 [273].

17.1.2.2 Phosgene

An orbital sequence for $COCl_2$ has been established with the aid of *ab initio* calculations using a double-zeta with polarization quality basis set [1857aa], *viz*:

$$[\text{core}](9a_1)^2(6b_1)^2(10a_1)^2(2b_2)^2(11a_1)^2(2a_2)^2(3b_2)^2(7b_1)^2(8b_1)^2$$

The characteristics of these orbitals are given in Table 17.2. The LUMO is π(CO) antibonding in character, and the HOMO and SHOMO are readily identifiable as chlorine and oxygen lone-pair orbitals respectively. However, it is important to note that the HOMO and SHOMO both have the same symmetry and they are very close in energy. An indication of the problems which this can cause was highlighted by the results of a series of *ab initio* calculations using increasingly sophisticated basis sets [1589c]; calculations with the extended and polarized basis sets, 4-31G and 4-31G*, predicted the HOMO to be the chlorine lone-pair orbital (in agreement with the results shown in Table 17.2), whereas use of the more restricted STO-3G, STO-4G, STO-5G and STO-6G basis sets suggested that the oxygen lone-pair should be the HOMO.

TABLE 17.2

ORBITAL CHARACTERISTICS OF THE MOLECULAR ORBITALS OF $COCl_2$, IN ORDER OF INCREASING STABILITY [1857aa]

Orbital	E_n/eV	Mulliken analysis			Character
		C	O	Cl	
$8b_1$	-12.92	0	11	89	n(Cl)
$7b_1$	-13.48	7	43	50	n(O),n(Cl)
$3b_2$	-13.54	2	28	70	n(Cl),n(O)
$2a_2$	-13.60	0	0	100	n(Cl)
$11a_1$	-14.42	2	2	96	n(Cl)
$2b_2$	-17.74	36	41	23	π(CO)
$10a_1$	-19.15	23	48	29	σ(CO)
$6b_1$	-19.35	27	35	38	$\sigma(CCl_2)+\pi_{xz}(CO)$
$9a_1$	-22.10	24	33	43	$\sigma(CCl_2)$

As noted for COF_2, there is considerable π–delocalization. The concept of π–delocalization into the C–Cl bonds of $COCl_2$ is not new, having been proposed, albeit in valence bond terms, as early as 1940 as a means of rationalizing a small discrepancy between the experimental and the computed dipole moments of phosgene [564,2082]. However, authors [*e.g.* 409a] still frequently treat phosgene as containing an unconjugated carbonyl group, and the conclusions drawn from such work must be treated with caution.

A vertical electron affinity of −3.40 eV has been obtained for $COCl_2$, using electron transmission spectroscopy; electron capture into a C–Cl σ–antibonding orbital was proposed [372a].

17.1.2.3 Carbonyl dibromide and the asymmetric carbonyl halides

Ab initio calculations on $COBr_2$ (C_{2v} symmetry) and the asymmetrically substituted carbonyl halides COClF, COBrF and COBrCl (which have only C_s symmetry) have shown that when a bromine atom is present in the molecule, the highest occupied molecular orbital has bromine lone–pair character [1857aa]. In contrast to this, the HOMO of COClF has mixed chlorine and oxygen character. The principal orbital characteristics for the most chemically significant orbitals of these molecules are given in Tables 17.3 and 17.4; it must be remembered that the low symmetry means that there is little bar to extensive mixing of the molecular orbitals.

TABLE 17.3

ORBITAL CHARACTERISTICS OF THE MOLECULAR ORBITALS OF $COBr_2$ IN ORDER OF INCREASING STABILITY [1857aa]

Orbital	Energy /eV	Mulliken analysis			Character
		C	O	Br	
$14b_1$	-11.73	1	1	98	n(Br)
$5a_2$	-12.26	0	0	100	n(Br)
$13b_1$	-12.53	7	39	54	n(O), n(Br)
$6b_2$	-12.58	1	15	84	n(Br)
$17a_1$	-13.04	2	1	97	n(Br)
$5b_2$	-17.32	36	54	10	π(CO)
$16a_1$	-18.54	29	33	38	σ(CO)
$12b_1$	-18.76	26	48	26	$\sigma(CF)+\pi_{xz}(CO)$
$15a_1$	-21.70	25	48	27	n(O),σ(CO),σ(CBr)

TABLE 17.4

ORBITAL CHARACTERISTICS OF THE UPPERMOST MOLECULAR ORBITALS OF COClF, COBrF AND COBrCl, IN ORDER OF INCREASING STABILITY [1857aa]

Orbital	Energy /eV	Mulliken analysis					Character
		C	O	F	Cl	Br	
(A) COClF							
16a'	-13.71	1	22	2	75		n(Cl)+n(O)
4a"	-13.82	2	18	0	80		n(Cl)+n(O)
15a'	-14.79	7	45	9	39		n(O)+n(Cl)
3a"	-16.39	19	45	21	15		π(CO)-n(F)
14a'	-17.85	14	28	37	21		n(F)+σ(CO)
13a'	-20.60	18	60	15	7		n(O)+σ(CO)
(B) COBrF							
22a'	-11.51	1	6	1		92	n(Br)
7a"	-11.84	0	8	0		92	n(Br)
21a'	-11.96	10	48	8		34	n(O)-n(Br)
6a"	-14.05	21	56	18		5	π(CO)-n(F)
20a'	-14.22	16	36	29		19	n(O)-n(F)
19a'	-16.81	21	64	8		7	n(O)+σ(CO)
(C) COBrCl							
25a'	-12.12	1	4		14	81	n(Br)
8a"	-12.41	0	6		1	93	n(Br)
24a'	-12.98	7	40		22	31	n(O)-σ(CBrCl)
7a"	-13.59	2	16		82	0	n(Cl)-π(CO)
23a'	-13.95	2	5		77	16	n(Cl)
6a"	-17.53	36	46		13	5	π(CO)+n(Cl)
22a'	-18.77	27	39		8	26	σ(CO)+n(Br)

17.1.2.4 Trends in the electronic structure of the carbonyl halides

The computed [1857aa] energy ordering of the n(O), π(CO) and σ(CO) orbitals of COX_2 (X = F, Cl or Br), COClF, COBrF and COBrCl are compared graphically in Fig. 17.5; *ab initio* methods involving the use of double-zeta plus polarization quality basis sets were used for each of the molecules. From Fig. 17.5, it is apparent that the sensitivity of the n(O), π(CO) and σ(CO) orbitals to halogen substitution is comparable. This is in contrast to predictions of earlier calculations, using STO-3G basis sets [1589a,1589c], which showed the energies of the n(O) orbitals to be relatively little affected by halogen substitution, and those of the π(CO) and σ(CO) orbitals to be particularly halogen dependent.

Of particular interest are the energies of the π(CO) levels of COF_2 and $COCl_2$ relative to that of COH_2. The π(CO) bond in planar COH_2 can be thought of as a 'pure' π bond because, by symmetry, there are no orbital contributions from the hydrogen atoms – this was clearly illustrated in Fig. 17.1. In contrast, all of the substituted molecules have some halogen *p*-orbitals of the same symmetry as the π(CO) molecular orbital (b_2 for COX_2, and a" for COXY). Qualitatively, the chlorine 3*p* orbitals lie at a higher energy than that of the 'pure' π(CO) molecular orbital of COH_2, whereas the reverse is true for the fluorine 2*p* orbitals. The π interaction with the halide ion therefore results in stabilization of the π(CO) level of $COCl_2$ and destabilization of that of COF_2 (see Fig. 17.6). Moreover, mixing will also occur between the halogen p_y orbitals and the π^*(CO) orbital [588b].

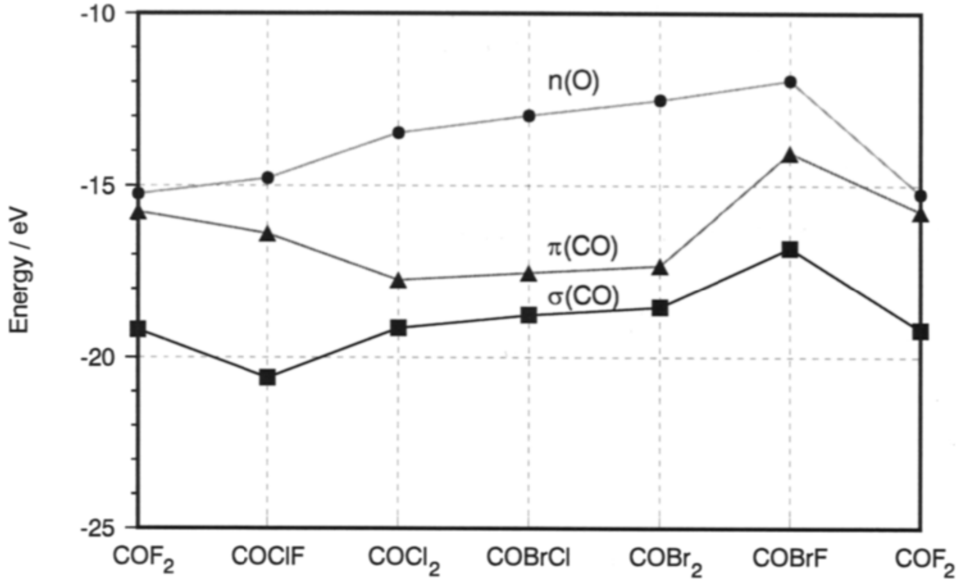


Fig. 17.5 The computed [1857aa] energy ordering of the n(O), π(CO) and σ(CO) orbitals of COX_2 (X = F, Cl or Br), COClF, COBrF and COBrCl.

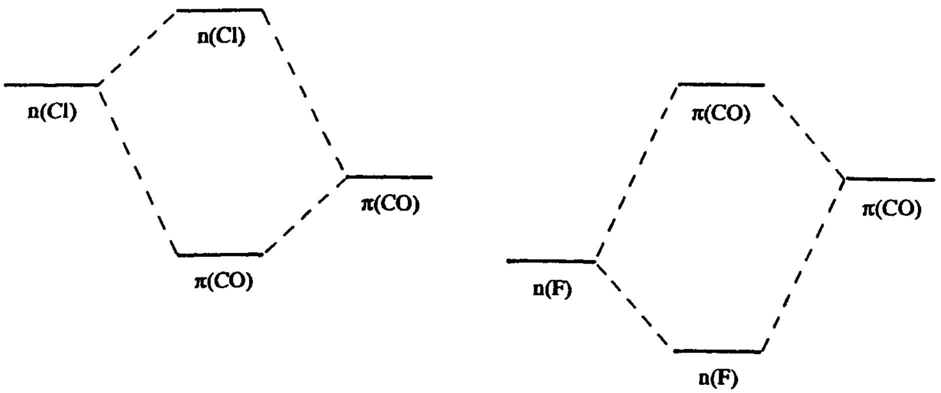


Fig. 17.6 The interactions between the halogen lone-pair levels and the π(CO) level in phosgene and carbonyl difluoride.

The π-components of Mulliken overlap populations derived from a series of calculations each employing STO-3G basis sets are given in Table 17.5. Using this admittedly simplistic approach, COF_2 has the weakest π(CO) interaction, and the strongest π(CX) bonding is seen when X = F. All of the molecules show significant, positive, π overlap populations and halogen substitution has an approximately additive effect. Interestingly, the π(CO) overlap populations in $COCl_2$ and $COBr_2$ are very similar to that of COH_2 (0.175). These results should not be overinterpreted as (not surprisingly) some basis set dependency was noted.

TABLE 17.5

MULLIKEN π-OVERLAP POPULATIONS FOR THE CARBONYL HALIDES [1857aa]

Molecule	C-O	C-F	C-Cl	C-Br
COF_2	0.166	0.027		
$COCl_2$	0.177		0.013	
$COBr_2$	0.176			0.013
COClF	0.172	0.026	0.013	
COBrF	0.171	0.027		0.012
COBrCl	0.177		0.013	0.013

Oberhammer and Boggs [1532] have computed (by *ab initio* m.o. techniques) the electronic effects of sequential replacement of the hydrogen atoms in formaldehyde by chlorine and/or fluorine atoms. The gross atomic charges on the constituent atoms of COClF, COHX and COX_2 (X = Cl or F) were computed, and are displayed (relative to those for COH_2) in Fig. 17.7. The three most noticeable features are that (a) the charge on the oxygen is effectively constant, (b) the charge on the carbon is greatly affected (changing by up to 1 a.u.), and (c) the effect of substitution from COH_2 to COX_2 is not simply additive – disubstitution results in a greater change than monosubstitution. It is also clear from Fig. 17.7 that the overall electron density of the carbonyl moiety is reduced by halogen substitution. By partitioning the gross charges into their σ and π constituents (see Fig. 17.8), it is clear that halogen substitution causes an increase in the π, and a decrease in the σ, electron densities of both the carbon and the oxygen atoms. However, whilst the influence of substitution upon the carbon π and the oxygen σ and π electron densities is only slight, its effect upon the carbon σ density is particularly marked. The decrease in carbon σ electron density upon disubstitution is two-to-three times the effect of monosubstitution, and fluorine substitution produces a more pronounced effect than chlorine substitution.

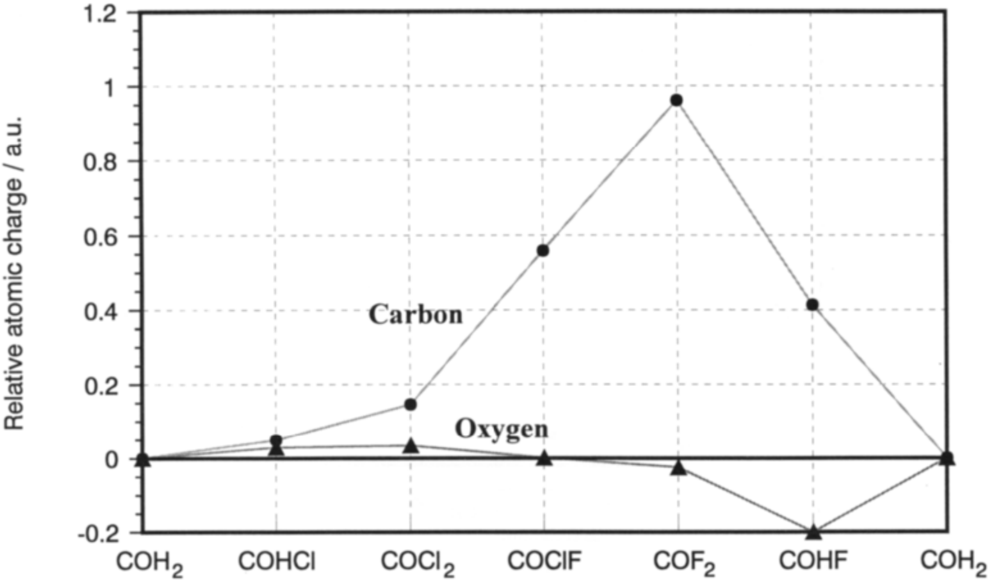


Fig. 17.7 Trends in the carbon and the oxygen atomic charges with fluorine or chlorine substitution of COH_2, with values relative to COH_2 in atomic units [1532].

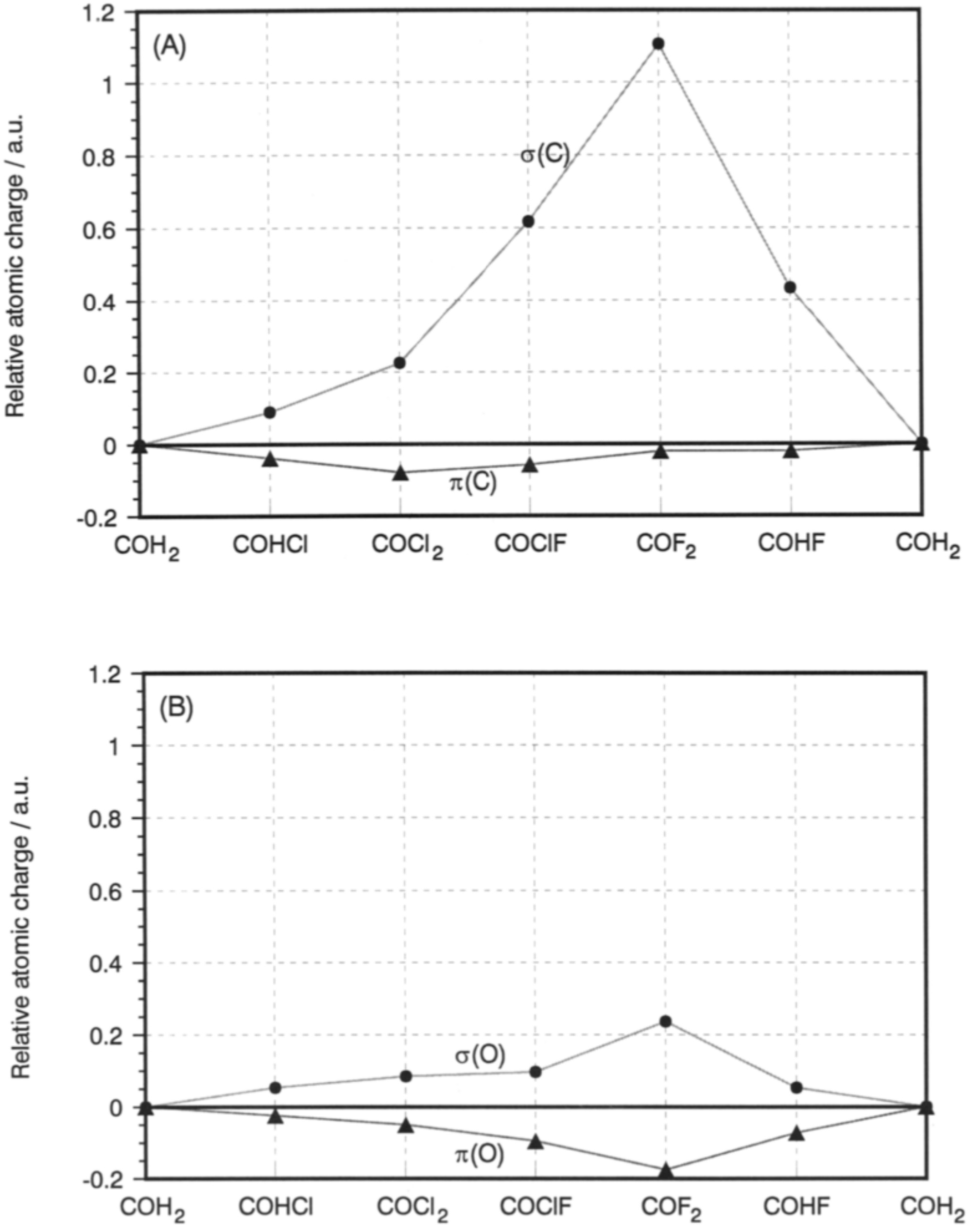


Fig. 17.8 Trends in the σ and π charge densities (A) of the carbonyl carbon atom or (B) the carbonyl oxygen atom, with values relative to those for COH_2 in atomic units [1532].

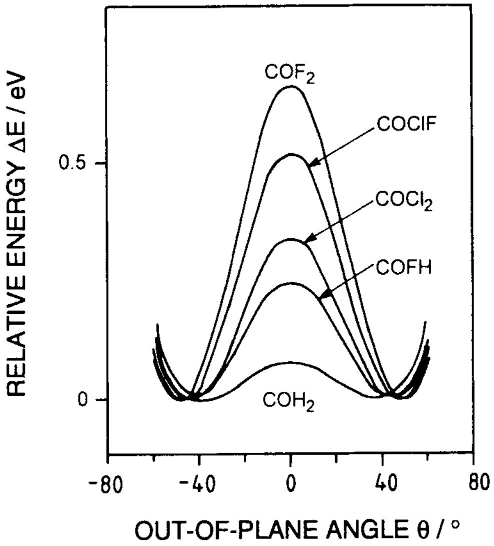


Fig. 17.9 **Computed potential energies along the out-of-plane bending coordinate for the first triplet states of COH_2, COFH, COF_2, COFCl and $COCl_2$ [1066].**

Although the ground states of the molecules are planar, their first excited singlet and triplet states are, for those cases where calculations have been performed, predicted to be markedly pyramidal [536,1066,1777]. The variation in potential energies of the lowest triplet states of COH_2, COHF, COF_2, $COCl_2$ and COClF, along the out-of-plane bending coordinate, have been calculated [1066] and are depicted in Fig. 17.9. Although a rather limited basis set (STO-3G) was used for the calculations, the trend of increasing barrier height with increasing electronegativity of the substituents is expected to be essentially correct. CNDO/2 calculations have also indicated that inductive effects of the fluorine atoms (with respect to hydrogen atoms) are crucial in determining the inversion barrier height [407]. The projected-unrestricted Hartree-Fock method (with a contracted [4*s*3*p*] Gaussian-type basis set and *fixed* C_{2v} symmetry) has been used to determine the nature of some singlet and triplet excited states of COF_2 [273]: both the singlet and triplet A_2 states were found to be weakly bound; the singlet and triplet B_1 and B_2 states were all repulsive.

A striking correlation between the decrease in electron density of the carbon $2p_z$ orbital and the calculated equilibrium out-of-plane angle, $\hat{\omega}$, for the excited state [1066] is shown in Fig. 17.10.

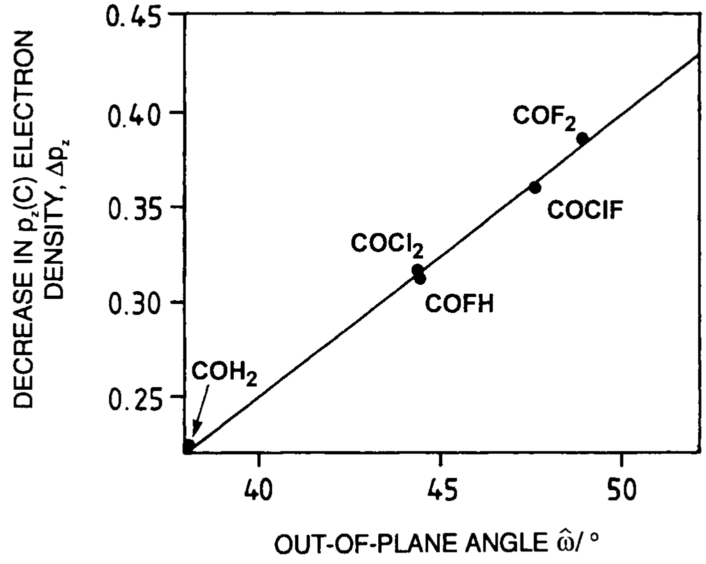


Fig. 17.10 **A graph of the relationship between the decrease in C p_z charge density and the computed equilibrium out-of-plane angle, $\hat{\omega}$, for COH_2, COFH, COF_2, COFCl and $COCl_2$ [1066].**

17.2 PHOTOELECTRON STUDIES

This section is subdivided into studies by u.v. photoelectron spectroscopy (u.p.s.) and X-ray photoelectron spectroscopy (x.p.s.). Although a distinction on the basis of the energy of the exciting radiation is somewhat arbitrary, the information obtained from u.p.s. complements rather than duplicates that from x.p.s. For the carbonyl halides, u.p.s. has been used to obtain the relative energy ordering of valence molecular orbitals, an indication of their atomic orbital parentage, and their bonding, non-bonding or anti-bonding nature; core binding energies have been obtained using x.p.s.

The molecular polarizabilities of COX_2 (X = F, Cl or Br) have been calculated, and the results obtained used to estimate electron impact ionization cross-sections: the values calculated are 5.50×10^{-16}, 13.11×10^{-16}, and 19.02×10^{-16} cm^2, respectively [374].

17.2.1 Ultraviolet photoelectron spectroscopic studies

The He I and He II photoelectron spectra of COF_2, $COCl_2$, $COBr_2$ and the He I photoelectron spectra of COClF, COBrF and COBrCl have been recorded and interpreted [1589a,1589c,1723,1857aa,2028]. The reported spectra are generally consistent, although some are complicated by the presence of contaminants and they have, as would be expected, been obtained with spectrometers of widely differing ultimate resolution. As an aid to the rationalization of the spectra and, ultimately, of the electronic structure of the ground-states of the molecules, ionization energies have been calculated by a number of techniques. As in Section 17.1, the simpler case of formaldehyde will be discussed before those of the carbonyl halides.

17.2.1.1 Basic principles

Simple molecular photoionization is the interaction of electromagnetic radiation with a molecule (in its ground state) to generate an ion (in a variety of different possible energy, E_n, and symmetry states) and a free electron {Equation (17.2)}. In this process, mass, momentum and energy are conserved, according to Equation (17.3).

$$\mathrm{M} + \mathrm{h}\nu \longrightarrow \mathrm{M}^+ + \mathrm{e}^- \qquad (17.2)$$

$$E(\mathrm{e}^-) = \mathrm{h}\nu + E(\mathrm{M}) - E_n(\mathrm{M}^+) \qquad (17.3)$$

$E(\mathrm{e}^-)$ represents the kinetic energy of the free electron (which is measured experimentally in photoelectron spectroscopy), and $E(\mathrm{M})$ and $E_n(\mathrm{M}^+)$ represent the total electronic energies of the ground state and ion states, respectively. The quantity $E(\mathrm{M}) - E_n(\mathrm{M}^+)$ represents the ionization energy, E_n, for the production of the ion in its n^{th} excited state, and it is this quantity which is determined in the u.p.s. experiment. Ionization energies of closed-shell molecules are often related directly to orbital energies by invoking Koopmans' approximation (or theorem), which is formulated in Equation (17.4). This zeroth level approximation implies

$$E_n = -E(\psi_n) \qquad (17.4)$$

that the n^{th} ionization energy, E_n, can be equated to the negative of the n^{th} orbital energy, $E(\psi_n)$, when calculated in the Hartree-Fock limit. The corollary of Koopmans' approximation is that the observed ordering of ionization energies in the photoelectron spectrum should map directly onto the orbital sequence of the ground state molecule. In practice, there are two principal reasons for the breakdown of Koopmans' approximation: neglect of both correlation effects (which are different for the ion and for the neutral molecule) and neglect of relaxation effects. A common means of calculating ionization energies is the ΔSCF method. However, whilst this procedure can in principle incorporate relaxation effects, it cannot accommodate correlation effects. Breakdowns of Koopmans' approximation are legion, the best known case being the ionization of dinitrogen.

It has been found empirically that the band intensities in photoelectron spectra can vary dramatically with photon energy. Thus, bands due to ionization from halogen-based (other than fluorine-based) molecular orbitals are reduced in intensity relative to bands that are either carbon-, oxygen- or fluorine-based, upon changing from He I to He II ionizing radiation. Thus, recording both He I and He II photoelectron spectra provides very useful empirical data for assignment of the photoelectron bands exhibited by COX_2 (X = Cl or Br) and the asymmetrical carbonyl halides, but is of less value for the assignments for COH_2 and COF_2.

Ionization energies can be measured either vertically (*i.e.* the most probable process) or adiabatically (*i.e.* from the lowest vibrational level in the ground state to the lowest vibrational level of the ion state). The greater the discrepancy in these values, the greater the distortion of the ion relative to the neutral molecule. As a generalization, the vertical and adiabatic ionization energies for ionization from a non-bonding orbital are expected to be very similar and the spectral bands sharp. In contrast to this, ionization from strongly bonding (or anti-bonding) orbitals leads to bands exhibiting extensive vibrational fine structure. Further, if the vibrational frequency measured from the photoelectron spectrum is reduced relative to its corresponding value in the vibrational spectrum of the neutral molecule, bond weakening has occurred upon ionization, and the molecular orbital from which the electron has been ejected may be assumed to be principally bonding in nature. The converse situation can also be invoked as a rationalization of increased vibrational ion state frequencies.

17.2.1.2 Formaldehyde

The He I photoelectron spectrum of COH_2 is shown in Fig. 17.11. As indicated in the Figure, the assignment of the spectrum follows the qualitative molecular orbital scheme in Fig. 17.1. The lowest ionization energy band, $2b_1$, consists of a narrow intense peak, with a short weak vibrational progression: the adiabatic and vertical ionization energies are equal. This is indicative of little perturbation of the geometry of the ion state, consistent with ionization of the non-bonding oxygen lone-pair.

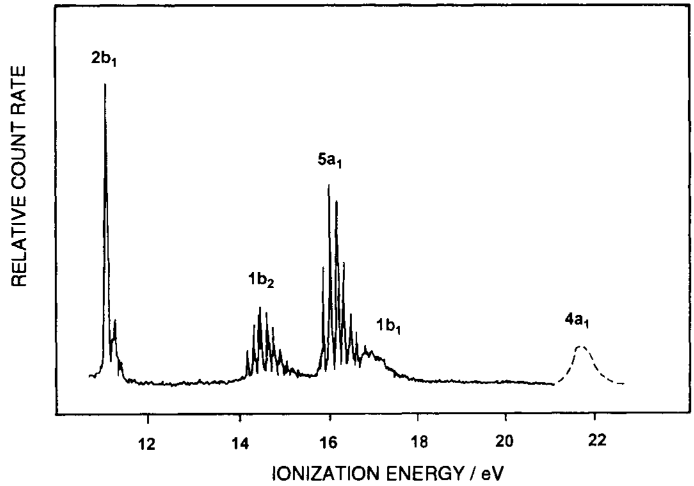


Fig. 17.11 The He I photoelectron spectrum of COH_2 [1723].

The presence of extensive vibrational structure on the $1b_2$ and $5a_1$ bands of the photoelectron spectrum is indicative of an ion geometry that is significantly different from the equilibrium molecular geometry. The carbonyl stretching frequency, ν_1, of COH_2 is 1744 cm^{-1}; the values of 1210 and 1270 cm^{-1} for the progressions in ν_1' associated with ionization from the $1b_2$ {π(CO)} and the $5a_1$ {n(O)/σ(CO)} orbitals, respectively, are consistent with these orbitals both having strong carbonyl bonding character.

17.2.1.3 Carbonyl difluoride

The first ionization energy of COF_2 predicted by La Paglia (*ca.* 13 eV) in 1963 [1208] on the basis of a study in which the Rydberg spectra of COF_2 and $COCl_2$ were compared with other related carbonyl-containing small molecules is surprisingly close to the values derived from photoelectron spectroscopic studies. The first ionization energy of COF_2 has also been estimated using electron-impact mass spectrometry yielding values of 14.6 [2035] and 13.17 eV [2212].

The He I and He II photoelectron spectra of COF_2 [284,1723,1857aa,2028] contain eight identifiable bands (marked A to H, Fig. 17.12), five of which (A, B, D, E and F) show clear evidence of extensive vibrational structure (highlighted in Fig. 17.13). Ionization energies for carbonyl difluoride, computed by a variety of techniques, are given in Tables 17.6 and 17.7: assignments of the p.e. spectra of COF_2 are given in Table 17.8.

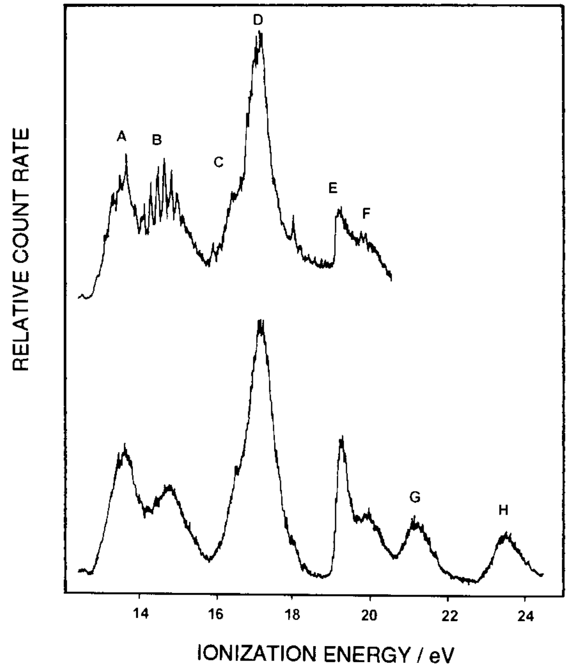


Fig. 17.12 The He I (upper) and He II (lower) photoelectron spectra of COF_2 [1857aa].

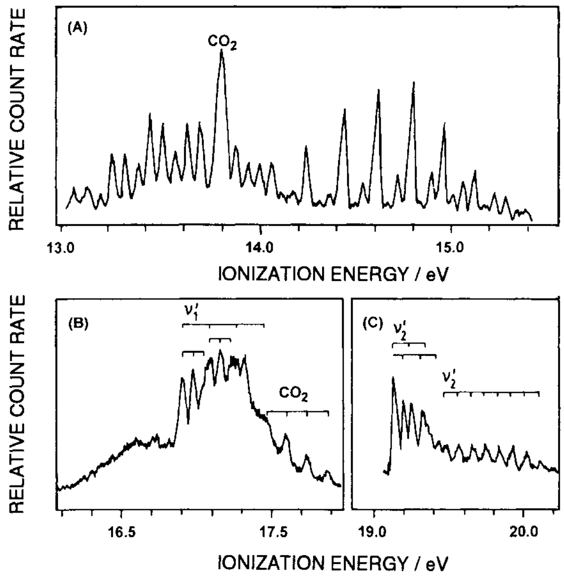


Fig. 17.13 **Expansions of the individual bands of the He I spectrum of COF_2 showing the vibrational progressions: (A) Bands A and B [1857aa], (B) Bands C and D [2028], and (C) Bands E and F [2028].**

Literature assignments of the He I spectrum of COF_2 include an analysis based solely on comparison of the experimental ionization energies with the predicted (INDO) values [373]. More generally, however, computational data have been supported by a detailed comparison of the observed ion state vibrational frequencies with the well established fundamental ground state frequencies of COF_2 [2028], by a comparison of the spectrum with that of COH_2 [284,1723], or by both.

Band A in the He I photoelectron spectrum of COF_2 shows extensive vibrational progressions {Fig. 17.13(A)}, a somewhat perplexing observation given its universally agreed assignment to the ionization of a non-bonding oxygen lone-pair orbital. The most likely explanation for this is significant distortion of $[COF_2]^+$ with respect to the neutral molecule [284,1723]. Support for this suggestion was gained recently when a calculation on the ground state of $[COF_2]^+$ (performed at the SCF level) predicted the ion structure to have a longer CO bond (by 0.01 nm), shorter CF bonds (by 0.007 nm) and a larger FCF angle (by 12°) than the corresponding calculation on COF_2 [1857aa].

The assignment of band B {Fig. 17.13(B)} to ionization from a π(CO) orbital is uncontroversial, and is supported by calculations, vibrational structure, and comparison with spectra of COH_2. Bands C–H of COF_2 have been assigned by direct reference to ionization energy calculations. Empirical observations are of little help here as (a) the bands overlap,

TABLE 17.6

CALCULATED VERTICAL IONIZATION ENERGIES OF COF_2, BASED ON KOOPMANS' APPROXIMATION

	E_n/eV						
	Ab initio[a]		*Ab initio*		INDO	CNDO[d]	MNDO
	[284, 1723][b]	[273][b]	[845][b]	[1857aa][c]	[373]	[2242]	[513]
$5b_1$	14.4	14.17	16.1	15.24	16.6	13.24	13.61
$2b_2$	14.8	14.42	16.5	15.76	17.5	13.60	14.18
$8a_1$	17.7	17.57	19.4	19.20	18.7	16.28	16.46
$4b_1$	18.0	18.00	19.7	19.12	20.5	16.45	16.97
$1a_2$	18.5	18.59	20.4	19.74	21.1	17.10	17.11
$7a_1$	20.4		22.4	21.88	23.1		
$1b_2$	21.0		23.0	22.21			
$3b_1$	22.0		24.0	23.50			
$6a_1$	24.1		26.3	26.02			

[a] Koopmans' theorem value scaled by a factor of 0.92. [b] Double-zeta. [c] Double-zeta with polarization. [d] No orbital assignment quoted.

(b) the perfluoro effect (*viz.* substitution of hydrogen by fluorine has a much greater stabilizing effect upon σ-bonds than upon π-bonds in planar molecules) is equivocal in distinguishing bands E and F, (c) the He I/He II intensity effects are small, and (d) the interpretation of the vibrational spacings (where present) is unhelpful. It is worth noting at this point that on the basis of the photoelectron spectra alone, it is impossible to determine whether the vibrational frequencies in the range 490–560 cm^{-1} are attributable to ν_3' or ν_5', the symmetrical or asymmetrical deformation modes, δ(OCF), respectively.

Photodissociation of $[COF_2]^+$ to give $[COF]^+$ and F· has been investigated using photoelectron/photoion coincidence techniques [1044]. Included in the report were a breakdown diagram and the translational energy releases computed from the time-of-flight peak contours. However, details of the kinetic energy releases, which were larger than expected, could not be fully rationalised. An appearance potential of 14.85 ± 0.2 eV was estimated for $[COF]^+$.

TABLE 17.7

CALCULATED VERTICAL IONIZATION ENERGIES OF COF$_2$, BASED ON ION STATE CALCULATIONS

	E_n/eV				
	ΔSCF		ΔINDO+FOCI[a]	OVGF[b]	E2PH-TDA[c]
	[845]	[1589c]	[373]	[1857aa]	[1857aa]
$^2B_1$	13.5	12.05	14.8	13.74	13.89
$^2B_2$	14.9	13.78	16.8	14.86	14.89
$^2B_1$	18.1		18.2	16.97	17.07
$^2A_1$	17.3	16.28	22.9	17.30	17.60
$^2A_2$	18.9		20.1	17.54	17.62
$^2A_1$	21.8		21.1	19.56	19.80
$^2B_2$	22.3			20.15	20.37
$^2B_1$	23.2			20.54	21.73
$^2A_1$	25.4			23.92	24.04

[a] FOCI - first-order configuration interaction. [b] Outer valence Green's function. [c] Extended two-particle-hole Tamm-Dancoff approximation.

TABLE 17.8

EXPERIMENTAL IONIZATION ENERGIES, VIBRATIONAL INTERVALS AND ASSIGNMENTS FOR THE PHOTOELECTRON SPECTRUM OF COF$_2$ [284,1723,1857aa,2028]

Band	E_n/eV	ν'/cm^{-1}			Assignment
	Vertical	ν'_1	ν'_2	ν'_3	
A	13.62	1580		540	n(O); 5b$_1$
B	14.80	1430	920	505	π(CO)-n(F); 2b$_2$
C	16.7(sh)				n(F); 4b$_1$
D	17.27	1500		555	σ(CO),n(F),n(O); 8a$_1$,1a$_2$
E	19.40			490	n(F),n(O),σ(CO); 7a$_1$
F	19.99		760		n(F)+π(CO); 1b$_2$
G	21.16				n(F),σ(CF),π_{xz}(CO); 3b$_1$
H	23.51		730		n(F),σ(CF); 6a$_1$

17.2.1.4 Phosgene

The first ionization energy of $COCl_2$ was originally determined by electron impact mass spectrometry [1439a] and the value obtained (11.77 eV) is in good agreement with that obtained later by u.p.s. (11.83 eV [349]).

Quite early in the development of photoelectron spectroscopy, two independent research groups reported the He I spectrum of $COCl_2$ [349,350,2028]. Whilst the spectra obtained were very similar, the assignments proposed by the two groups were fundamentally at variance (see Table 17.9). The differences centred upon the relative ordering (a) of the oxygen and chlorine lone-pair levels, and (b) of the σ(CO) and π(CO) levels. More recently, the He II spectrum of $COCl_2$ has been recorded (see Fig. 17.14) and ionization energy calculations have been performed, see Table 17.10.

The first two bands in the photoelectron spectra of $COCl_2$ (A and B in Fig. 17.14) are clearly associated with ionization from the HOMO and SHOMO, both orbitals of b_1 symmetry. The *specific* assignment of the two bands is, however, problematic and it illustrates the limitations of Koopmans' theorem when applied to systems in which two ion states of the same symmetry are close in energy.

TABLE 17.9

THE LITERATURE ASSIGNMENTS OF THE He I PHOTOELECTRON SPECTRUM OF PHOSGENE

Band[a]	Assignments	
	Chadwick [349]	Thomas and Thompson [2028]
A	O lone-pair	Cl lone-pair
B	Cl lone-pair (B and C)	Cl lone-pair
C		O lone-pair
D	Cl lone-pair	Cl lone-pair
E	Cl lone-pair	Cl lone-pair
F	σ	π(CO)
G	π(CO)	σ
H	σ	σ
I	σ	Not assigned

[a] See Fig. 17.14.

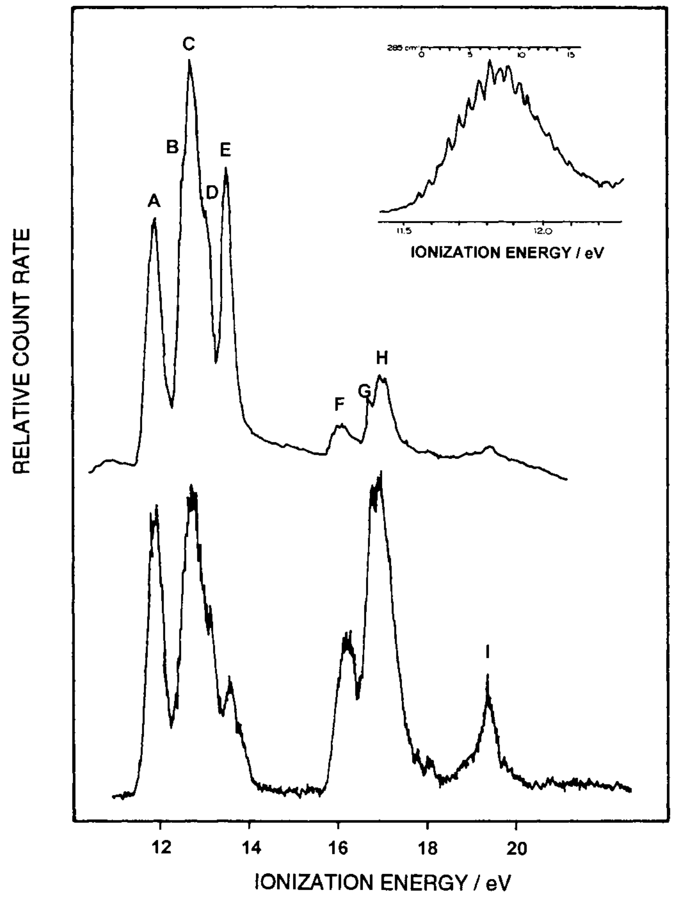


Fig. 17.14 **The He I (upper) and He II (lower) photoelectron spectra of $COCl_2$ [1589a]. Inset, band A of the He I photoelectron spectrum of $COCl_2$ showing the vibrational structure [349].**

Ab initio calculations [1857aa], using split valence and polarized basis sets, predict the HOMO to have essentially 90% chlorine lone-pair character, see Table 17.2. Experimentally, however, the large intensity increase of band A (compared with bands B–E, see Fig. 17.14) on changing from He I to He II ionizing radiation suggests that it results from ionization from an orbital with substantial oxygen character; this observation thus supports the assignment of the first band to ionisation from the SHOMO ($7b_1$) – a Koopmans' theorem violation. Recent work [1857aa], in which Green's function and configuration interaction techniques were used to calculate ionization energies, and in which the character of the singly occupied molecular orbitals in the ion states was examined, indicates that this assignment is

TABLE 17.10

CALCULATED VERTICAL IONIZATION ENERGIES OF $COCl_2$

Orbital	E_n/eV					
	KT STO-6G[a]	KT 4-31G*[a]	KT CNDO/2[b]	KT DZ+P[c]	OVGF[c,d]	E2PH-TDA[c,e]
$8b_1$	11.47	13.30	9.5	12.92	11.72	11.92
$7b_1$	11.82	12.94	11.4	13.48	12.26	12.52
$3b_2$	11.82	13.54	11.3	13.54	12.56	12.75
$2a_2$	12.33	13.60	11.5	13.60	12.43	12.71
$11a_1$	12.80	14.43	11.7	14.42	13.17	13.49
$2b_2$	16.73	17.82	18.4	17.74	16.40	16.54
$10a_1$	17.16	19.10	16.8	19.15	17.25	17.51
$6b_1$	18.02	19.22	19.3	19.35	17.37	17.62
$9a_1$	20.25	21.94	20.5	22.10	19.91	19.91 20.18[f]

[a] [1589c,1950c]. [b] A 4 eV correction factor has been applied to these values [349]. [c] [1857aa]. [d] Outer valence Green's function. [e] Extended two particle-hole Tamm-Dancoff approximation. [f] Shake-up potential.

misleading. The singly occupied m.o. of the ground ion state does contain substantial oxygen character but otherwise (*e.g.* by nodal character) it is most closely correlated with the HOMO ($8b_1$) of $COCl_2$.

A one-to-one correlation between the bands in the photoelectron spectra and the orbitals of neutral $COCl_2$ is clearly misleading. However, if an extant assignment is to be chosen that of Thomas and Thompson [2028] (in which band A is assigned to a chlorine based orbital) is the most accurate.

Bands C–E in the photoelectron spectrum of $COCl_2$ (Table 17.11) are assigned to ionizations from orbitals which are predominantly chlorine based and bands F and G are assigned to ionizations from the π(CO) and σ(CO) orbitals. *Ab initio* calculations (see Table 17.10) predict the σ(CO) $10a_1$ level to be significantly more stable than the π(CO) $2b_2$ level; hence the assignment of band F to ionization from the π(CO) and band G to σ(CO), in accord with Thomas and Thompson [2028]. The only evidence to support Chadwick's [349,350] counter-intuitive placing of the σ(CO) level above the π(CO) level are the results of semi-empirical CNDO/2 calculations. Bands H and I are assigned to ionization from the

TABLE 17.11

EXPERIMENTAL IONIZATION ENERGIES, VIBRATIONAL INTERVALS AND ASSIGNMENTS FOR THE PHOTOELECTRON SPECTRUM OF $COCl_2$ [349,1589a,1857aa]

Band	E_n/eV	ν'/cm^{-1}			Assignment
		ν'_1	ν'_2	ν'_3	
A	11.90			285	n(Cl); $8b_1$
B	12.5(sh)				n(O),n(Cl); $7b_1$
C	12.70				n(Cl),n(O); $3b_2$
D	13.1(sh)				n(Cl); $2a_2$
E	13.51			290	n(Cl); $11a_1$
F	16.09		540	260	π(CO); $2b_2$
G	16.72			280	σ(CO); $10a_1$
H	16.99	~1000			$\sigma(CCl_2)+\pi_{xz}(CO)$; $6b_1$
I	19.40				$\sigma(CCl_2)$; $9a_1$

$\sigma(CCl_2)$ levels, in accord with the results of the calculations (Table 17.10). The full spectral assignment for $COCl_2$ is summarized in Table 17.11.

Frost and coworkers have discussed the assignment of the photoelectron spectrum of COClH in the context of those for COH_2, $COCl_2$ and related molecules [694]. Some of the anomalies and uncertainties noted in these works are removed by the assignment presented in Table 17.11.

The photodissociation of $[COCl_2]^+$ has been investigated using photoelectron/photoion coincidence techniques [1044]. $[COCl_2]^+$ and $[COCl]^+$ were both observed in the time of flight spectrum recorded at the onset of the lowest ionization energy band in the photoelectron spectrum, suggesting quite a long dissociative lifetime. At higher internal energies, the $[COCl]^+$ intensity increased at the expense of $[COCl_2]^+$ until the former ion was observed without $[COCl_2]^+$. At ionization energies above 16.35 eV, Cl^+ was formed at the expense of $[COCl]^+$; an appearance potential for the formation of Cl^+ was estimated at 16.5 ± 0.2 eV. The translational energy releases computed from the time-of-flight peak contours were larger than expected, a feature that could not be fully rationalized.

17.2.1.5 Carbonyl dibromide

The He I and He II photoelectron spectra of $COBr_2$, which are presented in Fig. 17.15, show many similarities with those of phosgene. The assignments in Table 17.12 (suggested originally by Thomas and Thompson [2028]) were made on the basis of both the experimental He I/He II intensity variations and the results of ionization energy calculations [1857aa].

In contrast to the photoelectron spectra of COF_2, but in keeping with that of $COCl_2$, the lowest energy band in the spectrum of $COBr_2$ (band A, Fig. 17.15) is attributed to ionization from a halogen-based orbital, as are bands B, D and E. Band C, which gains in relative intensity in the He II spectrum, is assigned to the oxygen-based lone-pair. Bands F and G are assigned to ionizations from π(CO) and σ(CO), respectively, in accord with both

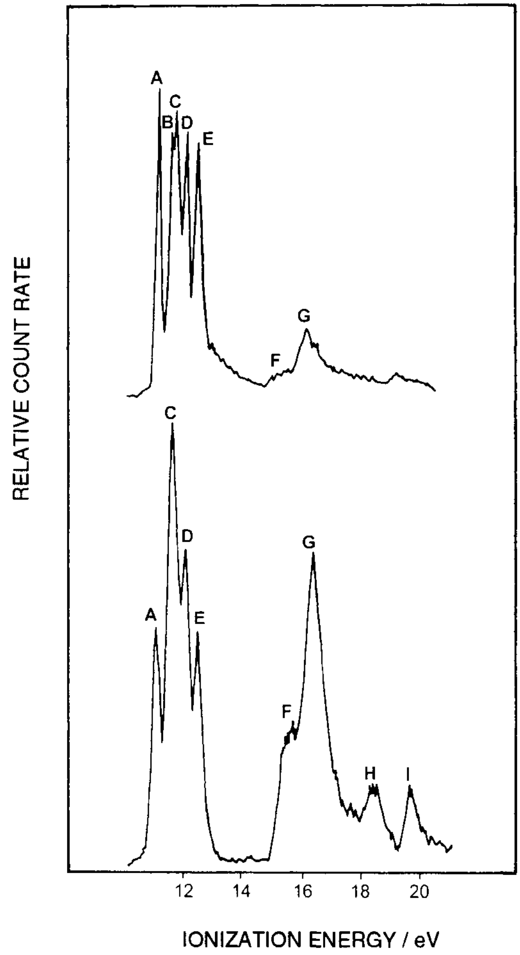


Fig. 17.15 The He I (upper) and He II (lower) photoelectron spectra of $COBr_2$ [1589a,1589c].

TABLE 17.12

EXPERIMENTAL AND CALCULATED IONIZATION ENERGIES, AND ASSIGNMENTS, FOR THE PHOTOELECTRON SPECTRUM OF $COBr_2$ [1857aa]

Band	E_n/eV[a]			Assignment
	Expt.	Calc.		
		OVGF[b]	E2PH-TDA[c]	
A	10.98	10.85	11.04	n(Br); $14b_1$
B	11.45	11.36	11.56	n(Br); $5a_2$
C	11.61	11.55	11.62	n(O); $13b_1$
D	11.92	11.73	11.97	n(Br); $6b_2$
E	12.36	12.05	12.28	n(Br); $17a_1$
F	15.56	15.92	15.86	π(CO); $5b_2$
G	16.12	16.72	16.62	σ(CO); $16a_1$
		16.64	16.69	$\sigma(CF)+\pi_{xz}(CO)$; $12b_1$
H	19.0	19.37	19.02	$\sigma(CO),\sigma(CBr_2)$; $15a_1$
I	20.1			Shake-up ionization

[a]Vertical ionization energies. [b]Outer valence Green's function. [c]Extended two particle-hole Tamm-Dancoff approximation.

the band profiles (as compared with those for COH_2, COF_2 and $COCl_2$) and the calculations (see Table 17.12).

Of the seven bands in the He I spectrum of $COBr_2$ (Fig. 17.15), only one (band F) exhibits any vibrational structure. The period of this structure (1690 cm^{-1} [2028]) indicates that it is associated with stretching of the carbonyl group – additional support for the assignment of band F to ionization from an orbital with π(CO) character.

17.2.1.6 Asymmetrical carbonyl halides

The He I photoelectron spectra of the mixed carbonyl halides COClF, COBrCl and COBrF are presented in Fig. 17.16 [1857aa]. They have been assigned (Table 17.13) by direct comparison with the 'parent' COX_2 molecules and with OVGF ionization energy calculations [1857aa]. In general the predicted ionization energies are underestimated for those bands in the region below 14 eV and overestimated for those bands above this region.

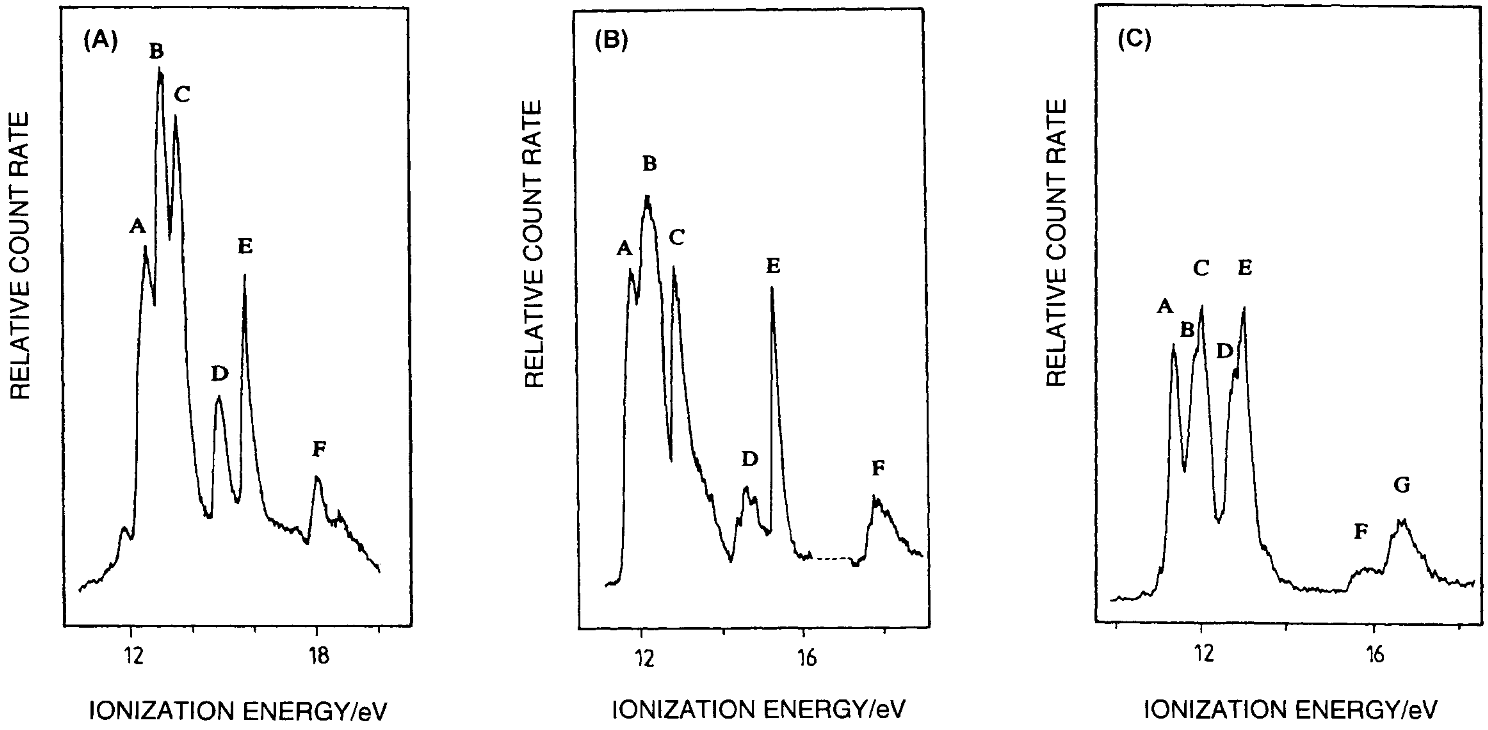


Fig. 17.16 The He I photoelectron spectra of (A) COClF, (B) COBrF and (C) COBrCl [1589a,1857aa].

TABLE 17.13

EXPERIMENTAL AND CALCULATED IONIZATION ENERGIES, AND ASSIGNMENTS, FOR THE PHOTOELECTRON SPECTRA OF COClF, COBrF AND COBrCl [1589a,1857aa]

Band	E_n/eV[a]		Assignment
	Expt.	Calc.[b]	
(A) COClF			
A	12.58	12.50	n(O); 16a'
B	13.10	12.83	n(Cl); 4a"
C	13.63	13.47	n(Cl); 15a'
D	14.87	15.10	π(CO); 3a"
E	15.64	15.97	n(F); 14a'
F	18.07	18.51	σ(CO); 13a'
(B) COBrF			
A	11.87	11.64	n(Br); 22a'
B	12.27	11.84	n(Br); 7a"
C	12.89	12.91	n(O)-n(Br); 21a'
D	14.57	15.06	π(CO)-n(F); 6a"
E	15.32	15.50	n(O)-n(F); 20a'
F	17.78	18.38	n(O)+σ(CO); 19a'
(C) COBrCl			
A	11.30	11.19	n(Br); 25a'
B	11.83	11.58	n(Br); 8a"
C	11.98	11.90	n(O)-σ(BrCCl); 24a'
D	12.73	12.49	n(Cl)-π(CO); 7a"
E	12.95	12.71	n(Cl); 23a'
F	15.75	16.15	π(CO)+n(Cl); 6a"
G	16.52	16.87	σ(CO)+n(Br); 22a'

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[a] Vertical ionization energies. [b] Outer valence Green's function method. Koopmans' Theorem values are also reported in [1857aa].

17.2.1.7 Empirical trends in the electronic structure of the carbonyl halides

The variation of experimental ionization energies for COX_2 (X = F, Cl or Br), COXF (X = Cl or Br) and COBrCl are illustrated in Fig. 17.17 and, although these largely parallel the *ab initio* n(O), π(CO) and σ(CO) orbital energies in Fig. 17.5, there are significant discrepancies in the trends, especially for COBrF. Ionization energies calculated using Green's function techniques [1857aa] map onto the experimental ionization energies far more closely, both in relative and absolute terms. A consideration of the trends in ionization potentials by Haque *et al.* [880a] is to be admired for its unique deductive style, but little else.

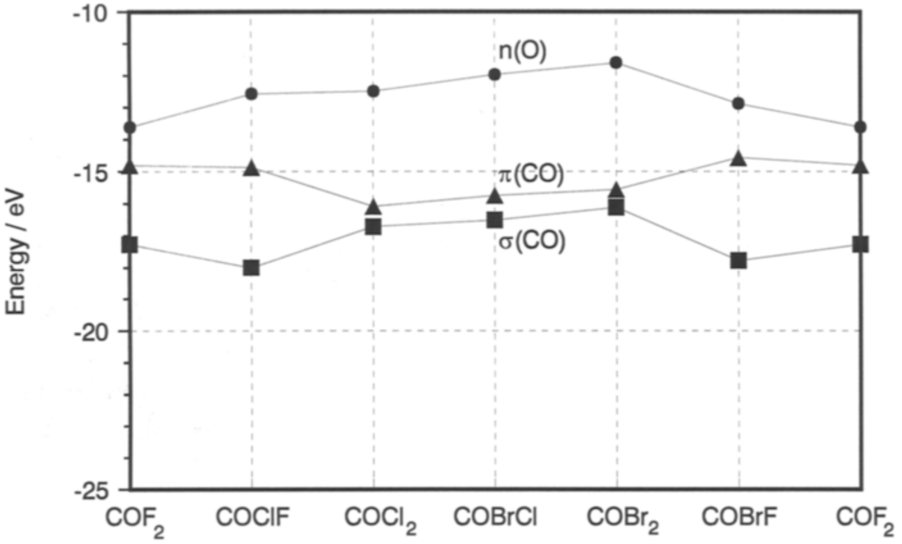

Fig. 17.17 **The empirical ionization energies for electrons removed from n(O), π(CO) and σ(CO) for COX_2 (X = F, Cl or Br), COXF (X = Cl or Br) and COBrCl.**

In Fig. 17.18, the carbonyl halide lone-pair oxygen ionization energies (determined by photoelectron spectroscopy) are plotted against the sum of the Pauling electronegativities of the halides. As might be expected, a reasonable (but not good) correlation is obtained between these parameters. A similar systematic trend is also obtained if the n(O) ionization energies are plotted against the ground-state carbonyl halide ν_1(CO) stretching frequencies. However, close correlation with r(CO) is not found – an observation that merits further investigation.

17.2.2 X-ray photoelectron spectroscopic studies

The C 1*s* binding energy of solid COF_2 has been shown to be 294.2 eV [728] and this value, together with the C 1*s* binding energies of a wide range of organic molecules, has

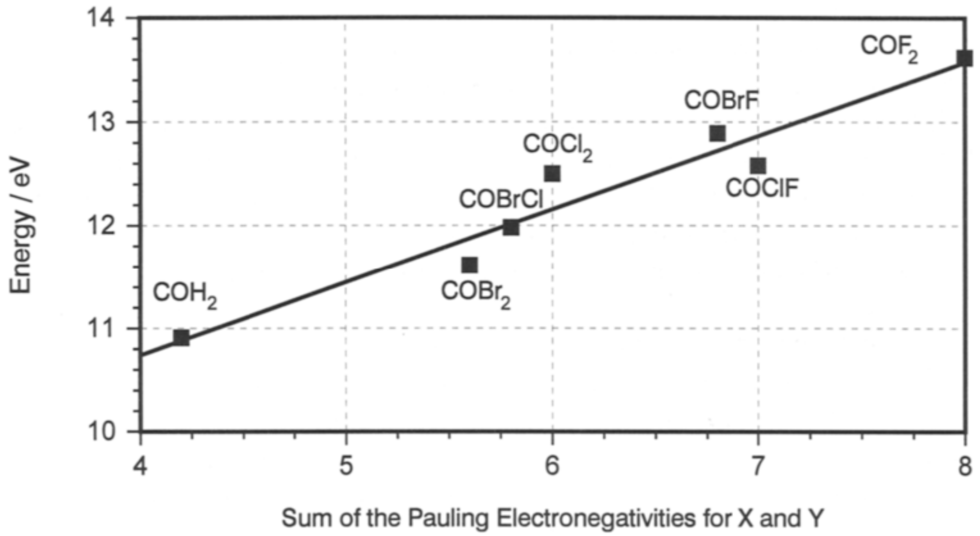

Fig. 17.18 **The ionization energy of the oxygen lone–pair plotted against the sum of the Pauling electronegativities of the substituents X and Y for COXY (X = Y = H, F, Cl or Br; X = Br, Y = Cl or F; X = Cl, Y = F); the line is a result of a conventional least–squares linear regression analysis of these data (R^2 = 0.936, n = 7).**

been correlated (in two independent studies) with an electronegativity–derived charge parameter [728] and with CNDO–derived carbon atomic charges [937]. A related study [1048] to determine the relationship between the carbon 1*s* and oxygen 1*s* binding energies of a sample of thirty–two carbonyl complexes revealed only a poor correlation. This latter observation was attributed [1048] to oxygen relaxation energy differences amongst the complexes, resulting from variable π–donor abilities of the groups attached to the carbonyl moieties. In particular, it was proposed by Jolly and Schaaf [1048] that COF_2 exhibits a high π–donor relaxation energy, a suggestion that is both contested by Adams [5] (whose CNDO/2 calculations indicate a small π relaxation energy, similar to that of COH_2) and is in conflict with earlier *ab initio* results [392a]. COF_2 was also included in a large scale computational study of substituent effects upon carbon, oxygen and fluorine 1*s* binding energies [392a].

17.3 ELECTRONIC ABSORPTION

In recent years there has been a revival of interest in the electronic absorption spectra of COF_2, COClF and $COCl_2$ owing to their formation as photooxidation products of chlorofluorocarbons, and their detection in the troposphere and stratosphere [1037,1718b, 1746a,2196a].

17.3.1 Carbonyl difluoride

The lowest excited electronic state of COF_2 (C_s point group) is a singlet of A" symmetry generated by a n⟶π* transition within the molecule [536]. *Ab initio* calculations [536,677b], using a variety of basis sets and extensive treatment of electron correlation, have indicated that this singlet state is associated with a pyramidal distortion of the molecule, and significant weakening of the CO bond {*r*(CO) = 0.1357 nm, *r*(CF) = 0.1325 nm, ∢FCO = 110.0° and ∢FCF = 112.8° [677b]}.

The lowest energy triplet state, of $^3A'$ symmetry, is generated by a π⟶π* transition, and is also associated with a pyramidal distortion of the molecule {*r*(CO) = 0.1354 nm, *r*(CF) = 0.1326 nm, ∢FCO = 110.1°, and ∢FCF = 112.4°} [677b]. These values can be compared with the equivalent parameters calculated for ground state COF_2 {*viz.* *r*(CO) = 0.1175 nm, *r*(CF) = 0.1316 nm, ∢FCO = 126.1°, and ∢FCF = 107.8° [677b]} and the best experimentally derived values {*viz.* *r*(CO) = 0.11717 nm, *r*(CF) = 0.13157 nm, ∢FCO = 126.145° and ∢FCF = 107.71° [1480]}. Despite the gross restrictions inherent in, or imposed by, many of the semiempirical approaches, some qualitatively similar excited state geometry changes have been computed [407,1414,1777]. Analysis of the excited state potential surfaces of COF_2 and related carbonyl halides has revealed an inversion barrier height ordering of COF_2 > COClF > $COCl_2$ > COFH > COH_2, which was discussed above (Section 17.1.2.4, Figs. 17.9 and 17.10) [1066]. Possible splitting of the absorption bands due to inversion doubling was predicted to be too small to be observed experimentally [1066,1444].

The first in depth study of the electronic spectrum of COF_2, at low resolution, revealed a remarkably rich spectrum of four broad bands, containing at least one hundred and twenty lines between 42100–82300 cm^{-1} [2212]. This is in contrast to an earlier report [1401], now unambiguously shown to be erroneous [2211], which suggested that the electronic spectrum of COF_2 was comprised of five bands over the region 48760–55190 cm^{-1}. The five bands originally attributed to COF_2 [1401] are now known to be due to the Cameron bands of impurity CO [2211].

The first transition (n⟶π*) has an onset at 42084 cm^{-1} and runs to *ca.* 56000 cm^{-1} where it merges with the second electronic transition [2212]. This first series of bands consists of around one hundred and forty vibrational components made up from twelve series each with a spacing of about 1030 cm^{-1} {ν'_1; ν(CO)}. Nölle *et al.* [1520a] have reinvestigated this region of the uv spectrum of COF_2 and obtained absolute absorption cross-sections which, together with a revised estimate of the quantum yield ($\Phi = 1$) were used to calculate photodissociation rate constants.

The second electronic transition (possibly also n⟶π*) starts at 56598 cm^{-1} and continues to around 61800 cm^{-1}; it has a maximum at *ca.* 59200 cm^{-1}. There are two vibrational progressions, starting points 56598 and 57317 cm^{-1} {a separation of 719 cm^{-1}; ν'_2; ν_s(CF)}, both with intervals of 500 cm^{-1} {ν'_3; δ_s(OCF)} [2212].

The third electronic series (n⟶σ*) is made up of only five broad bands (bandwidths *ca.* 450 cm^{-1}), the first of which is at 65597 cm^{-1}. The average separation is 779 cm^{-1}

(*i.e.* ν_2'). Overlapped with this series is the fourth absorption ($\pi \rightarrow \pi^*$) which is a continuous band with a maximum at 76000 cm^{-1} [2212].

A more recent high resolution, variable temperature (−78 to +25 °C) study [1057] upon the $\tilde{X} \rightarrow \tilde{A}$ band resulted in reassignment of the band origin to 39252 cm^{-1} and the identification of one hundred and seventy vibrational components, which have been rationalized into twenty-six progressions involving ν_1' (1056.2 cm^{-1}), ν_2' (834.1 cm^{-1}), ν_3' (470.0 cm^{-1}), ν_4' (1252.1 cm^{-1}) and ν_5' (669.1 cm^{-1}). In addition, a set of bands which were clearly closely spaced (1.1 cm^{-1}) doublets and a series of temperature dependent bands were observed (ν_6''). These observations are consistent with the predicted non-planarity of the $\tilde{A}$ state. Crude estimates of the height of the inversion barrier (8200 cm^{-1}), the out-of-plane angle ($\hat{\omega}$ = 148.2°) and of the changes in the CO and CF bond lengths (+0.26 Å and +0.06 Å, respectively) were deduced from the data [1057]. The large height of this barrier relative to those in COH_2 (354 cm^{-1}) and COHF (2550 cm^{-1}) is consistent with the delocalization, in the case of COF_2, of the nominally π(CO) bonding orbital over the whole molecule (see also Section 17.1.2.4).

Numerous methods have been used to predict the singlet $n \rightarrow \pi^*$ transition energy [82,463,486,535,536,597d,625,1573b,1777,2104a,2234,2242]. The most accurate was performed by Francisco *et al.* [677b] who performed a CAS-SCF calculation with a 6-31G* basis and obtained a value within 1% of that found experimentally [1057].

An *ab initio* calculation (using an STO-4G basis) gave an estimate of the singlet-triplet $\pi \rightarrow \pi^*$ energy of 20000 cm^{-1} (2.45 eV) [536], well below that experimentally determined (48000 cm^{-1}, 6 eV) using the trapped electron spectroscopic technique of ion cyclotron resonance [544]. MNDO and INDO predictions of the singlet-triplet $n \rightarrow \pi^*$ energy are likely to be poor estimates [2234]. There are no definitive experimental data for this transition, although Doiron and McMahon [544,597d] propose that its weak structure expected in the ion cyclotron resonance spectrum is hidden by the low energy tail of the singlet-triplet $\pi \rightarrow \pi^*$ peak.

Potential energy curves for singlet and triplet A_2, B_1 and B_2 states of COF_2 have been computed using *ab initio* projected-unrestricted Hartree-Fock theory with a contracted Gaussian type orbital basis set [273]. However, C_{2v} symmetry was strictly maintained for these excited states, so the poor agreement between the predicted and experimental band onsets (which was readily acknowledged by Brewer *et al.* [273]) comes as little surprise.

A method for calculating the magnitude of solvent shifts on electronic transitions has been developed and applied to COF_2; for a medium of dielectric constant equal to 80, a solvent shift of *ca.* 1000 cm^{-1} to higher energy (compared with the gas phase) was computed [230].

17.3.2 Phosgene

The experimental electronic spectrum of $COCl_2$ has received considerable attention [564,754,940,942,1007,1207,1444,1552,2134]. In addition, there have been several attempts, with varying degrees of success, at the prediction of the transition energies [625,1460] and the oscillator strengths [625]. The pioneering, high quality, experimental data of Henri and Howell [942] has now been supplemented and extended; however, their contribution (reported in 1930) remains an essential reference work.

The u.v. spectrum of $COCl_2$ shows a number of absorptions over the region 32869 to 93475 cm^{-1}. The system I onset is at 33551 cm^{-1} and the absorptions (which are superimposed on a strong continuum) do not reach a maximum (ε = 18 l mol^{-1} cm^{-1} [2245]) until 43100 cm^{-1} {Fig. 17.19(A)} [1444]. Variable temperature studies [754,1444]

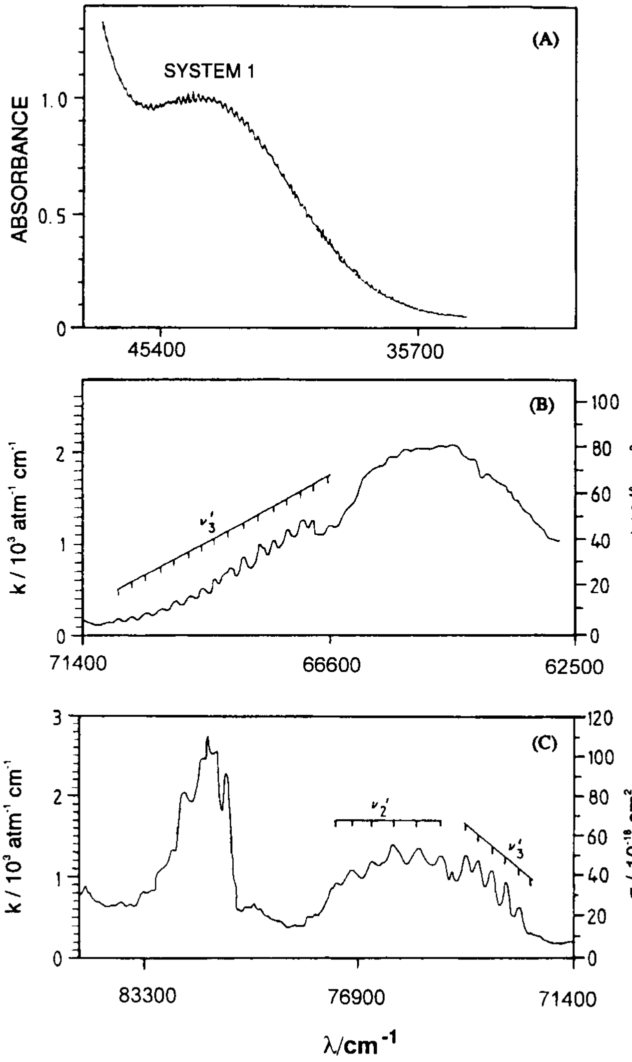

Fig. 17.19 The low resolution electronic absorption spectrum of $COCl_2$ over the ranges (A) 34500 to 49000 cm^{-1} [1444], (B) 62500 to 71430 cm^{-1} [1552], and (C) 71430 to 85470 cm^{-1} [1552].

have revealed that most of the discrete bands above 35100 cm^{-1} are hot bands; the continuum is also temperature sensitive [35,754]. Detailed vibrational analysis of the spectrum [754,1444] indicated a large change in equilibrium geometry between the ground and excited states (*cf*. Section 17.3.1).

Analysis of system I (origin assumed to be 32730 cm^{-1} for $CO^{35}Cl_2$) revealed excited state progressions in ν_5' (430 cm^{-1}) and ν_6' (581 cm^{-1}), as well as ground state progressions in ν_5'' (438 cm^{-1}) and ν_6'' (587 cm^{-1}) [754], thus revising the earlier values [942]. A more recent, higher resolution study [1444] revealed excited state progressions in ν_1' (1152 cm^{-1}), ν_2' (554 cm^{-1}), ν_3' (300 cm^{-1}), and ν_6' (435 cm^{-1}), with a ground state progression in ν_6'' (582 cm^{-1}) with a "false origin" at 33631 cm^{-1} [1444]. The system I bands are due to a spin-forbidden $^1A_1 \longrightarrow ^1A_2$ ($n \longrightarrow \pi^*$) transition [1444].

The data are consistent with a pyramidal excited state with weakened CCl and CO bonds, but with ∡ClCCl very similar to that exhibited by the ground state molecule. Computer fitting of the positions and intensities of the spectral lines yielded an inversion barrier height of 3170 cm^{-1}, and an equilibrium deviation from planarity of 147.5° [1444]. The vibrational potential function for the first excited state of phosgene has been studied, and it supports considerable delocalization of the π^* orbital, and significant mixing of the CO and CCl bonds in the ground state of the molecule [564,565].

Due to predissociation, the bands become increasingly diffuse towards higher energies, so much so that the doublet structure (splittings of 6 to 10 cm^{-1}, larger splittings to shorter wavelengths) of many of the bands above 36800 cm^{-1} is no longer apparent [754]. The doublet structure (which is temperature invariant and has the weaker component to longer wavelength) is a manifestation of the chlorine isotope effect, *i.e.* $CO^{35}Cl^{37}Cl$ absorbs at longer wavelength than the more abundant $CO^{35}Cl_2$. In addition, each band is asymmetric having a relatively sharp edge to short wavelengths, but a much less sharp edge towards longer wavelengths. This has been ascribed to bond lengthening at high rotational states [940].

Experimentation with $^{13}COCl_2$ has revealed a subtle shift in the vibrational peak maxima of system I, when compared with those of $^{12}COCl_2$ [2134], a finding that is consistent with the occurrence of predissociation in phosgene.

At higher energies (*i.e.* in the vacuum ultraviolet region), $COCl_2$ exhibits six absorption bands (Fig. 17.19) [1207,1552]. There is a broad absorption with a maximum at 64700 cm^{-1}, the short-wavelength end of which overlaps with a second vibrationally structured band whose maximum is at 66707 cm^{-1} (ν_3' = 267 cm^{-1}) [1207]. Vibrational structure was also found on the next two absorptions, which have band onsets of 72538 cm^{-1} (ν_3' = 335 cm^{-1}) and 74810 cm^{-1} (ν_2' = 562 cm^{-1}), respectively. Only two further absorption bands were detected, an intense feature with an onset at 80816 cm^{-1} and a broad band with an onset at 88253 cm^{-1} and a maximum at 89043 cm^{-1}; the latter displays a diffuse vibrational structure (ν_3' = 290 cm^{-1}). All of the instances of vibrational structure in the vacuum u.v. spectrum of $COCl_2$ are simple progressions in a_1 modes. Continuous absorption occurs above

95000 cm^{-1} (11.78 eV), a value which shows good correspondence with the adiabatic first ionization energy of phosgene, *viz.* 11.55 eV [349].

17.3.3 Carbonyl dibromide

The electronic absorption spectrum of gaseous carbonyl dibromide has not been studied in detail, but the absorption onset occurs at 31250 cm^{-1} and absorption is continuous up to 47620 cm^{-1}, the limit of the reported measurements [1821].

17.3.4 Carbonyl chloride fluoride

The electronic spectrum of COClF (Fig. 17.20), at both low and medium resolution, has been obtained [2244a,2245]. The absorption was attributed to a singlet–singlet $n \rightarrow \pi^*$ transition. Although no fine structure was detectable in the low resolution spectrum, at medium resolution a series of diffuse bands that merged to a continuum (at 42550 cm^{-1}) was reported [2244a,2245]; the diffuseness of the individual members of the progression was attributed to predissociation. A vibrational analysis of the spectrum proved inconclusive, but vibrational spacings of 307, 360, 553 and possibly 754 cm^{-1} were identified. In line with observations upon COF_2, a distorted excited state geometry was proposed [2244a,2245].

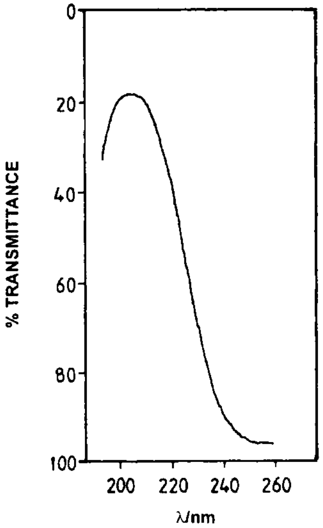

Fig. 17.20 The low resolution electronic absorption spectrum of COClF [2245].

In cyclohexane, a red shift of 3400 cm^{-1} occurs (relative to the gas phase absorption maximum, 49260 cm^{-1}, $\varepsilon = 35\ l\ mol^{-1}\ cm^{-1}$) [2245].

17.4 FLUORESCENCE

The chemiluminescent reaction [225]:

$$O_2(^1\Delta) + C_2F_4 \longrightarrow COF_2(S_1) + COF_2(S_0)$$

gives rise to a fluorescence which has been ascribed to emission from electronically excited COF_2; it has an origin at 42550 cm^{-1} (235 nm), peaks at *ca.* 34500 cm^{-1} (290 nm), and shows extensive vibrational structure {see Fig. 17.21(A)}. As a means of further characterizing this fluorescence, COF_2 was studied by multiphoton infrared excitation {see Fig. 17.21(B)} [989]. The observed emission from pure COF_2 was assigned to a transition between the first excited singlet state, π^*, and the ground state of the molecule, *i.e.* $S_1 \rightarrow S_0$ ($^1A_2 \rightarrow {}^1A_1$).

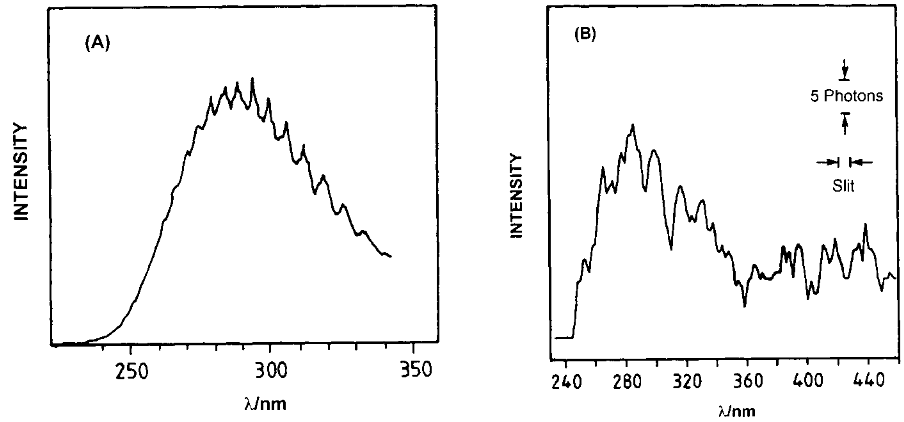

Fig. 17.21 The fluorescence spectrum of electronically excited COF_2 (A) as generated in the reaction between singlet oxygen and C_2F_4 [225], and (B) in the pure state (pressure 10.1 torr) over a period of 1 μs following laser irradiation (50 J cm^{-2}, 946 cm^{-1}) [989].

COF_2 has found favour as a target molecule in energy transfer studies as its vibrational energy transfer processes are relatively little affected by rotational complications, its ir vibrational modes are all allowed and its constituent atoms are all of comparable 'large' mass - a feature that means the vibrational modes are all easily accessible to one laser.

Laser excitation of the ν_2 mode of COF_2 has been shown to result in infrared fluorescence (indicated by the wavy lines in Fig. 17.22) from its ν_1, ν_4, ν_6 and ν_3/ν_5 states [18,227,340]. Subsequent to excitation of the ν_2 mode, a ladder-climbing process:

$$2COF_2(\nu_2) \longrightarrow COF_2(2\nu_2) + COF_2$$

results in the rapid population of the $2\nu_2$ state: as this overtone state is strongly Fermi mixed

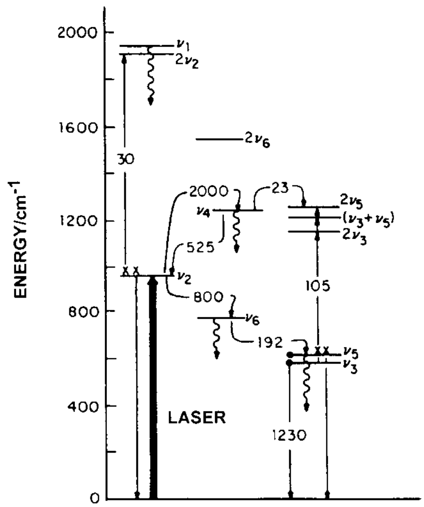

Fig 17.22 **Energy level diagram for COF_2; the indicated rate constants are in units of gas kinetic collisions, the wavelength of the fluorescence is given in parentheses [18,340].**

with the ν_1 state, this latter state is also populated. There is also evidence for hot band pumping of the $\nu_2 \rightarrow 2\nu_2$ transition, which would populate the ν_1 and $2\nu_2$ states [340]. The ν_2 state decays to the ν_4 and the ν_6 states, both of which ultimately decay to the ν_3 and ν_5 states. The probabilities for transfer from state to state have been calculated assuming a one-dimensional collision and purely repulsive exponential potential and harmonic wave functions; the reciprocal of the probabilities give the collision numbers that are indicated in bold in Fig. 17.22. Vibration-translation/rotation relaxation of the ν_3 and ν_5 states occurs over a time scale of *ca.* twelve hundred collisions.

An early attempt to observe fluorescence from phosgene was unsuccessful [576]. The chlorine K_α and K_β X-ray fluorescence spectra of phosgene (together with those of a wide range of organic compounds) have been recorded [755]. The emission was attributed to the filling of chlorine core level vacancies by valence electrons.

17.5 PHOSPHORESCENCE

Although there are no reported experimental data upon phosphorescent emission from the carbonyl halides under scrutiny in this book, there has been some effort expended in calculating the transition energies, polarizations and lifetimes for possible excited triplet states (see Table 17.14) [337,1344]. These predictions should expedite the interpretation of any data that may be obtained in the future, as the characteristics of the phosphorescence should depend quite markedly upon the nature of the emitting state. However, it should be noted that the predictions of Carroll *et al.* [337] give very small values for the transition energies.

An early prediction by El-Sayed [588b] that the halogen atoms should have a negligible influence upon the $\pi^* \rightarrow n$ phosphorescent lifetimes of these compounds (relative to COH_2) has, in more recent work [337], been refuted. A marked dependence in the predicted lifetimes is revealed in the data in Table 17.14, and this has been attributed [337] to mixing between the halogen and the oxygen atomic orbitals.

TABLE 17.14

CALCULATED TRANSITION ENERGIES AND LIFETIMES FOR SOME EXCITED TRIPLET STATES OF THE CARBONYL HALIDES

Molecule	Excited State	Transition	Transition Energy/eV	Lifetime/ms	Ref.
COF_2	$^3A_2$	$\pi^* \rightarrow n$[a]	6.21	7.4	1344
	$^3A_1$	$\pi^* \rightarrow \pi$[b]	7.23	10.0	1344
	$^3A_2$	$\pi^* \rightarrow n$	1.77	1.6	337
$COCl_2$	$^3A_2$	$\pi^* \rightarrow n$	2.03	9.3	337
$COBr_2$	$^3A_2$	$\pi^* \rightarrow n$	2.03	0.05	337
COI_2[c]	$^3A_2$	$\pi^* \rightarrow n$	2.03	0.01	337

[a] *z*-polarized. [b] *y*-polarized. [c] This molecule has never been isolated.

17.6 REACTIVITY PATTERNS

In the Sections above, various aspects of the electronic structure of the carbonyl halides have been discussed in some detail, and it is now appropriate to consider what insight this knowledge yields concerning their chemical reactivity. In particular, their reactivity towards nucleophilic and electrophilic substitutions will be examined.

The relative nucleophilicity of a carbonyl compound can be estimated from the energy of the oxygen lone-pair orbital, a measure of which is obtained from the n(O) ionization energies (see Table 17.15). On this basis the following reactivity towards Lewis acids is predicted:

$$COH_2 > COBr_2 > COBrCl > COCl_2 > COClF > COBrF > COF_2$$

Thus COF_2 is expected to exhibit little, and $COBr_2$ a more marked, tendency to act as a donor in the formation of molecular (Lewis acid–base) complexes. There has, as yet, been no experimental comparative study of the donor ability of the carbonyl halides.

The reactivity of a carbonyl compound with an electron donor is generally controlled (as long as steric crowding need not be considered) by the energy difference of the $\pi^*(CO)$ orbital of the former and the HOMO of the donor. Further, if the reactivity of just one type of donor is considered, then an inverse relationship is expected between carbonyl halide $\pi^*(CO)$ energy and reactivity (*i.e.* the higher the $\pi^*(CO)$ energy, the less reactive the carbonyl halide). On these grounds, the reactivity ordering (given below) was predicted from

TABLE 17.15

EXPERIMENTAL IONIZATION ENERGIES FOR THE n(CO) AND π(CO) LEVELS FOR THE CARBONYL HALIDES [1857aa,2071a]

Molecule	$E\{n(O)\}$/eV	$E\{\pi(CO)\}$/eV
COH_2	10.88	14.38
$COBr_2$	11.61	15.56
COBrCl	11.98	15.75
$COCl_2$	12.5(sh)	16.09
COClF	12.58	14.87
COBrF	12.89	14.57
COF_2	13.62	14.80

the results of *ab initio* molecular orbital calculations upon the carbonyl halides (STO-3G basis set for each molecule) [1589c]:

$$COCl_2 > COBrCl > COBr_2 > COClF > COBrF > COH_2 > COF_2$$

Unfortunately, the dearth of experimental data means that this reactivity ordering must remain in the realm of speculation. However, the addition of ammonia to formaldehyde and to carbonyl difluoride (*inter alia*) has been modelled, by *ab initio* methods, by Yamataka *et al.* [2226aa]. These authors expected (on the basis of the calculated $\pi^*(CO)$ energy levels) that COF_2 should be less reactive than COH_2 (as indicated above) but calculated the reverse reactivity order. They suggest that the reactivity of COF_2 may be controlled by the large positive charge density on the carbon atom rather than the ammonia-HOMO/carbonyl-π^*(CO) energy difference. *Ab initio* calculations on the carbonyl halides [1589c] suggest the following order of increasingly positive carbon charge density:

$$COF_2 > COClF > COCl_2 > COH_2$$

Thus, on the *very* limited data set available, it would appear that the formal positive charge at the carbon (see Fig. 17.7) is more important in determining the electrophilic reactivity of a carbonyl halide than the absolute energy of the π^*(CO) orbital.

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APPENDICES

A1 PHOSGENE: INDUSTRIAL OUTPUT

The earliest industrial uses for phosgene were in the manufacture of dyes and a few pharmaceuticals (see Chapter 4), for which production requirements were minimal. Large quantities of phosgene were not manufactured until 1915, when they were needed for use as a war gas (see Section 1.3.1). After World War I, the production of phosgene declined, but massive quantities were manufactured in anticipation of a resumption of the use of chemical warfare agents in WWII (see Section 1.7). Proper wide-scale industrial, non-military, manufacture of phosgene began in the mid-50s, for use in the production of TDI for polyurethane resins (see Section 4.7.1.1). In 1957, the US International Trade Commission (USITC) reported the production of phosgene to be about 2.5 kt, and production thereafter increased sharply throughout the 1960s and 1970s as the demand for isocyanates, and other materials manufactured from phosgene, expanded. The world production of phosgene in 1977 was approximately 1300 kt: current World production is estimated at 2700 kt. The current demand for phosgene is strong for most of its end uses, but owing to the disproportionate demand in polyurethane manufacture, the growth rate for phosgene may be expected to parallel the growth rate for polyurethanes for the foreseeable future. Based on new MDI and polycarbonate applications, captive phosgene production should continue to expand, although TDI growth will be more modest.

Phosgene is known to be produced in the USA, Japan, Germany, France, Belgium, Italy, Netherlands, Britain, Canada, Spain, India, Australia, Brazil, Hungary, Switzerland and China. No production of phosgene is known for the African continent, and comparatively little data are available for the Former Soviet Union.

Estimates for phosgene production for the two major marketing segments, USA and Western Europe, are given in Tables A1.1 and A1.2. These listings are subject to frequent change depending upon market conditions, changing ownership, plant closures, and start-up of new facilities. In addition, it should be noted that capacity estimates are frequently unreliable owing to most phosgene usage being captive. Sometimes the derived intermediates are also used at the site of manufacture, so that phosgene usage statistics can become obscured.

The United States is by far the largest manufacturer of phosgene, producing almost a half of the known world total. Of the dozen or so major manufacturers in the United States, only Van De Mark supplies the small merchant market. The remaining companies produce phosgene for consumption only on site. The US phosgene producers in 1994 are listed in Table A1.1. Updates of the US manufacturers, and their capacities, are published regularly in *Chemical Marketing Reporter*.

Estimates (1994) of the capacities for the Western European producers are listed in Table

A1.2. The total production capacity of phosgene for Eastern Asia, the third major marketing territory, is estimated to be 420 kt y^{-1}. Hence, the three principal marketing areas account for almost 90% of the estimated world production of 2700 kt y^{-1}.

At least five separate companies in Europe offer the process technology for phosgene manufacture under licence. These companies, and their particular processes, are described in Section 4.5.1.

TABLE A1.1

PHOSGENE PRODUCERS (USA)

Producer	Location	Capacity / kt y^{-1} [a]
BASF	Geismar, Louisiana	160
Dow	Freeport, Texas	70
Dow	La Porte, Texas	120
DuPont	Deepwater, New Jersey	35
General Electric	Burkville, Alabama	25
General Electric	Mount Vernon, Indiana	60
ICI Americas	Geismar, Louisiana	135
Miles	Baytown, Texas	200
Miles	New Martinsville, W. Virginia	115
Olin	Lake Charles, Louisiana	135
PPG	Barberton, Ohio	3
PPG	La Porte, Texas	25
Rhône-Poulenc	Institute, W. Virginia	50
Twin Lake	Lockport, New York	3
Van De Mark	Lockport, New York	10
Zeneca	Cold Creek, Alabama	15
	APPROXIMATE TOTAL	1200

[a] Based on end-use estimates

TABLE A1.2

PHOSGENE PRODUCERS (WESTERN EUROPE)

Producer	Location	Capacity / kt y^{-1} [a]
Belgium		
BASF	Antwerpen	30
Bayer-Shell	Antwerpen	70
Stauffer	Seneffe, Hainaut	20
France		
Rhône-Poulenc	Le Pont De Claix, Isère	120
SNPE	Toulouse, Haute-Garonne	15
Germany		
BASF	Ludwigshafen, Rheinland-Pfalz	10
Bayer	Brunsbüttel, Schleswig-Holstein	60
Bayer	Krefeld, Nordrhein-Westfalen	95
Bayer	Leverkusen, Nordrhein-Westfalen	165
Italy		
Enichem	Brinidisi, Puglia	35
The Netherlands		
General Electric	Bergen op Zoom, Noord-Brabant	15
ICI Holland	Rozenburg, Zuid-Holland	35
Spain		
General Electric Plastics	Cartagena	n.a.
Switzerland		
Ciba-Geigy	Monthey, Valais	2
United Kingdom		
ICI Chemicals & Polymers	Fleetwood, Lancashire	70
International Biosynthetics	Widnes, Cheshire	2
	APPROXIMATE TOTAL	750

[a] Based on end-use estimates

A2 CARBONYL HALIDES: SUPPLIERS OF RESEARCH QUANTITIES

The following is a selective list of some typical suppliers (USA and Western Europe) who are currently, or who have recently, produced research quantities of phosgene, isotopically-labelled phosgene, carbonyl difluoride or carbonyl chloride fluoride, for laboratory research or small-scale development studies. This list is always in a state of flux, but it is hoped that it will at least provide some useful starting points in the search for a supplier. Convenient laboratory syntheses of these materials are give in Appendix A5.

PHOSGENE

Aldrich Chemical Co., Inc.
BDH Laboratory Supplies (Merck Ltd.)
Bodman Chemicals
Carbolabs, Inc.
Crescent Chemical Co.
E M Science
Fairfield Chemical Co., Inc.
Fisons PLC
Fluka Chemical Corp.
Fluka Chemie AG
Great Lakes Chemical Corp.
Ken Seika Corp.
Lancaster Synthesis
Miles Inc.
Pfaltz & Bauer, Inc.
PPG Industries, Inc.
Pressure Chemical Co.
Raylo Chemicals
Sithean Corp.
SNPE
Stauffer Chemical Belgium

PHOSGENE-C13 ($^{13}COCl_2$)

Cambridge Isotope Laboratories, Inc.
Icon Services Inc.
MSD Isotopes (Merck Frosst, Inc.)

PHOSGENE-C14 ($^{14}COCl_2$)

Amersham Corp.
California Bionuclear Corp.
Mallinckrodt Chemical Works

PHOSGENE-O17 ($C^{17}OCl_2$)

Icon Services

PHOSGENE-O18 ($C^{18}OCl_2$)

Icon Services

CARBONYL DIFLUORIDE

Air Products & Chemicals, Inc.
Columbia Organic Chemical Co., Inc.
Fluorochem Ltd.
Hynes Chemical Research Corp.
K & K Laboratories
Matheson Gas Products, Inc.
PCR, Inc.
Pfaltz & Bauer
Precision Gas Products, Inc.
Strem Chemicals, Inc.

CARBONYL CHLORIDE FLUORIDE

Bodman Chemicals
Chemical Procurement Laboratories, Inc.
Ozark-Mahoning Co.
PCR, Inc.

A3 REGISTRY NUMBERS AND SYNONYMS

This appendix forms a short reference section giving many of the codes and alternative names which are used for phosgene, and the other carbonyl halides.

A3.1 REGISTRATION NUMBERS

The registration numbers for the three most important carbonyl halides are listed below:

PHOSGENE

CAS Registry No.	75-44-5
RTECS No.	SY5600000
U.N. No.	UN 1076
EEC No.	006-002-00-8
EINECS No.	200-870-3
Hazchem Code	2XE

CARBONYL DIFLUORIDE

CAS Registry No.	353-50-4
RTECS No.	FG6125000
U.N. No.	UN 2417
EINECS No.	206-534-2
Hazchem Code	2PE

CARBONYL CHLORIDE FLUORIDE

CAS Registry No.	353-49-1
EINECS No.	206-533-7

The other carbonyl halides are not listed in the European Inventory of Existing Chemical Substances (EINECS).

A3.2 CAS REGISTRY NUMBERS AND SYNONYMS FOR THE CARBONYL HALIDES

The CAS Registry numbers for the carbonyl halides, and their principal isotopomers, are given in Table A3.1. Synonyms and foreign language equivalents for phosgene are given in Table A3.2, and for carbonyl difluoride in Table A3.3.

TABLE A3.1

CAS REGISTRY NUMBERS

Carbonyl Halide	CAS Registry No.
$COCl_2$	75-44-5
$CO^{35}Cl_2$	67303-78-0
$CO^{37}Cl_2$	67303-79-1
$C^{18}O^{35}Cl_2$	75240-97-0
$C^{18}O^{37}Cl_2$	75240-99-2
$^{11}COCl_2$	63560-70-3
$^{13}CO^{35}Cl_2$	97458-61-2
$^{13}CO^{37}Cl_2$	75241-00-8
$^{13}C^{18}O^{35}Cl_2$	75240-98-1
$^{13}C^{18}O^{37}Cl_2$	75241-01-9
$^{14}COCl_2$	58420-88-5
COF_2	353-50-4
$^{13}COF_2$	2561-68-4
$^{13}C^{18}OF_2$	51759-97-8
$C^{18}OF_2$	2561-69-5
$COBr_2$	593-95-3
$CO^{79}Br_2$	63348-21-0
$CO^{81}Br_2$	63348-23-2
$CO^{79}Br^{81}Br$	63348-22-1
COI_2	13353-01-0
COClF	353-49-1
$CO^{35}ClF$	1956-77-0
$CO^{37}ClF$	1840-38-6
COBrF	753-56-0
COClBr	7726-12-7
COFI	1495-48-3

TABLE A3.2

SYNONYMS AND FOREIGN LANGUAGE EQUIVALENTS FOR PHOSGENE

Synonym	Comment
Carbonyl Dichloride	IUPAC Recommended
Carbonyl Chloride	Commonly used chemical name (DOT, OSHA)
Carbonic Acid Dichloride	ACS Nomenclature (*Chemical Abstracts*)
Carbonic Dichloride	Not recommended
Carbon Dichloride Oxide	Not recommended
Chloroformyl Chloride	Not recommended
Carbon Oxychloride	Not recommended
Oxychlorure de Carbone	French
Carbonylchlorid	German
Phosgen	German
Chlorkohlenoxyd	German
Kohlenoxychloride	German
Kohlensäuredichlorid	German
Ossichloruro di carbonio	Italian
Fosgene	Italian
Koolstofoxychloride	Dutch
Fosgeen	Dutch
Fosgen	Polish
NCI-C60219	Military
Combat Gas	Military
CG	Military (US)
Collongite	French Military; mixed with $SnCl_4$ or $TiCl_4$
D-Stuff	German Military

TABLE A3.3

SYNONYMS FOR COF_2

Synonym	Comment
Carbonyl Difluoride	IUPAC Recommended
Carbon Difluoride Oxide	Not recommended
Carbon Fluoride Oxide	Not recommended
Carbonic Difluoride	ACS Nomenclature (*Chemical Abstracts*)
Carbon Oxyfluoride	Not recommended
Difluoroformaldehyde	Not recommended
Perfluoro-formaldehyde	Not recommended
Fluorophosgene	Not recommended
Fluophosgene	Not recommended
Fluoroformyl Fluoride	Not recommended

A4 CHARACTER TABLES

The tetra-atomic molecules of concern throughout this book belong to one of two point groups: C_{2v} or C_s. The character tables for these groups are reproduced below:

$\mathbf{C_{2v}}$	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
$\mathbf{A_1}$	1	1	1	1	z	x^2, y^2, z^2
$\mathbf{A_2}$	1	1	-1	-1	R_z	xy
$\mathbf{B_1}$	1	-1	1	-1	x, R_y	xz
$\mathbf{B_2}$	1	-1	-1	1	y, R_x	yz

$\mathbf{C_s}$	E	σ_h		
A'	1	1	x, y, R_z	x^2, y^2, z^2, xy
A"	1	-1	z, R_x, R_y	yz

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A5 LABORATORY PREPARATIONS OF THE CARBONYL HALIDES

The following sections give convenient laboratory syntheses for phosgene and the related carbonyl halides.[¶] These are meant to give the reader an idea of the nature of the procedures involved, and the ease of handling these materials; we have found it often easier (and certainly cheaper) to prepare research quantities of these materials than to buy them (with the notable exception of phosgene itself). We draw the readers attention to the disclaimer at the front of this book.

Because of the extremely poisonous nature of the carbonyl halides, all preparations and subsequent handling of these materials must be conducted in a fume cupboard designed to cope with highly poisonous gases. Where applicable, indicator papers should be suspended in the fume cupboard in which operations involving the carbonyl halides are being carried out. A further recommended precaution is to wear a gas mask or fresh air breathing apparatus in the event of sudden fan failure or catastrophic emission of gas. These precautions, exemplified for phosgene in particular, are described in more detail in Chapter 3.

A5.1 THE PREPARATION OF PHOSGENE

Phosgene is readily and cheaply available, in cylinders, or as a solution in toluene (usually 12.5 or 20 % w/w), from commercial suppliers, so that it is rarely necessary to prepare the material in the laboratory. For the preparation of small quantities of phosgene solution of alternative concentrations, or in other solvents, the following procedure may be used, based upon the reaction of tetrachloromethane with sulfuric acid:

$$3CCl_4 + 2H_2SO_4 \longrightarrow 3COCl_2 + 4HCl + S_2O_5Cl_2$$

The apparatus, constructed as illustrated in Fig. 5.6., Section 5..2.1.1, consists of a round-bottomed flask, fitted with a water-cooled reflux condenser, a T-piece connector, and a stoppered dropping funnel fitted with a pressure equalising arm. Concentrated sulfuric acid, containing 2% w/w of ignited kieselguhr, was introduced into the flask and the dropping funnel charged with tetrachloromethane. The train of four Dreschel bottles were connected in the way

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[¶] The preparation of COFI is not a convenient synthesis, and the reader is referred to Section 16.4.1, and Kwasnik's original work [1196a,1751].

illustrated in the diagram; the first and third bottles in the series serving as suck-back traps, the second and fourth bottles being charged with toluene, or other suitable solvent, and 20 % aqueous sodium hydroxide solution, respectively. The sulfuric acid was heated on an oil bath to 120-130 °C and the tetrachloromethane added, initially drop-by-drop, until the rate of addition was monitored by means of the bubble flow.

Phosgene, contaminated to some degree with hydrogen chloride (typically 2 % w/w when toluene is employed), was absorbed in the non-aqueous solvent contained in the second Dreschel bottle.

A5.2 PREPARATION OF CARBONYL DIFLUORIDE

A 250 cm^3, four-necked round-bottomed glass flask was provided with a thermometer, 100 cm^3 dropping funnel equipped with a pressure equalizing and cooling jacket, a Teflon stirrer, a heater, and a reflux condenser mounted vertically with a cold finger having a high surface area. The condenser was cooled with cold water, while the cold finger was cooled with dry ice-propanone (-70 to -78 °C). The cold finger was linked to a 250 cm^3 evacuated glass storage vessel, cooled by liquid dinitrogen. Several bubblers were used to monitor the pressure during the experiment. The final product was stored in a stainless steel cylinder.

$$COCl_2 + 2NaF \longrightarrow COF_2 + 2NaCl$$

Sodium fluoride (3.8 g, 0.9 mol) and ethanenitrile (100 cm^3) were added to the round-bottomed flask, and the mixture was stirred and heated to 30-35 °C. Phosgene (3.5 g, 0.35 mol) was bubbled into ethanenitrile (30 cm^3) in the ice-cooled funnel. After all the required phosgene had been transferred from the phosgene cylinder (weight monitored using a digital top-pan balance), the phosgene solution was added dropwise to the stirred slurry at 30-40 °C. The solvent condensed in the upper condenser during the addition, which required about one hour. When the addition of phosgene had been completed, the reaction mixture was stirred at 30-45 °C for an additional 30 min. The product carbonyl difluoride (*ca.* 16.5-19.0 g, 70-80% conversion) was collected as a solid in a liquid dinitrogen cooled receiver. This product was then transferred under reduced pressure to the stainless steel cylinder for storage.

A5.3 PREPARATION OF CARBONYL DIBROMIDE

Carbonyl dibromide is not commercially available, and therefore must be prepared when required. It is conveniently prepared by the oxidation of tetrabromomethane with sulfuric acid:

$$CBr_4 + H_2SO_4 \longrightarrow COBr_2 + 2HBr + SO_3$$

Concentrated sulfuric acid (20 cm^3) was slowly added, *via* a dropping funnel, to molten tetrabromomethane (20 g; 0.06 mol) held in a reaction flask at about 90 °C. The flask, connected to a simple distillation unit, was then heated to 150-170 °C for 2 h, and the products collected in a high surface area trap cooled to -10 °C.

The deep red, impure product was then transferred to a vacuum line, and continuously evacuated at -95 °C for 30 min to remove the sulfur(IV) oxide co-product. In order to remove the dibromine impurity, the product was then condensed into an ampoule, fitted with a greaseless tap, containing mercury and allowed to warm to room temperature. The ampoule was closed, disconnected from the vacuum line, and agitated vigorously for 5 min within the fume cupboard. The ampoule was then reconnected to the vacuum apparatus, and the liquid twice distilled *in vacuo* into a storage bulb, fitted with a greaseless tap. The carbonyl dibromide was stored at room temperature in the dark. Yield: 5.8 g; 51%.

A5.4 PREPARATION OF CARBONYL CHLORIDE FLUORIDE

The commercial availability of carbonyl chloride fluoride is, to say the least, variable; appearing on suppliers lists (*e.g.* Fluorochem and Ozark-Mahoning) in some years, and not in others. When available, this material has a price that is disproportionately high relative to phosgene and carbonyl difluoride, reflecting the speciality nature of the compound and the absence of any bulk production.

Carbonyl chloride fluoride is conveniently prepared from the reaction of the trichlorofluoromethane, CCl_3F, with sulfur(IV) oxide:

$$CCl_3F + (n{+}1)SO_3 \longrightarrow COClF + ClSO_2(SO_3)_nCl$$

The apparatus consists of a three-necked flask fitted with a thermometer, long-stemmed dropping funnel and two vertically-mounted reflux condensers; the lower condenser being cooled to 10 °C, and the upper condenser being cooled to -30 °C. The flask was charged with oleum (65%; 600 g) and warmed to 28-34 °C. Trichlorofluoromethane (275 g; 2 mol) contained in the dropping funnel (the end of the delivery stem being immersed in the oleum) was added over a period of 5 h. The evolved gas was passed through a condenser and a wash bottle (containing sulfuric acid) into a cold trap cooled to - 78 °C. Analysis of the condensed product gave carbon dioxide; 3, CCl_3F; 23, and COClF; 74%, corresponding to a yield of about 60 %. The COClF is readily separated by low temperature distillation, and may be transferred for storage in a stainless steel cylinder.

A5.5 PREPARATION OF CARBONYL BROMIDE FLUORIDE

Commercially unavailable, carbonyl bromide fluoride can be prepared by the oxidation of tribromofluoromethane, CBr_3F, with sulfur(VI) oxide:

$$CBr_3F + SO_3 \longrightarrow COBrF + SO_2 + Br_2$$

A three-necked reaction flask was fitted with a thermometer, a dropping funnel containing tribromofluoromethane (50 g; 0.2 mol), and two vertically-mounted reflux condensers. The lower condenser was cooled with a flow of cold water, and the upper condenser was cooled with melting ice. Sulfur(VI) oxide (200 g; 2.5 mol) was carefully melted using a hot-air gun and poured into the reaction flask under an atmosphere of dry dinitrogen. The tribromofluoromethane was then added dropwise to the sulfur(VI) oxide at a temperature of 35-45 °C over a 45 min period. The gas evolved was passed through trichloroethene (300 cm^3) contained in a 30 cm column, and irradiated with light, supplied by a 100 W UV lamp, to remove elemental bromine, and then through concentrated sulfuric acid to remove sulfur(IV) oxide. The product was collected at -196 °C and transferred to the vacuum line to remove the small amount of carbon dioxide present by trap-to-trap distillation. The colourless gas was then distilled into a glass bulb (2 dm^3) fitted with a greaseless tap, and stored at room temperature. Yield: 13.6 g; 58 %.

A5.6 PREPARATION OF CARBONYL BROMIDE CHLORIDE

Carbonyl bromide chloride is not available commercially. It is readily prepared, however, by the oxidation of tribromochloromethane, CBr_3Cl with concentrated sulfuric acid:

$$CBr_3Cl + H_2SO_4 \longrightarrow COBrCl + 2HBr + SO_3$$

Tribromochloromethane (20 g; 0.07 mol) was placed in a three-necked flask fitted with a dropping funnel containing concentrated sulfuric acid (22 cm^3), a thermometer, and two vertically-mounted reflux condensers. The lower condenser was cooled with a flow of cold water and the upper condenser, cooled with a dry ice/propanone mixture. The reaction mixture was heated under reflux at about 130 °C for 3 h, after which time the condensers were replaced with a fractional distillation column. The fraction boiling in the range of 23-40 °C was collected. The deep red, impure distillate was transferred to a vacuum line and evacuated continuously, whilst held at -95 °C for 1 h, to ensure removal of sulfur(IV) oxide and phosgene. In order to remove the dibromine impurity, the product was then condensed into an ampoule, fitted with a greaseless tap, containing a stoicheiometric excess of mercury, and allowed to warm to room temperature. The ampoule was closed, disconnected from the vacuum line, and agitated vigorously for 5 min within the fume hood. The ampoule was then reconnected to the vacuum apparatus, and the liquid twice distilled *in vacuo* into a storage bulb, fitted with a greaseless tap to give a yield of $COClBr$ of 3.0 g; 30%.

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