

# Transport and Chemical Transformation of Pollutants in the Troposphere

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Series editors: Peter Borrell, Patricia M. Borrell, Tomislav Cvitaš,  
Kerry Kelly and Wolfgang Seiler





Transport and Chemical Transformation  
of Pollutants in the Troposphere

Volume 3

# Chemical Processes in Atmospheric Oxidation

Laboratory Studies of Chemistry  
Related to Tropospheric Ozone

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With 43 Figures and 48 Tables

ISBN 978-3-642-63902-9

Library of Congress Cataloging-in-Publication Data. Chemical processes in atmospheric oxidation: laboratory studies of chemistry related to tropospheric ozone / Georges le Bras, editor and coordinator. p. cm. – (Transport and chemical transformation of pollutants in the troposphere; v. 3) Includes index.

ISBN 978-3-642-63902-9 ISBN 978-3-642-59216-4 (eBook)

DOI 10.1007/978-3-642-59216-4

1. Atmospheric ozone. 2. Troposphere. 3. Atmospheric chemistry. 4.

Photochemical oxidants. I. Le Bras, Georges. II. Series. QC879.7.C53 1997, 551.5'11-dc20, 96-41132 CIP

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© Springer-Verlag Berlin Heidelberg 1997

Softcover reprint of the hardcover 1st edition 1997

Originally published by Springer-Verlag Berlin Heidelberg New York in 1997

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Cover Design: Struve & Partner, Heidelberg

Coverpicture from Georges Le Bras (LACTOZ)

SPIN 10514750 30/3136-5 4 3 2 1 0 – Printed on acid-free paper

## **Transport and Chemical Transformation of Pollutants in the Troposphere**

Series editors: Peter Borrell, Patricia M. Borrell, Tomislav Cvitaš, Kerry Kelly  
and Wolfgang Seiler

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## Foreword by the Series Editors

EUROTRAC is the European co-ordinated research project, within the EUREKA initiative, studying the transport and chemical transformation of pollutants in the troposphere. The project has achieved a remarkable scientific success since its start in 1988, contributing substantially both to the scientific progress in this field and to the improvement of the scientific basis for environmental management in Europe. EUROTRAC, which at its peak comprised some 250 research groups organised into 14 subprojects, brought together international groups of scientists to work on problems directly related to the transport and chemical transformation of trace substances in the troposphere. In doing so, it helped to harness the resources of the participating countries to gain a better understanding of the trans-boundary, interdisciplinary environmental problems which beset us in Europe.

The scientific results of EUROTRAC are summarised in this report which consists of ten volumes.

Volume 1 provides a general overview of the scientific results, prepared by the Scientific Steering Committee (SSC) and the International Scientific Secretariat (ISS) of EUROTRAC, together with brief summaries of the work of the fourteen individual subprojects prepared by the respective subproject coordinators.

Volumes 2 to 9 comprise detailed overviews of the subproject achievements, each prepared by the respective subproject coordinator and steering group, together with summaries of the work of the participating research groups prepared by the principal investigators. Each volume also includes a full list of the scientific publications from the subproject.

The final volume, 10, is the complete report of the Application Project, which was set up in 1993 to assimilate the scientific results from EUROTRAC and present them in a condensed form so that they are suitable for use by those responsible for environmental planning and management in Europe. It illustrates how a scientific project such as EUROTRAC can contribute practically to providing the scientific consensus necessary for the development of a coherent atmospheric environmental policy for Europe.

A multi-volume work such as this has many contributors and we, as general editors, would like to express our thanks to all of them: to the subproject coordinators who have borne the brunt of the scientific co-ordination and who have contributed so much to the success of the project and the quality of this report; to the principal investigators who have carried out so much high-quality scientific work; to the members of the International Executive Committee (IEC) and the SSC for their enthusiastic encouragement and support of EUROTRAC; to the

## VIII

participating governments in EUROTRAC, and in particular the German Government (BMBF) for funding, not only the research, but also the ISS publication activities; and finally to Mr. Christian Witschell and his colleagues at Springer Verlag for providing the opportunity to publish the results in a way which will bring them to the notice of a large audience.

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## **Preface by the LACTOZ steering group**

The LACTOZ project has been co-ordinated successively by R. Anthony Cox, Karl-Heinz Becker and Georges Le Bras. This report has been prepared by the Steering Committee of LACTOZ with contributions from I. Barnes and R.P. Wayne. The support of the European Commission for co-ordination of the project and the personal involvement of Heinz Ott and Giovanni Angeletti are gratefully acknowledged.

In Chapter 2 of the report describing the scientific results, when the work of an author, whose individual contribution can be found in a later chapter of this book, is mentioned, the appropriate chapter and section numbers have been provided. However when an author's name appears with a year it refers to a EUROTRAC final report.



# Table of Contents

<b>Chapter 1</b> .....	<b>1</b>
1.1 Summary.....	1
1.2 Original Objectives and LACTOZ Achievements.....	2
1.3 Application of LACTOZ Results.....	11
<b>Chapter 2 Scientific Results</b> .....	<b>13</b>
G. Le Bras and the LACTOZ Steering Group	
2.1 Reaction of OH radicals .....	13
2.2 Reactions of NO <sub>3</sub> radicals .....	20
2.3 Reactions of O <sub>3</sub> with alkenes .....	29
2.4 Reactions of peroxy radicals.....	34
2.5 Reactions of oxy radicals.....	53
2.6 Photochemical cross-sections and quantum yields .....	57
2.7 Oxidation of aromatic compounds.....	63
2.8 Oxidation of biogenic compounds.....	68
<b>Chapter 3 Individual Reports from LACTOZ Contributors</b> .....	<b>73</b>
3.1 Laboratory Studies of the Atmospheric Decay of Hydrocarbons in the NO <sub>x</sub> Free Atmosphere.....	73
<i>K. Bächmann, B. Kusserow, J. Polzer, J. Hauptmann and M. Hartmann</i>	
3.2 OH Initiated Oxidation of VOC under Variable NO <sub>x</sub> Conditions .....	79
<i>K.-H. Becker, I. Barnes, A. Bierbach, K.J. Brockmann, F. Kirchner, B. Klotz, H.G. Libuda, A. Mayer-Figge, S. Mönninghoff, L. Ruppert, W. Thomas, E. Wiesen, K. Wirtz and F. Zabel</i>	
3.3 Laboratory and Field Measurement Studies of the Tropospheric Chemistry of Nitrate and Peroxy Radicals.....	91
<i>J. P. Burrows, T. Behmann, J. N. Crowley, D. Maric, A. Lastätter- Weißmayer, G. K. Moortgat, D. Perner and M. Weißmayer</i>	
3.4 Tropospheric Degradation of Aromatics: Laboratory Kinetic Studies of some First Steps of the OH Initiated Oxidation.....	100
<i>P. Devolder, J.-P. Sawerysyn, C. Fittscheine, A. Goumri, L. Elmaimouni, B. Bigan and C. Bourbon</i>	
3.5 Laboratory Studies of the Formation of Hydroperoxides in Ozonolysis of Anthropogenic and Biogenic Alkenes .....	106
<i>S. Wolff, W. V. Turner, S. Gäb, S. Mönninghoff, L. Ruppert and K. Brockmann</i>	
3.6 Gas-Phase Reactions of Interest in Night-Time Tropospheric Chemistry .....	113
<i>J. Hjorth, N.R. Jensen, H. Skov, F. Capellani and G. Restelli</i>	

3.7	Laboratory Studies of Peroxy Radical Reactions of Importance for Tropospheric Chemistry .....	120
	<i>M. E. Jenkin, G. D. Hayman, R. A. Cox and T. P. Murrells</i>	
3.8	The Rates and Mechanisms for VOC Photo-oxidation Reactions under Simulated Tropospheric Conditions .....	128
	<i>J. A. Kerr, D. W. Stocker, M. Semadeni, J. Eberhard and C. Müller</i>	
3.9	Laboratory Studies of NO <sub>3</sub> and OH Reactions of Tropospheric Relevance .....	135
	<i>G. Le Bras, G. Poulet, N. Butkovskaya, V. Daële, D. Johnstone, I.T. Lançar, G. Laverdet, A. Mellouki, A. Ray, S. Téton and I. Vassali</i>	
3.10	Peroxy Radical Reactions of Tropospheric Interest .....	143
	<i>R. Lesclaux, A.A. Boyd, I. Bridier, F. Caralp, V. Catoire, F.F. Fenter, P.D. Lightfoot, B. Nozière, D.M. Rowley, B. Veyret and E. Villenave</i>	
3.11	Laboratory Studies of Some Thermal Reactions Involving NO <sub>y</sub> Species .....	151
	<i>E. Ljungström, M. Hallqvist, R. Karlsson, S. Langer and I. Wängberg</i>	
3.12	High-Resolution Measurements of the Absorption Cross-Sections for O <sub>3</sub> and NO <sub>2</sub> .....	157
	<i>T. Brion, A. Chakir, B. Coquart, D. Daumont, A. Jenouvrier, J. Malicet and M.F. Merienne</i>	
3.13	Laboratory Studies of Peroxy Radicals, Carbonyl Compounds and Ozonolysis Reactions of Tropospheric Importance .....	162
	<i>G. K. Moortgat, D. Bauer, J.P. Burrows, J. Crowley, F. Helleis, O. Horie, S. Koch, S. Limbach, P. Neeb, W. Raber, F. Sauer, C. Schäfer, W. Schneider, F. Simon and C. Zahn</i>	
3.14	Atmospheric Chemistry of Nitrogen-Containing Species.....	170
	<i>O. J. Nielsen and J. Sehested</i>	
3.15	Kinetic Studies of Reactions of Alkylperoxy and Haloalkylperoxy Radicals with NO. A Structure-Activity Relationship for Reactions of OH with Alkenes and Polyalkenes .....	179
	<i>J. Peeters, J. Vertommen, I. Langhans, W. Boullart, J. Van Hoeymissen and V. Pultau</i>	
3.16	Mechanism and Kinetics of the Reaction of OH with Volatile Organic Compounds.....	186
	<i>M. J. Pilling, A. E. Heard, S. M. Saunders and P. I. Smurthwaite</i>	
3.17	Reactions of <i>n</i> - and <i>s</i> -Butoxy Radicals in Oxygen. Importance of Isomerisation and Formation of Pollutants.....	192
	<i>K. Sahetchian and A. Heiss</i>	
3.18	Gas-Phase Ozonolysis of Alkenes and the Role of the Criegee Intermediate.....	200
	<i>W. Sander, M. Träubel and P. Komnick</i>	
3.19	Mechanistic and Kinetic Studies of Selected Oxidation Steps of Tropospheric Interest .....	208
	<i>R. N. Schindler</i>	

3.20	Reactions of OH Radicals with Organic Nitrogen-Containing Compounds.....	214
	<i>H. Sidebottom, J. Tracy and O. J. Nielsen</i>	
3.21	Kinetics and Mechanism for the Reaction of Ozone with Cycloalkenes .....	218
	<i>H. Sidebottom and J. Tracy</i>	
3.22	Mechanisms for the Oxidation of C <sub>5</sub> -C <sub>7</sub> Hydrocarbons.....	225
	<i>P. Warneck, H.-J. Benkelberg, G. Heimann and R. Seuwen</i>	
3.23	Studies of the Kinetics and Mechanisms of Interactions of Nitrate and Peroxy Radicals of Tropospheric Interest.....	232
	<i>R. P. Wayne, P. Biggs and C. E. Canosa-Mas</i>	
3.24	Time-Resolved Studies of the NO <sub>2</sub> and OH Formation in the Integrated Oxidation Chain of Hydrocarbons.....	241
	<i>R. Zellner, A. Hoffmann, W. Malms and V. Mörs</i>	
3.25	Adduct Formation of OH with Aromatics and Unsaturated Hydrocarbons and Consecutive Reactions with O <sub>2</sub> and NO <sub>x</sub> to Regenerate OH .....	247
	<i>C. Zetzsch, R. Koch, B. Bohn, R. Knispel, M. Siese and F. Witte</i>	
	<b>Chapter 4 LACTOZ Publications 1988–1995 .....</b>	<b>257</b>
	LACTOZ Publications 1988–1995	
	<b>Subject Index .....</b>	<b>311</b>

Transport and Chemical Transformation of  
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# Chapter 1

## 1.1 Summary

The EUROTRAC project has addressed the problem of transport and transformation of photo-oxidants in north-western Europe, including global-, regional- and local-scale effects occurring in the atmospheric boundary layer and free troposphere. Tropospheric ozone is also important for the climate because  $O_3$  is an active greenhouse gas. LACTOZ (LABoratory studies of Chemistry related to Tropospheric Ozone), one of two EUROTRAC laboratory subprojects, was begun with the aim of providing, through laboratory investigations of the kinetics and mechanisms of relevant gas-phase reactions, a quantitative description of the chemical production and loss of ozone from its precursor molecules – nitrogen oxides and volatile organic compounds – in the atmospheric boundary layer and free troposphere.

The results of the project have greatly improved our knowledge about the following identified problems corresponding to the specific objectives defined at the start of LACTOZ:

- the kinetics and mechanisms for the oxidative breakdown of simple organic compounds present in the free troposphere;
- the kinetics and mechanisms of the reactions involved in the transport and interconversion of  $NO_x$  into and within the free troposphere;
- the production and loss of odd hydrogen radicals required for accurate calculation of tropospheric free radical concentrations;
- the determination of the rates and mechanisms for OH attack on more complex organic compounds, including aromatic, oxygenated and nitrate compounds;
- the determination of the rate constants and branching ratios for reactions of peroxy and alkoxy radicals, derived from higher-molecular-weight organic compounds including isoprene, naturally emitted;
- the elucidation of  $NO_3$  chemistry with a view to modelling the night-time removal of  $NO_x$  and VOCs from the atmosphere and the impact of the overall oxidation of VOCs;

- the investigation of reactions acting as sources and sinks of HO<sub>x</sub> and RO<sub>2</sub> radicals in the boundary layer in support of anticipated field measurements of free radical concentrations.

The results of LACTOZ have provided an extended kinetic data base for the following classes of reactions: reactions of OH with VOCs, reactions of NO<sub>3</sub> with VOCs and peroxy radicals, reactions of O<sub>3</sub> with alkenes, reactions of peroxy radicals (self reactions, reaction with HO<sub>2</sub>, other RO<sub>2</sub>, NO, NO<sub>2</sub>), reactions of alkoxy radicals (reactions with O<sub>2</sub>, decomposition, isomerisation), thermal decomposition of peroxy nitrates. Photolysis parameters (absorption cross-section, quantum yields) have been refined or obtained for the first time for species which photolyse in the troposphere. Significantly new mechanistic information has also been obtained for the oxidation of aromatic compounds and biogenic compounds (especially isoprene). These different data allow the rates of the processes involved to be modelled, especially the ozone production from the oxidation of hydrocarbons. The data from LACTOZ are summarised in the tables given in this report and have been used in evaluations of chemical data for atmospheric chemistry conducted by international evaluation groups of NASA and IUPAC.

The data base has been used to establish structure-reactivity relationships and to provide quantitative rate coefficients and reliable reaction pathways for reactions for which no experimental data are available or have proved to be experimentally inaccessible. Such a strategy was adopted in view of the very large number of VOCs involved in the generation of tropospheric ozone. These structure-reactivity relationships are discussed in this report and in other publications.

As an application of LACTOZ, a concerted effort has been made during the last phase of LACTOZ to incorporate the data obtained into models describing and predicting ozone and photo-oxidant formation. As an example, the input data of the EMEP mechanism have been updated and extended by LACTOZ.

## 1.2 Original Objectives and LACTOZ Achievements

### 1.2.1 Aims and objectives

The aims of LACTOZ have been to provide, through laboratory investigation of the kinetics and mechanisms of relevant gas-phase reactions, a quantitative description of the chemical production and loss of ozone from its precursor molecules, nitrogen oxides and volatile organic compounds, in the regions of the troposphere.

The first area of focus was on the reactions involved in the photochemically initiated oxidative degradation of CO and simpler hydrocarbons (CH<sub>4</sub>, C<sub>2</sub> - C<sub>5</sub> alkanes, C<sub>2</sub> and C<sub>3</sub> unsaturated hydrocarbons, *etc.*) and the chemistry of NO<sub>x</sub>,

relevant for ozone production in the global troposphere. The objective was to provide rate coefficients and reaction mechanisms for a complete model description of the chemistry of  $\text{NO}_x$  and low molecular weight VOCs in the free troposphere and in air parcels transporting ozone precursors away from source regions.

The second area of focus was placed on the oxidative degradation of more complex volatile organic compounds (higher alkanes and alkenes; benzene, toluene and higher aromatic compounds; isoprene and other biogenic compounds; and oxygenated VOCs) which are important for ozone generation in the atmospheric boundary layer, closer to the sources of precursors. The chemistry of VOC oxidation initiated by the nitrate radical and by the reaction with ozone was also investigated, in addition to the photochemical oxidation initiated by OH. The reactions involved in the change in nitrogen speciation resulting from the formation of organic nitrates by the heavier VOCs were also studied.

Within the context of the above project foci, the following specific objectives were defined for LACTOZ

- to define quantitatively the kinetics and mechanisms for the elementary reactions involved in ozone production in the free troposphere, in particular:
  - the oxidative breakdown of simple organic compounds present in the free troposphere ( $\text{CH}_4$ , HCHO,  $\text{C}_2$ - $\text{C}_5$  alkanes, *etc.*);
  - the transport and interconversion of  $\text{NO}_x$  into and within the free troposphere;
  - the production and loss of odd hydrogen radicals required for accurate calculation of tropospheric free radical concentrations;
- to provide kinetic and mechanistic data necessary for the formulation of models describing the production of ozone in the polluted boundary layer including:
  - the determination of the rates and mechanisms for OH attack on more complex organic compounds including oxygenated species and nitrates;
  - the determination of the rate constants and branching ratios for reactions of peroxy and alkoxy radicals, derived from higher molecular weight organic compounds including natural hydrocarbons, isoprene and terpenes;
  - the elucidation of night-time  $\text{NO}_3$  chemistry with a view to modelling the removal of  $\text{NO}_x$  and VOCs from the atmosphere and the impact on the overall oxidation of VOCs;
  - the investigation of reactions acting as sources and sinks of  $\text{HO}_x$  (OH,  $\text{HO}_2$ ) and  $\text{RO}_2$  radicals in the boundary layer in support of anticipated field measurements of free radical concentrations.

In view of the very large number of VOCs involved in the generation of tropospheric ozone it was recognised that it will not be feasible to investigate the elementary steps in the oxidation of every VOC. Therefore, a strategy based on the establishment of structure-reactivity relationships was adopted to provide



quantitative rate coefficients and reliable reaction pathways for the diverse reactions of the many individual species.

The sequence of chemical reactions leading to oxidative degradation and ozone formation in the atmosphere is often determined by the relative rates of competing reaction pathways at several critical points in the degradation. The protocol adopted was therefore to establish these critical points and emphasis was then placed on provision of data allowing the relative importance of these competing processes to be quantitatively defined for a range of VOCs. These critical points were found to lie for example in the reactions of RO<sub>2</sub> and RO radicals.

### 1.2.2 Achievements

The high level of LACTOZ achievements can be best illustrated by comparing the results of the project as summarised in Chapter 2 of this report with the specific objectives, as defined in Section 1.2.1.

#### *1.2.2a The kinetics and mechanisms for the oxidative breakdown of simple organic compounds present in the free troposphere*

Hydroxyl radical attack on VOCs is the primary source of RO<sub>2</sub> radicals in the troposphere, and consequently the rates of the OH + VOC reactions have a strong influence on the local rate of O<sub>3</sub> formation (Fig. 1). Moreover, the mechanism of the OH reaction determines the structure of the peroxy radical formed, and hence, provides information on its subsequent degradation pathway.

The rates and mechanisms for OH attack on simple organic compounds have been established for sometime, and any uncertainty in their atmospheric lifetimes largely resides in the value of the concentration of the OH radical in the atmosphere. In LACTOZ, effort has been concentrated on oxidation mechanisms, particularly on the reactions of RO<sub>2</sub> and RO radicals, for understanding the degradation of small organic compounds.

The rate of ozone generation in a particular region of the troposphere is determined by the perturbation of the local photostationary state of NO<sub>x</sub> due to oxidation of NO to NO<sub>2</sub>, primarily by peroxy radicals, RO<sub>2</sub>, in the reaction:



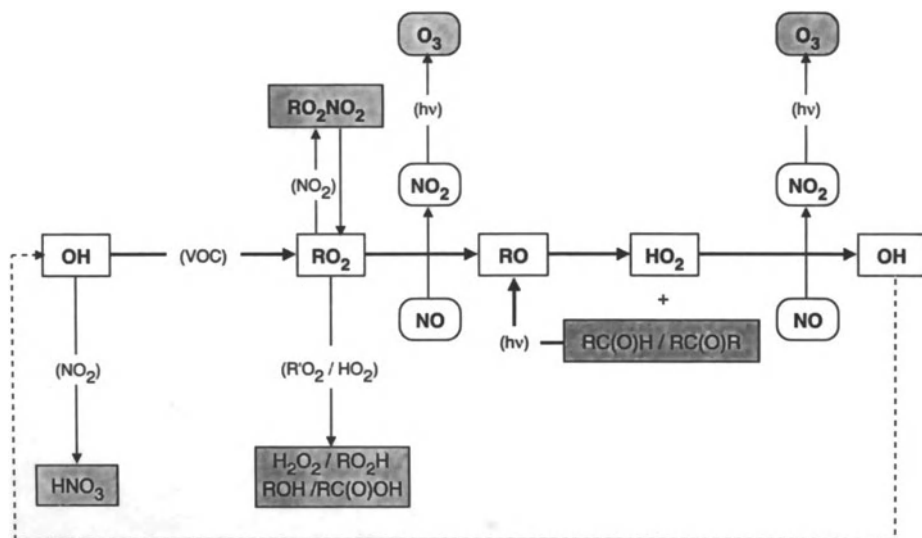
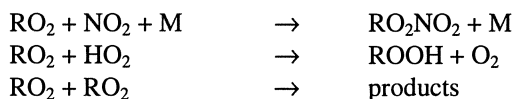


Fig. 1: VOC oxidation mechanism during daytime.

The importance of this reaction depends on the rates of competing reactions of  $\text{RO}_2$ , in particular, reaction with  $\text{NO}_2$  to form peroxy nitrates, with  $\text{HO}_2$  to form hydroperoxides and the reaction with other  $\text{RO}_2$ , forming a variety of products:



In the sunlit free troposphere, competition between  $\text{RO}_2 + \text{HO}_2$  and  $\text{RO}_2 + \text{NO}$  is the key to the effective local ozone production, and the work in LACTOZ has led to the establishment of the rate parameters for these two reactions for a variety of organic peroxy radicals. The kinetic data base created is sufficiently broad to enable structure-reactivity criteria to be applied to peroxy radicals for which there is as yet no experimental data. The change in the rate coefficients at 298 K for these two competing processes as a function of the organic group tends to show opposite trends. It is therefore important to take reactivity changes into account when the propensity for ozone formation is assessed for a given type of VOC under atmospheric regimes in which the  $\text{NO}$  and  $\text{HO}_2$  reactions are competing.

A complete quantitative mechanism for the atmospheric oxidation of  $\text{C}_1$  and  $\text{C}_2$  hydrocarbons was assembled and published as an interim product of LACTOZ.

### ***1.2.2b The kinetics and mechanisms of the reactions involved in the transport and interconversion of NO<sub>x</sub> into and within the free troposphere***

NO<sub>x</sub> plays a central role in ozone production in the troposphere through the photodissociation of NO<sub>2</sub> to produce O atoms, which subsequently react with O<sub>2</sub> to produce O<sub>3</sub>. It follows that the distribution of NO<sub>x</sub> in the troposphere has to be defined in order to assess photochemical ozone production. The transport of NO<sub>x</sub> depends on its chemical conversion to the various forms of nitrogen species, which have different atmospheric lifetimes. The objectives within this LACTOZ theme were to provide kinetic and mechanistic data for the processes which govern the partitioning of total active nitrogen (NO<sub>y</sub>) between the different forms (Fig. 2). Particular emphasis was placed on the formation of organic nitrogen compounds which are not removed by heterogeneous reactions.

Peroxyacetylnitrate (PAN) is an important species for transport of NO<sub>y</sub> because of its relatively low reactivity, particularly in the cold regions of the troposphere. Work in LACTOZ provided the first definitive rate data for the formation from its precursor species and decomposition of this molecule:



Data have also been obtained for various other peroxyacetylnitrate species formed from a number of different VOCs. Structure-reactivity relationships for the thermal stability of PAN type species have been established which provide the needed information for assessing the transport of NO<sub>y</sub> in this form, and also the relationships required in order to estimate the relative rates of the reactions of RO<sub>2</sub> with NO (leading to ozone production) and NO<sub>2</sub> (leading to the PAN reservoirs) have been established. Although the peroxyacetylnitrates are the most stable, other peroxyacetylnitrates could also be significant reservoirs for NO<sub>x</sub> in the coldest regions of the troposphere.

Alkyl nitrates, formed in a secondary channel of the reaction of RO<sub>2</sub> with NO, are another "stable" form of NO<sub>y</sub>. LACTOZ has provided a comprehensive data set for the formation of nitrates, mainly from the higher molecular weight VOCs. In addition, the rates of degradation of organic nitrates, by photolysis and by their reaction with OH radicals, can be determined from LACTOZ results, although some uncertainties remain in the production and loss of alkyl nitrates.

The project has provided the data necessary for a much more robust estimation of the partitioning of NO<sub>y</sub> between the active NO<sub>x</sub> forms and the reservoirs, both in the source regions and the remote troposphere.

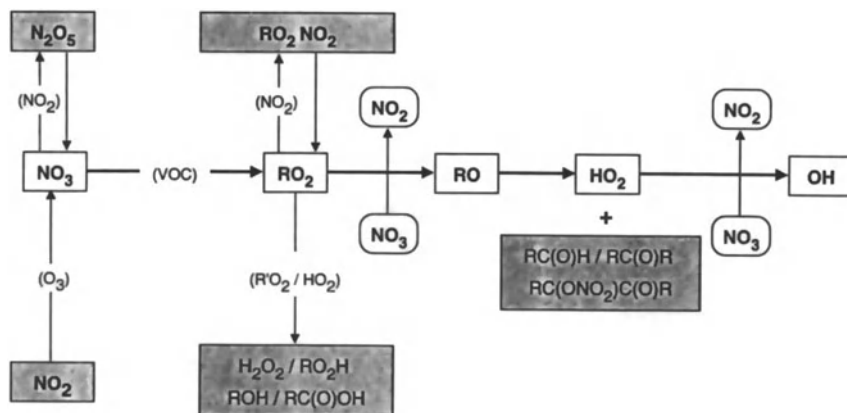


Fig. 2: NO<sub>y</sub> reaction system.

### 1.2.2c The production and loss of odd hydrogen radicals required for accurate calculation of tropospheric free radical concentrations

Atmospheric photolysis provides the predominant source of free radicals in the atmosphere. Photolysis of NO<sub>2</sub> produces O atoms which form ozone; ozone photolysis in the near UV produces O(<sup>1</sup>D) which reacts with H<sub>2</sub>O to produce OH radicals. A number of organic species absorb UV light and dissociate to yield organic peroxy and HO<sub>2</sub> radicals in the presence of O<sub>2</sub>.

One of the objectives of LACTOZ has been to provide absorption cross-sections and quantum yields so that photolysis rates can be calculated under atmospheric conditions. Emphasis has been on (a) refinement of data for the simple, well-characterised molecules (O<sub>3</sub>, HCHO) involved in HO<sub>x</sub> radical production, and (b) determination of data for photolysis of organic compounds formed as products in the degradation of alkanes, alkenes and selected multifunctional VOCs, mainly carbonyl compounds and nitrates, which produce HO<sub>x</sub> indirectly.

The reaction of ozone with alkenes produces OH and other radicals. Work in LACTOZ has provided quantitative data for the yield of OH for a variety of alkenes, including biogenic hydrocarbons. Yields of around 50 % were obtained for the reaction of ozone with typical alkenes, making this a source of atmospheric free radicals, which is especially significant at night-time when photolytic sources are absent.

The elucidation of the detailed chemistry of NO<sub>3</sub> radicals was a primary objective of LACTOZ since it was recognised that NO<sub>3</sub> initiated degradation of VOC could be significant for VOC oxidation and nitrogen speciation. NO<sub>3</sub> is formed from reaction of NO<sub>2</sub> with O<sub>3</sub> and is a key oxidising agent during night-time when photochemically produced radicals, primarily OH, are much less abundant. When NO<sub>3</sub> reacts with VOCs, RO<sub>2</sub> and ultimately HO<sub>x</sub> radicals are formed (Fig. 3).

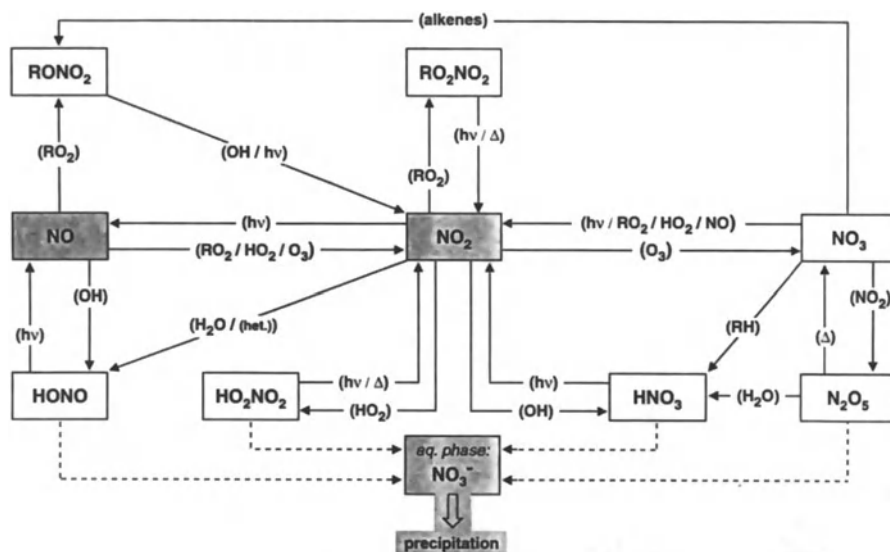


Fig. 3: VOC oxidation by  $\text{NO}_3$  during night-time.

Early in the LACTOZ project a significant discovery was made of the mechanism by which oxidation chains involving  $\text{NO}_3$  might be propagated through reactions such as:



When  $\text{R} = \text{H}$ ,  $\text{OH}$  radicals are generated. Kinetic and mechanistic data necessary for the description of the night-time radical chemistry initiated by  $\text{NO}_3$  has been now established.

### 1.2.2d The determination of the rates and mechanisms for OH attack on more complex organic compounds, including oxygenated and nitrate compounds

An objective of LACTOZ has been to provide accurate rate coefficient data for OH attack on the more complex, higher molecular weight VOCs. As a result of the studies there is now a much improved data set for aromatic compounds, alkenes, including isoprene and other biogenic hydrocarbons. Kinetic data have also been obtained for some oxygenated compounds and nitrates for the first time.

Understanding of the mechanisms of oxidative degradation following OH attack has improved substantially, in particular for the aromatic compounds and for higher alkanes ( $\text{C}_5$  and  $\text{C}_6$ ). These results provide a firmer basis for the formulation of models for assessing ozone production from these important primary pollutants. Work in LACTOZ has established for the first time a validated model for isoprene oxidation under both high and low  $\text{NO}_x$  conditions. This provides a basis for assessing ozone formation resulting from emissions of this important biogenic hydrocarbon.

Although ozone-alkene reactions were not specified in the original objectives of LACTOZ they constitute a loss process for ozone and are important for degradation of unsaturated hydrocarbons, in particular alkenes with multiple double bonds and complex structures, such as are found in the biogenic hydrocarbons. Emphasis in LACTOZ has been on the rates and mechanisms under atmospheric conditions. These studies led to downward revision of the rate constants of the O<sub>3</sub> alkene reactions, due to complications arising in many earlier investigations from secondary reactions of radicals produced in the primary step. Some important hitherto unknown aspects of ozone reactions, such as the formation of peroxides and their dependence on the water vapour concentrations, have been discovered in LACTOZ.

### ***1.2.2e The determination of the rate constants and branching ratios for reactions of peroxy and alkoxy radicals***

The initial attack of radicals on VOCs gives rise to the formation of RO<sub>2</sub> radicals which can undergo a variety of reactions. These reactions may lead to propagation of the radical chain, *e.g.* formation of RO, or termination of the chain leading to radical loss and formation of stable products, *e.g.* hydroperoxides, peroxy nitrates and nitrates. Propagation is necessary for ozone production, and thus these reactions are central to the scientific aim of LACTOZ: quantification of tropospheric ozone budget.

Outstanding progress has been made in RO<sub>2</sub> chemistry, both in terms of reactivity and reaction mechanisms. The data have been compiled and reviewed [1], and further progress in defining structure-reactivity aspects for more complex VOCs is documented in this Final Report. For example, the mechanism of isoprene oxidation involving six different RO<sub>2</sub> radicals, for low NO<sub>x</sub> and high NO<sub>x</sub> conditions, has recently been validated against observations.

The general mechanism for the atmospheric degradation of VOCs follows a pathway in which the initially produced RO<sub>2</sub> radical is transformed into an alkoxy radical, RO. The fate of the alkoxy radicals determines the nature of the first stable products of oxidation, the degree of fragmentation of the original carbon chain and the potential for photo-oxidant formation.

Alkoxy radicals have several potential reaction channels which compete under atmospheric conditions. The study of these reactions is difficult due to their complexity and the absence of suitable techniques for direct monitoring of the kinetics. The relative importance of these channels has been established accurately for several individual RO radicals and also for groups of RO radicals of similar structural type in the LACTOZ project. This aids the definition of the ozone forming potential for alkanes. A particularly important achievement is the characterisation of the isomerisation reactions of larger alkoxy radicals, which has been a significant uncertainty in modelling photochemical ozone formation in the polluted boundary layer.

Studies of the oxidation of aromatic compounds have established that the reaction of the initial adduct, formed by attack by OH, reacts with O<sub>2</sub> to produce HO<sub>2</sub> on a short timescale. This observation, together with the fast reaction rate for the OH reaction with substituted aromatic compounds, accounts for their efficient ozone production.

***1.2.2f The elucidation of night-time NO<sub>3</sub> chemistry with a view to modelling the removal of NO<sub>x</sub> and VOCs from the atmosphere and the impact on the overall oxidation of VOCs***

Quantification of the NO<sub>3</sub> initiated degradation of VOC at night-time has required the establishment of rate coefficients for a wide range of VOCs present in the lower atmosphere. A substantial body of data for the reaction rates of NO<sub>3</sub> with VOCs has been obtained in LACTOZ, covering both man-made and naturally produced organic compounds. The mechanisms and products have also been investigated. As a result, it is now possible to make quantitative estimates of the rate of night-time HNO<sub>3</sub> production from NO<sub>x</sub> via the homogeneous pathway as opposed to the heterogeneous route via N<sub>2</sub>O<sub>5</sub>. Night-time production of organic nitrates, which are reservoirs for NO<sub>x</sub>, can also be estimated. The atmospheric chemistry of the NO<sub>3</sub> radical has been reviewed within LACTOZ [2].

***1.2.2g The investigation of reactions acting as sources and sinks of HO<sub>x</sub> and RO<sub>2</sub> radicals in the boundary layer in support of anticipated field measurements of free radical concentrations***

At the beginning of LACTOZ there was a well developed theory of the 'fast photochemistry' governing tropospheric free radical concentrations. However, the theory had not been validated by field measurements. Successful development of instruments for field measurements of OH and RO<sub>2</sub> radicals have led to the anticipated capability to observe atmospheric free radical chemistry and validate the models describing their production and loss, and the related production rates of ozone. A number of field campaigns for the study of radical chemistry have been conducted in Europe. Work in LACTOZ has made a substantial contribution to the data base for gas-phase reactions which control OH, HO<sub>2</sub> and related radical concentrations in the daytime troposphere; this information is needed to interpret the results of these experiments.

The issue of night-time radical chemistry initiated by NO<sub>3</sub> was not prominent at the start of LACTOZ. Although O<sub>3</sub> is not generated in this process, NO<sub>3</sub> chemistry is now considered to be of importance for the modification of the precursors for ozone formation, for example at high latitudes in wintertime, when anthropogenic pollutants can accumulate. Observations of night-time oxidation chemistry, including NO<sub>3</sub> and RO<sub>2</sub> radicals in the boundary layer, are also now feasible. LACTOZ data will enable the interpretation of these experiments.

### 1.3 Application of LACTOZ Results

We consider here some applications of work performed within LACTOZ and discuss ways in which the information gained has been disseminated.

Laboratory data on the kinetics, reaction mechanisms and pathways of elementary reactions occurring in the atmosphere form the basis for models describing and predicting photo-oxidant formation. Experience in the incorporation of the chemical information into the models by the Chemical Mechanism Working Group (CMWG) has shown that critical evaluation of currently used chemistry is required. In this respect, a successful exercise was the evaluation and improvement carried out by LACTOZ of the chemistry contained within the EMEP MSC-W model of photo-oxidants.

One of the objectives of the modelling procedures is to predict the extent to which specific VOCs contribute to ozone formation in the atmosphere. Kinetic information on the initiation step (attack by OH, NO<sub>3</sub>, O<sub>3</sub>) is required, and a great deal of new data of this kind has been acquired within LACTOZ. However, work within LACTOZ has also confirmed that the efficiency of ozone generation is not determined by the efficiency of the initial step alone (even in a single VOC system). In particular, the conversion of NO to NO<sub>2</sub> is required for ozone to be formed, and the length of the radical chain thus has a direct bearing on ozone generation. A great deal of new information on this aspect of VOC oxidation has been provided by LACTOZ. The VOC/NO<sub>x</sub> ratio in turn influences the nature and extent of the chain propagation and termination reactions. Thus, detailed understanding of all the steps in the mechanism (including photochemical processes) is necessary in defining useful measures of ozone generation in mixtures of VOC representative of real air masses.

A consequence of these considerations is that it is not possible to give a straightforward definition of an ozone forming potential of a given VOC. One index of ozone formation potential that has found some favour is the Photo-oxidant Creation Potential (POCP). This index is derived from a model calculation that includes detailed chemistry, but it has to be interpreted with caution because it applies to a single model domain. Another measure, which has the virtue of being objectively calculable from laboratory data, is the NOCON factor, defined as the total number of NO molecules converted to NO<sub>2</sub> for the first stage of the oxidation of each VOC molecule. The parameters required for the determination of the NOCON factor are the branching ratios for chain termination in the interaction of RO<sub>2</sub> with NO and for reaction with O<sub>2</sub>, compared with decomposition and isomerisation, of the corresponding RO radicals.

It has become increasingly apparent that omission of biogenic species from tropospheric models leads to incorrect evaluation of photo-oxidant chemistry, particularly in rural areas. LACTOZ has provided substantial new data, largely on



isoprene, which is an important component of the biogenic emissions. However, there are many other species, including the terpenes, which have not yet been subject to detailed investigation because of considerable experimental difficulties. The aim of future work should be to describe the impact of the major biogenic components both on the formation and the destruction of ozone in the atmosphere for meteorological conditions that apply in Europe.

In 1992, a complete mechanism for the oxidation of C<sub>1</sub> and C<sub>2</sub> hydrocarbons was formulated by the LACTOZ Steering Committee. The intended application is in global models for studies of methane oxidation and the tropospheric ozone budget. These studies have provided useful input to the Intergovernmental Panel on Climate Change (IPCC) assessment of the atmospheric chemistry of greenhouse gases.

Much of the work within LACTOZ has been published in the open literature and has also been recorded in the Annual Reports to EUROTRAC. Workshops have been held annually, and the proceedings published as reports by the European Commission. In addition, groups of workers within LACTOZ have written two extensive reviews summarising knowledge on the physics and chemistry of two of the key radicals and their involvement in atmospheric chemistry. These reviews discuss (i) the nitrate radical and (ii) peroxy radicals, RO<sub>2</sub>, and were both published by *Atmospheric Environment* and by the European Commission. Similarly, reviews are currently in preparation on (i) the chemistry, and especially the oxidation pathways and mechanisms, of aromatic compounds, and (ii) chemical mechanisms for use in models and the methods for their experimental evaluation.

# Chapter 2

## Scientific Results

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### 2.1 Reaction of OH radicals

#### 2.1.1 Introduction

Reactions with the hydroxyl radical provide the major removal pathway for most VOCs in the global troposphere. As a consequence, the rate constants for OH + VOC reactions determine the timescales, and hence the spatial distribution of VOCs. The timescales of VOC loss by reaction with OH are also identical with the timescales of formation of secondary pollutants and photochemical oxidants, including ozone. The data base for OH reaction rate coefficients is generally well defined and has been the subject of regular evaluations and updates including contributions from LACTOZ. The specific objectives of LACTOZ contributions are:

- to define and extend the current kinetic data base for compounds relevant to the formation of ozone, in particular for compounds which have only recently been identified as oxidation products of primary pollutants;
- to determine the product distribution for OH initiated oxidation reactions and to derive structure-reactivity relationships for OH attack at different sites of the parent VOC;
- to develop techniques for the estimation of photochemical ozone formation potentials of VOCs and for the reduction of oxidation mechanisms for incorporation into tropospheric chemical-dynamic models.

Of these objectives, only the first is related to overall OH radical reaction rate studies. The latter two rely largely on the full complexity of the oxidation chain including reactions of RO<sub>2</sub> and RO radicals as well as their interactions with NO<sub>x</sub>.

### 2.1.2 Results

A number of new kinetic studies of reactions of OH radicals with VOCs have been performed in LACTOZ. The results are summarised in Tables 1a and 1b. Pilling has studied the rate coefficients for reactions of OH with C<sub>4</sub> alcohols and esters using DF/LIF and LP/LIF techniques. Becker has used a relative rate technique to determine the rate coefficients for reactions of OH with products originating from the oxidation of isoprene, 2- and 3-methyl-3-butene-1,2-diol and 1,2-epoxy-3-methyl-3-butene. Similar experiments have also been performed by this group on doubly unsaturated 1,6 and 1,4-dicarbonyl compounds, carbonyl nitrates and dinitrates. These compounds are suspected to be the primary ring-opening products in the oxidation of aromatic compounds and from the NO<sub>3</sub> initiated oxidation of alkenes, respectively. The rate coefficients for the reactions of OH with a series of alkenes and with methyl glyoxal, a product from the oxidation of isoprene, have been determined using a DF/RF technique (Devolder). Rate data for the reactions of OH radicals with various ethers have been obtained using LP-LIF (Le Bras/Poulet) and relative rate techniques (Kerr). Surprisingly, all the ethers show negative temperature dependence. Schindler has measured rate coefficients for reactions of OH with a number of oxiranes. These compounds are secondary pollutants which arise from the NO<sub>3</sub> and O<sub>3</sub> initiated oxidation of alkenes. Kinetic studies for reactions of OH with benzene and its substituted analogues (toluene, phenol, benzaldehyde, cresols) have been performed as a function of temperature using a relative rate technique in an irradiated flow reactor over the pressure range 130–1000 mbar (Kerr). Nielsen has measured rate coefficients for reactions of OH with a number of *n*-nitroalkanes, *n*-alkyl nitrates and nitrites using a pulse radiolysis technique. These studies have been complemented by Sidebottom using a relative rate technique. An important mechanistic finding arising from this work is that for the compounds CH<sub>3</sub>NO<sub>2</sub>, CH<sub>3</sub>ONO<sub>2</sub> and CH<sub>3</sub>ONO both abstraction and addition channels appear to be important.

**Table 1a:** Rate constants for reactions of OH radicals with VOCs determined at 298 K.

VOC	$k$ ( $\text{cm}^3 \text{s}^{-1}$ )	Method <sup>a</sup>	Reference <sup>b</sup>
<b>Alkanes</b>			
methane	$5.4 \times 10^{-15}$ <sup>c</sup>	LP/LIF	Pilling (92)
	$6.3 \times 10^{-15}$	DF/LIF	Le Bras (93)
propane	$1.1 \times 10^{-12}$	DF/LIF	Le Bras (93)
cyclohexane	$6.7 \times 10^{-12}$	DF/LIF	Pilling (92)
1,2-dichloroethane	$2.0 \times 10^{-12}$	LP/LIF	Pilling (93)
<b>Alkenes</b>			
isobutene	$5.7 \times 10^{-11}$	LP/RF	Devolder (92)
1,2-butadiene	$1.9 \times 10^{-11}$	DF/LIF	Pilling (92)
isoprene	$9.7 \times 10^{-11}$	FP/RF	Zetzsch (93)
	$9.7 \times 10^{-11}$	LP/RF	Devolder (92)
cyclohexene	$6.6 \times 10^{-11}$	LP/RF	Devolder (92)
trans-1,2-dichloroethene	$1.9 \times 10^{-12}$	DF/LIF	Pilling (93)
<b>Alcohols</b>			
<i>n</i> -butanol	$8.4 \times 10^{-12}$	LP/LIF	Pilling (92)
<i>i</i> -butanol	$9.0 \times 10^{-12}$	LP/LIF	Pilling (92)
<i>t</i> -butanol	$8.1 \times 10^{-13}$	DF/LIF	Pilling (92)
	$1.1 \times 10^{-12}$	LP/LIF	Le Bras (94)
<i>i</i> -amylalcohol	$1.3 \times 10^{-11}$	DF/LIF	Pilling (92)
2-methyl-3-butene-1,2-diol	$8.2 \times 10^{-11}$	RR/FTIR	Becker (93)
3-methyl-3-butene-1,2-diol	$1.3 \times 10^{-10}$	RR/FTIR	Becker (93)
3-hexene-3,4-diol-2,5-dione	$2.7 \times 10^{-10}$	RR/FTIR	Becker (94)
<b>Ethers</b>			
di-methyl ether	$2.8 \times 10^{-12}$	LP/LIF	Le Bras (94)
di-ethyl ether	$1.3 \times 10^{-11}$	LP/LIF	Le Bras (93)
	$1.3 \times 10^{-11}$	RR/GC	Kerr (92)
di- <i>n</i> -propyl ether	$2.2 \times 10^{-11}$	LP/LIF	Le Bras (94)
di- <i>i</i> -propyl ether	$1.0 \times 10^{-11}$	LP/LIF	Le Bras (93)
methyl- <i>n</i> -butyl ether	$1.5 \times 10^{-11}$	RR/GC	Kerr (92)
methyl- <i>t</i> -butyl ether	$3.1 \times 10^{-12}$	LP/LIF	Le Bras (94)
methyl- <i>i</i> -pentyl ether	$6.3 \times 10^{-12}$	LP/LIF	Le Bras (94)
methyl- <i>t</i> -amyl ether	$5.0 \times 10^{-12}$	LP/LIF	Pilling (92)
ethyl- <i>n</i> -butyl ether	$2.3 \times 10^{-11}$	RR/GC	Kerr (92)
	$2.1 \times 10^{-11}$	LP/LIF	Le Bras (94)
ethyl- <i>t</i> -butyl ether	$8.8 \times 10^{-12}$	LP/LIF	Le Bras (94)
di- <i>n</i> -butyl ether	$2.7 \times 10^{-11}$	LP/LIF	Le Bras (93)
	$3.0 \times 10^{-11}$	RR/GC	Kerr (92)
di- <i>n</i> -pentyl ether	$3.4 \times 10^{-11}$	RR/GC	Kerr (92)
<b>Carbonyls</b>			
methyl-ethyl ketone	$1.2 \times 10^{-12}$	RR/GC	Moortgat (90)
methyl-vinyl ketone	$1.9 \times 10^{-11}$	RR/GC	Moortgat (90)
methyl glyoxal	$7.7 \times 10^{-12}$	LP/RF	Devolder (93)
	$1.7 \times 10^{-11}$	RR/GC	Moortgat (90)
methacrolein	$3.3 \times 10^{-11}$	RR/GC	Moortgat (90)
cyclohexanone	$4.3 \times 10^{-12}$	LP/LIF	Pilling (93)

Table 1a: continued

VOC	$k$ ( $\text{cm}^3 \text{s}^{-1}$ )	Method <sup>a</sup>	Reference <sup>b</sup>
<b>Carbonyls (unsaturated)</b>			
<i>cis</i> -butenedial	$5.2 \times 10^{-11}$	RR/FTIR	Becker (92)
<i>trans</i> -butenedial	$2.4 \times 10^{-11}$	RR/FTIR	Becker (92)
<i>cis/trans</i> -4-oxo-2-pental	$5.5 \times 10^{-11}$	RR/FTIR	Becker (92)
<i>cis</i> -3-hexene-2,5-dione	$6.9 \times 10^{-11}$	RR/FTIR	Becker (93)
<i>trans</i> -3-hexene-2,5-dione	$4.0 \times 10^{-11}$	RR/FTIR	Becker (93)
E,Z-hexa-2,4-dienedial	$1.1 \times 10^{-10}$	RR/FTIR	Becker (93)
E,E-hexa-2,4-dienedial	$8.8 \times 10^{-11}$	RR/FTIR	Becker (93)
E,E-2-methyl-hexa-2,4-dienedial	$1.2 \times 10^{-10}$	RR/FTIR	Becker (93)
maleic anhydride	$1.5 \times 10^{-12}$	RR/FTIR	Becker (92)
3H-furan-2-one	$4.4 \times 10^{-11}$	RR/FTIR	Becker (92)
5-methyl-3H-furan-2-one	$6.9 \times 10^{-11}$	RR/FTIR	Becker (92)
<b>Esters</b>			
<i>n</i> -propyl acetate	$2.9 \times 10^{-12}$	LP/LIF	Pilling (93)
vinylacetate	$2.5 \times 10^{-11}$	DF/LIF	Pilling (93)
methyl methacrylate	$2.6 \times 10^{-11}$	DF/LIF	Pilling (92)
<b>Oxiranes</b>			
ethylene oxide	$1.1 \times 10^{-13}$		Schindler (92)
1,2-epoxypropane	$5.1 \times 10^{-13}$		Schindler (92)
1,2-epoxybutane	$3.1 \times 10^{-12}$		Schindler (92)
1,2-epoxyhexane	$1.2 \times 10^{-11}$		Schindler (92)
tetramethyloxirane	$1.4 \times 10^{-12}$		Schindler (92)
butadienmonoxide	$1.2 \times 10^{-11}$		Schindler (92)
2-methyl-2-vinyl-oxirane	$2.6 \times 10^{-11}$		Schindler (92)
1,2-epoxi-5-hexene	$5.4 \times 10^{-11}$		Schindler (92)
2-propenyl-oxirane	$5.8 \times 10^{-11}$	RR/FTIR	Becker (94)
<b>Nitroalkanes</b>			
nitromethane	$1.6 \times 10^{-13}$	PR/UV	Nielsen (94)
nitroethane	$1.5 \times 10^{-13}$	PR/UV	Nielsen (94)
nitro- <i>n</i> -propane	$3.4 \times 10^{-13}$	PR/UV	Nielsen (94)
nitro- <i>n</i> -butane	$1.5 \times 10^{-12}$	PR/UV	Nielsen (94)
nitro- <i>n</i> -pentane	$3.3 \times 10^{-12}$	PR/UV	Nielsen (94)
<b>Nitrates</b>			
methyl nitrate	$3.3 \times 10^{-13}$	PR/UV	Nielsen (91)
ethyl nitrate	$5.3 \times 10^{-13}$	PR/UV	Nielsen (91)
<i>n</i> -propyl nitrate	$8.0 \times 10^{-13}$	PR/UV	Nielsen (91)
<i>n</i> -butyl nitrate	$1.7 \times 10^{-12}$	PR/UV	Nielsen (91)
<i>n</i> -pentyl nitrate	$3.1 \times 10^{-12}$	PR/UV	Nielsen (91)
1,2-propandiol dinitrate	$< 3 \times 10^{-13}$	RR/FTIR	Becker (90)
1,2-butandiol dinitrate	$1.7 \times 10^{-12}$	RR/FTIR	Becker (90)
2,3-butandiol dinitrate	$1.1 \times 10^{-12}$	RR/FTIR	Becker (90)
<i>a</i> -nitrooxy acetone	$< 4.3 \times 10^{-13}$	RR/FTIR	Becker (90)
1-nitrooxy-butanone-2	$9.1 \times 10^{-13}$	RR/FTIR	Becker (90)
3-nitrooxy-butanone-2	$1.3 \times 10^{-12}$	RR/FTIR	Becker (90)
<i>cis</i> -1,4-dinitrooxy butene-2	$1.5 \times 10^{-11}$	RR/FTIR	Becker (90)
3,4-dinitrooxy butene-1	$1.0 \times 10^{-11}$	RR/FTIR	Becker (90)

Table 1a: continued

VOC	k (cm <sup>3</sup> s <sup>-1</sup> )	Method <sup>a</sup>	Reference <sup>b</sup>
<b>Nitrites</b>			
methylnitrite	2.6 × 10 <sup>-13</sup>	PR/UV	Nielsen (90)
ethylnitrite	7.0 × 10 <sup>-13</sup>	PR/UV	Nielsen (90)
<i>n</i> -propyl nitrite	1.2 × 10 <sup>-12</sup>	PR/UV	Nielsen (90)
<i>n</i> -butyl nitrite	2.7 × 10 <sup>-12</sup>	PR/UV	Nielsen (90)
<i>n</i> -pentyl nitrite	4.2 × 10 <sup>-12</sup>	PR/UV	Nielsen (90)
<b>Aromatics</b>			
benzene	1.2 × 10 <sup>-12</sup>	RR/GC	Kerr (93)
	k <sub>0</sub> = 1.0 × 10 <sup>-12</sup>	DF/RF	Devolder (94)
toluene	k <sub>0</sub> = 1.7 × 10 <sup>-29</sup> cm <sup>6</sup> /s	DF/RF	Devolder (94)
	6.1 × 10 <sup>-12</sup>	RR/GC	Kerr (93)
	k <sub>0</sub> = 6.0 × 10 <sup>-12</sup>	DF/RF	Devolder (94)
	k <sub>0</sub> = 4.0 × 10 <sup>-28</sup> cm <sup>6</sup> /s	DF/RF	Devolder (94)
<i>p</i> -xylene	4.7 × 10 <sup>-12</sup> (N <sub>2</sub> )	RR/FTIR	Becker (94)
	6.6 × 10 <sup>-12</sup> (air)	RR/FTIR	Becker (94)
	1.1 × 10 <sup>-11</sup> (N <sub>2</sub> )	RR/FTIR	Becker (94)
	1.5 × 10 <sup>-11</sup> (air)	RR/FTIR	Becker (94)
phenol	2.9 × 10 <sup>-11</sup>	RR/GC	Kerr (93)
benzaldehyde	1.2 × 10 <sup>-11</sup>	RR/GC	Kerr (93)
<i>o</i> -cresol	4.9 × 10 <sup>-11</sup>	RR/GC	Kerr (93)
<i>m</i> -cresol	5.3 × 10 <sup>-11</sup>	RR/GC	Kerr (93)
<i>p</i> -cresol	5.9 × 10 <sup>-11</sup>	RR/GC	Kerr (93)
naphthalene	2.3 × 10 <sup>-11</sup>	FP/RF	Zetzsch (93)

<sup>a</sup> T = 292 K

<sup>b</sup> These references are to EUROTRAC Annual Reports. The year in parentheses is the year of the report not the publishing year.

<sup>c</sup> LP/LIF: laser photolysis/laser induced fluorescence  
 DF/LIF: discharge flow/laser induced fluorescence  
 FP/RF: flash photolysis/resonance fluorescence  
 LP/RF: laser photolysis/resonance fluorescence  
 RR/GC: relative rate technique/gas chromatography  
 PR/UV: pulse radiolysis/UV adsorption  
 RR/FTIR: relative rate technique/Fourier transform IR absorption

**Table 1b:** Rate constants for reactions of OH radicals with VOCs. Results from temperature dependence studies.

VOC	A (cm <sup>3</sup> s <sup>-1</sup> )	E <sub>a</sub> /R (K)	Reference*
<b>Alkanes</b>			
methane	2.6 × 10 <sup>-12</sup>	1765	Le Bras (93)
<b>Alkenes</b>			
isobutene	3.6 × 10 <sup>-12</sup>	-840	Devolder (92)
isoprene	7.2 × 10 <sup>-12</sup>	-783	Devolder (92)
cyclohexene	1.4 × 10 <sup>-11</sup>	-490	Devolder (92)
<b>Ethers</b>			
di-methyl ether	6.4 × 10 <sup>-12</sup>	234	Le Bras (94)
di-ethyl ether	5.2 × 10 <sup>-12</sup>	-262	Kerr (92)
	6.6 × 10 <sup>-12</sup>	-208	Le Bras (93)
di- <i>n</i> -propyl ether	1.1 × 10 <sup>-11</sup>	-210	Le Bras (94)
di- <i>i</i> -propyl ether	4.1 × 10 <sup>-12</sup>	-274	Le Bras (93)
di- <i>n</i> -butyl ether	5.5 × 10 <sup>-12</sup>	-502	Kerr (92)
	3.8 × 10 <sup>-12</sup>	-599	Le Bras (93)
di- <i>n</i> -pentyl ether	8.5 × 10 <sup>-12</sup>	-417	Kerr (92)
methyl- <i>n</i> -butyl ether	5.4 × 10 <sup>-12</sup>	-309	Kerr (92)
methyl- <i>i</i> -butyl ether	5.0 × 10 <sup>-12</sup>	133	Le Bras (94)
methyl- <i>i</i> -pentyl ether	4.7 × 10 <sup>-12</sup>	-82	Le Bras (94)
ethyl- <i>n</i> -butyl ether	6.6 × 10 <sup>-12</sup>	-362	Le Bras (94)
	7.3 × 10 <sup>-12</sup>	-335	Kerr (92)
ethyl- <i>i</i> -butyl ether	4.4 × 10 <sup>-12</sup>	-210	Le Bras (94)
<b>Aromatics</b>			
benzene	2.6 × 10 <sup>-12</sup>	-231	Kerr (94)
toluene	7.9 × 10 <sup>-13</sup>	-614	Kerr (94)
phenol	3.7 × 10 <sup>-13</sup>	-1270	Kerr (94)
benzaldehyde	5.3 × 10 <sup>-12</sup>	-243	Kerr (94)
<i>o</i> -cresol	9.8 × 10 <sup>-13</sup>	-1170	Kerr (94)
<i>m</i> -cresol	5.2 × 10 <sup>-12</sup>	-686	Kerr (94)
<i>p</i> -cresol	2.2 × 10 <sup>-12</sup>	-943	Kerr (94)
naphtalene	4.7 × 10 <sup>-12</sup>	-475	Zetzsch (93)

\* These references are to EUROTRAC Annual Reports. The year in parentheses is the year of the report not the publishing year.

Kinetic data for reactions of OH with VOCs determined in LACTOZ show good agreement with literature data. However, the LACTOZ data base also contains OH rate coefficients for compounds which have not previously been investigated.

Based on an analysis of the overall rate coefficients for the reactions of OH radicals with alkenes, Peeters has developed a structure-reactivity relationship for prediction of the relative yields of OH addition to specific sites in the parent alkenes. For mono-alkenes and non-conjugated poly-alkenes the site-specific rate coefficients depend on the stability of the ensuing hydroxyalkyl radical, which can be either a primary, secondary or tertiary radical. For conjugated dienes, the structure-reactivity analysis requires additional consideration of the resonance stabilisation energies of the adduct radicals. The quality of the predictions have been tested for a large number of alkenes and found in most cases to be in agreement with experiment within 10 %.

Whereas kinetic measurements of OH reactions are usually designed to monitor the loss of OH, measurements of the kinetic behaviour of OH in oxidation studies can also be utilised to extract mechanistic information. Zellner has applied time-resolved laser absorption studies of OH to monitor the formation of HO<sub>2</sub> radicals (converted into OH in the presence of NO) in the Cl atom initiated oxidation of a large number of alkanes, alkenes and aromatic compounds. It has been demonstrated that by this technique the total yield of hydroxyperoxy radicals and, by implication, the number of NO molecules converted into NO<sub>2</sub>, can be monitored. Zetzsch has applied highly sensitive OH measurements in oxidation studies of aromatic compounds to extract both the thermal stability of OH aromatic adducts and the extent of radical recycling occurring in the loss reactions of these adducts in the presence of O<sub>2</sub> and NO.

Mechanistic studies, aimed at direct determination of product distributions in the photo-oxidation of VOCs under simulated tropospheric conditions, have been performed (Warneck, Becker, Kerr). From the product distributions observed in the steady-state photo-oxidation of a number of C<sub>5</sub>-C<sub>7</sub> alkanes and alkenes, branching ratios for site specific H atom abstraction and OH addition, respectively, have been determined (Warneck). For 2,3-dimethyl butane the ratio of tertiary to primary H atom abstraction was found to be 1.0:0.20. The dominance of abstraction from the tertiary site was also confirmed for 2-methyl butane (*i*-pentane). In addition, reactions of OH with asymmetric alkenes show a higher propensity for addition to a terminal position at room temperature. For instance, the fractions of OH addition to the 1-position of 1-butene, 2-methyl-1-butene and 3-methyl-1-butene have been determined as 0.74, 0.89 and 0.76, respectively (Warneck). Warneck has also investigated the product distribution in the oxidation of toluene under NO<sub>x</sub> free conditions. The major finding was that 56 % of the total products could be assigned to ring-retaining mechanisms, whereas 25 % resulted from ring cleavage (see Section 4.7). Becker has performed product investigations for the oxidation of isoprene and aromatic compounds (toluene and *p*-xylene). For isoprene the identification of diols such as 2- and 3-methyl-3-butene-1,2-diol were taken as evidence for the mechanism shown in Fig. 11. In contrast to Warneck the experiments of Becker were carried

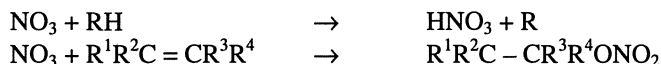


out under conditions closer to those of the atmosphere. Under these conditions, ring-retaining (phenol-type) products are negligible. The OH initiated photo-oxidation of n-hexane has been studied using a collapsible Teflon smog chamber (Kerr). The primary products quantified include 3-hexylnitrate, 2-hexylnitrate, n-butylnitrate, 3-hexanone, 2-hexanone, formaldehyde and acetaldehyde. From these product distributions valuable information on the branching ratios for reactions of the various alkoxy radicals produced in the system were obtained.

## 2.2 Reactions of NO<sub>3</sub> radicals

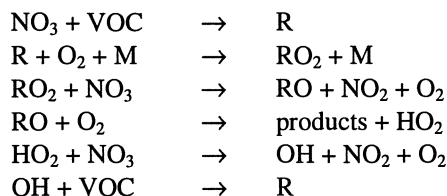
### 2.2.1 Introduction

Evidence for the presence of the nitrate radical during night-time in the troposphere has led to considerable effort in establishing its role in atmospheric chemistry. Two main types of reactions of NO<sub>3</sub> with volatile organic compounds have been identified, hydrogen atom abstraction and addition to unsaturated systems:



Abstraction reactions of NO<sub>3</sub> are generally slow, although reaction with dimethyl sulfide and oxygenated aromatics are facile and probably dominate the atmospheric removal of these species. Since the reaction rate of NO<sub>3</sub> with alkenes is often higher than that for the reaction with O<sub>3</sub>, production of NO<sub>3</sub> radicals from O<sub>3</sub> leads to a faster effective oxidation rate by O<sub>3</sub>. The major products identified from reactions of NO<sub>3</sub> with alkenes are carbonyl nitrates and unsubstituted carbonyl compounds. Thus, the reactions of NO<sub>3</sub> radicals play an important role in the conversion of NO<sub>x</sub> into both the permanent sink species, HNO<sub>3</sub>, and into temporary reservoir species such as carbonyl nitrates which can lead to long-range transport of odd nitrogen. Nitric acid results from both hydrogen abstraction from saturated organic compounds or from hydrolysis of N<sub>2</sub>O<sub>5</sub> formed from the reaction of NO<sub>3</sub> with NO<sub>2</sub>.

It has recently been shown that the reaction of NO<sub>3</sub> with organic compounds initiates a chain reaction and can lead to a night-time source of OH radical [3]:



The importance of this oxidation sequence depends on the availability of  $\text{NO}_3$  to propagate the chain via reaction with alkylperoxy and  $\text{HO}_2$  radicals.

## 2.2.2 Reactions of $\text{NO}_3$ with organic molecules

### *Abstraction reactions of $\text{NO}_3$ radicals*

Rate constants for the reaction of  $\text{NO}_3$  radicals with a number of alkanes have been determined using conventional discharge flow-visible absorption methods (Ljungström, Wayne) and by a stopped-flow technique (Wayne) (Table 2). Rate constants, determined as a function of temperature, for the reaction of  $\text{NO}_3$  with ethane, n-butane and 2-methyl propane show that, as expected, the activation energy increases in the order primary > secondary > tertiary. Product studies have not been reported for the reaction of  $\text{NO}_3$  with alkanes although the available rate data are consistent with a hydrogen atom abstraction process. Alkyl radical formation has also been used to explain the secondary reactions observed in discharge-flow investigations of  $\text{NO}_3$  alkane reactions (Wayne). The reactivity of  $\text{NO}_3$  is low and hence loss of alkanes in the troposphere due to reaction with  $\text{NO}_3$  is minor compared to their removal by the daytime attack of hydroxyl radicals.

The reactivity of various oxygenated organic compounds with respect to reactions with  $\text{NO}_3$  radicals has been reported (Ljungström, Schindler, Wayne) (Table 2). Many of these compounds have been used as industrial solvents and fuel additives, and are formed in the troposphere as degradation products from a variety of VOCs. Wayne has determined rate constants for the reactions of  $\text{NO}_3$  with  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{COCH}_3$  using discharge-flow and stopped-flow methods, respectively. The low activation energy for the reaction with  $\text{CH}_3\text{CHO}$  indicates a process involving hydrogen atom abstraction from the aldehyde group. The reactivity of  $\text{CH}_3\text{COCH}_3$  is similar to that observed for ethane, suggesting that the carbonyl group has little influence on the  $\text{CH}_3$  group reactivity. Kinetic and mechanistic studies on the reactions of  $\text{NO}_3$  radicals with a series of alcohols, ethers and esters have been described (Ljungström). Rate constants were measured as a function of temperature at low pressures with a discharge-flow visible-absorption absolute rate technique. Rate data were also obtained at 295 K and atmospheric pressure using a relative rate method, employing FTIR spectroscopy for monitoring the loss of reactants. Agreement between the rate constants determined from the two experimental techniques was excellent. The rate coefficients obtained for the reaction of  $\text{NO}_3$  radicals with both alcohols and ethers are significantly higher than would be expected on the basis of carbon-hydrogen bond strengths in these molecules. This effect could arise from stabilisation of the transition states for the reactions arising from an interaction between the nitrate radical and the oxygen atom of the hydroxy or ether groups.

**Table 2:** Rate constants for the reactions of NO<sub>3</sub> with VOCs at 298 K.

VOC	Method	$k$ (cm <sup>3</sup> s <sup>-1</sup> )	Reference *
<b>Alkanes</b>			
methane	DSF-VA	$< 4 \times 10^{-19}$	Wayne (94)
ethane	DF-VA	$8.3 \times 10^{-19}$	Wayne (94)
<i>n</i> -butane	DF-VA	$4.5 \times 10^{-17}$	Wayne (94)
<i>n</i> -hexane	DF-VA	$1.4 \times 10^{-16}$	Ljungström (91)
2-methyl propane	DF-VA	$1.1 \times 10^{-16}$	Wayne (94)
<b>Oxygenated Organics</b>			
acetaldehyde	DF-VA	$2.5 \times 10^{-15}$	Wayne (94)
acetone	DSF-VA	$8.5 \times 10^{-18}$	Wayne (90)
methanol	DF-VA	$9.0 \times 10^{-16}$	Ljungström (94)
ethanol	DF-VA	$1.6 \times 10^{-15}$	Ljungström (94)
2-propanol	DF-VA	$4.0 \times 10^{-15}$	Ljungström (94)
dimethyl ether	DF-VA, RR	$2.6 \times 10^{-16}$	Ljungström (93)
diethyl ether	DF-VA, RR	$2.8 \times 10^{-15}$	Ljungström (93)
methyl <i>t</i> -butyl ether	DF-VA, RR	$6.4 \times 10^{-16}$	Ljungström (93)
di- <i>n</i> -propyl ether	DF-VA, RR	$6.5 \times 10^{-15}$	Ljungström (93)
di- <i>i</i> -propyl ether	DF-VA, RR	$5.5 \times 10^{-15}$	Ljungström (93)
<i>t</i> -amyl methyl ether	DF-VA, RR	$2.2 \times 10^{-15}$	Ljungström (93)
ethyl <i>t</i> -butyl ether	DF-VA, RR	$1.1 \times 10^{-14}$	Ljungström (93)
methyl formate	DF-VA	$3.6 \times 10^{-18}$	Ljungström (92)
methyl acetate	DF-VA	$7.0 \times 10^{-18}$	Ljungström (92)
methyl propionate	DF-VA	$3.3 \times 10^{-17}$	Ljungström (92)
methyl butyrate	DF-VA	$4.8 \times 10^{-17}$	Ljungström (92)
ethyl formate	DF-VA	$1.7 \times 10^{-17}$	Ljungström (92)
ethyl acetate	DF-VA	$1.3 \times 10^{-17}$	Ljungström (92)
ethyl propionate	DF-VA	$3.3 \times 10^{-17}$	Ljungström (92)
propyl formate	DF-VA	$5.4 \times 10^{-17}$	Ljungström (92)
propyl acetate	DF-VA	$5.0 \times 10^{-17}$	Ljungström (92)
1,2-epoxyethane	DF-MS	$3.9 \times 10^{-16}$	Schindler (91)
1,2-epoxybutane	DF-MS	$1.5 \times 10^{-15}$	Schindler (91)
1,2-epoxyhexane	DF-MS	$5.7 \times 10^{-15}$	Schindler (91)
3,4-epoxy-1-butene	DF-MS	$7.3 \times 10^{-15}$	Schindler (91)
3,4-epoxy-3-methyl-1-butene	DF-MS	$1.8 \times 10^{-14}$	Schindler (91)

Table 2: continued

VOIC	Method	$k$ (cm <sup>3</sup> s <sup>-1</sup> )	Reference *
<b>Alkenes</b>			
ethene	DSF-VA	$1.7 \times 10^{-16}$	Wayne (94)
	EC-RR	$9.3 \times 10^{-17}$	Becker (88)
1-butene	DF-VA	$1.1 \times 10^{-14}$	Wayne (90)
	EC-RR	$7.8 \times 10^{-15}$	Ljungström (90)
	EC-RR	$1.3 \times 10^{-14}$	Becker (88)
<i>cis</i> -2-butene	DF-MS	$3.6 \times 10^{-13}$	Schindler (92)
<i>trans</i> -2-butene	DF-MS	$3.8 \times 10^{-13}$	Schindler (88)
2-methyl propene	EC-RR	$3.2 \times 10^{-13}$	Becker (88)
	DF-MS	$3.8 \times 10^{-13}$	Schindler (92)
2-methyl-2-butene	DF-MS	$7.8 \times 10^{-12}$	Schindler (92)
2,3-dimethyl-2-butene	DF-MS	$4.0 \times 10^{-11}$	Schindler (92)
	DF-MS	$4.5 \times 10^{-11}$	Le Bras (89)
	PR-KS	$4.5 \times 10^{-11}$	Nielsen (88)
1-pentene	DF-VA	$1.8 \times 10^{-14}$	Wayne (92)
1-hexene	DF-VA	$1.5 \times 10^{-14}$	Wayne (92)
cyclopentene	DF-VA	$5.9 \times 10^{-13}$	Ljungström (92)
cyclohexene	DF-VA	$6.3 \times 10^{-13}$	Ljungström (92)
1-methyl cyclohexene	DF-VA	$1.5 \times 10^{-11}$	Ljungström (92)
1,3-butadiene	DF-MS	$1.0 \times 10^{-13}$	Le Bras (89)
	EC-RR	$1.9 \times 10^{-13}$	Becker (88)
2,3-dimethyl-1,3-butadiene	DF-MS	$2.0 \times 10^{-12}$	Le Bras (89)
2-methyl-1,3-butadiene (isoprene)	DF-MS	$7.8 \times 10^{-13}$	Le Bras (90/91), Schindler (90/91)
	EC-RR	$6.0 \times 10^{-13}$	Becker (90)
$\alpha$ -pinene	EC-RR	$6.5 \times 10^{-12}$	Becker (88)
$\beta$ -pinene	EC-RR	$2.8 \times 10^{-12}$	Becker (88)
$\Delta^3$ -carene	EC-RR	$8.1 \times 10^{-12}$	Becker (88)
<i>d</i> -limonene	EC-RR	$1.1 \times 10^{-11}$	Becker (88)
<b>Aromatics</b>			
toluene	RR	$6.1 \times 10^{-17}$	Carlier (89)
<i>o</i> -xylene	RR	$3.7 \times 10^{-16}$	Carlier (89)
<i>m</i> -xylene	RR	$2.5 \times 10^{-16}$	Carlier (89)
<i>p</i> -xylene	RR	$4.2 \times 10^{-16}$	Carlier (89)
1,2,3-trimethyl benzene	RR	$2.5 \times 10^{-15}$	Carlier (89)
1,2,4-trimethyl benzene	RR	$2.1 \times 10^{-15}$	Carlier (89)
1,3,5-trimethyl benzene	RR	$1.4 \times 10^{-15}$	Carlier (89)

\* These references are to EUROTRAC Annual Reports. The year in parentheses is the year of the report not the publishing year.

DSF-VA: discharge stopped flow - visible absorption

DF-VA: discharge flow - visible absorption,  $p < 5$  Torr

DF-MS: discharge flow - mass spectrometry

EC-RR: environmental chamber - relative rate

RR: relative rate, atmospheric pressure of air

PR-KS: pulse radiolysis - kinetic spectroscopy

The rate data for reaction of  $\text{NO}_3$  with aliphatic esters show that the presence of the ester group in an organic molecule has little influence on the reactivity compared to the parent alkane. The reactivity trends exhibited by the nitrate radical for reactions with alcohols, ethers and esters are similar to those shown for the analogous reactions of hydroxyl radicals. The major products identified from the  $\text{NO}_3$  radical-initiated oxidation of alcohols, ethers and esters under atmospheric conditions were esters, carbonyls and alkyl nitrates. Similar products arise from the reactions of OH radicals with these molecules under atmospheric conditions.

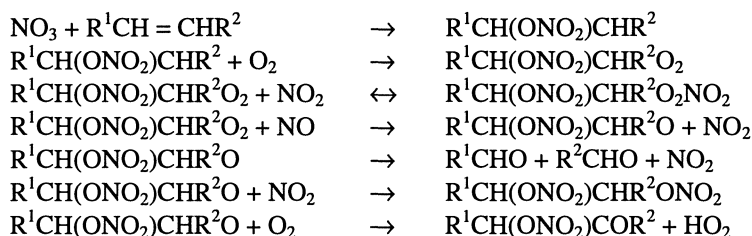
The rate constants for reactions of  $\text{NO}_3$  with oxygenated organic compounds are too low for these reactions to contribute to the overall atmospheric removal of these species, although they could provide a non-negligible source of  $\text{HNO}_3$  under night-time conditions. Schindler has measured rate constants for reaction of  $\text{NO}_3$  with saturated epoxides using a discharge-flow mass-spectrometry technique. The reactivity of the epoxides is around two orders of magnitude higher than that for the analogous alkanes, indicating the influence of ring-strain in these reactions.

Dimethyl sulfide is the most abundant of all the biogenic organo-sulfur compounds, and the available data show that the H atom abstraction reaction with  $\text{NO}_3$  could contribute significantly to the conversion of  $\text{NO}_x$  to  $\text{HNO}_3$  in polluted coastal regions (Hjorth, Le Bras/Poulet).

### *Reaction of $\text{NO}_3$ with alkenes*

Rate constants for the gas-phase reactions of  $\text{NO}_3$  with a variety of alkenes, dialkenes, cycloalkenes and terpenes have been measured using both relative (Becker, Ljungström) and absolute rate techniques (Nielsen, Le Bras/Poulet, Ljungström, Schindler, Wayne), (Table 2). The various data sets are, in general, in good agreement and help to identify patterns of reactivity that may have diagnostic and predictive value. Wayne has carried out work on correlations of rate constants with ionisation potentials for reactions of  $\text{NO}_3$  with alkenes. The correlations provide accurate predictions of room temperature rate coefficients and Arrhenius parameters for the reaction of  $\text{NO}_3$  with a wide range of alkenes, which may be used to estimate unknown rate constants or indicate experimental inconsistencies. The increase in rate constant with increasing degree of alkyl substitution at the double bond strongly suggests attack by the electrophilic  $\text{NO}_3$  radical at the double bond site. Arrhenius parameters, obtained from rate coefficient measurements as a function of temperature, are consistent with this view. Rate constants for reaction of  $\text{NO}_3$  with cyclic alkenes are slightly higher than those for structurally similar acyclic alkenes. This may reflect the loss of strain energy on formation of the radical adducts.

A number of product studies on the reactions of  $\text{NO}_3$  with alkenes have been carried out using mainly FTIR spectroscopy (Becker, Hjorth, Le Bras/Poulet, Ljungström, Schindler). The product and intermediate distributions for all the alkenes investigated followed a similar pattern and can be represented in terms of the following simplified mechanism:



Under atmospheric conditions, the nitro-oxyalkyl peroxy radicals will probably form mainly the corresponding nitro-oxy alkoxy radicals. Thermal decomposition, yielding carbonyl compounds and  $\text{NO}_2$ , and reaction with  $\text{O}_2$  giving carbonyl nitrates, appear to be the dominant reactions under most atmospheric conditions. The extent to which carbonyl nitrates can act as temporary reservoirs for  $\text{NO}_x$  will largely depend on their photolysis rates or reactions with OH radicals.

Product studies on the reaction of  $\text{NO}_3$  with isoprene showed that the addition occurs mainly at the 1-position and that 3-methyl-4-nitroxy-2-butenal is the main reaction product (Hjorth). Results from an FTIR spectroscopy study on product formation in the reaction of  $\text{NO}_3$  radicals with cyclic alkenes provided evidence that dicarbonyls are important products arising from ring opening processes (Ljungström).

Evidence for epoxide formation from  $\text{NO}_3$  reactions with alkenes has been reported (Hjorth, Schindler). These results show that oxirane formation occurs via a radical adduct, in which rotation about the C-C bond can occur before elimination of  $\text{NO}_2$ . Reactions of  $\text{NO}_3$  with isoprene and 2-butene at low pressure and at low  $\text{O}_2$  concentrations gave mainly oxiranes, whereas in air at atmospheric pressure, oxirane yields were negligible. However, even at atmospheric pressures, the reaction of  $\text{NO}_3$  with 2,3-dimethyl-2-butene gave an oxirane yield of around 20 %. Thus, it is apparent that, at least with some alkenes, oxirane formation may be important under tropospheric conditions.

Combination of the available rate constant data with estimates of the atmospheric concentrations of  $\text{O}_3$ ,  $\text{NO}_3$  and OH indicates that the reaction of  $\text{NO}_3$  with substituted alkenes and terpenes may be the dominant tropospheric oxidation process for these species. Formation of carbonyl nitrates in the reactions could be important in the long-range transport of odd nitrogen.

### ***Reactions of $\text{NO}_3$ with aromatic compounds***

Carrier has determined rate constants for the reactions of  $\text{NO}_3$  with a series of aromatic compounds using a relative rate method (Table 2). Agreement with literature values is reasonable. The gas-phase reactions of  $\text{NO}_3$  radicals with benzene, toluene and xylene isomers have been studied in  $\text{N}_2\text{O}_5/\text{NO}_2/\text{aromatic}/\text{air}$  mixtures at room temperature and atmospheric pressure (Hjorth). Products were identified by *in situ* FTIR spectroscopy, and after sampling, on charcoal column or a XAD-2 trap by gas chromatography coupled to mass spectrometry.

Benzene was found to be virtually unreactive, with only trace yields of nitrobenzene detected. Reaction with toluene and xylenes gave benzaldehydes and benzyl nitrates as major products, which indicate that the reaction with  $\text{NO}_3$  proceeds mainly by hydrogen abstraction from a methyl group. Minor yields of aromatic nitroderivatives were observed in the reactions suggesting that the nitrate radical may also react by addition to the aromatic ring system.

### 2.2.3 Reaction of $\text{NO}_3$ with peroxy radicals

Reactions of  $\text{NO}_3$  with  $\text{HO}_2$  and simple  $\text{RO}_2$  radicals ( $\text{CH}_3\text{O}_2$ ,  $\text{C}_2\text{H}_5\text{O}_2$  and  $\text{CH}_3\text{C}(\text{O})\text{O}_2$ ) have been investigated within LACTOZ (Table 3), as possible chain propagation steps in the mechanism suggested for the night-time oxidation of VOCs (see above).

**Table 3:** Rate constants for the reactions of  $\text{NO}_3$  with  $\text{HO}_2$  and  $\text{RO}_2$  radicals at 298 K.

$\text{RO}_2$	Method	$k$ ( $\text{cm}^3 \text{s}^{-1}$ )	Reference <sup>a</sup>	
$\text{HO}_2$		$\text{NO}_3 + \text{HO}_2 \rightleftharpoons \text{NO}_2 + \text{OH} + \text{O}_2, k_1$		
		$\text{NO}_3 + \text{HO}_2 \rightleftharpoons \text{HNO}_3 + \text{O}_2, k_2$		
	DF-EPR	$3.6 \times 10^{-12}/k_1$ $0.9 \times 10^{-12}/k_2$	Le Bras (88)	
	MP	$3.5 \times 10^{-12}/k_1 + k_2$	Wayne (88)	
	FP-LA	$4.7 \times 10^{-12}/k_1 + k_2$	Zellner (88)	
	DF-MS/RF	$2.5 \times 10^{-12}/k_1$ $1.9 \times 10^{-12}/k_2$	Schindler (91)	
	EC-FTIR/TDL	$< 8.0 \times 10^{-13}/k_1^b$	Hjorth (92)	
$\text{CH}_3\text{O}_2$		$\text{NO}_3 + \text{RO}_2 \rightleftharpoons \text{NO}_2 + \text{RO} + \text{O}_2$		
	MP	$2.3 \times 10^{-12}$	Burrows, Moortgat, Le Bras (89)	
	DF-LIF	$1.3 \times 10^{-12}$	Le Bras (93)	
	DF-LIF	$1.0 \times 10^{-12}$	Wayne (93)	
	$\text{CD}_3\text{O}_2$	DF-MS	$1.4 \times 10^{-12}$	Moortgat (93)
	$\text{C}_2\text{H}_5\text{O}_2$	DF-LIF	$2.5 \times 10^{-12}$	Wayne (94)
		DF-LIF	$2.2 \times 10^{-12}$	Le Bras (94)
$\text{CH}_3\text{C}(\text{O})\text{O}_2$	SFR-FTIR	$\sim 2 \times 10^{-11}$	Wayne (94)	

<sup>a</sup> These references are to EUROTRAC Annual Reports. The year in parentheses is the year of the report not the publishing year.

<sup>b</sup> This value has not been confirmed so far.

DF-EPR: discharge flow - electron paramagnetic resonance

MP: modulated photolysis

FP-LA: flash photolysis - laser absorption

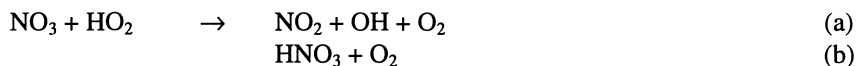
DF-MS/RF: discharge flow-mass spectrometry / resonance fluorescence

EC-FTIR/TDL: environmental chamber - Fourier transform IR spectroscopy/tuneable diode laser spectroscopy

DF-LIF: discharge flow-laser induced fluorescence

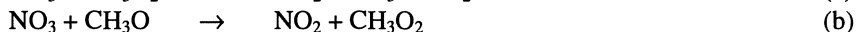
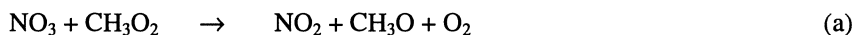
SFR- FTIR: slow flow reactor - Fourier transform IR spectroscopy

Several studies of the  $\text{NO}_3 + \text{HO}_2$  reaction have been carried out (Le Bras/Poulet, Wayne and Cox, Zellner, Schindler, Hjorth) using four different techniques. The discharge flow-EPR method has been used to determine rate constant data at room temperature for the two possible reaction channels (Le Bras/Poulet):



Good agreement with the value of the overall rate constant was obtained in the other studies (Wayne and Cox, Zellner, Schindler). The predominance of channel (a) was confirmed by Schindler and is in agreement with other reported work [4]. In contrast, channel (a) was found insignificant in an indirect study of the dark reaction of  $\text{HO}_2\text{NO}_2/\text{N}_2\text{O}_5/^{13}\text{C}^{18}\text{O}/\text{air}$  mixtures at room temperature and atmospheric pressure (Hjorth). However, this result has not been confirmed so far.

The  $\text{NO}_3 + \text{CH}_3\text{O}_2$  reaction has been investigated at 298 K in discharge-flow reactors, with LIF analysis of  $\text{CH}_3\text{O}$  in the reaction system:



The two studies performed (Le Bras/Poulet, Wayne) yielded  $k_a$  and  $k_b$  values which were in agreement. The rate constant obtained for the  $\text{NO}_3 + \text{CD}_3\text{O}_2$  reaction in a discharge-flow mass-spectrometric study (Moortgat) agrees with these  $k_a$  values.

Similar discharge-flow LIF studies were recently performed for the  $\text{NO}_3 + \text{C}_2\text{H}_5\text{O}_2$  reaction which was also found to convert  $\text{RO}_2$  ( $\text{C}_2\text{H}_5\text{O}_2$ ) into  $\text{RO}$  ( $\text{C}_2\text{H}_5\text{O}$ ) (Wayne, Le Bras/Poulet). The rate constant values obtained in both studies were in agreement.

The rate constant of the reaction of  $\text{NO}_3$  with another peroxy radical, the peroxyacetyl radical ( $\text{CH}_3\text{C}(\text{O})\text{O}_2$ ) was also measured in a slow discharge flow reactor at 300–423 K (Wayne), using thermal decomposition of PAN as a source of the organic radicals.

The results obtained for reactions of  $\text{NO}_3$  with  $\text{RO}_2$  ( $\text{R} = \text{H}, \text{CH}_3$  and  $\text{C}_2\text{H}_5$ ) show that rate constants at 298 K are comparable ( $1 - 3.6 \times 10^{-12} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$  at 298 K), and they all proceed through  $\text{RO}_2/\text{RO}$  conversion. These reactions can consequently be rather fast and make important the proposed chain mechanism of VOC oxidation during nighttime in moderately polluted atmosphere. In addition, if the high rate constant found for the  $\text{NO}_3 + \text{CH}_3\text{C}(\text{O})\text{O}_2$  reaction was confirmed ( $k \approx 2 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$  at 298 K); this reaction could affect PAN concentrations [5].



### 2.2.4 Reactions of NO<sub>3</sub> with inorganic molecules

The equilibrium constant for  $\text{NO}_2 + \text{NO}_3 + \text{M} \leftrightarrow \text{N}_2\text{O}_5 + \text{M}$  has been measured at room temperature by direct monitoring of the species by optical absorption in  $\text{O}_3/\text{N}_2\text{O}_5/\text{NO}_2/\text{NO}_3/\text{air}$  mixtures (Table 4, Hjorth). This is an important parameter in the calculation of the NO<sub>y</sub> atmospheric partitioning.

The rate constant for the thermal decomposition of NO<sub>3</sub> ( $\text{NO}_3 + \text{M} \rightarrow \text{NO} + \text{O}_2 + \text{M}$ ) has been derived from a computer simulation of the same experiments (Hjorth). The deduced lifetime of NO<sub>3</sub> would be of 10 min at 295 K and 1 atmosphere pressure.

Several other reactions of NO<sub>3</sub> with inorganic molecules have been investigated and found to be negligible or too slow to be of atmospheric significance. These include reactions of NO<sub>3</sub> with itself and ozone (Wayne) with HCl, HBr and HI (Le Bras/Poulet, Wayne), the reaction of NO<sub>3</sub> with NO<sub>2</sub> as a source of NO (Ljungström) and the reaction of electronically excited NO<sub>3</sub> with N<sub>2</sub> as a source of N<sub>2</sub>O (Burrows, Zellner).

**Table 4:** Rate constants for the reactions of NO<sub>3</sub> radicals with inorganic species.

reaction	$k$ (cm <sup>3</sup> s <sup>-1</sup> )	$T$ (K)	Method	Reference *
$\text{NO}_3 + \text{NO}_2 + \text{M} \leftrightarrow \text{N}_2\text{O}_5 + \text{M}$ (1)/(-1)	$K_e = k_1/k_{-1} = (3.73 \pm 0.41) \times 10^{-11}$ (cm <sup>3</sup> molecule <sup>-1</sup> )	298	EC	Hjorth (90)
$\text{NO}_3 + \text{M} \rightarrow \text{NO} + \text{O}_2 + \text{M}$	$(1.6 \pm 0.7) \times 10^{-3}$ (s <sup>-1</sup> ) (1013 mbar in air)	295	EC	Hjorth (90)
$\text{NO}_3 + \text{NO}_3 \rightarrow \text{NO}_2 + \text{NO}_2 + \text{O}_2$	$2.7 \times 10^{-16}$	298	LP-LA DSF-LA	Wayne (89)
$\text{NO}_3 + \text{NO}_2 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2$	$(5.2 \pm 1.5) \times 10^{-14} \exp [(-1477 \pm 260)/T]$ $3.7 \times 10^{-16}$	296–332 298	EC-FTIR/TDL	Ljungström (91)
$\text{NO}_3 + \text{O}_3 \rightarrow \text{NO}_2 + 2 \text{O}_2$	$\leq 1 \times 10^{-19}$	298	DSF-LA	Wayne (93)

\* These references are to EUROTRAC Annual Reports. The year in parentheses is the year of the report not the publishing year.

EC: environmental chamber

LP-LA: laser photolysis-laser absorption

DSF-LA: discharge stopped flow-laser absorption

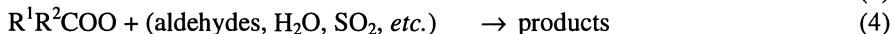
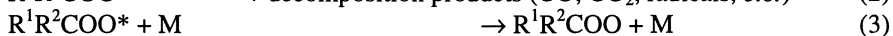
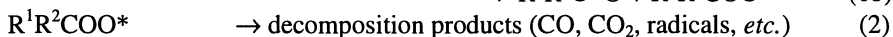
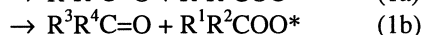
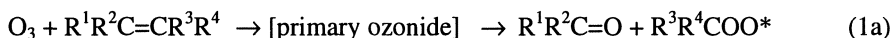
DF-EPR: discharge flow-electron paramagnetic resonance

EC-FTIR/TDL: environmental chamber - Fourier transform IR spectroscopy/tunable diode laser spectroscopy

## 2.3 Reactions of O<sub>3</sub> with alkenes

### 2.3.1 Introduction

Ozone-alkene reactions are important sinks for both ozone and alkenes, and provide important sources of OH and other radicals, carbonyl compounds, hydrogen peroxide, organic hydroperoxides and acids in the troposphere. Atmospheric photo-oxidation chemistry cannot be adequately described without considering the ozonolysis of alkenes, in particular biogenic compounds, such as isoprene (see also Section 4.8 and Fig. 13) and terpenes. In the presence of NO<sub>x</sub>, the ozonolysis of biogenic hydrocarbons eventually can lead to ozone generation rather than its loss. The Criegee reaction mechanism, presently accepted for the ozonolysis of alkenes is shown in Fig 4, the key steps being reactions (1a) and (1b) – the two decomposition channels of the primary ozonide, (2) – the decomposition of the excited biradical (several pathways possible), (3) – its collisional deactivation and (4) – reactions of the stabilised biradical:



The value of the rate constants for the reactions of O<sub>3</sub> with alkenes ( $k_1$ ) at room temperature are fairly well documented. However, corrections for OH reactions have to be made, resulting in lower rate constants compared to the currently accepted values. The temperature dependence of the rate constants is known only for a limited number of alkenes and corrections for OH reactions are also required in this case.

The knowledge of the chemistry of the Criegee biradicals R<sup>1</sup>R<sup>2</sup>COO is very poor: the branching ratios  $k_{1a}/k_{1b}$ , the rate constants  $k_4$ , and the product distributions of reactions (2) and (4) are largely uncertain.

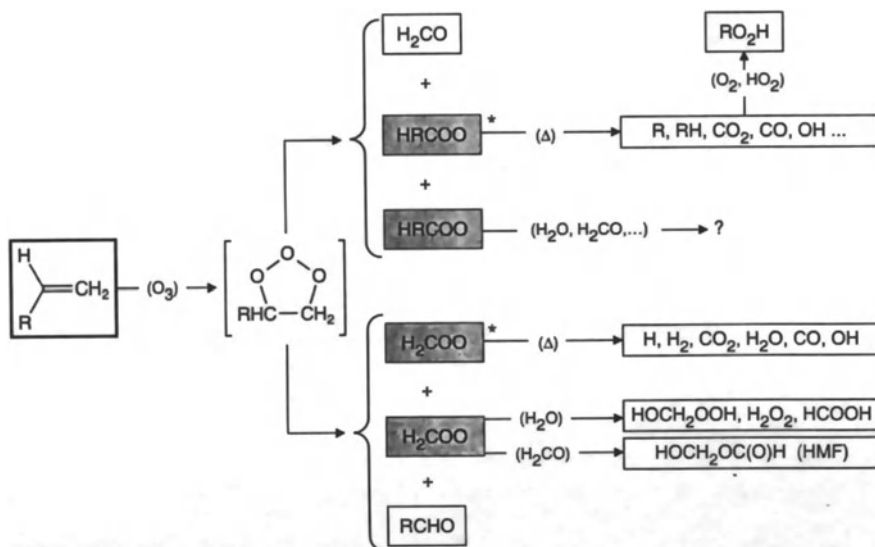


Fig. 4: Reaction scheme for the gas-phase ozonolysis of a simple alkene.

### 2.3.2 Results

Research within LACTOZ has addressed some of the open questions with respect to reaction rate constants, product formation and the general reaction mechanism. Overall reaction rate constants,  $k_f$ , have been measured as a function of temperature for a number of cyclic alkenes (Sidebottom), (Table 5a). The observed variation of Arrhenius parameters with the number of carbon atoms in the ring suggests that the ozonolysis rate is strongly influenced by the release of the ring strain, which is connected to the change of the C=C double bond in the cyclic alkene into the single bond in the intermediate trioxolane. In agreement with this view,  $k_f$  is larger for cyclopentene and cycloheptene. Careful studies in remeasuring the rate constant for the fundamental reaction of O<sub>3</sub> with ethene have been carried out (Becker). The value obtained is about 30 % smaller than the previously recommended value [6], (Table 5b). In addition, rate constants were measured at room temperature for the O<sub>3</sub> reaction with unsaturated alcohols and 2-propenyl-oxirane, both being products of the oxidation of isoprene (Becker).

**Table 5a:** Rate constants for O<sub>3</sub> reactions at different temperatures and atmospheric pressure in air.

Compound	A (cm <sup>3</sup> s <sup>-1</sup> )	E <sub>a</sub> /R (K)	k (cm <sup>3</sup> s <sup>-1</sup> )	Reference *
<i>cis</i> -2-butene	3.1 × 10 <sup>-15</sup>	939	1.3 × 10 <sup>-16</sup>	Sidebottom (93)
2-methyl-2-butene	5.2 × 10 <sup>-15</sup>	734	4.5 × 10 <sup>-16</sup>	Sidebottom (93)
cyclopentene	1.6 × 10 <sup>-15</sup>	348	4.9 × 10 <sup>-16</sup>	Sidebottom (93)
1-methyl-1-cyclopentene	-	-	6.7 × 10 <sup>-16</sup>	Sidebottom (93)
1-chloro-1-cyclopentene	4.4 × 10 <sup>-16</sup>	1008	1.5 × 10 <sup>-17</sup>	Sidebottom (93)
cyclohexene	2.6 × 10 <sup>-15</sup>	1062	8.5 × 10 <sup>-17</sup>	Sidebottom (93)
1-methyl-1-cyclohexene	5.3 × 10 <sup>-15</sup>	1039	1.7 × 10 <sup>-16</sup>	Sidebottom (93)
4-methyl-1-cyclohexene	2.2 × 10 <sup>-15</sup>	951	8.2 × 10 <sup>-17</sup>	Sidebottom (93)
1-nitro-1-cyclohexene	-	-	1.2 × 10 <sup>-18</sup>	Sidebottom (93)
cycloheptene	1.3 × 10 <sup>-15</sup>	493	2.4 × 10 <sup>-16</sup>	Sidebottom (93)
<i>cis</i> -cyclooctene	7.8 × 10 <sup>-16</sup>	217	3.7 × 10 <sup>-16</sup>	Sidebottom (93)
<i>cis</i> -cyclododecene	1.1 × 10 <sup>-15</sup>	1080	2.9 × 10 <sup>-17</sup>	Sidebottom (93)

\* These references are to EUROTRAC Annual Reports. The year in parentheses is the year of the report not the publishing year.

k-values: at 298 K

**Table 5b:** Rate constants for O<sub>3</sub> reactions at 295 K and atmospheric pressure in air.

Compound	k (cm <sup>3</sup> s <sup>-1</sup> )	Reference <sup>a</sup>
2-methyl-3-butene-1,2-diol	4.8 × 10 <sup>-18</sup>	Becker (94)
3-methyl-3-butene-1,2-diol	6.3 × 10 <sup>-17</sup>	Becker (94)
2-propenyl-oxirane	3.3 × 10 <sup>-18</sup>	Becker (94)
ethene <sup>b</sup> (298 K)	1.2 × 10 <sup>-18</sup>	Becker (94)

<sup>a</sup> These references are to EUROTRAC Annual Reports. The year in parentheses is the year of the report not the publishing year.

<sup>b</sup> corrected for OH radical reactions.

Two groups (Becker, Sander) have presented some evidence for the need to complete the generally accepted Criegee mechanism (1)-(4) by additional reaction pathways:

- The absence of methylacetate as a product in the ozonolysis of 2-methylpropene is interpreted in terms of a "non-Criegee" mechanism (Sander);
- The observed pressure independence of the product distribution in the ozone-ethene reaction between 100 and 1030 mbar indicates that the branching ratio  $k_3/k_4$  may not be pressure dependent, in this pressure region. The pressure independence of the H<sub>2</sub> yield has been shown, even down to 1 mbar (Becker). These findings are not in agreement with reaction step (3) by which excited Criegee intermediates are stabilised.

The yield of OH radicals in the ozonolysis of a number of cycloalkenes has been determined by scavenging OH with cyclohexane (Sidebottom). The derived OH yield of about 40 % was found to be similar to that of *cis*-2-butene, providing support for the suggestion that OH yields from ozone-alkene reactions depend

largely on the degree of alkyl groups substitution at the double bond site (Table 6a). From the number of alkene molecules by one O<sub>3</sub> molecule, the following OH yields were determined (Moortgat): ethene (5 %), *cis*-2-butene (40 %), *trans*-2-butene (60 %), isobutene (60 %) and isoprene (10–15 %).

**Table 6a:** OH radical yields of O<sub>3</sub> reactions at 298 K and atmospheric pressure in air.

Compound	OH yield (%)	Reference *
ethene	< 10 (a)	Sidebottom (94)
	< 5 (b)	
	5 (a)	
<i>cis</i> -2-butene	40 (a)	Moortgat (94)
<i>trans</i> -2-butene	60 (a)	Moortgat (94)
isobutene	60 (a)	Moortgat (94)
isoprene	24 (b)	Schindler (93)
	10–15 (a)	Moortgat (94)
cyclopentene	46 (a)	Sidebottom (94)
	62 (b)	
cyclohexene	39 (a)	Sidebottom (94)
	38 (b)	
cycloheptene	44 (a)	Sidebottom (94)
	46 (b)	
<i>cis</i> -cyclooctene	39 (a)	Sidebottom (94)
	35 (b)	
<i>cis</i> -cyclodecene	40 (a)	Sidebottom (94)
	35 (b)	

\* These references are to EUROTRAC Annual Reports. The year in parentheses is the year of the report not the publishing year.

(a): based on reactions stoichiometry

(b): based on product analysis

Special emphasis has been laid on the formation of H<sub>2</sub>O<sub>2</sub>, hydroperoxides and hydroxy-hydroperoxides. Systematic studies of their yields for a number of alkenes have been made with and without the addition of water vapour (Becker, Gäb, Moortgat). In the case of ethene, the formation of 2-hydroxyethyl hydroperoxide clearly can be related to the reaction OH + ethene. It was also possible to compare the product yields of hydroperoxides from the alkene + O<sub>3</sub> reactions in the gas phase with that in the aqueous phase (Gäb), (Table 6b). The product distribution is different and, in general, the yields of  $\alpha$ -hydroxy-hydroperoxides in the aqueous phase are 10 times higher than in the gas phase. In the presence of formaldehyde, the simplest Criegee intermediate, CH<sub>2</sub>OO, forms hydroxymethyl formate (Becker, Moortgat), which eventually decomposes into formic acid.

**Table 6b:** Hydroperoxide formation yields (%) of O<sub>3</sub> reactions with alkenes (mol % of reacted alkene).

Hydroperoxide	Ethene	Propene	Isoprene	$\alpha$ -Pinene	$\beta$ -Pinene
H <sub>2</sub> O <sub>2</sub>	0.4 (a) - (b)	0.3 (a) - (b)	0.7 (a) < 0.1 (b)	0.3 (a) < 0.1 (b)	0.6 (a) < 0.1 (b)
CH <sub>3</sub> O <sub>2</sub> H	- (a) - (b)	4.1 (a) - (b)	5.0 (a) - (b)	0.8 (a) - (b)	- (a) - (b)
HOCH <sub>2</sub> O <sub>2</sub> H	0.2 (a) 27.9 (b)	0.2 (a) 2.7 (b)	0.5 (a) 11.1 (b)	0.1 (a) - (b)	0.3 (a) 0.2 (b)
CH <sub>3</sub> CH(OH)O <sub>2</sub> H	- (a) - (b)	- (a) 11.1 (b)	- (a) - (b)	- (a) - (b)	- (a) - (b)
HOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> O <sub>2</sub> H	< 0.1 (a) - (b)	- (a) - (b)	- (a) - (b)	- (a) - (b)	- (a) - (b)
total	0.6 (a) 27.9 (b)	4.6 (a) 13.8 (b)	6.2 (a) 24.2 (b)	1.2 (a) 11.3 (b)	0.9 (a) 16.2 (b)

(a): no addition of H<sub>2</sub>O, (b): aqueous-phase, "-": not detected  
Gäb EUROTRAC Annual Report 1994.

**Table 7:** Product yields in the gas-phase ozonolysis of isoprene (units are mol-%: mole of product formed per mole of isoprene reacted).

Products	Becker (94) <sup>a</sup>			Moortgat (92)
	(900 mbar air)	(+ H <sub>2</sub> O) <sup>b</sup>	(+ C <sub>6</sub> H <sub>12</sub> ) <sup>c</sup>	
methacrolein	24 ± 2	28 ± 2	28 ± 2	22 ± 3
methyl vinyl ketone	11 ± 1	15 ± 2	12 ± 2	11 ± 2
formaldehyde	53 ± 3	62 ± 5	62 ± 7	56 ± 6
remaining carbonyl compounds	47 ± 15			
CO	24 ± 2	25 ± 2	30 ± 4	21 ± 2
CO <sub>2</sub>	18 ± 4	21 ± 9	~ 24	16 ± 3
formic acid	~ 3 <sup>c</sup>	1 – 25 <sup>c</sup>	1 – 25 <sup>c</sup>	3.5
ketene	~ 1	~ 1	~ 1	1.4
propene	2.3 ± 1.0	3 ± 1		< 9
H <sub>2</sub>	2.0 ± 0.2	~ 2	~ 2	
epoxides	< 4	< 4		
CH <sub>3</sub> OH	1.1 ± 0.3			
CH <sub>3</sub> OOH	5		5	
HOCH <sub>2</sub> OOH	0.5		0.6	
H <sub>2</sub> O <sub>2</sub>	~ 1		0.9	
OH	Schindler (93) <sup>a</sup> :	24 <sup>d</sup>	Moortgat (94) <sup>a</sup> :	10 – 15

<sup>a</sup> These references are to EUROTRAC Annual Reports. The year in parentheses is the year of the report not the publishing year. <sup>b</sup> H<sub>2</sub>O-vapour, 2–13 mbar; <sup>c</sup> Addition of 400–1000 ppm C<sub>6</sub>H<sub>12</sub>;

<sup>d</sup> Dependent on reaction time; <sup>e</sup> Measured with CO as scavenger.

A considerable amount of work has been devoted to product studies of the  $O_3$  reaction with isoprene (Becker, Moortgat), (Table 7). Ozonolysis of alkenes, in particular biogenic compounds, presents a significant source of OH radicals,  $H_2O_2$  and a number of organic hydroperoxides. It is necessary to study the product yields also in the presence of  $NO_x$  to elucidate the potential for ozone formation. Complementary field studies on the contribution of OH production from ozone reactions and the formation of the different hydroperoxides are suggested. The gas-to-particle conversion during the ozonolysis of alkenes, especially biogenic compounds, should also be studied (blue haze problem).

## 2.4 Reactions of peroxy radicals

### 2.4.1 Introduction

Organic peroxy radicals,  $RO_2$ , are the first intermediate species formed during the oxidation of organic compounds in the atmosphere. In spite of their low reactivity, their reactions are important in determining the overall oxidation mechanism of organic compounds and the tropospheric ozone balance. They react principally with the nitrogen oxides NO and  $NO_2$ , and with other peroxy radicals, *e.g.*  $R'O_2$  and  $HO_2$ . A great deal of work has been devoted in LACTOZ to studies of these reaction types, which has resulted in the collection of much new data and led to a much better understanding of the reactivity of peroxy radicals. A comprehensive review of  $RO_2$  chemistry "Organic Peroxy Radicals: Kinetics, Spectroscopy and Tropospheric Chemistry", prepared by members of the LACTOZ group, has been published in Atmospheric Environment [1].

In polluted areas, reactions of  $RO_2$  radicals with nitrogen oxides are of major importance. The reaction of  $RO_2$  with NO results in the production of  $NO_2$  and hence formation of ozone in the troposphere, and the reaction with  $NO_2$  forms temporary reservoir peroxyoxynitrate species. Much attention has been given in LACTOZ to the kinetics of these reactions, which has contributed to substantial improvement of the kinetic data base.

In remote atmospheres, where  $NO_x$  concentrations are very low, reactions of peroxy radicals with  $HO_2$ , or with other peroxy radicals, compete with the reaction with  $NO_x$  and result in the formation of various oxidised compounds such as aldehydes, alcohols, organic acids and hydroperoxides. Several studies performed as part of LACTOZ have provided important data for modelling these processes in the atmosphere.

Investigations performed within LACTOZ have mainly focused on the determination of structure-reactivity relationships for  $RO_2 + NO_x$ ,  $RO_2 + HO_2$ ,  $RO_2 + RO_2$  and  $RO_2 + R'O_2$  reactions. Reliable structure-reactivity relationships

have been established for the  $\text{RO}_2 + \text{NO}$  reaction so that rate constants can be reliably estimated for any  $\text{RO}_2$  reaction with  $\text{NO}$ . Significant progress has been made on the  $\text{RO}_2 + \text{HO}_2$  reactions, and it is now clear that the rate constants increase markedly with the size of the peroxy radical but are practically insensitive to halogen substitution. The situation is not as clear for  $\text{RO}_2 + \text{RO}_2$  self-reactions, despite the large number of results reported. An important result has emerged from the data, showing that the presence of various functional groups in the  $\text{RO}_2$  radical gives rise to a significant increase in the rate constant of the self-reaction compared to the behaviour of similar unsubstituted alkylperoxy radicals. Thus, fairly good values of the rate constant can now be estimated according to the structure of  $\text{R}$  in a given peroxy radical. Cross-reactions of the type  $\text{RO}_2 + \text{R}'\text{O}_2$  can play a significant role in the chemistry of hydrocarbon-rich atmospheres and new data have been obtained recently. They show, in particular, that reactions of the acetylperoxy radical are all probably quite fast and that these should be taken into account in tropospheric models and in mechanism reduction procedures.

In addition to kinetic and mechanistic studies, information on UV spectra has been obtained for all the peroxy radicals investigated.

Most of the work on peroxy radicals has been carried out by three of the LACTOZ groups (Cox/Hayman/Jenkin, Lesclaux and Moortgat).

#### 2.4.2 $\text{RO}_2 + \text{HO}_2$ reactions

$\text{RO}_2 + \text{HO}_2$  reactions are generally fast and, owing to the fairly high concentration of  $\text{HO}_2$  in the atmosphere, they play an important role under low concentrations of  $\text{NO}_x$ . Investigations of such reactions have represented a significant part of the LACTOZ project. The reactions that have been studied and the corresponding results are given in Table 8. Structure-reactivity relationships are fairly easy to establish for this particular class of reactions, as all rate constant values are within a factor of about three. There is no clear systematic effect of functional groups on the rate constants except for halogen substitution, which seems to lead to lower values for the rate constants. Apparently, the main factor influencing the rate constant is the size of the radical. The lowest rate constants are those of  $\text{CH}_3\text{O}_2$  and of the corresponding halogen-substituted radicals, around  $6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The rate constant increases rapidly with size to over  $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for larger radicals and reaches values of  $1.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for *c*- $\text{C}_5\text{H}_9\text{O}_2$  and *c*- $\text{C}_6\text{H}_{11}\text{O}_2$ . The data suggest the following rate constants (units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ):  $6 \times 10^{-12}$  for  $\text{CH}_3\text{O}_2$  and halogenated peroxy radicals,  $1.0 \times 10^{-11}$  for  $\text{C}_2$ – $\text{C}_3$  radicals and  $1.5 \times 10^{-11}$  for larger radicals ( $\text{C}_4$  and over) and acylperoxy radicals. All reactions exhibit a strong negative temperature dependence. Exponential factors vary from  $800\text{K}/T$  to  $1600\text{K}/T$ , most of them being in the range  $1000$ – $1200\text{K}/T$ .



**Table 8:** Rate constants and branching ratios for the reactions:  $\text{RO}_2 + \text{HO}_2$ ,  $\text{RO}_2 + \text{RO}_2$  and  $\text{RO}_2 + \text{R}'\text{O}_2$ .

Rate Coefficient <sup>a</sup> $k$ (298 K) ( $\text{cm}^3 \text{s}^{-1}$ )	Branching Ratio <sup>b</sup> $k_a$ (298 K)/ $k$ (298 K)	Reference <sup>c</sup>
<b>RO<sub>2</sub> + HO<sub>2</sub> Reactions</b>		
<b>HO<sub>2</sub> + HO<sub>2</sub></b>		
$(2.4 \pm 0.2) \times 10^{-12}$ (1013 mbar O <sub>2</sub> )		Cox (88)
$(2.8 \pm 0.3) \times 10^{-12}$ (1013 mbar air)		Cox (88)
$(3.8 \pm 0.4) \times 10^{-13} \exp[(580 \pm 32)/T]$		(1)
$(1.2 \pm 0.4) \times 10^{-33} [\text{M}] \exp [(1150 \pm 97)/T]$ (248–573 K; 133–1013 mbar air)		
$4.1 \times 10^{-12}$ (1013 mbar air)		
<b>CH<sub>3</sub>O<sub>2</sub> + HO<sub>2</sub></b>		
$(5.4 \pm 1.1) \times 10^{-12}$ (303 K; 13.3 mbar)		(2)
$(6.8 \pm 0.9) \times 10^{-12}$ (303 K; 1013 mbar)		(2)
$(4.8 \pm 0.2) \times 10^{-12}$ (933 mbar)		(3)
$(5.2 \pm 1.5) \times 10^{-12}$		Zellner (89)
$(4.4 \pm 0.7) \times 10^{-13} \exp [(780 \pm 55)/T]$ (248–573 K; 280–1013 mbar)		(1)
$6.0 \times 10^{-12}$		
<b>HOCH<sub>2</sub>O<sub>2</sub> + HO<sub>2</sub></b>		
$5.6 \times 10^{-15} \exp [(2300 \pm 1100)/T]$ (275–333 K)		Veyret (88)
$1.3 \times 10^{-11}$		
$(1.2 \pm 0.3) \times 10^{-11}$		(4)
<b>C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> + HO<sub>2</sub></b>		
$(1.6 \pm 0.2) \times 10^{-13} \exp [(1200 \pm 40)/T]$		Lesclaux
$1.1 \times 10^{-11}$		
<b>HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> + HO<sub>2</sub></b>		
$(4.8 \pm 0.5) \times 10^{-12}$ (13.3 mbar)		Cox (89)
$(1.5 \pm 0.3) \times 10^{-11}$ (1013 mbar)		Hayman (94)



Table 8: continued

Rate Coefficient <sup>a</sup> $k$ (298 K) (cm <sup>3</sup> s <sup>-1</sup> )	Branching Ratio <sup>b</sup> $k_a$ (298 K)/ $k$ (298 K)	Reference <sup>c</sup>
<b>C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O<sub>2</sub> + HO<sub>2</sub></b> (3.75±0.32) × 10 <sup>-13</sup> exp[(980±230)/T] (1.0±0.2) × 10 <sup>-11</sup>		Lesclaux (93)
<b>CCl<sub>3</sub>O<sub>2</sub> + HO<sub>2</sub></b> (4.81±0.46) × 10 <sup>-13</sup> exp[(706±31)/T] 5.1 × 10 <sup>-12</sup>		Lesclaux (94)
<b>CHCl<sub>2</sub>O<sub>2</sub> + HO<sub>2</sub></b> (5.6±1.2) × 10 <sup>-13</sup> exp[(700±64)/T] 5.9 × 10 <sup>-12</sup>		Lesclaux (94)
<b>CH<sub>2</sub>ClO<sub>2</sub> + HO<sub>2</sub></b> (3.31±0.61) × 10 <sup>-13</sup> exp[(830±60)/T] (5.4±0.6) × 10 <sup>-12</sup>		Lesclaux (93)
<b>CH<sub>2</sub>BrO<sub>2</sub> + HO<sub>2</sub></b> (6.7±3.8) × 10 <sup>-12</sup>		Lesclaux (94)
<b>RO<sub>2</sub> + RO<sub>2</sub> Reactions</b>		
<b>CH<sub>3</sub>O<sub>2</sub> + CH<sub>3</sub>O<sub>2</sub> → 2 CH<sub>3</sub>O + O<sub>2</sub></b> <b>↳ CH<sub>3</sub>OH + HCHO + O<sub>2</sub></b> (4.79±0.54) × 10 <sup>-13</sup> [x] (1.27±0.14) × 10 <sup>-13</sup> exp [(365±40)/T] (248–573 K) 4.4 × 10 <sup>-13</sup>		Moortgat (88) Veyret (88)
2.13×10 <sup>-13</sup> exp[(220±70)/T](268–353 K; 1013 mbar) [x] 3.28×10 <sup>-13</sup> exp[(92±40)/T] (268–353 K; 13.3 mbar) [x] 4.5 × 10 <sup>-13</sup> (13.3 and 1013 mbar) [x]	0.24	Cox (89) Cox (89)
	(y+exp(1131±30/T))/(19±5)) <sup>-1</sup> (6) (223–333 K) 0.30	
(4.8±0.5) × 10 <sup>-13</sup> (300 K; 320 mbar)		(7)
	0.25±0.04 (1013 mbar)	Becker (90)

Table 8: continued

Rate Coefficient <sup>a</sup> $k$ (298 K) ( $\text{cm}^3 \text{s}^{-1}$ )	Branching Ratio <sup>b</sup> $k_a$ (298 K)/ $k$ (298 K)	Reference <sup>c</sup>
<b>HOCH<sub>2</sub>O<sub>2</sub> + HOCH<sub>2</sub>O<sub>2</sub> <math>\xrightarrow{a}</math> 2 HOCH<sub>2</sub>O + O<sub>2</sub></b> <b><math>\xrightarrow{b}</math> CH<sub>2</sub>(OH)<sub>2</sub> + HC(O)OH + O<sub>2</sub></b>		
$(5.9 \pm 1.1) \times 10^{-12}$	0.89	Veyret (88)
<b>C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> + C<sub>2</sub>H<sub>5</sub>O<sub>2</sub></b>		
$2.49 \times 10^{-13} \exp[-518/T] + 9.39 \times 10^{-16} \exp(960/T)$ (220–330K, 1013 mbar)	0.54±0.03	Becker (90)
$6.7 \times 10^{-14}$	0.65	Moortgat (91)
<b>CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> + CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub></b>		
$(2.1 \pm 0.3) \times 10^{-12}$	0.67	Hayman (92/93)
<b>HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> + HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub></b>		
$(2.3 \pm 0.3) \times 10^{-12}$ (1013 mbar/MMS) [x]	0.50	Hayman (93)
<b>CH<sub>3</sub>C(O)O<sub>2</sub> + CH<sub>3</sub>C(O)O<sub>2</sub></b>		
$2.8 \times 10^{-12} \exp[(526 \pm 90)/T]$ (253–368 K; 800 mbar)		Veyret (88)
$1.6 \times 10^{-11}$ $(1.4 \pm 0.2) \times 10^{-11}$ 0.5±0.1 (1013 mbar)		Moortgat(94)
<b>C<sub>2</sub>H<sub>5</sub>C(O)O<sub>2</sub> + C<sub>2</sub>H<sub>5</sub>C(O)O<sub>2</sub> <math>\xrightarrow{(O_2)}</math> 2 C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> + 2 CO<sub>2</sub></b>		
$(1.7 \pm 1) \times 10^{-11}$ (prelim.)		Veyret (90)
<b>CH<sub>3</sub>C(O)CH<sub>2</sub>O<sub>2</sub> + CH<sub>3</sub>C(O)CH<sub>2</sub>O<sub>2</sub></b>		
$(8.0 \pm 2.0) \times 10^{-12}$	0.75	Lesclaux (92)
<b>CH<sub>2</sub> = CHCH<sub>2</sub>O<sub>2</sub> + CH<sub>2</sub> = CHCH<sub>2</sub>O<sub>2</sub></b>		
$(6.8 \pm 1.3) \times 10^{-13}$ $(7.1 \pm 1.0) \times 10^{-14} \exp[(700 \pm 100)/T]$ $(7.3 \pm 1.5) \times 10^{-13}$	0.61	Hayman (92) Lesclaux (93)

Table 8: continued

Rate Coefficient <sup>a</sup> $k$ (298 K) (cm <sup>3</sup> s <sup>-1</sup> )	Branching Ratio <sup>b</sup> $k_a$ (298 K)/ $k$ (298 K)	Reference <sup>c</sup>
$(\text{CH}_3)_3\text{CO}_2 + (\text{CH}_3)_3\text{CO}_2 \rightarrow 2 (\text{CH}_3)_3\text{CO} + \text{O}_2$ $1.0 \times 10^{-11} \exp[-3890/T]$ $2.1 \times 10^{-17}$		Veyret (90)
$\text{HOC}(\text{CH}_3)_2\text{CH}_2\text{O}_2 + \text{HOC}(\text{CH}_3)_2\text{CH}_2\text{O}_2$ $1.4 \times 10^{-14} \exp[1740/T]$ (303–398 K) $4.8 \times 10^{-12}$	0.6±0.2	Lesclaux (94)
$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}_2)\text{CH}_3 + \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}_2)\text{CH}_3$ $(8.4 \pm 1.0) \times 10^{-13}$ [X]		Hayman (94)
$1\text{-C}_5\text{H}_{11}\text{O}_2 + 1\text{-C}_5\text{H}_{11}\text{O}_2$	> 0.16 (1013 mbar)	Becker (90)
$n\text{-C}_5\text{H}_{11}\text{O}_2 + n\text{-C}_5\text{H}_{11}\text{O}_2$	0.58 (overall)	Warneck (90)
$c\text{-C}_5\text{H}_9\text{O}_2 + c\text{-C}_5\text{H}_9\text{O}_2$ $2.9 \times 10^{-13} \exp[-555/T]$ (248–364 K, 1013 mbar) $4.5 \times 10^{-14}$		Lightfoot (91)
$(\text{CH}_3)_3\text{CCH}_2\text{O}_2 + (\text{CH}_3)_3\text{CCH}_2\text{O}_2$ $3.02 \times 10^{-19} (T/298)^{9.46} \exp[4260/T]$ (248–373 K; 38–1013 mbar) $(1.04 \pm 0.09) \times 10^{-12}$	0.40±0.01	Veyret (90)
$c\text{-C}_6\text{H}_{11}\text{O}_2 + c\text{-C}_6\text{H}_{11}\text{O}_2$ $2.0 \times 10^{-13} \exp[-487/T]$ (248–364 K, 1013 mbar) $3.9 \times 10^{-14}$		Lightfoot (91)
$(\text{CH}_3)_2\text{C}(\text{OH})\text{C}(\text{O}_2)(\text{CH}_3)_2 + (\text{CH}_3)_2\text{C}(\text{OH})\text{C}(\text{O}_2)(\text{CH}_3)_2$ $(1.1 \pm 0.25) \times 10^{-14}$	1.0	Hayman (94)
$\text{C}_6\text{H}_5\text{CH}_2\text{O}_2 + \text{C}_6\text{H}_5\text{CH}_2\text{O}_2$ $(2.75 \pm 0.15) \times 10^{-14} \exp[(1680 \pm 140)/T]$ $(7.7 \pm 1.5) \times 10^{-12}$	0.4 0.74	Lesclaux (93) Warneck (93)

Table 8: continued

Rate Coefficient <sup>a</sup> $k$ (298 K) ( $\text{cm}^3 \text{s}^{-1}$ )	Branching Ratio <sup>b</sup> $k_a$ (298 K)/ $k$ (298 K)	Reference <sup>c</sup>
$\text{CF}_3\text{O}_2 + \text{CF}_3\text{O}_2$ $4.0 \times 10^{-12}$		Wayne (94)
$\text{CCl}_3\text{O}_2 + \text{CCl}_3\text{O}_2$ $(3.31 \pm 0.55) \times 10^{-13} \exp[(745 \pm 58)/T]$ $4.0 \times 10^{-12}$	1.0	Lesclaux (94)
$\text{CHCl}_2\text{O}_2 + \text{CHCl}_2\text{O}_2$ $(2.65 \times 10^{-13} \exp[(800)/T])$ $3.9 \times 10^{-12}$ $4.0 \times 10^{-12}$	> 0.95	Lesclaux (94) Wayne (94)
$\text{CH}_2\text{ClO}_2 + \text{CH}_2\text{ClO}_2$ $(1.95 \pm 0.27) \times 10^{-13} \exp[(880 \pm 50)/T]$ $(3.7 \pm 0.4) \times 10^{-12}$ $1.0 \times 10^{-12}$	> 0.85	Lesclaux (93) Wayne (94)
$\text{CHBr}_2\text{O}_2 + \text{CHBr}_2\text{O}_2$ $2.5 \times 10^{-12}$		Wayne (94)
$\text{CH}_2\text{BrO}_2 + \text{CH}_2\text{BrO}_2$ $(1.05 \pm 0.4) \times 10^{-12}$ $2.0 \times 10^{-12}$	1.0	Lesclaux (94) Wayne (94)
$\text{CH}_3\text{CHBrCH}(\text{O}_2)\text{CH}_3 + \text{CH}_3\text{CHBrCH}(\text{O}_2)\text{CH}_3$ $7.1 \times 10^{-15} \exp[1360/T]$ $7.0 \times 10^{-13}$		Lesclaux (94)
<b>RO<sub>2</sub> + R'O<sub>2</sub> Reactions</b>		
$\text{C}_2\text{H}_5\text{O}_2 + \text{CH}_3\text{O}_2$ $(2.0 \pm 1.0) \times 10^{-13}$	0.5	Lesclaux (93)

Table 8: continued

Rate Coefficient <sup>a</sup> <i>k</i> (298 K) (cm <sup>3</sup> s <sup>-1</sup> )	Branching Ratio <sup>b</sup> <i>k<sub>a</sub></i> (298 K)/ <i>k</i> (298 K)	Reference <sup>c</sup>
$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{CH}_3\text{O}_2 \xrightarrow{\text{a}} \text{CH}_3\text{C}(\text{O})\text{O} + \text{CH}_3\text{O} + \text{O}_2$ $\xrightarrow{\text{b}} \text{CH}_3\text{C}(\text{O})\text{OH} + \text{HCHO} + \text{O}_2$		
$9.6 \times 10^{-12}$	0.87	Moortgat (91,94)
	$k_{\text{a}} = 3.21 \times 10^{-11} \exp[-440/T]$ $k_{\text{b}} = 2.68 \times 10^{-16} \exp[2510/T]$ (233–333 K, 1013 mbar)	
$7.6 \times 10^{-12}$		Lesclaux (94)
$\text{C}_3\text{H}_5\text{O}_2 + \text{CH}_3\text{O}_2$ $(3.4 \pm 1.5) \times 10^{-13} \exp[(430 \pm 160)/T]$		Lesclaux (94)
$1.5 \times 10^{-12}$		
$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2 + \text{CH}_3\text{O}_2$ $(3.8 \pm 0.4) \times 10^{-12}$	0.3	Lesclaux (92)
$\text{CH}_2=\text{CHCH}_2\text{O}_2 + \text{CH}_3\text{O}_2$ $(2.0 \pm 1.0) \times 10^{-12}$	0.45	Lesclaux (93)
$\text{C}_5\text{H}_{11}\text{O}_2 + \text{CH}_3\text{O}_2$ $1.1 \times 10^{-12}$		Lesclaux (94)
$c\text{-C}_6\text{H}_{11}\text{O}_2 + \text{CH}_3\text{O}_2$ $(3.0 \pm 1.5) \times 10^{-14}$	0.3	Lesclaux (93)
$\text{C}_6\text{H}_5\text{CH}_2\text{O}_2 + \text{CH}_3\text{O}_2$ $< 10^{-12}$		Lesclaux (94)
$\text{CCl}_3\text{O}_2 + \text{CH}_3\text{O}_2$ $(4.0 \pm 2.0) \times 10^{-12}$	0.65	Lesclaux (93)
$\text{CH}_2\text{ClO}_2 + \text{CH}_3\text{O}_2$ $(2.5 \pm 1.2) \times 10^{-12}$	0.65	Lesclaux (93)
$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{C}_2\text{H}_5\text{O}_2$ $1.0 \times 10^{-11}$		Lesclaux (94)

Table 8: continued

Rate Coefficient <sup>a</sup> (298 K) (cm <sup>3</sup> s <sup>-1</sup> )	Branching Ratio <sup>b</sup> $k_a$ (298 K)/ $k$ (298 K)	Reference <sup>c</sup>
$C_3H_5O_2 + C_2H_5O_2$ $> 10^{-12}$		Lesclaux (94)
$C_5H_{11}O_2 + C_2H_5O_2$ $> 10^{-13}$		Lesclaux (94)
<i>c</i> - $C_6H_{11}O_2 + C_2H_5O_2$ $< 10^{-14}$		Lesclaux (94)
$C_2H_5C(O)O_2 + C_2H_5O_2 \xrightarrow{a} C_2H_5O_2 + C_2H_5O + CO_2$ $\xrightarrow{b} C_2H_5C(O)OH + CH_3CHO + O_2$ $\pm 1.5 \times 10^{-12}$ (prelim.)	0.25 $k_a = (1 \pm 1) \times 10^{-12}$ $k_b = (3 \pm 0.5) \times 10^{-12}$	Veyret (90)
$(CH_3)_2CHC(CH_3)_2O_2 + s\text{-}C_3H_7O_2$ $< 10^{-17}$		Warneck (91)
$CH_3C(O)O_2 + c\text{-}C_6H_{11}O_2$ $> 10^{-11}$		Lesclaux (94)
$CH_3C(O)CH_2O_2 + CH_3C(O)O_2$ $0 \pm 1.0 \times 10^{-12}$	0.5	Lesclaux (92)
<b>overall RO<sub>2</sub> reactions resulting from OH + isoprene</b>	0.7–0.8	Becker (93)

[x]  $k_{\text{observed}}$  with  $k < k_{\text{observed}} < 2k$

<sup>a</sup> rate coefficients at 298 K and temperature dependence when available.

<sup>b</sup> ratio of rate of RO formation / total rate at 298 K; temperature dependence given when available.

<sup>c</sup> These references are to EUROTRAC Ann. Reps. The year in parentheses is the year of the report not the publishing year.

MMS molecular modulation spectroscopy

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(2) M. E. Jenkin, R. A. Cox, G. D. Hayman, L. J. Whyte; *J. Chem. Soc. Faraday Trans. 2*, **84** (1988) 913.

(3) G. K. Moortgat, R. A. Cox, G. Schuster, J. P. Burrows, G. S. Tyndall; *J. Chem. Soc. Faraday Trans. 2*, **85** (1989) 809.

(4) J. P. Burrows, G. Moortgat, G. Tyndall, R. Cox, M. Jenkin, G. D. Hayman, B. Veyret; *J. Phys. Chem.* **93** (1989) 2375.

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(7) F. G. Simon, W. Schneider, G. K. Moortgat; *Int. J. Chem. Kinetics* **22** (1990) 791.

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It should be noted that the trends observed for the rate constants, particularly regarding the size of alkylperoxy radicals and halogen substitution, are generally opposite to those observed for the  $\text{RO}_2 + \text{NO}$  reactions. This is an important result, since the two types of reactions are in competition in the ozone formation processes.  $\text{RO}_2 + \text{NO}$  are propagating reactions, whereas  $\text{RO}_2 + \text{HO}_2$  are terminating reactions, the products of the latter reactions being non-radical, generally hydroperoxides. An alternative reaction channel, producing a carbonyl compound and  $\text{H}_2\text{O}$  has been identified for the  $\text{HOCH}_2\text{O}_2$ ,  $\text{CH}_3\text{OCH}_2\text{O}_2$  and  $\text{CH}_2\text{ClO}_2$  reactions, with a branching ratio of 40–50 %, but this reaction channel seems to be minor in the other reactions investigated. The formation of an organic acid along with ozone in reactions of acylperoxy radical reactions with  $\text{HO}_2$  has been confirmed.

### 2.4.3 $\text{RO}_2 + \text{RO}_2$ reactions

Self-reactions of peroxy radicals may occur in the atmosphere under low  $\text{NO}_x$  concentrations, particularly since the reactions are fast, with rate constants which can reach values as high as  $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . In addition, self-reactions must be well characterised for laboratory studies of other reactions of peroxy radicals, particularly those with  $\text{HO}_2$  and  $\text{R}'\text{O}_2$ . The general mechanism for  $\text{RO}_2$  self-reactions is the following:



$\text{ROH}$  is an alcohol,  $\text{R}_{\text{H}}\text{O}$  an aldehyde or a ketone and  $\alpha$  the branching ratio of the non-terminating channel (1a):  $\alpha = k_{1a}/k_1$ . A possible third channel, forming the peroxide  $\text{ROOR}$ , has never been observed. The non-terminating channel generates an alkoxy radical which can further react with  $\text{O}_2$  to yield a carbonyl compound and  $\text{HO}_2$ , decompose, or isomerise to generate a different peroxy radical. Rate constants for self-reactions have been determined by either ignoring subsequent reactions, thus giving an observed rate constant,  $k_{\text{obs}}$ , or modelling the complete reaction mechanism for a determination of the real rate constant. All rate constants measured during the LACTOZ project are collected in Table 8. The determination of the elementary rate constant requires knowledge of the branching ratio  $\alpha$ , which has been determined for several reactions (Table 8). The values of  $\alpha$  are fairly insensitive to the structure of alkylperoxy radicals and to the presence of functional groups (with the exception of halogen substitution) and generally fall in the range 0.4–0.7 at 298 K. In contrast,  $\alpha$  seems to be close to 1 for all halogen substituted radicals, for all investigated temperatures.

#### *Primary peroxy radicals ( $\text{RCH}_2\text{O}_2$ )*

The self reactions of the simplest primary alkylperoxy radicals have rate constant values at 298 K of about  $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . These rate constants for non-linear alkyl groups apparently increase with chain branching, e.g.  $1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for neopentylperoxy. These values seem to be the

lower and upper limits for primary alkylperoxy radicals and more data would be required to refine the structure-reactivity relationships for this class of radicals.

The most striking feature of the results is the dramatic increase of the rate constant following substitution of an H atom in the alkylperoxy radicals with halogen atoms, an OH group, a carbonyl group, unsaturated bond or aromatic ring. Apparently, this effect is independent of the position of the substituent ( $\alpha$  or  $\beta$ ) relative to the peroxy function. In the case of the methylperoxy radical, for example, the presence of a F atom, Cl atom(s), or an OH group, increases the rate constant by more than a factor of 10. The effect of bromine, in contrast, seems smaller. The enhancement is even larger with the presence of a carbonyl group (e.g. acetylperoxy) or an aromatic ring (e.g. benzylperoxy). Rate constants for such primary peroxy radicals bearing a particular functional group generally fall in the range  $2 - 8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

The acetylperoxy radical, and probably other acylperoxy radicals  $\text{RC(O)O}_2$ , exhibit even higher rate constants:  $1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Acylperoxy radicals are certainly the most reactive peroxy radicals, as emphasised below for other type of reactions.

A negative temperature dependence of the rate constant seems to be a general characteristic for self-reactions of primary alkylperoxy radicals, with most exponential factors being in the range 0–1000 K/T.

### ***Secondary peroxy radicals (RCHO<sub>2</sub>R')***

Only few data are available for self-reactions of secondary alkylperoxy radicals. One of the principal contributions of the project has been the study of the cyclo-alkylperoxy radicals  $c\text{-C}_5\text{H}_9\text{O}_2$  and  $c\text{-C}_6\text{H}_{11}\text{O}_2$  radicals. The corresponding rate constants are 40 times smaller than the only linear secondary peroxy radical studied so far,  $i\text{-C}_3\text{H}_7\text{O}_2$ , and exhibit a slight positive temperature dependence. More data would be necessary for a better description of such reactions but, due to their relatively low rate constants ( $< 5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ), their contribution to atmospheric chemistry is negligible.

It should be emphasised, however, that the presence of a functional group may result in an even more dramatic increase of the rate constant than in the case of primary radicals. This has been shown in the cases of radicals resulting from the addition of Br atoms or OH radicals to 2-butene (Moortgat, Hayman), the rate constant approaching  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for these particular cases. More data are needed to confirm whether this effect occurs for the presence of other functional groups.

### ***Tertiary peroxy radicals (RR'R''CO<sub>2</sub>)***

No new data have been reported for tertiary alkylperoxy radicals. It has been confirmed that the rate constant of the t-butylperoxy radical self-reaction is very

slow, with a fairly high activation energy. However, as above, a dramatic increase of the rate constant has been observed in the presence of an OH group at the  $\beta$  position with respect to the peroxy function (Hayman). However, the reaction is still slow ( $5.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) and has no relevance to atmospheric chemistry.

#### 2.4.4 $\text{RO}_2 + \text{CH}_3\text{O}_2$ cross-reactions

$\text{CH}_3\text{O}_2$  is the most abundant alkylperoxy radical in hydrocarbon-rich atmospheres. It is of interest to assess the role of  $\text{RO}_2 + \text{CH}_3\text{O}_2$  cross-reactions since a series of rate constants has been obtained for such reactions, either resulting from indirect determinations (secondary reactions of  $\text{RO}_2 + \text{RO}_2$  reactions) or from direct measurements. Rate constants for this class of reactions are reported in Table 8.

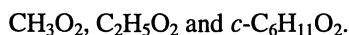
It is observed that the rate constants are generally intermediate between the rate constants for self-reactions of  $\text{RO}_2$  and  $\text{CH}_3\text{O}_2$ . A geometric mean such as

$$k(\text{RO}_2 + \text{CH}_3\text{O}_2) = 2 \sqrt{k(\text{RO}_2 + \text{RO}_2) \times k(\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2)}$$

appears to provide a good estimate of the cross-reaction rate constant. However, it is observed that when the  $\text{RO}_2$  self-reactions are fast,  $k(\text{RO}_2 + \text{CH}_3\text{O}_2)$  is much closer to  $k(\text{RO}_2 + \text{RO}_2)$  than to  $k(\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2)$ . This is the case, for example, for acetyl, acetylonyl and chloromethylperoxy radicals. If this behaviour is indeed general, a better approximation would be to set  $k(\text{RO}_2 + \text{CH}_3\text{O}_2)$  equal to  $k(\text{RO}_2 + \text{RO}_2)$ . This would be incorrect for slow reactions, but as far as atmospheric chemistry is concerned, slow reactions are unimportant.

#### 2.4.5 $\text{RO}_2 + \text{CH}_3\text{C}(\text{O})\text{O}_2$ cross-reactions

A few cross-reactions of  $\text{RO}_2$  radicals with the acetylperoxy radical have been investigated:



The reactions are very fast, with rate constants close to  $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This is even true for the secondary radical  $c\text{-C}_6\text{H}_{11}\text{O}_2$ , in spite of the much lower rate constant observed for the self-reaction ( $4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). This may be important since the acetylperoxy radical is also an abundant radical in the atmosphere and, if all cross-reactions of this type are as fast as those reported above, they should be taken into account in modelling the chemistry of remote atmospheres.

#### 2.4.6 Reactions of $\text{RO}_2$ radicals with nitrogen oxides

As emphasised above, reactions of  $\text{RO}_2$  radicals with NO are important propagating reactions, resulting in the formation of  $\text{NO}_2$  which, on photolysis, yields  $\text{O}_3$ . The reactions of a series of peroxy radicals, derived from both

hydrocarbons and halocarbons, have been investigated. The rate constants are given in Table 9 (see also Fig. 5a). Two significant trends can be observed. The rate constants increase markedly with halogen substitution (probably related to the electron accepting nature of these substituents), whereas they decrease with the size of the organic peroxy radical (probably due to the opposite effect). It is interesting to note that the very low rate constant measured for the reaction of the  $(\text{CH}_3)_3\text{CC}(\text{CH}_3)_2\text{CH}_2\text{O}_2$  radical ( $1.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) is almost one order of magnitude smaller than the highest rate constants observed for halogenated peroxy radicals. As emphasised above, the trend observed with the size of radical is opposite to that observed for  $\text{RO}_2 + \text{HO}_2$  reactions. Thus, the latter, which is a terminating reaction, is favoured for this particular class of radicals. Note that the acetylperoxy radical reaction is one of the fastest reactions.

**Table 9:** Rate constants for the reactions of  $\text{RO}_2$  radicals with  $\text{NO}_x$ ;

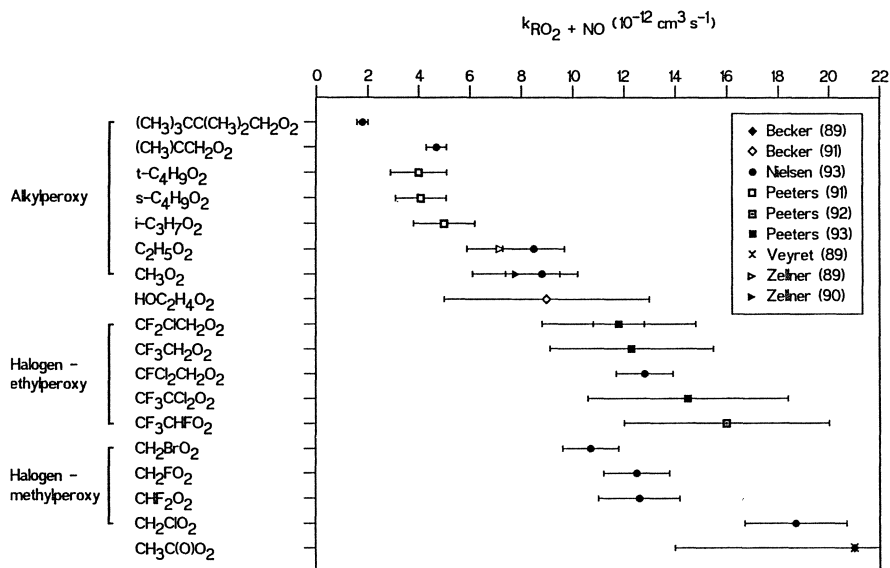
$\text{RO}_2 + \text{NO}, k_1$

$\text{RO}_2 + \text{NO}_2, k_2$

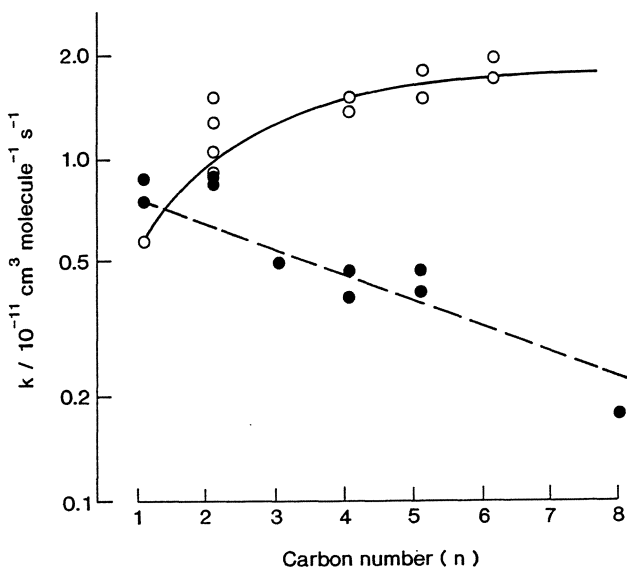
$\text{RO}_2$	Total Pressure (mbar)	Temperature (K)	$k_2$ ( $10^{-12} \text{ cm}^3 \text{ s}^{-1}$ )	$k_1$ ( $10^{-12} \text{ cm}^3 \text{ s}^{-1}$ )	$k_2/k_1$	Reference <sup>a</sup>
$\text{CH}_3\text{O}_2$	10.3/ $\text{N}_2$	298		$7.8 \pm 1.7$		Zellner (90)
		298		$8.8 \pm 1.4$		Nielsen (93)
$\text{C}_2\text{H}_5\text{O}_2$	10.3/ $\text{N}_2$	298	$1.8 \pm 0.1$	$7.2 \pm 1.3$		Zellner (89)
		298		$8.5 \pm 1.2$		Nielsen (93)
$\text{HOC}_2\text{H}_4\text{O}_2$	1013/air	298		$9 \pm 4^b$		Becker (91)
<i>i</i> - $\text{C}_3\text{H}_7\text{O}_2$	2.7/He	290		$5.0 \pm 1.2$		Peeters (91)
<i>t</i> - $\text{C}_4\text{H}_9\text{O}_2$	2.7/He	290		$4.0 \pm 1.1$		Peeters (91)
<i>s</i> - $\text{C}_4\text{H}_9\text{O}_2$	2.7/He	290		$4.1 \pm 1.0$		Peeters (91)
$\text{CH}_3\text{C}(\text{O})\text{O}_2$	1013/ $\text{N}_2$	298	$9.6 \pm 0.9$	$21 \pm 7$		Becker (89)
						Veyret (89)
$(\text{CH}_3)_3\text{CCH}_2\text{O}_2$		298		$4.7 \pm 0.4$		Nielsen (93)
$(\text{CH}_3)_3\text{CC}(\text{CH}_3)_2\text{CH}_2\text{O}_2$		298		$1.8 \pm 0.2$		Nielsen (93)
$\text{C}_6\text{H}_5\text{C}(\text{O})\text{O}_2$	1013/ $\text{N}_2$	315			0.62	Becker (91)
$\text{CF}_3\text{CHFO}_2$	2.0/He	290		$15.6 \pm 4$		Peeters (94)
$\text{CF}_3\text{CH}_2\text{O}_2$		290		$12.3 \pm 3.2$		Peeters (93)
$\text{CF}_2\text{ClCH}_2\text{O}_2$		290		$11.8 \pm 3.0$		Peeters (93)
$\text{CF}_3\text{CCl}_2\text{O}_2$		290		$14.5 \pm 3.9$		Peeters (93)
$\text{CH}_2\text{FO}_2$		298		$12.5 \pm 1.3$		Nielsen (93)
$\text{CH}_2\text{ClO}_2$		298		$18.7 \pm 2.0$		Nielsen (93)
$\text{CH}_2\text{BrO}_2$		298		$10.7 \pm 1.1$		Nielsen (93)
$\text{CHF}_2\text{O}_2$		298		$12.6 \pm 1.6$		Nielsen (93)
$\text{CFCl}_2\text{CH}_2\text{O}_2$		298		$12.8 \pm 1.1$		Nielsen (93)
$\text{CF}_2\text{ClCH}_2\text{O}_2$		298		$11.8 \pm 1.0$		Nielsen (93)
		290		$11.8 \pm 3.0$		Peeters (94)
$\text{CH}_3\text{SCH}_2\text{O}_2$	1000	298	$(9.2 \pm 0.9)$			Nielsen (94)

<sup>a</sup> These references are to EUROTRAC Annual Reports. The year in parentheses is the year of the report not the publishing year.

<sup>b</sup> reaction channel  $\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2$



**Fig. 5a:** Rate constants for the reactions  $\text{RO}_2 + \text{NO}$ .



**Fig. 5b:** Room Temperature data for reactions of alkyl peroxy and  $\beta$ -hydroxy alkyl peroxy radicals with  $\text{HO}_2$  (open circles) and  $\text{NO}$  (closed circles) as a function of carbon number.

**Table 10:** Branching ratios for nitrate formation at about 1000 mbar in air;  
 $\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2$ ,  $k_1$        $\text{RO}_2 + \text{NO} \rightarrow \text{RONO}_2$ ,  $k_2$

Precursor Radical R	Temperature (K)	$k_2/(k_2+k_1)$	Reference <sup>a</sup>
<b>propane</b>			
1-propyl	295	0.019	Becker (90)
2-propyl	295	0.049	Becker (90)
<b>n-butane</b>			
1 butyl	295	0.041	Becker (90)
<b>isobutane</b>			
2-methyl-1-propyl	295	0.075	Becker (90)
<i>t</i> -butyl	295	0.180	Becker (90)
<b>isobutene</b>			
2-methyl-1-hydroxy-2-propyl	300	0.40 <sup>b</sup>	Peeters (89)
	295	0.057 <sup>c</sup>	Becker (90)
<b>2-butanone</b>			
2-keto-3-butyl	293	0.0021	Becker (89)
	323	0.0025	Becker (89)
<b>isopentane</b>			
3-methyl-1-butyl	295	0.043	Becker (88)
2-methyl-1-butyl	295	0.039	Becker (88)
3-methyl-2-butyl	295	0.074	Becker (88)
2-methyl-2-butyl	295	0.044	Becker (88)
<b>n-pentane</b>			
1-pentyl	295	0.061	Becker (90)
<b>n-hexane</b>			
1-hexyl	295	0.121	Becker (90)
<b>cyclohexane</b>			
cyclohexyl	273	0.113	Becker (89)
	293	0.074	Becker (89)
	323	0.046	Becker (89)
	343	0.025	Becker (89)
<b>n-heptane</b>			
2-, 3- and 4-heptyl	295	0.265 <sup>d</sup>	Kerr (88)
1-heptyl	295	0.195	Becker (90)
<b>n-octane</b>			
1-octyl	295	0.360	Becker (90)
2-, 3- and 4-octyl	295	0.370	Becker (90)
<b>isoprene</b>	295	0.10 <sup>d</sup>	Becker (90)

<sup>a</sup> These references are to EUROTRAC Annual Reports. The year in parentheses is the year of the report not the publishing year.

<sup>b</sup> 2 Torr total pressure He, value seems to be too large.

<sup>c</sup> Represents the total nitrate yield for the OH radical initiated oxidation in the presence of  $\text{NO}_x$ .

<sup>d</sup> Mean branching ratio for 2-, 3- and 4-heptylperoxy radicals; temperature dependence obtained by  $k_2/k_1 = 1.4 \times 10^{-3} \exp(1640/T)$ .

It should be noted that in nearly all experiments carried out within LACTOZ, overall rate constants have been measured. However, the channel,  $\text{RO}_2 + \text{NO} \rightarrow \text{RONO}_2$  relative to the  $\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2$  channel, gains importance for larger  $\text{RO}_2$  radicals. The branching ratios for nitrate formation have been shown to increase to more than 30 % (Table 10).

When the absolute reaction rate constants are not available, the ratio  $k(\text{RO}_2 + \text{NO}_2)/k(\text{RO}_2 + \text{NO})$  is an important parameter, giving the relative importance of the terminating and the non-terminating reaction channels. This ratio has been determined for a few typical radicals (Becker).

The reactions of  $\text{RO}_2$  radicals with  $\text{NO}_2$  are also very important. They are terminating reactions, in competition with the propagating  $\text{RO}_2 + \text{NO}$  reactions (Fig. 5b), and they form peroxy nitrates which can contribute to the transport of nitrogen oxides if they are sufficiently stable. The most important reaction influencing the formation of ozone is the reaction of the acetylperoxy radical with  $\text{NO}_2$  forming PAN. The kinetics and thermodynamics of the forward and reverse reactions have been investigated in detail (Becker, Lesclaux), resulting in the currently recommended rate constant values. Examination of the absolute values of rate constants for reactions of  $\text{RO}_2$  radicals with  $\text{NO}_2$  at the high pressure limit, determined from LACTOZ investigations and also those reported in the literature, shows that they all appear to be very close to each other, *e.g.*  $(7 \pm 2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Thus, this value can be recommended for all  $\text{RO}_2 + \text{NO}_2$  reactions. However, fall-off effects must be taken into account for the reactions of smaller radicals (Table 11).

**Table 11:** Kinetic parameters for the thermal decomposition of peroxy nitrates,  $\text{RO}_2\text{NO}_2 (+\text{M}) \rightarrow \text{RO}_2 + \text{NO}_2 (+\text{M})$ .

R	$k_{298\text{K}}, 1 \text{ bar N}_2$ ( $\text{s}^{-1}$ )	$E_a, 1 \text{ bar}$ ( $\text{kJ/mol}$ )	$A, 1 \text{ bar}$ ( $10^{16} \text{ s}^{-1}$ )
$\text{C}_6\text{H}_{11}$	4.8	$87.4 \pm 6.4^a$	$1^b$
$\text{CH}_3\text{CH}_2$	$3.7^c$	$86.2 \pm 4.0^{c,d}$	$0.47^c$
$\text{CH}_3\text{C}(\text{O})\text{CH}_2$	$2.6^c$	$85.6 \pm 15^{c,d}$	$0.26^c$
$\text{CF}_2\text{ClCH}_2$	2.3	$90.9 \pm 5.9^a$	$2^b$
$\text{CFCl}_2\text{CH}_2$	2.1	$91.2 \pm 5.3^a$	$2^b$
$\text{C}_6\text{H}_5\text{CH}_2$	1.8	$89.8 \pm 7.2^a$	$1^b$
$\text{CH}_3$	1.65	$83.8 \pm 5.9$	0.080
$\text{HOCH}_2$	$1.0^c$	$85.3^b$	$0.09^c$
$\text{CH}_2\text{I}$	0.8	$91.8 \pm 6.8^a$	$1^b$
$\text{CH}_3\text{OCH}_2$	0.45	$93.5 \pm 5.4^d$	1.11
$\text{CH}_2\text{Cl}$	$0.26^c$	$91.7 \pm 2.9^{c,d}$	$0.31^c$
$\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{CH}_3)$	0.23	$94.9 \pm 7.3^a$	$1^b$
$\text{C}_6\text{H}_5\text{OCH}_2$	0.22	$95.0 \pm 6.8^a$	$1^b$
$\text{CCl}_3$	$0.19^c$	$96.8 \pm 1.4^{c,d}$	$1.8^c$
H	0.083	$89.2 \pm 2.2^d$	0.036
$\text{CCl}_2\text{F}$	$0.066^c$	$100.3 \pm 1.8^{c,d}$	$2.5^c$
$\text{CF}_3$	0.043	$97.7 \pm 1.0^d$	0.57
$\text{CClF}_2$	$0.040^c$	$98.7 \pm 1.8^{c,d}$	$0.8^c$
$(\text{CH}_3)_2\text{NC}(\text{O})$	0.00123	$111.5 \pm 5.8^d$	4.3
$\text{CH}_3\text{OC}(\text{O})$	0.00084	$107.0 \pm 4.5^d$	0.48
$\text{C}_6\text{H}_5\text{OC}(\text{O})$	0.00052	$110.0 \pm 7.7^a$	$1^b$
$\text{CH}_3\text{C}(\text{O})$	$0.00040^c$	$112.9 \pm 1.9^{c,d}$	$2.5^c$
$\text{C}_2\text{H}_5\text{C}(\text{O})$	0.00035	$115.9 \pm 2.2^d$	7.2
$\text{C}_6\text{H}_5\text{C}(\text{O})$	0.00031	$116.4 \pm 3.8^d$	7.9
$\text{ClC}(\text{O})$	$0.00017^c$	$115.1 \pm 3.2^{c,d}$	$2.6^c$
$\text{CCl}_3\text{C}(\text{O})$	$0.00012^c$	$120.6 \pm 5.2^{c,d}$	$16.4^c$
$\text{CFCl}_2\text{C}(\text{O})$	0.00012	$118.0 \pm 5.2^a$	$6^b$
$\text{CF}_2\text{ClC}(\text{O})$	0.00010	$118.6 \pm 5.2^a$	$6^b$
$\text{CF}_3\text{C}(\text{O})$	0.00008	$119.1 \pm 5.0^a$	$6^b$

<sup>a</sup> derived from  $k$  and estimated  $A$ , error reflects uncertainties of  $k$  and  $A$ ;<sup>b</sup> estimated by analogy from measured  $A$  or  $E_a$  of similar molecules<sup>c</sup>  $p_{\text{tot}} = 800 \text{ mbar}$ ;<sup>d</sup>  $2\sigma$  error;<sup>e</sup>  $p_{\text{tot}} = 600 \text{ mbar}$ ;

(Becker, EUROTRAC Annual Report 1994)



**Appendix to Table 11:** Predictions of rate constants  $k$  for the thermal decomposition of peroxy nitrates.

1. Select  $d_x$  values for  $^{13}\text{C}$  NMR shift of RX (X: OCH<sub>3</sub>, Cl, F, H, OH, CH<sub>3</sub>).

2. Enter the equation below with the proper numbers of  $a_x$ ,  $b_x$ ,  $c_x$  and  $d_x$  from the table.

$$k [\text{s}^{-1}] = A \cdot \exp\left(-\frac{E_a}{RT}\right) = 3 \times 10^{-3} \cdot \exp\left(\frac{a_x \delta_x + b_x}{R(c_x \delta_x + d_x)}\right) \cdot \exp\left(-\frac{a_x \delta_x + b_x}{RT}\right)$$

$$E_{a,1 \text{ atm}} [\text{J/mol}] = a_x \delta_x + b_x$$

X	OCH <sub>3</sub>	Cl	F	H	OH	CH <sub>3</sub>
$a_x$ ( $\text{J} \times \text{mol}^{-1} \text{ppm}^{-1}$ )	307.5	226.5	358.0	153.4	277.1	170.9
$b_x$ ( $\text{J} \times \text{mol}^{-1}$ )	65 160	76 530	57 050	85 030	69 300	82 530
$c_x$ ( $\text{K} \times \text{ppm}^{-1}$ )	0.7011	0.5437	0.8212	0.3458	0.6136	0.3927
$d_x$ (K)	199.95	224.47	180.23	245.53	209.75	239.72

(Becker)

#### 2.4.7 Thermal decomposition of peroxy nitrates

Studies on the thermal stability of peroxy nitrates have been extended (Becker). From the results of measurements of thermal decomposition rate constants for 28 peroxy nitrates (Table 11), the following conclusions can be drawn:

- acyl peroxy nitrates are thermally much more stable than any of the alkyl peroxy nitrates;
- the thermal stability of peroxy nitrates is governed by the bond strength RO<sub>2</sub>-NO<sub>2</sub> which is highly dependent on the electron density at the carbon atom next to the -O<sub>2</sub>NO<sub>2</sub> group. Electron withdrawing substituents increase the thermal stability of peroxy nitrates compared to substituents which are less electron withdrawing. For alkyl peroxy nitrates inductive effects are the most important;
- the electronegativities of the atoms next to the C atom of the >CO<sub>2</sub>NO<sub>2</sub> group will therefore determine the thermal stability of RO<sub>2</sub>NO<sub>2</sub>. For acyl peroxy nitrates mesomeric effects are important and cannot be neglected.

Because of the importance of electron density, the activation energies for thermal decomposition of peroxy nitrates are highly correlated with  $^{13}\text{C}$ -NMR signal shifts of the corresponding R-X compounds (X= OCH<sub>3</sub>, Cl, F, H, OH, CH<sub>3</sub>). From these correlations an expression has been derived which can be used to estimate rate constants and activation energies for the thermal decomposition of peroxy nitrates (see appendix to Table 11). Rate data for the decomposition of CH<sub>2</sub>IO<sub>2</sub>NO<sub>2</sub> indicate that these equations are not valid in cases where the substituents are heavy atoms. Using the equations, activation energies for the thermal decomposition of all measured peroxy nitrates can be estimated within error limits to  $\pm 6 \text{ kJ mol}^{-1}$  (experimental error limits: 2–7  $\text{kJ mol}^{-1}$ ), with the exception of those peroxy nitrates containing heavy atom substituents. All rate constants, which are calculated from the equation (see appendix to Table 11), agree with the measured values within a factor of 6, and 70 % of them agree with the measured values within a factor of 3. The experimental errors of the rate constants are usually

between 10 and 50 %. Table 12 gives the relevant parameters of the equilibrium constant for  $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2 \rightleftharpoons \text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$ . Knowledge concerning the thermal stability of peroxy nitrates is now sufficiently advanced that the stability of peroxy nitrates, for which no experimental data is available, can be estimated with reasonable confidence. Possible exceptions are peroxy nitrates with a sulfur bonded to the peroxy group. Evidence has been found that these species might be stable enough, *e.g.*  $\text{CH}_3\text{S}(\text{O})_2\text{O}_2\text{NO}_2$  (Hjorth) to play a role as  $\text{NO}_x$  carriers in the marine troposphere. Determination of the rate constants for photolysis and reaction with the OH radical of several representative peroxy nitrates should be considered in order to compare the rates of these reactions with those for thermal decomposition of the more stable peroxy nitrates.

**Table 12:** Equilibrium constant\*  $K_e$  ( $\text{cm}^3 \text{ molecule}^{-1}$ );  
 $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2 \leftrightarrow \text{H}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$ .

---

$K_e = 0.9 \times 10^{-28} \exp[(14.000 \pm 200)/T]$	
	(200–300 K)
$= (2.3 \pm 0.3) \times 10^{-8}$	
	(298 K)
$\Delta S_{298}^\circ = 174.0$	$\pm 11 \text{ J K}^{-1} \text{ mol}^{-1}$
$\Delta H_{298}^\circ = -118.8$	$\pm 4.0 \text{ kJ mol}^{-1}$
$\Delta H_0^\circ = E_0 = -115.1$	$\pm 4.0 \text{ kJ mol}^{-1}$

---

\* Equilibrium constants for other peroxy nitrates can be derived from decomposition rate constants given in Table 11, taking into account that all measurements of  $k$  ( $\text{RO}_2 + \text{NO}_2$ ) give values very close to each other,  $k_\infty(\text{RO}_2 + \text{NO}_2) \sim (7.0 \pm 3) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ .  
 Becker (89/90) and Veyret (89/90)

## 2.5 Reactions of oxy radicals

### 2.5.1 Introduction

Oxy radicals (RO) are important intermediates in all VOC oxidation chains. They are formed in the chain propagating channels of the reactions of  $\text{RO}_2$  radicals with NO and in the self-reactions of  $\text{RO}_2$ . Three principal reaction pathways for RO radicals have been identified under atmospheric conditions:

- reaction with  $\text{O}_2$ , forming a carbonyl compound and  $\text{HO}_2$ ;
- dissociation, involving C-C bond splitting and formation of a carbonyl compound and a new alkyl radical;
- isomerisation via an intramolecular H atom shift forming a hydroxyalkyl radical.

**Table 13:** Rate constants for decomposition / isomerisation of alkoxy radicals and branching ratios  $\beta$  at 298 K in air at atmospheric pressure,

$$\beta = (k_{\text{dec}} + k_{\text{iso}}) / (k_{\text{dec}} + k_{\text{iso}} + k_{\text{O}_2} [\text{O}_2]).$$

RO	$k_{\text{dec}} + k_{\text{iso}} \text{ (s}^{-1}\text{)}$	$\beta$	Reference <sup>a</sup>
CH3O	< 50	< $4 \times 10^{-3}$	Zellner (90)
	dominant reaction with O <sub>2</sub>		Lesclaux (93)
HOCH <sub>2</sub> O	dominant reaction with O <sub>2</sub> and H atom elimination		Lesclaux (93)
CH <sub>2</sub> ClO	dominant reaction with O <sub>2</sub> (small HCl elimination)		Lesclaux (93)
CHCl <sub>2</sub> O	dominant decomposition		Lesclaux (93)
CCl <sub>3</sub> O	dominant decomposition		Lesclaux (93)
propoxy <sup>b</sup>	$\leq 1 \times 10^3$	$\leq 0.01$	Zellner (93) <sup>d</sup>
<i>i</i> -propoxy	$\leq 3.0 \times 10^2$	$\leq 0.01$	Zellner (92) <sup>d</sup>
CH <sub>3</sub> C(O)CH <sub>2</sub> O	dominant decomposition		Lesclaux (93)
	dominant decomposition		Hayman (93)
CH <sub>3</sub> CH(O $\cdot$ )CH <sub>2</sub> Cl	$\leq 2 \times 10^3$	$\leq 0.05$	Zellner (92) <sup>d</sup>
CH <sub>2</sub> = CHCH <sub>2</sub> O	< $10^3$	0	Hayman (91)
	dominant reaction with O <sub>2</sub>		Lesclaux (93)
<i>n</i> -butoxy <sup>d</sup>	$3.8 \times 10^3$	0.09	Zellner (92) <sup>d</sup>
<i>i</i> -butoxy	$1.1 \times 10^3$	0.03	Zellner (92) <sup>d</sup>
HOC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> O	dominant decomposition		Lesclaux (93)
CH <sub>3</sub> CH(O)OC <sub>2</sub> H <sub>5</sub>	> $10^5$	> 0.75	Kerr (92)
<i>n</i> -pentoxy <sup>a</sup>	$7.1 \times 10^3$	0.16	Zellner (92) <sup>d</sup>
(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> O	> $3 \times 10^5$	$\sim 1$ <sup>c</sup>	Lesclaux (90)
2-pentoxy	$7.5 \times 10^4$	$\sim 0.9$ <sup>c</sup>	Warneck (90)
3-pentoxy	$5 \times 10^3$	$\sim 0.13$ <sup>c</sup>	Warneck (90)
neopentoxy	competition between O <sub>2</sub> reaction and decomposition		Lesclaux (93)
<i>c</i> -C <sub>5</sub> H <sub>9</sub> O	dominant decomposition		Lesclaux (93)
<i>n</i> -hexoxy <sup>d</sup>	$3.3 \times 10^4$	0.48	Zellner (92) <sup>d</sup>
2-hexoxy	99 % 1,5-isomerization		Kerr (93)
3-hexoxy	74 % 1,5-isomerization 7 % reaction with O <sub>2</sub> 19 % decomposition		Kerr (93)
<i>c</i> -C <sub>6</sub> H <sub>11</sub> O	$3 \times 10^3$	0.07	Zellner (93) <sup>d</sup>
	competition between O <sub>2</sub> reaction and decomposition		Lesclaux (93)
benzyloxy	dominant reaction with O <sub>2</sub>		Lesclaux (93)
<i>n</i> -heptoxy <sup>d</sup>	$4.4 \times 10^4$	0.53	Zellner (92) <sup>d</sup>
<i>n</i> -oxtoxy <sup>d</sup>	$4.7 \times 10^4$	0.55	Zellner (92) <sup>d</sup>

<sup>a</sup> These references are to EUROTRAC Annual Reports. The year in parentheses is the year of the report not the publishing year.

<sup>b</sup> includes all oxy radicals originating from *n*-alkane; isomer unspecified.

<sup>c</sup> based on an assumed ratio coefficient for RO + O<sub>2</sub> of  $8 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ .

<sup>d</sup> based on measurements at 50 mbar of O<sub>2</sub>, but extrapolated to 1 bar of air.

**Table 14:** Rate constants for the reactions of alkoxy radicals with O<sub>2</sub> at 298 K.

RO	$k$ (cm <sup>3</sup> s <sup>-1</sup> )	Reference <sup>a</sup>
CH <sub>3</sub> O	$1.8 \times 10^{-15}$	Zellner (90)
C <sub>2</sub> H <sub>5</sub> O	$1.1 \times 10^{-14}$	Zellner (89)
	$8.8 \times 10^{-15}$	Zellner (92)
CH <sub>2</sub> ClCH <sub>2</sub> O	$(8 \pm 2) \times 10^{-15}$	Zellner (92)
propoxy <sup>b</sup>	''	''
<i>i</i> -propoxy	''	''
CH <sub>3</sub> CH(O <sup>•</sup> )CH <sub>2</sub> Cl	''	''
<i>n</i> -butoxy <sup>b</sup>	''	''
<i>i</i> -butoxy	''	''
<i>n</i> -pentoxy <sup>b</sup>	''	''
<i>n</i> -hexoxy <sup>b</sup>	''	''
<i>n</i> -heptoxy <sup>b</sup>	''	''
<i>n</i> -octoxy <sup>b</sup>	''	''

<sup>a</sup> These references are to EUROTRAC Annual Reports. The year in parentheses is the year of the report not the publishing year.

<sup>b</sup> includes all oxy radicals originating from *n*-alkane; structure of isomer unspecified.

In the first of these processes, the carbonyl compound generated contains the same number of carbon atoms as the parent VOC. Formation of HO<sub>2</sub> radicals leads to subsequent NO to NO<sub>2</sub> conversion associated with HO<sub>x</sub> radical recycling. The second process (dissociation) gives rise to breakdown of the carbon chain, and as a consequence the resulting carbonyl compound is of smaller size than the present VOC and reflects oxidative breakdown of the VOC. The third process (isomerisation) may lead to several NO to NO<sub>2</sub> conversion as the carbon atoms in the molecule are oxidised by internal H abstraction. The alkyl radicals generated in both dissociative and isomerisation reactions lead to formation of RO<sub>2</sub> radicals and hence enhanced NO to NO<sub>2</sub> conversion. Thus, the three alternative reaction pathways for oxy radicals have a large influence on the total net O<sub>3</sub> generation.

Despite the importance of RO radical reactions, study of their kinetic parameters is not very advanced. This is because, apart from the simplest RO's such as CH<sub>3</sub>O and C<sub>2</sub>H<sub>5</sub>O, convenient production and detection techniques are not available for these species. As a consequence, rate data must be derived from relative product yields or by using indirect techniques. The results obtained within LACTOZ are summarised in Tables 13 and 14.

A large data base for the reactions of RO radicals has been provided by the work of Zellner. This group has used time resolved detection of both OH and NO<sub>2</sub> in the pulse-initiated oxidation of VOCs to determine branching ratios and absolute rate coefficients for the different reaction channels of RO radicals. However, in these studies the integrated oxidation chain for a particular VOC was investigated and hence the results for the RO reactions are weighted averages over a number of different RO radicals. Although detailed information is lost, this approach has the advantage that it can provide oxy radical lumped oxidation mechanisms for VOCs and provides information on total NO to NO<sub>2</sub> conversion. The major finding of this work is that the rate coefficients for reactions of different oxy radicals with O<sub>2</sub>,

except for  $\text{CH}_3\text{O}$ , are essentially independent of the structure of the radical ( $k \approx 8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). This implies that for the conditions of the lower troposphere the lifetime of RO is limited to 25  $\mu\text{s}$ . Alternative reaction channels of RO such as decomposition and isomerisation are only important if their rate coefficients exceed  $\approx 10^4 \text{ s}^{-1}$ . For n-alkane oxidation this is only the case for compounds  $\geq \text{C}_5$  (Zellner).

Information on the reaction pathways for oxy radicals has also been derived from kinetic and mechanistic studies of  $\text{RO}_2$  self-reactions. Lesclaux has shown that primary oxy radicals such as  $\text{CH}_3\text{O}$ ,  $\text{C}_2\text{H}_5\text{O}$ , allyloxy and benzyloxy predominantly react with  $\text{O}_2$  under tropospheric conditions. However, for cyclo- $\text{C}_6\text{H}_{11}\text{O}$  and neo-pentoxy radicals a competition between fragmentation and reaction with  $\text{O}_2$  was observed. Decomposition of the oxy radicals cyclo- $\text{C}_5\text{H}_9\text{O}$ ,  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}$  and  $\text{HO}(\text{CH}_3)_2\text{CH}_2\text{O}$  was found to be the major reaction channel. Information on the behaviour of the acetonoxo ( $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}$ ) and methoxy-methoxy ( $\text{CH}_3\text{OCH}_2\text{O}$ ) radicals using  $\text{RO}_2$  reaction kinetic studies has been provided (Jenkin). For  $\text{CH}_3\text{OCH}_2\text{O}$  an unusual reaction pathway, namely the elimination of an H atom, was identified in addition to the reaction with  $\text{O}_2$ .

Two groups (Kerr, Warneck) have provided reactivity data for oxy radicals using product distribution studies. From investigations on the oxidation of diethylether Kerr has derived relative reaction probabilities for the 1-ethoxyethoxy ( $\text{CH}_3\text{CH}(\text{O})\text{OC}_2\text{H}_5$ ) radical. It was found that under lower tropospheric conditions this radical mainly decomposes by  $\text{CH}_3$  elimination to produce ethylformate as the dominant product (84 %). The atmospheric fate of 3-hexoxy and 2-hexoxy radicals, which are generated in the OH initiated oxidation of n-hexane, has also been investigated. It was shown that for both radicals that 1,5-H atom shift isomerisations are the dominant reaction pathways. In contrast, for the 2-hexoxy radical a significant fraction also reacts by decomposition and/or interaction with  $\text{O}_2$ . Surprisingly, these findings for the different reactivities of the hexoxy radicals are in very good agreement with suggested empirical predictions. Product distribution studies aimed at providing kinetic and mechanistic information on the reactions of oxy radicals have also been performed (Warneck). As a consequence of the large fractions of cyclic compounds observed in the oxidation of cyclohexane the cyclo-hexoxy radical must be stable with respect to C-C bond cleavage. Warneck also studied the behaviour of the different pentoxy radicals (1-, 2- and 3-pentoxy) which are formed in the OH initiated oxidation of n-pentane. For the 1- and 2-pentoxy radicals H-atom shift isomerisation reactions forming hydroxypentyl radicals are clearly dominant, whereas this is not the case for the 3-pentoxy radical.

Despite the collection of a reasonably large number of rate coefficients for reactions of RO radicals under atmospheric conditions within LACTOZ, the available data base is still too small to derive general conclusions and/or structure-reactivity relationships for these radicals. Moreover, since the branching ratios for the different reaction channels of RO radicals are expected to be strongly

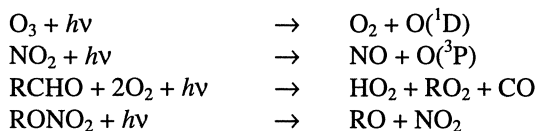
dependent on temperature, there is a remaining need for temperature dependent studies on the reactions of RO radicals.

## 2.6 Photochemical cross-sections and quantum yields

### 2.6.1 Introduction

Photochemical processes play a critical role in the chemistry of the atmosphere, since they control the daytime production of reactive free radicals, which initiate chemical transformations of many trace compounds. The photodissociation of atmospheric molecules occurs by absorption of solar ultraviolet (UV) and/or visible (VIS) radiation. The rate of photolysis is determined by the absorption cross-sections of the dissociated molecule and by the quantum yield for the various products channels at the absorbing wavelengths.

An important priority of the LACTOZ programme was placed on the high precision measurement of absorption cross-sections of molecules related to the production of tropospheric ozone. Emphasis was placed on  $\text{NO}_2$ ,  $\text{O}_3$  and on organic molecules formed in the photo-oxidation of VOCs which are responsible for generating odd hydrogen radicals (aldehydes and ketones) and the release of  $\text{NO}_x$  from reservoir molecules (PAN, organic nitrates). The species involved are generated in the following photolytic processes:



For selected compounds, quantum yields were determined as a function of wavelength and pressure, resembling the conditions of the tropospheric environment.

### 2.6.2 Ozone ( $\text{O}_3$ )

The absorption cross-sections for  $\text{O}_3$  have been measured with a resolution of 0.01 nm over the whole spectral range of the Hartley and Huggins bands (195–345 nm) at ambient temperature and at temperatures down to 218 K (Malicet). A negligible temperature effect (< 1 %) was observed at the maximum in the Hartley band near 250 nm. In contrast, a strong variation of the absorption cross-sections was observed in the Huggins band in the range 300 to 345 nm when the temperature was lowered from 295 to 218 K. This effect of temperature is shown in Fig. 6.

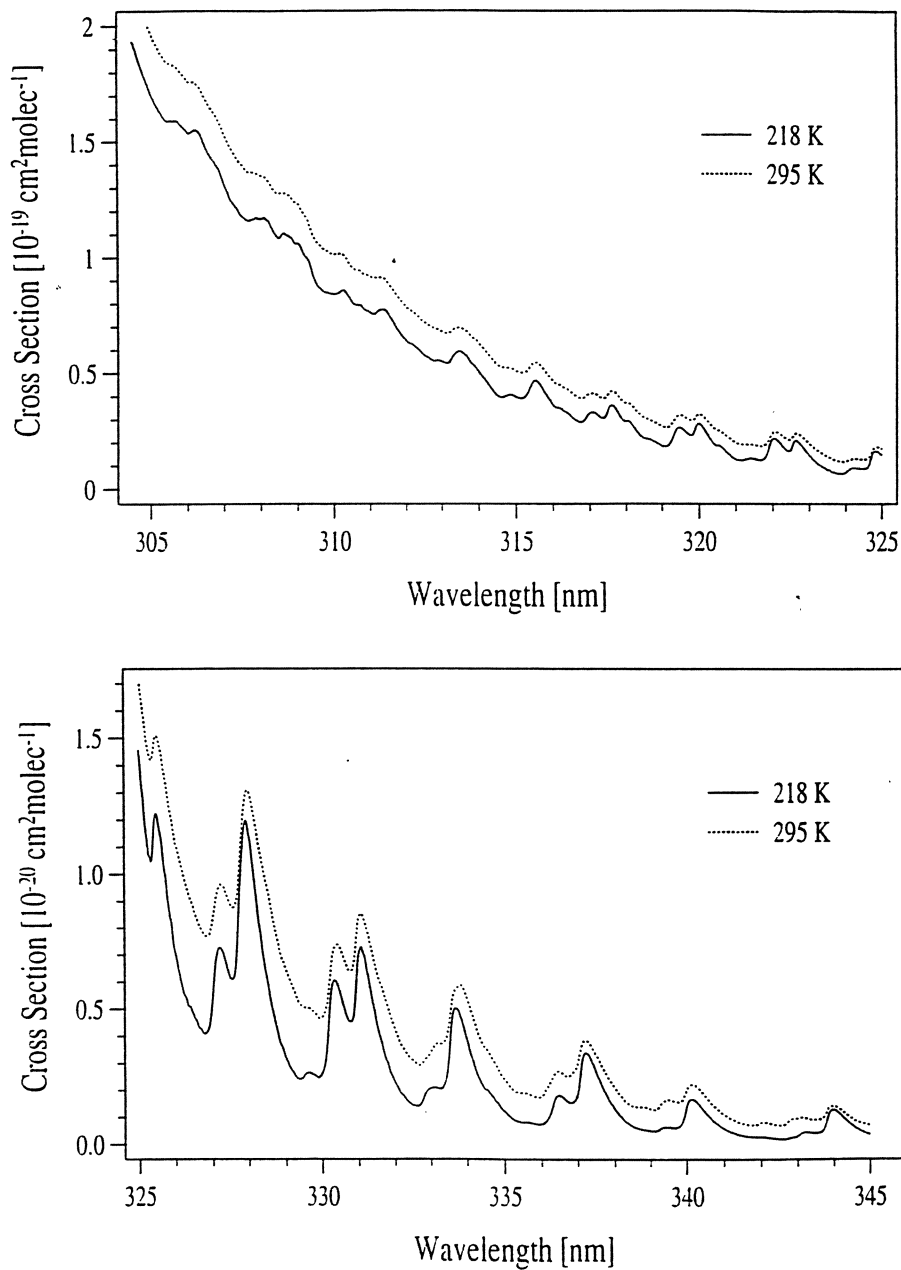
Absorption Cross Sections of O<sub>3</sub>

Fig. 6: O<sub>3</sub> Absorption cross-section between 305 and 345 nm at 295 and 218 K (Malicet).

### 2.6.3 Nitrogen dioxide (NO<sub>2</sub>)

New high resolution (0.01 nm) measurements of the absorption cross-sections of NO<sub>2</sub> were performed in the 300–500 nm range at 293, 240 and 220 K using a coolable 5m long path absorption cell (Malicet). Experiments were carried out at very low NO<sub>2</sub> pressures in order to reduce absorption contributions of the dimer, N<sub>2</sub>O<sub>4</sub>. A definite temperature effect (up to 6 %) was observed in the structured region of the spectrum.

### 2.6.4 Formaldehyde (HCHO)

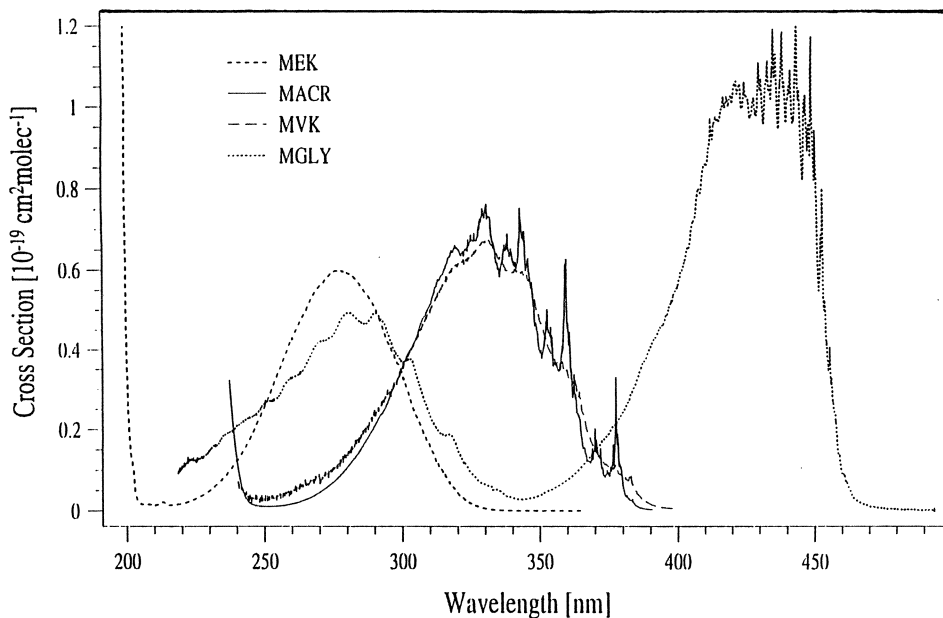
Absorption cross-sections of formaldehyde was obtained in the range 240–360 nm at 298 and 220 K by diode array spectroscopy with a spectral resolution of 0.022 nm (Moortgat). These values are consistently higher (up to 10 %) than those previously measured.

### 2.6.5 Carbonyl compounds

The absorption spectra and chemical degradation pathways of four selected carbonyl compounds, methylethylketone (MEK, CH<sub>3</sub>COC<sub>2</sub>H<sub>5</sub>), methylvinylketone (MVK, CH<sub>3</sub>COCH=CH<sub>2</sub>), methacrolein (MACR, CH<sub>2</sub>=C(CH<sub>3</sub>)CHO) and methylglyoxal (MGLY, CH<sub>3</sub>COCHO) have been investigated (Moortgat). MVK, MACR and MGLY are formed in the photo-oxidation of isoprene, initiated by the reaction of OH radicals and/or O<sub>3</sub>, whereas MEK arises as a product in the photo-oxidation of butane. The measured spectra show that absorption of MEK extends to 330 nm, whereas the absorptions of MVK and MACR extend to 400 nm, and to 540 nm for MGLY (Fig. 7).

Quantum yields for decomposition were estimated from product analysis studies, following broad-band photolysis performed using sun lamps (290–360 nm). All these compounds showed increasing product yields at lower pressures in the total pressure range 50 to 760 Torr. The overall quantum yields of the primary processes are summarised in Table 15. In a separate study, the photolysis of MGLY was investigated and the CO quantum yield measured as a function of wavelength over the same pressure range (Moortgat). The quantum yields increase significantly from 0.01 at 410 nm to unity at 280 nm and displayed a strong pressure dependence, decreasing with increasing pressure.





**Fig. 7:** UV visible absorption cross-sections of several carbonyl compounds.

MEK = methylethylketone, MACR = methacrolein, MVK = methylvinylketone and MGLY = methylglyoxal (Moortgat).

**Table 15:** Calculated photolysis frequencies (J-values) for 30° and 70° solar zenith angle of organic nitrates and carbonyl compounds in the lower troposphere, using the given quantum yields  $\phi$ .

Compound	$\phi$	J value <sup>a</sup> ( $10^{-6}$ ) s <sup>-1</sup>	
		30°	70°
<b>Nitrates (Becker)</b>			
peroxyacetylnitrate	1	0.491	0.134
$\alpha$ -nitrooxy acetone	1	26.7	10.4
1-nitrooxy-2-butanone	1	15.1	5.42
3-nitrooxy-2-butanone	1	38.7	15.2
1,2-propandiol dinitrate	1	7.56	3.29
1,2-butandiol dinitrate	1	10.4	4.72
2,3-butandiol dinitrate	1	7.69	3.31
3,4-dinitrooxy-1-butene	1	4.52	1.81
1,4-dinitrooxy-1-butene	1	4.54	1.41
<b>Carbonyl compounds (Moortgat)</b>			
methylethylketone	0.34	3.19	0.932
methylvinylketone	0.05	20.7	13.8
methacrolein	0.03	12.6	8.37
methylglyoxal	b	39.6	29.3

<sup>a</sup> Calculated photolysis frequencies using radiation transfer model of MPI, Mainz.

<sup>b</sup> f = wavelength dependent quantum yield function (Moortgat).

The photolytic lifetimes for average tropospheric conditions were calculated on the basis of the cited quantum yields: 4 days for MEK, 14 h for MEK, 22 h for MACR and 35 min for MGLY. These results indicate that photolysis processes in the troposphere dominate (in the case of MGLY) or are in competition with removal reactions initiated by OH radicals.

### 2.6.6 Dicarbonyl compounds

Three unsaturated 1,4-dicarbonyl compounds, (butenedial, 4-oxo-2-pentenal and 3-hexene-2,5-dione), formed in the OH initiated oxidation of aromatic compounds, were studied in both UV and VIS regions (Becker). The results indicate that both reaction with OH radicals and photolysis are major atmospheric sinks for these species. In contrast, doubly unsaturated 1,6-dicarbonyl compounds (e.g. 2,4-hexadienedial) were found to photolyse extremely rapidly in the UV range at 254 nm, but negligibly in the visible range. These results may suggest that the latter compounds are not photolysed in the troposphere (Becker).

### 2.6.7 Nitrates and dinitrates

UV spectra of various keto-nitrates ( $\text{RCOCH}(\text{ONO}_2)\text{R}$ ) and dinitrates ( $\text{RCH}(\text{ONO}_2)\text{CH}(\text{ONO}_2)\text{R}$ ) (Table 15) were measured in the range 240–340 nm using diode array spectroscopy with spectral resolution of 0.7 nm (Becker). In the region of tropospheric interest ( $> 290$  nm), the absorption cross-sections of keto-nitrates are approximately one order of magnitude higher than those of the dinitrates. The results indicate that, assuming a quantum yield of unity, photolysis of the saturated difunctional nitrates will generally be somewhat more important than loss via reaction with OH radicals in the troposphere. However, for unsaturated nitrates, loss via reaction with OH radicals will dominate over photolysis in the troposphere.

Photo-oxidation studies of the nitrates and dinitrates investigated revealed that  $\text{NO}_2$  and PAN are important products (Becker). Thus, the photolysis of keto-nitrates and dinitrates will result in the release of  $\text{NO}_2$  from these species. As a consequence, organic nitrates formed in the reactions of  $\text{NO}_3$  with alkenes during night-time will act only as temporary reservoirs for  $\text{NO}_x$ .

### 2.6.8 Other photolytic studies

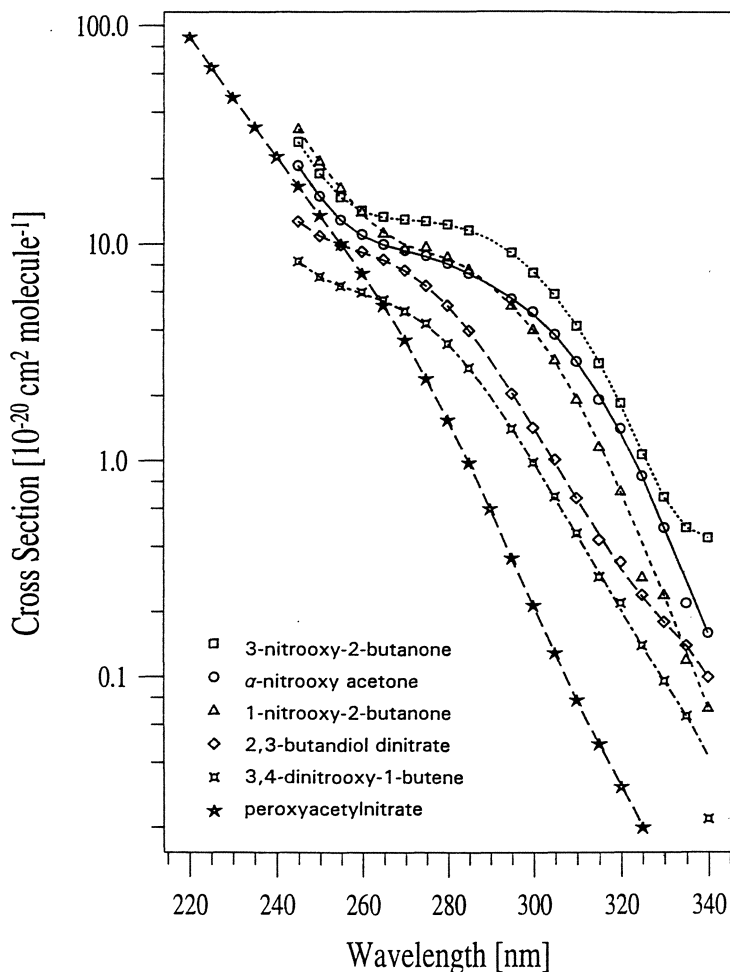
#### *Nitrate radical ( $\text{NO}_3$ )*

Photolysis of  $\text{NO}_3$  at 662 nm in  $\text{N}_2$  was performed in order to study the possible reaction of vibrationally excited  $\text{NO}_3(^2\text{A}')$  with  $\text{N}_2$  to yield  $\text{N}_2\text{O}$  and  $\text{NO}_2$  (Burrows). An upper limit for the quantum yield (0.006) for  $\text{N}_2\text{O}$  formation was obtained. Zellner has observed a value of 0.014 in a recent flash photolysis study of this reaction.

Wavelength-dependent quantum yield studies of the photolysis of  $\text{NO}_3$  were performed in the range 580–640 nm (Moortgat). The dominant photolysis channel was confirmed to be  $\text{NO}_2 + \text{O}(^3\text{P})$  at 298 K.

**Peroxyacetylnitrate, PAN ( $\text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$ )**

The UV absorption spectrum of PAN (Fig. 8) was determined in the range 235–330 nm using a diode array spectrometer (Becker). This study gave larger cross-sections for wavelengths  $> 300$  nm than previously reported and gives photolysis rate coefficients at 298 K which are higher by about a factor 3 than currently recommended [7].



**Fig. 8:** UV absorption cross-sections of several organic nitrates and dinitrates (Becker).

**Pyruvic Acid ( $\text{CH}_3\text{COCO}_2\text{H}$ )**

Photo-oxidation studies of pyruvic acid, a product found in the photo-oxidation of methylglyoxal, have been carried out (Warneck). Quantum yields of the primary reaction steps are given in Table 15.

### ***Alkyl nitrites (RONO)***

Excimer laser photolysis of ethyl nitrite was studied at 248 and 351 nm as a function of O<sub>2</sub> pressure (Zellner). In contrast to methyl nitrite, the photolysis produced not only C<sub>2</sub>H<sub>5</sub>O radicals but also methyl radicals with high yield. This study indicates that photolysis of higher alkyl nitrites is not an appropriate source for the laboratory generation of alkoxy radicals.

## **2.7 Oxidation of aromatic compounds**

### **2.7.1 Introduction**

Aromatic hydrocarbons (benzene, toluene, xylene isomers) are a major class of organic compounds associated with the urban environment and model calculations appear to indicate that they might contribute more than 30 % of the photo-oxidant formation in urban areas. However, the mechanisms currently used in models of tropospheric chemistry to describe the photo-oxidation of aromatic compounds are highly speculative. Studies within LACTOZ have involved both direct and smog chamber investigations and have provided data on many different aspects of the mechanisms for oxidation of aromatic compounds related to tropospheric ozone and oxidant formation. Most of this work was carried out by four of the LACTOZ groups (Becker, Devolder, Kerr, Zetzsch).

### **2.7.2 Results**

The kinetics of the primary oxidation steps of the OH initiated oxidation of the alkylated benzenes, i) abstraction of an H atom from an alkyl side group, and ii) addition to the ring, as outlined in Fig. 9, are reasonably well established (Becker, Devolder, Kerr, Zetzsch). Branching ratios for abstraction/addition have been obtained for toluene and the xylene isomers, however, data for higher alkylated benzenes are poor. Reversible addition to the aromatic ring is the dominant pathway and accounts for approximately 90 % of the reaction.

Zetzsch has measured reaction rate constants for the reactions of the aromatic OH adduct with O<sub>2</sub>, NO<sub>2</sub> and NO (Table 16) (units: cm<sup>3</sup>molecule<sup>-1</sup> s<sup>-1</sup>, at 298 K):

#### **toluene-OH adduct**

$$k(\text{O}_2) = 5.5 \times 10^{-16}$$

$$k(\text{NO}_2) = 3.6 \times 10^{-11}$$

$$k(\text{NO}) < 3 \times 10^{-14}$$

#### **p-xylene-OH adduct**

$$k(\text{O}_2) = 8.0 \times 10^{-16}$$

$$k(\text{NO}_2) = 3.2 \times 10^{-11}$$

$$k(\text{NO}) < 10^{-14}$$

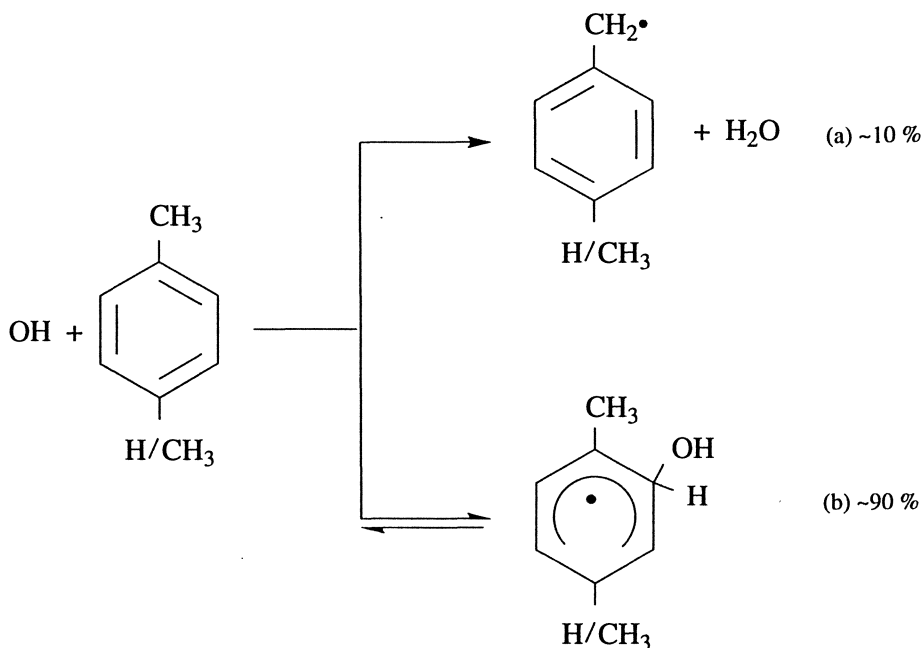


Fig. 9: Primary OH reaction with toluene and p-xylene.

These data show that under atmospheric conditions the adducts will react predominantly with  $\text{O}_2$  to form hydroxycyclohexadienylperoxy radicals. The subsequent reactions of these peroxy radicals leading to ring-opening are still unclear. Several possible reaction pathways which result in formation of dicarbonyl and unsaturated dicarbonyl compounds are outlined in Fig. 10. Experiments on radical cycling (Zetzsch) indicate that the reaction of the aromatic-OH adducts with  $\text{O}_2$  produce  $\text{HO}_2$  radicals with high yield on a short timescale. The mechanism leading to this so-called "prompt  $\text{HO}_2$ " formation in the aromatic compound oxidation systems is presently unclear.

Careful attempts to detect hydroperoxides and peroxy nitrates, expected products of the reactions of the hydroxycyclohexadienylperoxy radicals with  $\text{HO}_2$  and  $\text{NO}_2$ , respectively, were unsuccessful. This has been taken, in conjunction with work on the effect of  $\text{NO}_x$  on the kinetics and products of the aromatic compound oxidation, as an indication that such peroxy radicals are very short-lived. It has been suggested, therefore, that the peroxy radicals are not able to oxidise  $\text{NO}$  as is the case for alkane and alkene atmospheric oxidation.

**Table 16:** Rate constants for the reactions of radicals derived from aromatic VOCs with O<sub>2</sub>, NO and NO<sub>2</sub>.

Radical	$k_{O_2} \times 10^{16}$ (cm <sup>3</sup> s <sup>-1</sup> )	$k_{NO} \times 10^{14}$ (cm <sup>3</sup> s <sup>-1</sup> )	$k_{NO_2} \times 10^{11}$ (cm <sup>3</sup> s <sup>-1</sup> )	Reference *
benzene-OH				
(300 mbar N <sub>2</sub> , 298 K)	2.1	< 1	2.5	Zetzsch (90)
(133 mbar Ar, 299 K)	1.6			Zetzsch (91)
( " , 314 K)	2.1			Zetzsch (91)
( " , 330 K)	3.0	< 3	2.5	Zetzsch (92)
( " , 354 K)	3.7			Zetzsch (91)
toluene-OH				
(1.3 mbar He, 353 K)			4	Devolder (89)
(130 mbar N <sub>2</sub> , 298 K)	5	< 3	3.7	Zetzsch (90)
(133 mbar Ar, 330 K)	5.5	< 3	3.6	Zetzsch (92)
phenol-OH				
(130 mbar Ar, 298 K)	250	< 7	3.4	Zetzsch (90)
(130 mbar Ar, 330 K)	300	< 7	3.6	Zetzsch (92)
benzyl				
(1.3 mbar He, 297 K)	$0.72 \times 10^4$	0.063	6.0	Devolder (91)
<i>o</i> -methylbenzyl				
(1.3 mbar He, 297 K)	$1 \times 10^4$		5	Devolder (90)
"	$0.93 \times 10^4$	0.105	5.7	Devolder (91)
<i>m</i> -methylbenzyl				
(1.3 mbar He, 297 K)	$1.1 \times 10^4$		5	Devolder (90)
"	$1.1 \times 10^4$	0.127	5.6	Devolder (91)
<i>p</i> -xylene-OH				
(130 mbar Ar, 330 K)	8.0	< 10	3.2	Zetzsch (92)
<i>m</i> -cresol-OH				
(130 mbar Ar, 330 K)	800	< 3	4.0	Zetzsch (92)
aniline-OH				
(130 mbar Ar, 330 K)	10	< 10	5.0	Zetzsch (92)
naphthalene-OH				
(130 mbar Ar, 400 K)	1.1	-	-	Zetzsch (93)

\* These references are to EUROTRAC Annual Reports. The year in parentheses is the year of the report not the publishing year.

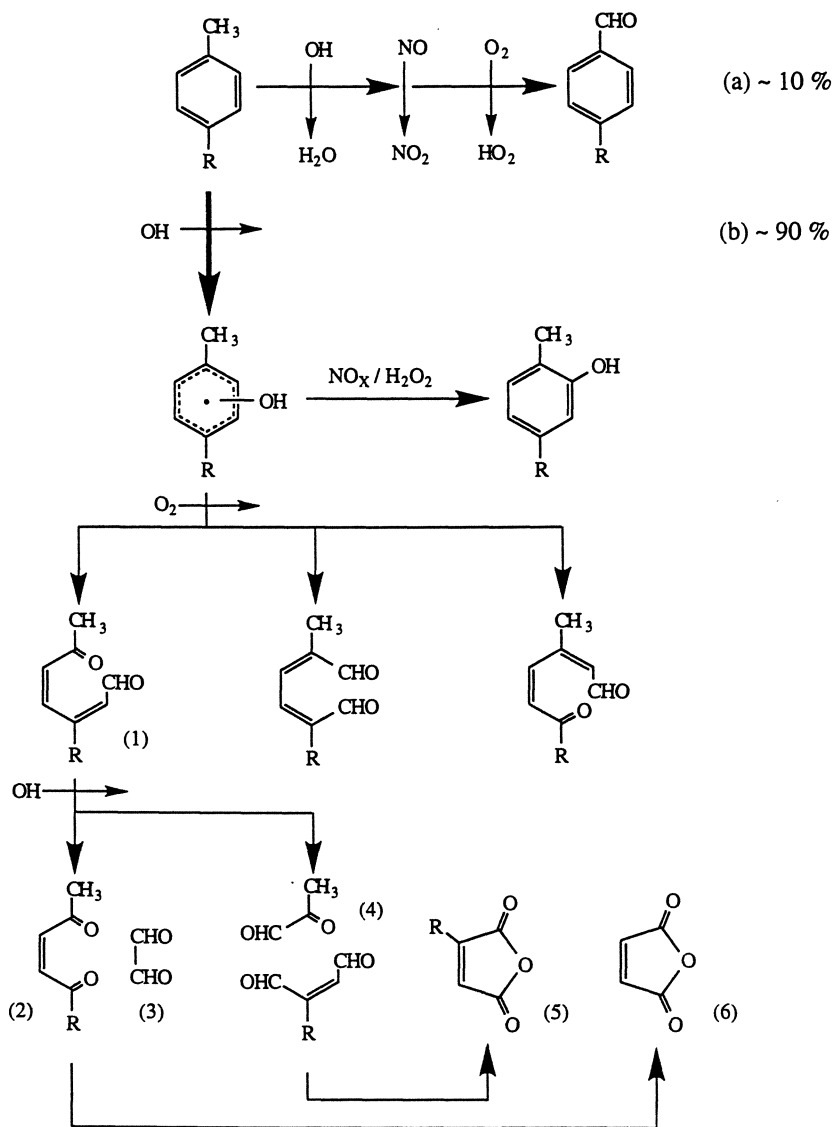
Yields have been determined for hydroperoxide formation from the alkyl side-groups ethylbenzene-2-hydroperoxide, 17 % C from OH + ethylbenzene; benzylhydroperoxide, 5 % C from OH + toluene (Bachmann). Low yields of methylhydroperoxide are reported for both systems, and ethylhydroperoxide was also observed in the reaction of OH with ethylbenzene.

Warneck has determined the product yields for the reaction OH + toluene under NO<sub>x</sub> free conditions in air at atmospheric pressure and with very high partial pressures of toluene and H<sub>2</sub>O<sub>2</sub>, both on the order of 1000 ppm. Hydrogen peroxide was used as the photolytic source of OH radicals and the toluene concentration was kept high in order to minimise secondary OH reactions. High yields of cresols were observed which could be best explained by a mechanism involving H atom abstraction from the OH adduct by O<sub>2</sub>. A similar study also gave high yields of cresols (Bachmann). Becker tried to confirm these findings under conditions more

similar to those typical of the troposphere. It was also found that, at high aromatic compound concentrations and high levels of  $\text{H}_2\text{O}_2$ , cresol formation was important. Addition of  $\text{NO}_x$  to the system increased the cresol formation. The cresol yield was measured relative to that of benzaldehyde, which is a product of the abstraction channel. However, at low concentration cresol yields were minimal. From these results it has been concluded that under atmospheric conditions cresols in the case of toluene and alkylated phenols in the case of the xylene isomers will be only very minor products. This conclusion is further supported by the absence of quinone-type products in aromatic compound product studies; quinones were shown to be formed in high yields in the reactions of OH with phenolic-type compounds. These conclusions, however, do not necessarily include benzene which is more difficult to study and in which the oxidation mechanism may be different to that of the alkylated benzenes. Results from studies of Cl atom reactions with benzene indicate a 50 % yield for phenol formation from the reaction of  $\text{O}_2$  with the benzene-OH adduct (Zellner).

Becker has performed detailed product studies on the OH reaction with toluene and *p*-xylene. At present, product formation can best be explained by the mechanism shown in Fig. 10 where muconaldehydes (hexa-2,4-diene-1,6-dial) are proposed as direct products of the reaction of the aromatic-OH adduct with  $\text{O}_2$ . Several of these muconaldehydes have been synthesised and their reactions with OH radicals investigated (Becker). These reactions result in the formation of unsaturated 1,4-dicarbonyl compounds, glyoxal, methylglyoxal and maleic anhydride, which have also been observed in the reaction of OH with toluene and *p*-xylene. It has been demonstrated that the unsaturated 1,4-dicarbonyl species react very rapidly with OH and photolyse, yielding products which possibly accelerate  $\text{O}_3$  formation in smog chamber type studies. Many of the aromatic oxidation products especially the unsaturated 1,6-dicarbonyl species are known either to be toxic or are potentially toxic with both carcinogenic and mutagenic properties [8].

Becker has carried out smog-chamber type experiments on the photolysis of cyclohexane/ $\text{NO}_x$  mixtures in air which show that addition of toluene to the system produces  $\text{O}_3$  much faster than the toluene-free system. However, the maximum value of  $\text{O}_3$  reached in both cases remains approximately the same and  $\text{NO}_x$  is observed to be scavenged in the toluene system. At present the mechanism by which  $\text{NO}_x$  is scavenged in photoreactors is not clear. Formation of PAN and nitro aromatic compounds are observed, however, their yields are very low. The unidentified scavenging process could possibly be an artefact which results in a progressive slowing down of the  $\text{O}_3$  formation rate in smog chamber experiments. The carbon balance found in aromatic compound product studies is presently only approximately 50 % C. Persistent product spectra, observed during the oxidation of toluene and *p*-xylene, can very probably be attributed to 3,3-dihydroxy hexane-2,4,5-trione in the case of *p*-xylene and in the case of toluene to a similar hydrated vicinal polyketone. Based on an estimated IR absorption cross-section for the carbonyl band of these compounds, it has been shown that these compounds could account for another 30 % C in the product studies of both aromatic compounds.



(a) Abstraction Channel (b) OH-Addition-Channel

(1) 6-Oxo-2,4-heptadienal (R=H), 3-Methyl-6-oxo-2,4-heptadienal (R=CH<sub>3</sub>)

(2) 4-Oxo-2-pentenal (R=H), 3-Hexene-2,5-dione (R=CH<sub>3</sub>)

(3) Glyoxal (4) Methylglyoxal

(5) Methyl maleic anhydride (R=CH<sub>3</sub>), Maleic anhydride (R=H) = (6)

Fig. 10: Mechanism of atmospheric toluene (R=H) and p-xylene (R=CH<sub>3</sub>) oxidation.



With the exception of phenolic-type compounds the reactions of  $\text{NO}_3$  radicals with alkylated benzenes will be unimportant under atmospheric conditions. A product study has shown that aromatic aldehydes and aromatic nitrates are the main products of these reactions (Hjorth).

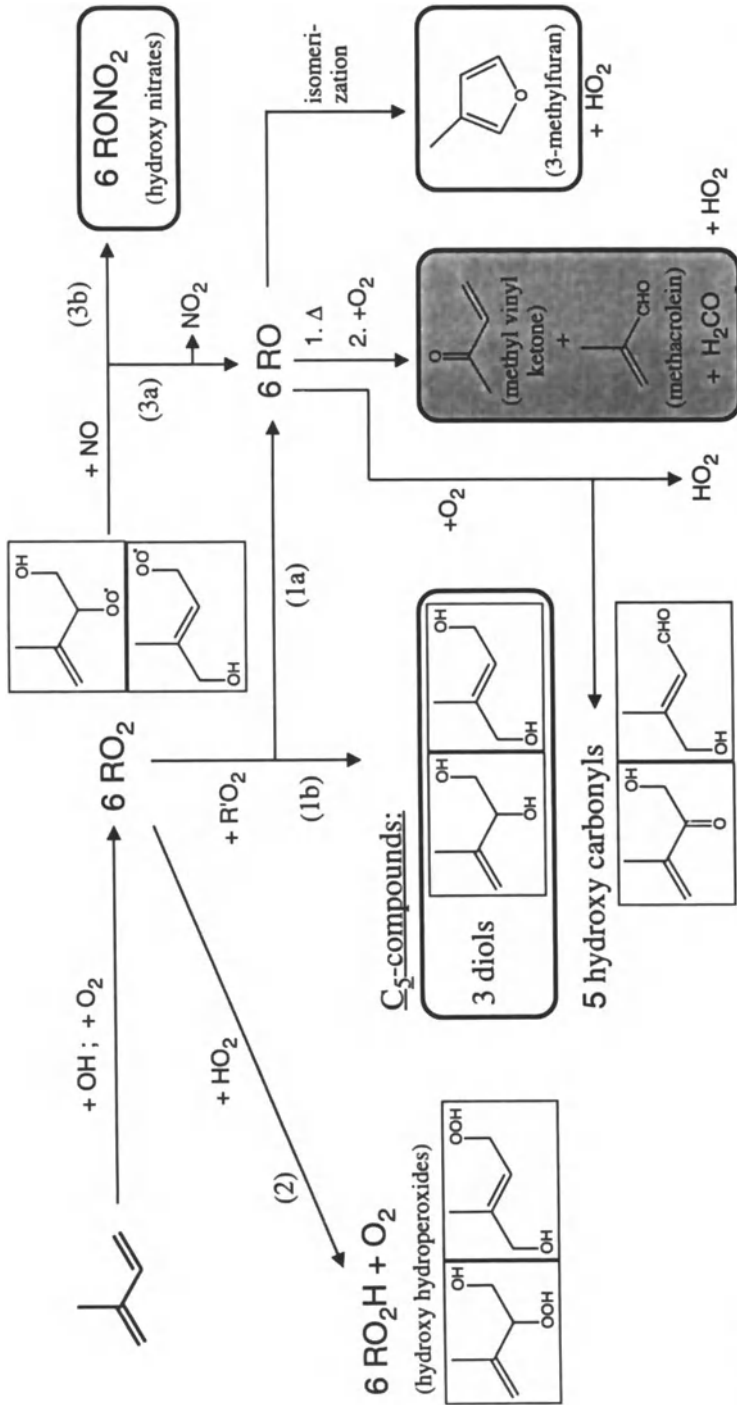
## 2.8 Oxidation of biogenic compounds

### 2.8.1 Introduction

Terpenes are emitted from forests and other vegetation in Europe, the importance of each individual compound depending on tree type and location. Isoprene is the main hydrocarbon emission of certain trees. Many biogenic VOCs show a significant diurnal variation because emission strengths are strongly dependent on temperature, humidity, *etc.* We collect here some general comments based on LACTOZ results about the atmospheric oxidation of these species. A more detailed discussion, accompanied by identification of the laboratories where the research was conducted, can be found in earlier sections dealing with the specific chemistry (*e.g.* reaction with OH,  $\text{NO}_3$ , *etc.*). Almost all mechanistic information that is available refers to isoprene. Isoprene is, of course, the building block of the terpenes, although its behaviour may well differ from that of the terpenes because of the location of the two double bonds and its higher volatility.

### 2.8.2 Oxidation mechanism of isoprene

Isoprene and the terpenes may be attacked by OH,  $\text{NO}_3$  and  $\text{O}_3$ . The rate coefficients at room temperature for reaction with isoprene are of the order of  $10^{-10}$ ,  $10^{-12}$  and  $10^{-17}$   $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. In the case of attack by OH, and in the presence of oxygen, a peroxy-hydroxy radical is formed; up to six isomers may be produced. Product studies indicate that the initial addition is to one of the terminal carbon atoms. The peroxy-hydroxy radical may then either react with NO or with other  $\text{RO}_2$  radicals (including  $\text{HO}_2$ ) to form a variety of products, as indicated in Fig. 11. Under conditions where the peroxy-hydroxy radical reacts exclusively with NO, approximately 50 % of the carbon balance is accounted for by three main products: methacrolein, methyl vinyl ketone and formaldehyde. Other carbonyl products and hydroxy-nitrates are thought to make up the carbon balance although there is presently no clear indication of the exact identity of these compounds or their yields.

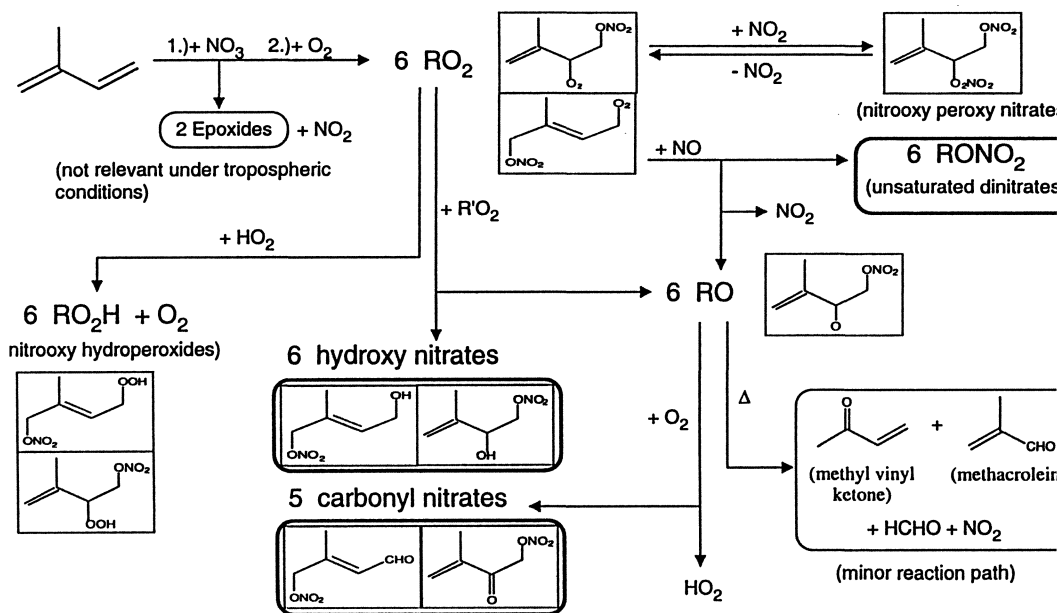


**Legend:**

The numbers written in front of the products give the number of different compounds which can be expected (cis-/trans-isomerism in the case of 1,4-substituted compounds is neglected). The meaning of the different frames is:

- example      products identified in laboratory studies      products identified in laboratory studies and field measurements

**Fig. 11:** Mechanism for the OH initiated oxidation of isoprene (simplified scheme).

**Legend:**

The numbers written in front of the products give the number of different compounds which can be expected (cis-/trans-isomerism in the case of 1,4 substituted compounds is neglected). Dashed frames show example structures, compounds in solid frames have been identified in laboratory studies.

**Fig. 12:** Mechanism for the NO<sub>3</sub> initiated oxidation of isoprene (simplified scheme).

Attack of NO<sub>3</sub> on isoprene apparently proceeds in much the same manner, but there is considerable controversy about the precise reaction pathway because of the variety of peroxy radicals that can be formed. The products, such as 4-nitroxy-2-methyl-1-butan-3-one and methacrolein, are consistent with the initial addition of NO<sub>3</sub> to the terminal carbon atoms to form nitro-oxy-peroxy radicals in the presence of oxygen; apparently the NO<sub>3</sub> adds preferentially to position 1 (Fig. 12). 3-methyl-4-nitroxy-2-butanal was found as the main product in these experiments. The nitro-oxy-peroxy radicals can react with NO<sub>2</sub>, in the presence of O<sub>2</sub>, to yield thermally unstable nitroxy-peroxynitrate compounds. One particularly important feature of the addition of NO<sub>3</sub> is the extent to which the initial adduct, which might eliminate NO<sub>2</sub> to form an epoxide, is actually converted to the nitro-oxy-peroxy radicals in the atmosphere.



Reaction of isoprene with ozone follows a rather different course. Ozone adds across one or other of the double bonds, and the ozonide may then fragment in several possible ways, to form methacrolein, methylvinylketone, epoxides and Criegee radicals as indicated in Fig. 13. Methacrolein, methylvinylketone and formaldehyde are the main carbonyl compounds that have been identified. The ratio of methacrolein to methylvinylketone yields is considerably higher than that found for the reaction of OH with isoprene. The fates of the Criegee radicals, and even if they are formed at all, are the subject of much disagreement, but the matter is of some importance, since these radicals might provide a source of OH at night. The Criegee mechanism cannot account for all the observed products found in the oxidation studies. Note that, necessarily, the laboratory studies on ozonolysis are carried out in the absence of NO<sub>x</sub>, the presence of which may or may not alter relative and absolute product yields.

This summary will indicate that, even for the simplest of the molecules, isoprene, there remain uncertainties about the degradation pathways. One problem concerns poor carbon balance in almost all of the studies of attack by OH, NO<sub>3</sub> and O<sub>3</sub>. Another concerns the effect of humidity on product distributions. Yet a further question hangs over the significance of the ozonolysis reactions as a source of OH radicals. Almost nothing is known about the mechanisms and specific pathways of reactions of the terpenes, and there are substantial experimental obstacles to investigation of these systems. Much further work is clearly warranted, in order to determine whether ozone is only lost in its reaction with biogenic VOCs or whether the reactions might constitute a source of atmospheric ozone when NO<sub>x</sub> is present.

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## Chapter 3

### Individual Reports from LACTOZ Contributors

#### 3.1 Laboratory Studies of the Atmospheric Decay of Hydrocarbons in the NO<sub>x</sub> Free Atmosphere

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##### Summary

Analysis methods for the determination of hydroperoxides and hydroxyhydroperoxides in reaction mixtures were developed and applied to photolysis mixtures of aliphatic and aromatic hydrocarbons, carbonyls, alcohols and halogenated hydrocarbons. HPLC with chemiluminescence, electrochemical and fluorescence detection was used for selective detection of hydroperoxides and hydroxyhydroperoxides and gas chromatography with mass spectrometric and flame ionisation detection for the analysis of all reaction products.

Laboratory experiments of the oxidation of hydrocarbons under NO<sub>x</sub> free conditions were made in 2 L and 10 L deactivated glass vessels by the photolysis of H<sub>2</sub>O<sub>2</sub>.

Hydroperoxides were found as reaction products of alkanes, alkylsubstituted aromatic hydrocarbons, ketones, chlorinated and iodated hydrocarbons. They were major products in the oxidation of alkanes.

### **Aims of the research**

The atmospheric decay of hydrocarbons is studied intensively only for methane. The aim of our research was to develop analytical methods that could help to study the decay of hydrocarbons with longer chain. The hydroperoxides were of special interest.

Separation and detection methods for the specific and sensitive determination of hydroperoxides in laboratory experiments and in rain water must be developed. In addition, methods for the analysis of the whole product distribution were necessary. These methods should have been applied to the analysis of different reaction mixtures.

### **Principal findings during the project**

During the project, we developed HPLC and GC methods for the determination of hydroperoxides.

#### ***HPLC***

The separation of hydroperoxides with HPLC was developed with commercially available hydroperoxides and a post column derivatisation with luminol on an RP-2 phase.

Due to the lack of detection methods for organic hydroperoxides, we developed three different detection methods for HPLC analysis.

#### **1. Post-column reaction with luminol**

The detection of hydroperoxides in this method is based on chemiluminescence. The system was optimised using *t*-butylhydroperoxide, *t*-amylhydroperoxide and cumenehydroperoxide. Cytochrome C was used as a catalyst, the eluent was 0.25 M borate buffer. Detection limits were 5 nmol of active oxygen, which was only sufficient for laboratory experiments.

#### **2. Polarographic detection**

A polarographic detector was used with the method of Funk [1]. For electrochemical detection it is necessary to use an electrolyte as eluent. A new separation method was developed for this reason. The reduction of O<sub>2</sub>, which could not be completely excluded, at the detector potential of -1400 mV led to distortion of the chromatogram. Because of this problem, the detection limit was 1 ppm. In the later research, this problem could be solved partially with a method which allowed the degassing of the sample. Detection limits were improved by a factor of 2.

#### **3. Fluorometric detection**

In general, fluorometric detection achieves very good detection limits. Therefore we searched a method to derivatize hydroperoxides in a post column

reaction to fluorescent products. Kok *et. al.* [2, 3] used a fluorometric system to measure  $H_2O_2$  and the total hydroperoxide content. The reaction of hydroperoxides with p-hydroxyphenylacetic acid in the presence of a catalyst (peroxidase) leads to a fluorescent dimer of the acid.

Peroxidase is not useful for all hydroperoxides. Better results were achieved with microperoxidase. Detection limits of 0.2  $\mu\text{mol/L}$  were achieved.

### ***Solid-phase enrichment***

A method for the enrichment of hydroperoxides on solid phases has been developed. The enrichment is performed on a small volume of RP-18 material, the solid phase is dried and the sample eluted with acetone. An enrichment factor of 50 can be reached.

### ***Detection of 1-hydroxyhydroperoxides with chemiluminescence***

The exposed method is based on the detection of hydrogen peroxide with the peroxyoxalate chemiluminescence method [4].

In the first step the 1-hydroxy hydroperoxides are separated by reversed-phase HPLC in acidic solution as described by Hellpointner [5]. After the separation, pH value as well as temperature are raised to enforce the decomposition of the labile 1-hydroxy hydroperoxides to hydrogen peroxide and the corresponding aldehyde. After mixing of eluent and reagent stream, the solution passes a flow cell placed in front of the window of a photomultiplier tube where the emitted light of the chemiluminescence reaction is registered. The main difficulties arise from high contents of hydrogen peroxide (*e.g.* rain samples).

Because of the high sensitivity of the chemiluminescence, limits of detection reached presently are 0.06  $\mu\text{mol/L}$  (6 pmol absolute 0.4 ng HMHP).

In several rain samples 1-hydroxymethyl, 1-hydroxyethyl and 1-hydroxypropyl hydroperoxides could be determined.

### ***Analysis of peroxy compounds in photolysis mixtures of hydrocarbons***

A number of hydrocarbons were photolysed in a reaction vessel according to the system described by Prof. Warneck, MPI Mainz. Measurements were made with fluorometric and polarographic detection. The photolysis experiment were reproducible with a standard deviation of 3–6 %. Several hydroperoxides could be identified by "cross"-identifications by comparing the retention times of different photolysed hydrocarbons, aldehydes, ketones and alcohol's with the unknown peaks.

### ***Determination of hydroperoxides by GC/MS and GC/FID***

In our recent investigations, a low temperature GC/MS system (HP 5890/5970) with a vapour sample inlet system is applied to the determination of all oxidation



products > C<sub>2</sub> including the alkylhydroperoxides. This system is described in the annual report 1993. We analysed photolysis mixtures of alkanes, aromatic hydrocarbons, alkenes, ketones and chlorinated hydrocarbons. Quantitations were made in the full scan mode and later with a flame ionisation detector. Carbon balances were made for alkanes and aromatics. They were 93–102 % (20 min photolysis) and 45–73 % (90 min photolysis), respectively.

### Alkanes

We conducted photolysis experiments with methane, ethane, propane, *n*- and *i*-butane, *n*- and *i*-pentane and *n*-hexane. Hydroperoxides were the main products in all experiments. Other products were carbonyls, alcohols and organic acids. Peroxides were found only when hydrocarbons are present in high excess in the reaction mixture. In the photolysis of hydrocarbons > C<sub>4</sub> no peroxides were found. We discuss the experiment with *n*-butane as an example.

Quantitations were made based on the "effective carbon number" concept of Sternberg *et al.* [6] with a FID. Response factors of the hydroperoxides were calculated as the corresponding alcohol's. Carbon balances are good, indicating that this increment method is suitable also for hydroperoxides.

The decrease in recovery with increasing reaction time is due to the forming of low boiling products, *i.e.* methanol, formaldehyde, CO and CO<sub>2</sub> which cannot be analysed with our analytical system.

The distribution of products of the attack on primary and secondary H-atoms is in good agreement with calculations of Atkinson [7].

**Table 1:** Reaction products in the photo-oxidation of butane. 54 ppm (= 24.07 μmol) *n*-butane 2.5 + 60 ppm (= 26.60 μmol) H<sub>2</sub>O<sub>2</sub>. We identified additionally: ethanol, propanal, methylhydroperoxide, formic acid and acetic acid.

	Reaction time 20 min	Reaction time 53 min
<i>n</i> -Butane	1.13 μmol*	2.57 μmol*
Butanal	0.03 μmol	0.05 μmol
Butanone	0.11 μmol	0.48 μmol
2-Butanol	0.03 μmol	0.09 μmol
Ethylhydroperoxide	–	0.07 μmol
1-Butanol	–	0.01 μmol
2-Hydroperoxy butane	0.89 μmol	1.67 μmol
1-Hydroperoxy butane	0.10 μmol	0.16 μmol
Reacted carbon (%)	102	98

\* Loss due to oxidation.

**Table 2:** Percentage distribution of the attack on primary and secondary H of *n*-butane with OH radicals, experimental and calculated.

attack on	calculated	measured (20 min photolysis)
primary H	14 %	12 %
secondary H	86 %	88 %

### ***Influence of the composition of the reaction mixture on the product distribution***

At the beginning of our research we made experiments to determine the influence of the composition of the reaction mixture to the product distribution. First we kept the concentration of  $H_2O_2$  constant and varied the concentration of *n*-butane at constant reaction times. As expected, the whole product concentration raised with increasing concentration of *n*-butane. The relative composition changes, the hydroperoxides are decreasing while the other oxidation products are increasing with increasing concentration of *n*-butane. Similar results were achieved when the concentration of *n*-butane is kept constant and the concentration of  $H_2O_2$  is varied. With increasing the  $H_2O_2$  / *n*-butane ratio the amount of hydroperoxides increases because the reaction of the hydroperoxy radical with  $\cdot OOH$  predominates the self reaction.

We also changed the concentration of the reaction mixture without changing the  $H_2O_2$  / *n*-butane ratio. No change in product distribution could be found.

### ***Alkenes***

No hydroperoxides could be found in photolysis experiments with 1-butene. Some substances in the experiments with 1-pentene and 1-hexene could not be identified. Main products were ketones.

### ***Ketones***

We photolysed 2 and 3-pentanone. We found ethylhydroperoxide in the experiment with 3-pentanone and methylhydroperoxide and propylhydroperoxide in the oxidation of 2-pentanone as product of the Norrish reaction. Other products were diketones and organic acids. Some main products at late retention time could not be identified. Tests with HPLC/fluorescence detection indicate that they are hydroperoxides.

### ***Aromatic hydrocarbons***

The decay of benzene, toluene, ethylbenzene and the xylenes was investigated. Hydro-peroxides were found in the experiments with alkyl substituted aromatics. Main products were organic acids. These experiments were described in the annual report 1993.

### ***Chlorinated hydrocarbons***

No hydroperoxide was found in the case of methylenchloride. Main product was phosgene. Chloracetylchloride was the main product in the photo-oxidation of 1,2-dichlorethane. 1,2-dichlorethylhydroperoxide could be identified with mass spectrometry and HPLC / fluorescence. Other products were chloracetaldehyde and chloracetic acid.

### ***Achievements during the project***

During the project we developed analytical methods for the selective and sensitive determination of hydroperoxides and hydroxyhydroperoxides. They can be used as analytical tools for laboratory experiments and partially for field measurements. A method for GC/MS and CG/FID allowed the analysis of all reaction products.

### **Acknowledgement**

We are grateful to the BMBF for financial support.

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## 3.2 OH Initiated Oxidation of VOC under Variable NO<sub>x</sub> Conditions

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### Summary

During the reporting period the following investigations have been carried out:

- Determination of rate coefficients for the reactions of NO<sub>3</sub> radicals with unsaturated hydrocarbons
- Determination of alkene yields from the reaction of OH with alkanes
- Investigation of the thermal stability of peroxy nitrates
- Determination of branching ratios for RO<sub>2</sub> + NO reactions: yields of alkyl nitrates
- Atmospheric chemistry of ketonitrates and dinitrates: OH reaction kinetics and UV absorption spectra
- Mechanistic study of the ozonolysis of ethene
- Investigation of the oxidation of isoprene, initiated by reaction with OH and with O<sub>3</sub>
- Kinetic and mechanistic studies of the reaction of simple alkylated aromatics with OH
- Investigation of the reactions of unsaturated carbonyl compounds as products of the oxidation of aromatics under atmospheric conditions

### Experimental

As described in previous LACTOZ reports the experiments were carried out in glass reaction chambers with volumes ranging from 37 to 1080 L at a total pressure of 1000 mbar synthetic air and at temperatures between 243 and 323 K. Most of the analyses of reactants and products for the different types of experiments were performed using long-path *in situ* Fourier transform IR spectroscopy (FTIR), however, other techniques such as gas chromatography, HPLC and TDL spectroscopy were also applied. UV absorption spectra were measured using a diode array spectrometer.

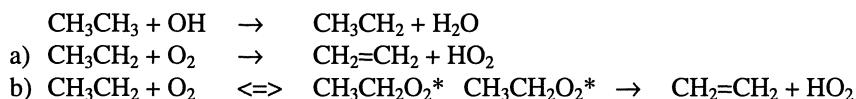
## Principal results

### *Reaction of NO<sub>3</sub> radicals with unsaturated hydrocarbons*

Rate coefficients have been determined for the reactions of NO<sub>3</sub> with a number of aliphatic mono- and dialkenes and monoterpenes with a relative kinetic method. The measured rate coefficients are listed in Chapter 2, Table 2. The products of the reactions were also investigated using *in situ* FTIR. The formation of thermally unstable nitro-oxy-peroxynitrate-type compounds was observed. The final products included aldehydes/ketones, nitro-oxy-aldehydes and -ketones and dinitrate compounds.

### *Alkene formation in the OH initiated oxidation of saturated hydrocarbons*

The primary step in the OH initiated atmospheric oxidation of saturated hydrocarbons is abstraction of an H atom to form an alkyl radical and water. The predominant fate of the alkyl radical is addition of oxygen to form a peroxy radical. However, it is known for ethyl radicals that a pathway exists which leads to formation of ethene and HO<sub>2</sub> radicals. Two mechanisms have been discussed in the literature, a) a direct abstraction of an H atom by O<sub>2</sub> and b) a Lindemann mechanism involving an excited alkylperoxy radical:



The formation yields for alkene production in the OH initiated oxidation of a number of saturated hydrocarbons (alkanes) have been determined. The 254 nm photolysis of H<sub>2</sub>O<sub>2</sub> was employed as the OH source and GC-MS for detection of the products. The following alkanes were investigated: *n*-butane, *n*-pentane, 2,3-dimethylbutane and cyclopentane.

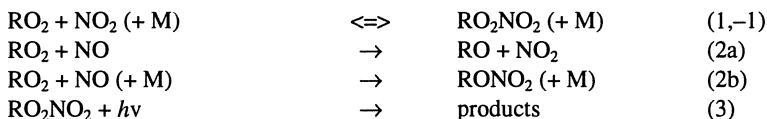
The alkene yields measured in the experiments are shown in Table 1. The yields have been corrected for loss due to reaction with OH radicals. For all the alkanes investigated formation of alkenes was observed, but the yields were always well below 1 %. The results show that the reaction of alkyl radicals with O<sub>2</sub> to form alkenes is not a significant process under normal tropospheric conditions.

**Table 1:** Formation yield for alkene production in the OH initiated oxidation of saturated hydrocarbons.

Saturated hydrocarbon	Alkene formation yield [%]
<i>n</i> -Butane	1-butene (0.18 ± 0.02) <i>trans</i> -butene (0.15 ± 0.03)
<i>n</i> -Pentane	1-pentene (0.014 ± 0.003) <i>cis</i> - and <i>trans</i> -2-pentene (0.053 ± 0.012)
2,3-Dimethylbutane	2,3-dimethyl-1-butene (0.62 ± 0.18) 2,3-dimethyl-2-butene (0.16 ± 0.03)
Cyclopentane	cyclopentene (0.024 ± 0.003)

### *Thermal stability of peroxy nitrates*

Peroxy nitrates are formed in the troposphere by the recombination of  $\text{RO}_2$  radicals and  $\text{NO}_2$ . The relevant chemical reactions which determine the importance of peroxy nitrates as temporary reservoirs of  $\text{NO}_x$  are the following:



Within the framework of LACTOZ, rate coefficients  $k_{-1}$  were systematically measured as a function of temperature and total pressure for a variety of different groups R, see Chapter 2, Table 11. In addition,  $k_{2a}$  was estimated for  $\text{R} = \text{HOC}_2\text{H}_4$ , the ratios  $k_1/(k_{2a}+k_{2b})$  were measured for several R, and UV absorption cross sections were determined for the most abundant peroxy nitrate, PAN, see Chapter 2, Fig. 7. The following conclusions can be drawn from the results of this work:

- The thermal stability of peroxy nitrates increases with the electron withdrawing effect of R thus implying, for example, that  $\text{CF}_3\text{O}_2\text{NO}_2$  is considerably more stable than  $\text{CH}_3\text{O}_2\text{NO}_2$ .
- The strongest effect on the thermal stability is induced by a carbonyl group adjacent to the peroxy group, *e.g.* in  $\text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$  (PAN). With respect to their importance in the lower troposphere, peroxy nitrates can thus be divided into two groups: those with no adjacent carbonyl group (alkylperoxy nitrates, substituted alkylperoxy nitrates) with thermal lifetimes in the order of seconds at 298 K and 1 atm, and those containing a carbonyl group adjacent to the peroxy group (acetylperoxy nitrate and substituted acetylperoxy nitrates) with lifetimes in the order of hours at the same conditions. The effect of electronegative substituents or carbonyl groups distant from the peroxy group on the lifetime of a peroxy nitrate is only minor — acetyl peroxy nitrate, for example, is very short-lived as compared to PAN.
- A linear relationship has been established between the Arrhenius parameters for the dissociation of a particular peroxy nitrate  $\text{RO}_2\text{NO}_2$  and the  $^{13}\text{C}$ -NMR shifts in the corresponding compounds  $\text{RX}$  ( $\text{X} = \text{H}, \text{Cl}, \text{CH}_3$ ). The physical background of this correlation is that both the  $^{13}\text{C}$ -NMR shift of the C atom next to the peroxy group and the  $\text{OO}-\text{N}$  bond strength depend on the electron density at this C atom. Based on these correlations, thermal lifetimes of peroxy nitrates of the type  $\text{C}-\text{O}_2\text{NO}_2$  can be estimated from tabulated NMR data of the corresponding compounds  $\text{RX}$  with an uncertainty of about a factor of 5.
- Experimental results on the ratio  $k_1/(k_{2a}+k_{2b})$  for acetylperoxy radicals are about 30 % lower than previously assumed leading to 30 % less PAN formation from acetylperoxy radicals.

- New measurements of the UV absorption spectrum of PAN resulted in larger cross sections for wavelengths  $\geq 300$  nm, leading to photolysis rate coefficients at 298 K which are higher by about a factor of 3 than a previous estimate [1].

### ***Product yields of alkyl nitrates in the oxidation of hydrocarbons***

Values of the branching ratios  $k_{2b}/(k_{2a}+k_{2b})$  at 298 K have been determined for the OH initiated oxidation of a number of alkanes and alkenes. All of these branching ratios are listed in Chapter 2, Table 10, where the quoted errors are  $2\sigma$  and represent experimental precision only. Data for the branching ratios for the reactions of alkyl radicals with  $\geq C_4$  are known only for *n*-butane and *n*-heptane. From a knowledge of the branching ratios for the secondary alkylperoxy radicals and also of the ratio of primary to secondary alkylperoxy radicals, the branching ratios for primary alkylperoxy radicals formed in the reactions of OH with *n*-butane, *n*-pentane, *n*-hexane and *n*-heptane were also determined and are also listed in Chapter 2, Table 10. These results show clearly that the branching ratio increases with increasing chain length of the hydrocarbon.

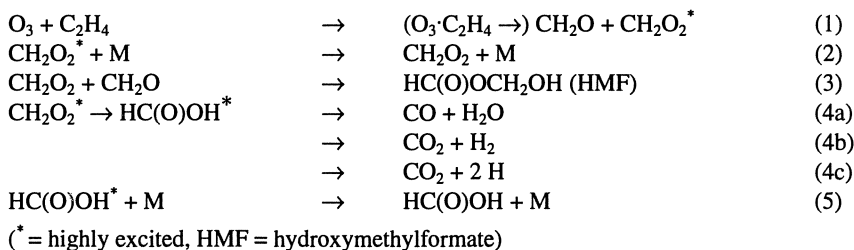
### ***Atmospheric chemistry of ketonitrates and dinitrates***

Rate coefficients have been measured for the reaction of OH radicals with a number of organic ketonitrates ( $R-CO-CH(ONO_2)-R$ ) and dinitrates ( $R-CH(ONO_2)-CH(ONO_2)-R$ ) using a relative kinetic method. The compounds investigated included 1,2-propane-, 1,2-butane-, and 2,3-butanediol dinitrate, *a*-nitro-oxy acetone, 1-nitro-oxy-2-butanone, 3-nitro-oxy-2-butanone, 3,4-dinitro-oxy-1-butene and *cis*-1,4-dinitro-oxy-2-butene (LACTOZ 90). The rate coefficients are listed in Chapter 2, Table 1a. and this study represented the first determination of the OH rate coefficients for these compounds.

UV absorption spectra have been measured for the ketonitrates and dinitrates (LACTOZ 89). In the region of atmospheric interest ( $\lambda > 270$  nm) the absorption cross sections of the carbonyl nitrates are approximately a factor of 10 higher than those of the dinitrates. From the measured cross sections photolysis frequencies have been calculated for the organic ketonitrates and dinitrates. Although the photolysis frequencies represent upper limits the results indicate that photolysis will generally be somewhat more important than loss via reaction with OH radicals for saturated difunctional nitrates. However, for unsaturated nitrates loss due to reaction with OH will dominate over photolysis as an atmospheric sink. The product studies show that photolysis of ketonitrates/dinitrates will result in the re-release of  $NO_2$  and the formation of PAN-type compounds.

### Ozonolysis of ethene

The currently accepted mechanism for the gas-phase reaction between ozone and ethene is represented by reactions (1)–(5) [2, 3]:



The following results have been obtained within the framework of LACTOZ with respect to the above mechanism:

- Usually, the loss of  $\text{C}_2\text{H}_4$  and  $\text{O}_3$  due to reaction (1) is enhanced by side reactions involving OH and  $\text{HO}_2$  radicals. By using cyclohexane as an OH scavenger,  $k_1 = (1.21 \pm 0.06) \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$  at 298 K was obtained from the first order decay of  $\text{C}_2\text{H}_4$  in the presence of a large excess of  $\text{O}_3$ . This value is lower by ca. 30 % than the previously recommended value [3].
- $\text{H}_2$  was measured for the first time in order to derive more reliable branching ratios for the reaction channels (4b) and (4c). With CO added as an OH scavenger, the  $\text{H}_2$  yield relative to the total amount of  $\text{C}_2\text{H}_4$  consumed increased from 12.1 %  $\text{H}_2$  (no CO added) to 15.5 %  $\text{H}_2$  ( $[\text{CO}] \geq 5 \times 10^{16} \text{ molecules cm}^{-3}$ ).
- Based on the experimental  $\text{H}_2$  yields with and without CO added and the yields of CO and  $\text{CO}_2$  in the absence of radical scavengers, the following product yields (corrected for side reactions and relative to the amount of  $\text{C}_2\text{H}_4$  consumed in reaction (1)) were determined:  
26.4 ± 0.5 %  $\text{CO}_2$ , 15.8 ± 0.3 %  $\text{H}_2$ , 10.5 ± 0.6 % H.
- The pressure dependence of the yields of CO,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CH}_2\text{O}$ , and  $\text{HC(O)OH}$  was investigated in order to examine the pressure dependent steps (2) and (5). From the measured product yields, based on 64 experiments, the following conclusions are drawn:
  - The  $\text{H}_2$  yield (relative to the total amount of  $\text{C}_2\text{H}_4$  consumed) is independent of total pressure between 1 and 1030 mbar.
  - Within error limits, the yields of the products CO,  $\text{CO}_2$ ,  $\text{HC(O)OH}$ , and  $\text{CH}_2\text{O}$  do not depend on total pressure between 100 and 1030 mbar.
  - The results above both suggest that collisional deactivation of  $\text{CH}_2\text{OO}^*$  and  $\text{HC(O)OH}^*$  (reactions (2) and (5)) are not effective. Ground state  $\text{CH}_2\text{OO}$ , if existing in this system, should be formed directly, implying a (at least) bimodal energy distribution of the Criegee radical formed in reaction (1).
  - When total pressures are 10 mbar or lower, a change of the mechanism occurs, leading to significantly higher yields of CO and  $\text{CO}_2$  and, simultaneously, lower yields of  $\text{CH}_2\text{O}$ .



Further mechanistic studies are under way to explain this result.

- 5) The products of the ozonolysis of ethene in the presence of added water vapour were analysed for the hydroperoxides  $\text{H}_2\text{O}_2$ ,  $\text{HOCH}_2\text{OOH}$  (hydroxymethyl hydroperoxide = HMHP) and  $\text{HOC}_2\text{H}_4\text{OOH}$  (2-hydroxyethyl hydroperoxide = 2-HEHP).

These experiments led to the following conclusions:

- $\text{H}_2\text{O}_2$ , HMHP and 2-HEHP are formed in gas-phase reactions.
- The yields of  $\text{H}_2\text{O}_2$  and HMHP increase with increasing partial pressure of  $\text{H}_2\text{O}$ , levelling off at high humidities. The yield of HMHP passes a distinct maximum of 4 % when the partial pressure of  $\text{H}_2\text{O}$  is increased.
- The major fraction of  $\text{H}_2\text{O}_2$  is formed in a reaction other than  $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ .
- The formation of both  $\text{H}_2\text{O}_2$  and HMHP is attributed to the reaction of  $\text{CH}_2\text{OO}$  with water vapour.
- For the reaction  $\text{CH}_2\text{OO} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{products}$ , a rate coefficient of  $(2.4 \pm 1.4) \times 10^{-19} \text{ cm}^3 \text{ s}^{-1}$  was determined, relative to the rate coefficient of the reaction  $\text{CH}_2\text{OO} + \text{SO}_2$  [2].
- 2-HEHP is formed via a reaction sequence initiated by the OH addition to ethene. The simplest explanation of the observed amounts of  $\text{H}_2\text{O}_2$  and  $\text{HOCH}_2\text{OOH}$  is the reaction of ground state Criegee radicals with water:  
 $\text{CH}_2\text{OO} + \text{H}_2\text{O} \rightarrow \dots \rightarrow \text{H}_2\text{O}_2 + \text{HCHO}; \text{CH}_2\text{OO} + \text{H}_2\text{O} \rightarrow \dots \rightarrow \text{HOCH}_2\text{OOH}$ .

Further experiments are necessary to establish the existence of ground state Criegee radicals and to elucidate their reactions.

### *Oxidation of isoprene*

The products of the reaction with OH, especially in the absence of  $\text{NO}_x$ , and of the reaction with  $\text{O}_3$  have been investigated. In addition rate coefficients for the reactions with OH and  $\text{O}_3$  were measured for some recently identified products of the isoprene oxidation. The concentrations of the reactants were in the low ppm range (usually 1–10 ppm). OH radicals were generated either by continuous UV photolysis of  $\text{H}_2\text{O}_2$  (254 nm) with or without NO present, or by photolysis of  $\text{CH}_3\text{ONO}$ .

These are the main findings of the investigations:

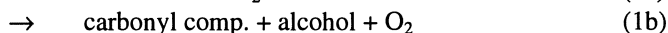
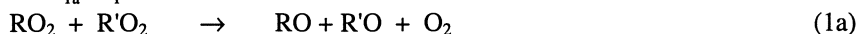
#### Isoprene + OH

In the presence of high  $\text{NO}_x$  concentrations (1–5 ppm), methacrolein (MAC,  $19 \pm 1$  [%-molar yield]), methyl vinyl ketone (MVK,  $29 \pm 3$ ) and formaldehyde ( $53 \pm 5$ ) were the main products in good agreement with the literature [4]. Formation of other carbonyl compounds and of nitrates could clearly be observed in the IR spectra of the products, but the yields were not quantified.

In the absence of  $\text{NO}_x$ , MAC ( $16 \pm 2$ ), MVK ( $15 \pm 2$ ) and  $\text{H}_2\text{CO}$  ( $33 \pm 3$ ) are also formed, but in significantly lower yields, as confirmed recently by Miyoshi *et al.* [5]. Remaining carbonyl compounds, which could not be identified, were evaluated from their IR absorption ( $18 \pm 7$ ) and in contrast to the  $\text{NO}_x$  experiments, strong absorptions of hydroxy- and/or hydroperoxy-groups were observed. Their yield was estimated to be  $48 \pm 20$  % based on an average absorption coefficient. From this group of compounds two diols, 2- and 3-methyl-3-butene-1,2-diol, were unambiguously identified. Their yields are relatively low (5 and 2 %), but this first-time identification is a clear indication that the peroxy radicals formed in the OH initiated oxidation of isoprene follow the reaction mechanism described in the Chapter 2, Fig. 11.

From a comparison of the MAC and MVK yields in the presence to those in the absence of  $\text{NO}_x$ , an overall value has been estimated for the branching ratio of the  $\text{RO}_2 + \text{R}'\text{O}_2$ -reactions, occurring in the isoprene + OH reaction system:

$$a = k_{1a} / k_1 = 0.7-0.8$$



#### Isoprene + $\text{O}_3$

Product yields were measured for isoprene /  $\text{O}_3$  / air mixtures. In some experiments either water vapour (2–13 mbar) or cyclohexane (~ 500 ppm) was added to the mixture. While cyclohexane acts as a scavenger for OH radicals, water is expected to react with the proposed intermediate biradicals [6, 7]:

- As in the OH reaction, MAC, MVK and formaldehyde are the main products, but in substantially different yields. The ratio MAC / MVK ranges around 2.3 (OH: 0.6–1).
- Among the unidentified compounds there is a large fraction of carbonyl- and/or carboxyl compounds: ~ 50 %. As for the OH experiments this number was obtained by use of an average absorption coefficient.
- The yields of the three main products increase in the presence of water vapour, as well as in the presence of cyclohexane. The simultaneous presence of both scavengers leads to still higher yields for these carbonyl compounds. This trend, as well as the absolute yields, agrees well with literature data obtained under comparable conditions [8–10]. The explanation for this behaviour is not clear. One idea is that high concentrations of water vapour and cyclohexane suppress reactions of biradicals and OH radicals, respectively, with other products such as MAC, MVK and formaldehyde, so that higher yields are measured for these products. Also the IR spectrum of the non-identified products changes clearly with different concentrations of water vapour, but the nature of these products is still speculative. Nevertheless, it is evident that water vapour participates in the  $\text{O}_3$  reaction.

- The formation of the low molecular weight compounds CO, CO<sub>2</sub>, H<sub>2</sub>, propene, ketene, methanol and methyl hydroperoxide can be explained by the decomposition of biradicals as shown in Chapter 2, Fig. 13. In view of the atmospheric relevance of the ozonolysis of alkenes, especially the influence of water vapour on the reaction mechanism and the product formation needs careful investigation. Under such conditions heterogeneous effects cannot be neglected and large-scale reaction chambers would be useful to account for such effects.

#### Kinetics of reactions of isoprene oxidation products with OH and O<sub>3</sub>

Rate coefficients for the reactions of OH and O<sub>3</sub> with 2- and 3-methyl-3-butene-1,2-diol and 1,2-epoxy-3-methyl-3-butene, the latter having been reported very recently as product from isoprene + O<sub>3</sub> [11], were determined by use of a relative rate technique. In the O<sub>3</sub> experiments sufficient CO was added to scavenge > 90 % of OH radicals eventually being formed. For the O<sub>3</sub> reaction of the diols absolute measurements were carried out in addition by monitoring the decay of O<sub>3</sub> under pseudo-first order conditions. Absolute and relative rate data were in good agreement. The average values at 295 ± 2 K are:

$$\begin{aligned} k(2\text{-methyl-3-butene-1,2-diol} + \text{O}_3) &= (4.8 \pm 0.6) \times 10^{-18} \text{ cm}^3 \text{ s}^{-1} \\ k(3\text{-methyl-3-butene-1,2-diol} + \text{O}_3) &= (6.3 \pm 1.0) \times 10^{-17} \text{ cm}^3 \text{ s}^{-1} \\ k(1,2\text{-epoxy-3-methyl-3-butene} + \text{O}_3) &= (3.3 \pm 0.3) \times 10^{-18} \text{ cm}^3 \text{ s}^{-1} \end{aligned}$$

The rate coefficients for the OH reaction are listed in Chapter 2, Table 1a. All compounds investigated show high reactivity to both, OH and O<sub>3</sub>, with the OH reaction dominating under "normal" tropospheric conditions. For OH, the experimental values are a factor of two higher than expected from the usual structure-reactivity estimation methods.

This high reactivity towards the important atmospheric photo-oxidants, probably valid also for similar isoprene oxidation products like unsaturated hydroxy carbonyls, hydroxy nitrates or hydroxy hydroperoxides, is an indication that these reactions need more consideration in laboratory experiments as well as photo-oxidation models.

#### *Atmospheric chemistry of simple alkylated aromatics*

##### Kinetics of the OH initiated oxidation of *p*-xylene and toluene

The rate coefficients for reaction of toluene and *p*-xylene with OH radicals have been determined and it was found that these rate coefficients are dependent on the O<sub>2</sub> concentration. Values of  $(1.11 \pm 0.06) \times 10^{-11}$  and  $(1.45 \pm 0.12) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  were obtained as rate coefficients for the reaction of *p*-xylene with OH radicals in 750 Torr N<sub>2</sub> and synthetic air, respectively. Intermediate values could not be determined, since, even in the presence of the smallest measurable partial pressure of O<sub>2</sub>, the same rate coefficient as in synthetic air was obtained. The rate coefficients for the reaction of toluene with OH radicals rose from

$(4.74 \pm 0.11) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  in  $\text{N}_2$  to a maximum value of  $(6.61 \pm 0.17) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  in the presence of 12 Torr  $\text{O}_2$ . It has been observed that the measured rate coefficients also depend on the concentrations of the organic constituents of the reaction mixture. This observation has been confirmed by experiments using different starting concentrations of the aromatics and reference compounds. Under atmospheric conditions, reaction with  $\text{O}_2$  will be the main fate of the initially formed OH-aromatic adducts.

#### Products of the OH initiated oxidation of toluene and *p*-xylene

Table 2 shows the products that have presently been identified and quantified for the *p*-xylene and toluene OH initiated oxidation systems. In the case of *p*-xylene 51.8 % of reacted carbon has been detected using FTIR and 51.7 % using the GC-MS technique. In the case of toluene 40.3 % of the reacted carbon has been detected by FTIR spectroscopy. Table 3 shows products which have been identified, but not yet quantified.

Table 2: Quantified products from the reaction of *p*-xylene and toluene with OH radicals using FTIR and GC-MS. Yields are given in percent of reacted carbon detected.

Technique Product	FTIR		GC-MS
	toluene <sup>1</sup>	<i>p</i> -xylene <sup>1</sup>	<i>p</i> -xylene <sup>2</sup>
CO		8.0 ± 1.4	
CO <sub>2</sub>		4.0 ± 0.4	
Benzaldehyde	7.1 ± 1.8		
<i>p</i> -Tolualdehyde		6.4 ± 1.5	11.2 ± 4
2,5-Dimethylphenol		(8.0 by GC-FID)	5.8 ± 2
<i>cis</i> -3-Hexene-2,5-dione		8.3 ± 1.9	14.4 ± 4
Maleic anhydride	4.2 ± 1.1		
Methylglyoxal	4.4 ± 1.1	2.2 ± 0.5	
Acetic acid	5.2 ± 1.3	3.8 ± 0.3	20.0 ± 3
Glyoxal	3.7 ± 0.9	4.0 ± 1.7	
Formic acid	12.9 ± 3.2	5.1 ± 1.0	
Formaldehyde	2.3 ± 0.6	1.2 ± 0.2	
Ketene	0.5 ± 0.1	0.3 ± 0.1	
Total amount	40.3	51.8	51.7

<sup>1</sup> Identified by FTIR in a 1080 L reaction chamber using 1–2 ppm as initial concentration of the aromatic hydrocarbon.

<sup>2</sup> Identified by GC-MS in a 36.5 L chamber using 50–200 ppm as initial concentration of the aromatic hydrocarbon.

Because of a large discrepancy in the yields of phenol-type compounds in the aromatic oxidation system systems, a detailed study has been made of the processes leading to cresol formation in the oxidation of toluene. The studies were performed using different initial concentrations of toluene,  $\text{NO}_2$  and  $\text{H}_2\text{O}_2$  and it has been observed that there is an increase of the *o*-cresol yield with increasing concentrations of  $\text{NO}_x$  and  $\text{H}_2\text{O}_2$ . At low starting concentrations of toluene,  $\text{NO}_x$  and  $\text{H}_2\text{O}_2$ , the cresol formation was found to be low and will not be significant under tropospheric conditions.

**Table 3:** Products qualitatively identified in the reaction of toluene and *p*-xylene with OH radicals.

Toluene	<i>p</i> -Xylene
Acetylene <sup>1</sup>	
Methanol <sup>1</sup>	Methanol <sup>1</sup>
Methylhydroperoxide <sup>1</sup>	Methylhydroperoxide <sup>1</sup>
4-Oxo-2-pental <sup>1</sup>	4-Oxo-2-pental <sup>1</sup>
Benzylalcohol <sup>2</sup>	4-Methylbenzylalcohol <sup>4</sup>
Phenol <sup>2</sup>	2-Hydroxy-4-methylbenzaldehyde <sup>4</sup>
Cresol-isomers <sup>2</sup>	4-Methylbenzoic acid <sup>4</sup>
Benzoic acid <sup>2</sup>	Methylmaleic anhydride <sup>1</sup>
<b>evidence of formation</b>	
Methylmaleic anhydride <sup>3</sup>	
Methylhexadienial isomers <sup>3</sup>	
Hydroxymethylhexadienial isomers <sup>3</sup>	
Butenedial <sup>5</sup>	2-Methylbutenedial <sup>5</sup>

<sup>1</sup> Identified by FTIR in a 1080 L reaction chamber

<sup>2</sup> Identified by GC-MS after solvent trapping from the 1080 L chamber

<sup>3</sup> Identified by DF-MS in a flow reactor

<sup>4</sup> Identified by GC-MS from a stirred reactor

<sup>5</sup> Investigations have shown that butenedial (2-methylbutenedial) is the precursor for maleic anhydride (methylmaleic anhydride) formation

### *Atmospheric chemistry of unsaturated carbonyl compounds*

The largest ring-fragmentation products identified in the OH initiated oxidation of aromatics so far are unsaturated 1,4-dicarbonyls (see Tables 2 and 3), and there is indirect evidence that the primary ring-opening products of aromatics are doubly unsaturated 1,6-dicarbonyls like 2,4-hexadienedial (CHO-CH=CH-CH=CH-CHO), also known as muconaldehydes, and its methylated derivatives. Therefore, the atmospheric chemistry of such unsaturated carbonyl compounds has been investigated. The kinetic data determined for these compounds are listed in Chapter 2, Table 1a.

#### Mono unsaturated 1,4-dicarbonyls

Unsaturated 1,4-dicarbonyls (butenedial, 4-oxo-2-pental, 3-hexene-2,5-dione) were found to undergo an oxidative cyclisation process under VIS ( $\lambda_{\max} = 360$  nm) and UV photolysis ( $\lambda_{\max} = 254$  nm), leading to the formation of maleic anhydride. Additionally, butenedial and 4-oxo-2-pental were found to form 3H-furan-2-one and 5-methyl-3H-furan-2-one (a-angelicalactone), respectively. The major atmospheric sinks of butenedial, 4-oxo-2-pental, 3-hexene-2,5-dione and the furanones will be reaction with OH radicals and photolysis. OH product studies revealed the additional formation of smaller oxidation products like dicarbonyls and carbonyls. The potentially fast photolysis of these compounds is of great significance, it might represent an important radical source in the atmospheric oxidation of aromatics.

### Doubly unsaturated 1,6-dicarbonyls

The kinetic data listed in Chapter 2, Table 1a show a very fast reaction of these compounds with OH radicals, while the NO<sub>3</sub> reactions were found to be slow. Furthermore, an extremely rapid UV photolysis was determined; irradiation with VIS lamps did not result in photolysis. The major atmospheric sinks of 2,4-hexadienedials will therefore be the reaction with OH radicals. The fast OH reactions and rapid UV photolysis can explain why it has not yet been possible to unambiguously identify 2,4-hexadienedials in aromatic oxidation systems, especially where the UV photolysis of H<sub>2</sub>O<sub>2</sub> is used as the OH radical source.

The primary photo-oxidation products of doubly unsaturated 1,6-dicarbonyls are smaller carbonyls like butenedial, (methyl)glyoxal and their follow-up products. These compounds have been identified in the atmospheric oxidation of aromatics.

### Kinetics and mechanism of the OH initiated oxidation of acetylformoin

Acetylformoin (3-hydroxy-hexane-2,4,5-trione: CH<sub>3</sub>-CO-CH(OH)-CO-CO-CH<sub>3</sub>) is a suspected major product of the OH initiated oxidation of 3-hexene-2,5-dione, itself a product of the OH initiated oxidation of *p*-xylene. This compound has been synthesised in its isomeric enediol form 3-hexene-3,4-diol-2,5-dione. The rate coefficients for the reaction with OH radicals was found to be  $(2.7 \pm 0.7) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . The residual FTIR spectrum of its OH initiated photo-oxidation was found to be identical to that obtained from the OH initiated oxidation of 3-hexene-2,5-dione, the major product has been tentatively identified as hexane-3,3-diol-2,4,5-trione (CH<sub>3</sub>-CO-C(OH)<sub>2</sub>-CO-CO-CH<sub>3</sub>). These results suggest that acetylformoin readily enolises and then rapidly reacts with OH radicals to give products of the type observed for the OH initiated oxidation of 3-hexene-3,4-diol-2,5-dione.

## Conclusions

Significant progress has been made in product studies of the reaction of NO<sub>3</sub> radicals with alkenes, however, further studies, in particular, with biogenic hydrocarbons are necessary. It was shown conclusively that the formation yields of alkenes from the reaction of OH radicals with alkanes is insignificant under atmospheric conditions. The investigations on the thermal stability of peroxy-nitrates are so advanced that it is now possible to estimate atmospheric lifetimes for nearly all types of peroxy-nitrate. Possible exceptions, that need further studies, are sulfur and iodine containing compounds. The mechanistic studies on the ozonolysis of alkenes have turned out to be more complicated than originally anticipated. Further investigations on different product channels and the mechanisms involving, *e.g.* Criegee intermediates, are necessary. The investigations of the reaction pathways of simple alkylated aromatics have led to a new view of the ring-opening mechanism and point to the need for more detailed investigations on unsaturated carbonyl compounds which appear to be major

secondary products. Also of major importance for further work is the identification of the fate of  $\text{NO}_x$  during the aromatic oxidation. Much more work is required to obtain a reliable and representative mechanism that can be used for modelling.

### Acknowledgements

Financial support by the State NRW, BMBF, IFP and the EC is gratefully acknowledged.

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### 3.3 Laboratory and Field Measurement Studies of the Tropospheric Chemistry of Nitrate and Peroxy Radicals

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#### Summary

Both laboratory and field measurement studies of RO<sub>2</sub> and NO<sub>3</sub> radicals were part of this LACTOZ study. The discovery of a rapid reaction between NO<sub>3</sub> and RO<sub>2</sub> and its involvement in a potentially important night-time oxidation mechanism for VOC are discussed. Investigation of the photo-excitation of mixtures of NO<sub>2</sub>, NO<sub>3</sub> and O<sub>3</sub> around 662 nm showed that reaction of NO<sub>3</sub>(A<sup>2</sup>E') with N<sub>2</sub> is not likely to be a source of N<sub>2</sub>O and provided an upper limit for rate coefficient for the reaction of NO<sub>3</sub> with O<sub>3</sub>. N<sub>2</sub>O is produced by 185 nm photolysis of NO, NO<sub>2</sub> and even air, as well as heterogeneously from NO<sub>2</sub>, NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> mixtures. Finally the development of a tropospheric ambient RO<sub>2</sub> detector, the analysis of RO<sub>2</sub> measurements and their impact on our understanding of the chemistry of the daytime and night-time planetary boundary layer are discussed.

#### Aims of the scientific research

The nitrate radical (NO<sub>3</sub>) is formed in the atmosphere primarily by the reaction of nitrogen dioxide (NO<sub>2</sub>) with ozone (O<sub>3</sub>). At the outset of this project the potential importance of the role of NO<sub>3</sub> as an oxidant in the troposphere had just been recognised. In order to assess the latter accurate physico-chemical models, describing the behaviour of NO<sub>3</sub> in the troposphere, are needed. These require a detailed understanding of the elementary photochemical or chemical reactions and physical processes such as deposition or transport, which determine the tropospheric lifetime of NO<sub>3</sub>.

HO<sub>2</sub> and organic peroxy radicals (RO<sub>2</sub>) play a variety of roles and functions in the tropospheric chemistry:

- i) the reactions of HO<sub>2</sub> and RO<sub>2</sub> lead to the formation peroxides;
- ii) during the day the reaction of HO<sub>2</sub>/RO<sub>2</sub> with NO producing NO<sub>2</sub> plays a key role in the photochemical production of O<sub>3</sub>;
- iii) HO<sub>2</sub> and possibly RO<sub>2</sub> in air masses with low NO<sub>x</sub> participate in a daytime catalytic cycle destroying O<sub>3</sub>.



As  $\text{NO}_3$  is photolysed rapidly during the day, its maximum concentration occurs at night. The reaction of  $\text{NO}_3$  with volatile organic compounds (VOC) is therefore anticipated to represent a night-time source of  $\text{RO}_2$  radicals.

The studies undertaken within this project aimed to combine laboratory studies of the tropospheric reactions of  $\text{NO}_3$  and  $\text{RO}_2$  with relevant field measurement studies. The objective of the latter was the investigation of the validity of the current understanding of the tropospheric role of  $\text{NO}_3$  and  $\text{RO}_2$ . The primary target species for the field studies was therefore  $\text{RO}_2$ .

## Principal scientific findings

### *Laboratory studies of $\text{NO}_3$ and $\text{RO}_2$ reactions*

Previous studies from this laboratory and elsewhere (notably by Atkinson and co-workers) had shown that  $\text{NO}_3$  reacted rapidly with a variety of VOC (*e.g.* DMS or isoprene or terpenes) and inorganic radicals such as  $\text{NO}_2$  and Cl. Similarly it was already known that the equilibrium between  $\text{NO}_2$ ,  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  played an important role in determining the atmospheric fate of  $\text{NO}_3$ .

#### Reaction of $\text{NO}_3$ with $\text{RO}_2$

The reaction between  $\text{NO}_3$  and  $\text{CH}_3\text{O}_2$  was studied in the modulated photolysis at 254 nm of  $\text{HNO}_3$ ,  $\text{CH}_4$  and  $\text{O}_2$  mixtures. The reaction of  $\text{CH}_3\text{O}_2$  with  $\text{NO}_3$  was shown to be rapid and its rate coefficient at 298 K estimated for the first time: the value for  $k(\text{CH}_3\text{O}_2 + \text{NO}_3)$  reported was  $(2.3 \pm 0.7) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [1]. The recognition of a source of  $\text{NO}_3$  from the liquid decomposition of  $\text{HNO}_3$  led to a re-analysis of this system with the rate coefficient  $k(\text{CH}_3\text{O}_2 + \text{NO}_3)$  being now estimated to be approximately  $1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [2].

A study of the reaction of  $\text{C}_2\text{H}_5\text{O}_2$  with  $\text{NO}_3$  was undertaken by photolysing mixtures of  $\text{HNO}_3$ ,  $\text{C}_2\text{H}_6$  and  $\text{O}_2$ . The reaction appeared to be fast but an unequivocal value for the rate coefficient was not established. Finally an upper limit for the reaction of  $\text{NO}_3$  with  $\text{O}_3$  was established with  $k(\text{NO}_3 + \text{O}_3) 2 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [3].

Further studies of the reaction between  $\text{NO}_3$  and  $\text{CH}_3\text{O}_2$  using a discharge flow coupled with mass spectrometry and studies and the photo-oxidants of HCHO,  $\text{CH}_3\text{CHO}$  and  $\text{CO}_2$  are reported by Moortgat elsewhere in this report.

#### Liquid-phase decomposition of $\text{HNO}_3$

The liquid-phase decomposition of  $\text{HNO}_3$  was investigated by observing the oxides of nitrogen produced when a flow of  $\text{N}_2$  or  $\text{O}_2$  was passed through freshly prepared  $\text{HNO}_3$  [2]. In addition to  $\text{HNO}_3$  both  $\text{NO}_2$  and  $\text{NO}_3$  were identified directly in the gas phase. These results indicate that concentrated liquid  $\text{HNO}_3$

disproportionates to form  $N_2O_5$  and  $H_2O$ . There may also be other channels which directly form  $NO_2$ .

As tropospheric aerosol typically has a substantial  $H_2O$  content, this reaction was not considered to be of significance for tropospheric chemistry. However stratospheric aerosol is dry and consequently this reaction may occur. Further studies are required to confirm this conclusion.

#### Atmospheric significance of $NO_3$

Two studies were undertaken concerning the atmospheric role of  $NO_3$ . The first was a theoretical study which focused on the  $NO_3$  initiated oxidation of DMS and the consequences of a chain propagated by the reactions of  $NO_3$  with  $RO_2$  and  $HO_2$  [4]. The second took place as part of a review of the physics, chemistry and atmospheric significance of  $NO_3$  [5].

The DMS study indicated that a potentially significant source of night-time OH results from the reaction of  $NO_3$  with DMS. The concept of a night-time chain initiated by  $NO_3$  reactions with VOC was further developed in Wayne *et al.* [5].

#### ***Photochemical and chemical sources of $N_2O$***

$N_2O$  is one of the most important tropospheric "greenhouse" gases, and its transport into the stratosphere is considered to be the dominant source of stratospheric oxides of nitrogen. The tropospheric abundance of  $N_2O$  has been shown to be increasing by approximately 0.2 % per year in recent times. The anaerobic denitrification/reduction of  $NO_3^-$  and the nitrification  $NH_4^+$  in soils have been postulated as important microbial sources of  $N_2O$ .

The interest in this investigation surrounded the quantification of the potential atmospheric importance of a photochemical source of  $N_2O$  involving the photoexcitation of  $NO_3$  into its  $A^2E'$  state by (0,0) band absorption followed by its reaction with  $N_2$  [6]. Mixtures of  $NO_2$  and  $O_3$  in air were photolysed by a 662 nm light source, comprising a Tungsten lamp and interference filter.  $N_2O$  was observed by means of a sampling gas chromatograph equipped with an ECD detector.

Overall an upper limit for the quantum yield for  $N_2O$  production,  $F_{N_2O}$ , of 0.6 % was established [7]. However control experiments showed that  $N_2O$  was also produced in the dark experiments and in the effective absence of  $N_2$ . The  $F_{N_2O}$  value is at least a factor of 2 lower than that obtained by Zellner *et al.* [8].

In spite of the efforts to deactivate the surface of the relatively large reaction vessel, the observed  $N_2O$  production was best explained by a heterogeneous reaction involving  $NO_2$ ,  $NO_3$  or  $N_2O_5$ .

Although the  $NO_3$  photoexcitation source was considered unlikely to be a significant atmospheric source of  $N_2O$ , the potential importance of a chemical heterogeneous source of  $N_2O$ , discovered in this study, at the earth's surface as

heterogeneous source of  $N_2O$ , discovered in this study, at the earth's surface as compared to the biological source needs to be quantified. The chemical conversion of  $NO_2$ ,  $NO_3$  or  $N_2O_5$  to  $N_2O$  has been up to the present ignored as a significant source of  $N_2O$ .

In a further study the following sources of  $N_2O$  were investigated

- i) the association reaction of  $O(^1D)$  with  $N_2$ ;
- ii) the photolysis of  $NO$  in  $N_2$  at 185 nm;
- iii) the photolysis of  $NO_2$  in  $N_2$  at 185 nm;
- iv) the photolysis of synthetic air at 185 nm.

The rate coefficient for the reaction of  $O(^1D)$  with  $N_2$ ,  $k(O(^1D) + N_2 + M)$ , at 298 K was found to be  $(8.8 \pm 3.3) \times 10^{-37} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  in reasonable agreement with previous studies. This confirms that this reaction is not a significant atmospheric source of  $N_2O$ .

The photolysis at 184 nm of both mixtures of  $NO$  and  $NO_2$  in  $N_2$  resulted in significant formation of  $N_2O$ . Surprisingly photolysis of air also generated  $N_2O$ . This could only be explained by the involvement of excited states of  $O_2$ . Any  $N_2O$  formation mechanism require a long lived state of  $NO$ . The latter is most likely the  $NO(^4P)$  state [7] and this mechanism generates a new stratospheric radical.

### ***Peroxy radical measurements***

As part of this study, two potential  $RO_2$  measurement techniques have been investigated: the chemical amplification and tuneable diode laser absorption spectroscopy. The first approach has proven to be successful for the measurement of ambient mixing ratios of the sum of all peroxy radicals which react with  $NO$  to form  $NO_2$ .

The second approach utilises the low-lying electronic transitions and vibrational overtones in the 1 to 2  $\mu\text{m}$  spectral region. This method has the spectroscopic advantage of high specificity. As a first step in the development of this technique a prototype spectrometer was developed which could operate in this region [9, 10]. As a second step the first observation of a high resolution spectrum of  $HO_2$  around 1.5  $\mu\text{m}$  was obtained [11]. Further work is currently underway to investigate the use of an external resonator laser system to enable highly sensitive intracavity measurements of  $HO_2$  to be made.

### **Development of the chemical amplifier detector**

The idea of using chemical amplification for the measurement of  $RO_2$  was first proposed by Stedman. It utilises the chain reaction of  $HO_2$  with  $NO$  followed by  $OH$  with  $CO$ . This initial concept was found to be difficult to calibrate ([12] and references therein). A calibrated chemical amplifier system was developed in this laboratory for the first time [13]. This system detects  $RO_x$  (*i.e.* the sum of  $RO_2$ ,  $HO_2$ ,  $RO$  and  $OH$ ) which participate effectively in the  $NO/CO$  chain reaction. As

the concentrations of RO and OH are much smaller than HO<sub>2</sub> and RO<sub>2</sub> in the troposphere, the detector effectively measures the sum of RO<sub>2</sub> and HO<sub>2</sub>. This detector requires a detailed understanding of the chemical mechanism which generate NO<sub>2</sub> from RO<sub>2</sub> or HO<sub>2</sub>. Prior to the advent of LACTOZ, the theoretical study reported in Hastie *et al.* [13] would not have been feasible.

#### RO<sub>x</sub> measurement campaigns 1991–1994

In 1991 RO<sub>x</sub> measurements in continental air were made in Mainz and in Israel. In autumn and winter the instrument was used to study RO<sub>x</sub> in the remote northern and southern Atlantic oceans, aboard the German research vessel Polar Stern from 50° N to 40° S. In 1993 the instrument took part in the first FIELDVOC campaign in Brittany in May and June and participated in the OCTA Project measurements at Izana Tenerife in July and August. In 1994 RO<sub>x</sub> measurements were undertaken as part of the second FIELDVOC campaign in Portugal and as part of the PRICE Project at the Schauinsland TOR station in southern Germany. The details of the measurements made, the results and their interpretation are reported elsewhere [14–18].

#### Ambient RO<sub>x</sub> measurements – daytime

The boundary layer measurements of RO<sub>x</sub> at land sites have resulted in the following conclusions about daytime RO<sub>2</sub> and tropospheric chemistry:

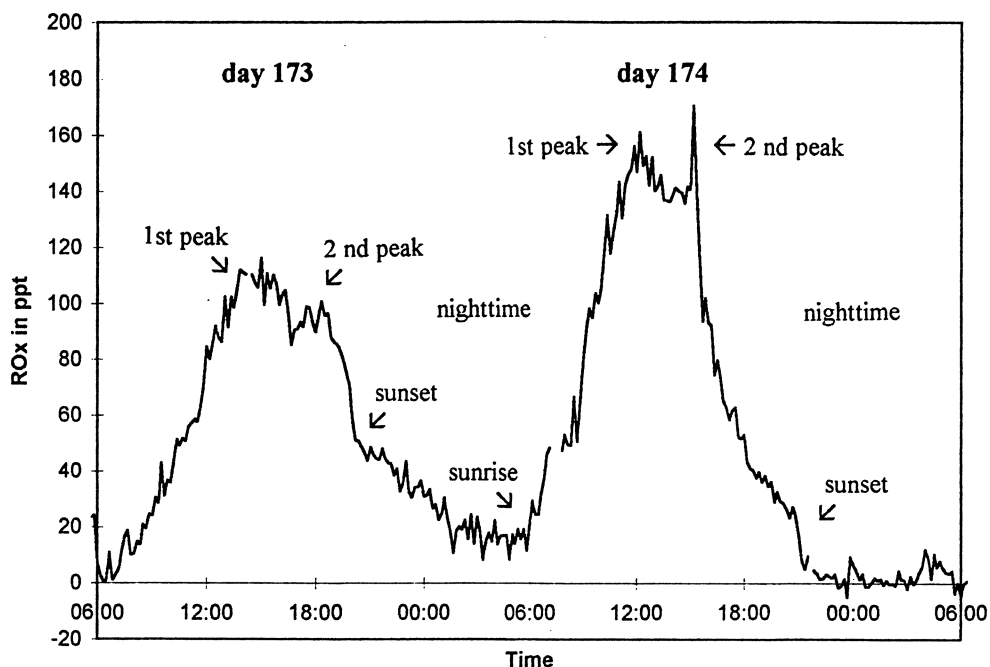
- a) in the absence of NO<sub>x</sub> and VOC, RO<sub>x</sub> values are quite low with maximum mixing ratios at midday ≤ 30 ppt;
- b) in the presence of NO<sub>x</sub> and VOC, high values of RO<sub>x</sub> are obtained: the highest recorded RO<sub>x</sub> mixing ratio being » 150 ppt;
- c) the rate of production of O<sub>3</sub> in polluted air appears to be reasonably well determined by  $S_{k_{RO_2+NO}}[NO][RO_2]$ , implying that the rate determining step for tropospheric O<sub>3</sub> production is the reaction of RO<sub>2</sub> with NO forming NO<sub>2</sub>;
- d) the [NO]/[NO<sub>2</sub>] appears to be explained by the reactions of NO with O<sub>3</sub>, RO<sub>2</sub> with NO and the photolysis of NO<sub>2</sub> at desert sites (Israel) and in the free troposphere (Izana);
- e) the [NO]/[NO<sub>2</sub>] at the coastal site Brittany can only be explained by the presence of an additional NO oxidising agent.

The last observation has resulted in the hypothesis that either halogen oxides (*e.g.* BrO) or Sulfur radicals may be active in tropospheric chemistry at least in coastal environments ([19] and references therein).

Analysis of the RO<sub>x</sub> measurements from the remote parts of the North and South Atlantic can be summarised as follows:

- a) RO<sub>x</sub> is low typically being < 10 ppt at midday;
- b) an unidentified source of RO<sub>x</sub> is required in the North Atlantic between approximately 10 and 35° N;

- d) a small additional loss process for  $RO_x$  is required in both hemispheres;  
 e) for remote maritime air the observed loss of  $O_3$  is similar to that predicted by the reaction of  $RO_x$  with  $O_3$ .



**Fig. 1:**  $RO_2$  mixing ratio measured during the FIELDVOC Portugal Campaign 1994.

The observation b) is best explained by the existence of a biogenic maritime source of VOC in the upwelling region off the coast of Africa, or by an as yet unidentified anthropogenic pollution source. The observation d) may imply that loss of  $RO_x$  occurs on aerosol or via a homogeneous reaction with an as yet unidentified radical.

#### Ambient $RO_x$ measurements – night-time

The night-time measurements of  $RO_x$  have shown the following:

- in remote maritime air the mixing ratio of  $RO_x$  is less than 2 ppt;
- in coastal environments  $RO_x$  significant levels *i.e.* above 2 ppt have been observed *e.g.* Brittany;
- in forests unambiguous  $RO_x$  signals of up to 30 ppt have been observed.

An example of two days' data from the FIELDVOC campaign in Portugal in 1994 is shown in Fig. 1. Large night-time RO<sub>2</sub> signals are clearly visible on day 173. In addition a double maxima is observed in the daytime RO<sub>2</sub> on both days. The appearance of RO<sub>x</sub> is linked to the presence of VOC, O<sub>3</sub> and NO<sub>x</sub>. Qualitatively this is in agreement with the hypotheses of Platt *et al.* [4] and Wayne *et al.* [5].

### Assessment

The original objective of the EUROTRAC project LACTOZ was to provide kinetic and mechanistic data to enable a quantitative description of the tropospheric ozone budget in numerical models. Following the review by the EUROTRAC-SSC in 1991 the priorities set for the second phase of LACTOZ were understanding

- a) Ozone production in the free troposphere;
- b) Complex VOC and NO<sub>x</sub> chemistry in the boundary layer.

In addition it was pointed out at this time that *the inclusion of "box modelling" and specially designed "field measurements" in order to test or evaluate chemical mechanisms, in particular with measurements of photochemically generated free radicals such as OH and HO<sub>2</sub> was necessary.*

The discovery of the rapid reactions of organic peroxy radicals with NO<sub>3</sub> and the recognition of their importance in tropospheric chemistry has been a significant achievement within this project. Similarly the development of a method for the detection of RO<sub>x</sub> has provided a large number of measurements of RO<sub>x</sub> to be made in the planetary boundary layer and a few to be made in the free troposphere (Izana, Tenerife). This has allowed box models of HO<sub>2</sub> and RO<sub>2</sub> chemistry to be developed and the inadequacies of our current understanding to be pointed out. In conclusion the aims and objectives of LACTOZ have been well served by the achievements of this project.

### Acknowledgements

The work described in this study was funded in part by the University of Bremen, the Max-Planck-Institut für Chemie Mainz and the Max-Planck-Gesellschaft zur Förderung der Wissenschaft and by the following EU research contracts STI-056-J-C, ST2J-0193, EV4V-0093-C and EV5-CT91-0040 and by the German Ministry of Research and Technology under Project No. 325-4007-07 INT 037. We acknowledge the active co-operation of G. LeBras, G. Poulet and U. Platt in this project.

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### 3.4 Tropospheric Degradation of Aromatics: Laboratory Kinetic Studies of some First Steps of the OH Initiated Oxidation

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#### Summary

We have performed laboratory measurements of rate constants of a few first steps of the tropospheric oxidation mechanism of some monocyclic aromatic hydrocarbons; the following reactions have been studied: OH radical with benzene or toluene (+M); benzyl radicals (from OH abstraction pathway) with O<sub>2</sub>, NO and NO<sub>2</sub>; on the other hand, the branching ratios (abstraction/addition + abstraction) have been measured by a direct spectroscopic technique. All these measurements have been achieved thanks to the Discharge Flow (DF) technique with detection of OH by Resonance Fluorescence (RF) and other radicals by Laser Induced Fluorescence (LIF).

#### Aims of the research

Although the specific and significant impact of aromatics upon tropospheric chemistry in urban areas is well documented [1], the exact mechanism of their tropospheric oxidation remained largely uncertain at the beginning of LACTOZ. Taking toluene as an example, the first reaction steps are as represented on the scheme of Fig. 9 [2, 3].

The abstraction path, with a yield of roughly 10 % [3], leads to the intermediate benzaldehyde which is known to exhibit subsequent fast reactions [4]. The major addition path (≈ 90 %), results in the formation of a radical adduct (of cyclohexadienyl type) which is suspected to lead ultimately to a variety of ring-containing or ring-cleavage products [1]. Whether or not there is an intermediate step of rearomatization (formation of *o*-cresol) is still a matter of controversy, Although very recent smog chamber experiments point to a negligible contribution of this pathway in real atmospheric conditions.

Our research aimed at the following objectives:

- (i) Measurements of the rate constants with O<sub>2</sub>, NO and NO<sub>2</sub> of a few benzyl-type radicals derived from toluene or xylenes. No reaction rate with NO<sub>2</sub> was reported so far, whereas the data for O<sub>2</sub> and NO were very limited.
- (ii) Measurements of the branching ratios between abstraction and addition.

These branching ratios were only inferred from end product analysis [3] and thus could be questioned since the carbon mass balance was usually very poor during the oxidation of aromatics (no more than 60 % of the initial reactant recovered in the collected end products). We have measured the branching ratios by a direct spectroscopic method based on a monitoring of the benzyl radical relative concentrations by LIF.

- (iii) Since the low pressure discharge flow technique has been used throughout our investigation, it has been necessary to measure the reaction rate constants (OH + benzene (+ M)) and (OH + toluene (+ M)) in our specific conditions in a preliminary compulsory step. These experiments have provided the preliminary data to perform subsequent experiments.

## Principal results

### *Rate constants for the intermolecular reactions (OH + toluene + He) and (OH + benzene + He); rate constant of the adducts with NO<sub>2</sub>*

These reactions have been investigated by the discharge-flow technique with detection of OH by resonance fluorescence. OH radicals were generated by the classical transfer reaction: (H + NO<sub>2</sub> → OH + NO). The experimental parameters were as follows: pressure of helium: 0.5/9.5 Torr,  $T = 298$  or  $353$  K.

Both reactions are in the fall-off range in our experimental conditions; our global results (over the pressure range 0.5/10 Torr) can be fitted to derive the Troe parameters  $k_0$  and  $k_\infty$  according to the classical Troe formula [5].

The corresponding results are presented in Table 1.

**Table 1:** Fall-off Troe parameters for OH + benzene (+ He) and OH + toluene (+ He) reactions.

		$k_0/\text{cm}^6 \text{ molec}^{-2} \text{ s}^{-1}$	$k_\infty/\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
benzene	(297 ± 3)K	(1.7 ± 0.5)10 <sup>-29</sup>	(10 ± 2)10 <sup>-13</sup>
	353 K	(1 ± 0.2)10 <sup>-29</sup>	(10 ± 1)10 <sup>-13</sup>
toluene	(295 ± 3)K	(4 ± 0.5)10 <sup>-28</sup>	(6.0 ± 0.7)10 <sup>-12</sup>
	353 K	(2 ± 0.5)10 <sup>-28</sup>	(4 ± 0.7)10 <sup>-12</sup>

The main reaction product (*i.e.* path b) with both benzene and toluene is an adduct (a cyclohexadienyl-type radical) which is known to exhibit back decomposition towards OH [6]; since these adduct radicals react very quickly with NO<sub>2</sub> [7], the OH decay kinetics proved to be very sensitive to NO<sub>2</sub> concentration in our experimental conditions, in agreement with numerical simulations. By taking into account the adduct unimolecular back decomposition rates of Zetzsch and co-workers [6], we have been able to estimate a few reaction rates of these adducts with NO<sub>2</sub> and O<sub>2</sub>:

benzene (353K, 1 Torr He):

$$k(\text{adduct} + \text{NO}_2) = (4 \pm 2) 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

toluene (353K, 1 Torr He):

$$k(\text{adduct} + \text{NO}_2) = 4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

toluene (353K, 1 Torr He):

$$k(\text{adduct} + \text{O}_2) < 5 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$$

### *Rate constants for O<sub>2</sub>, NO and NO<sub>2</sub> with a few benzyl-type radicals*

The benzyl radical is the reaction product of the abstraction path (path a) of the reaction of toluene with OH. Similarly, methylbenzyl radicals are formed during the OH abstraction reactions with xylenes and trimethylbenzenes. We have measured the reaction rate constants with O<sub>2</sub>, NO and NO<sub>2</sub> of a series of benzyl-type radicals, including a few fluorosubstituted ones in purpose of comparison.

The experimental technique was the fast discharge flow at low pressure (a few Torr) with detection of radicals by LIF.

The benzyl radicals were generated by chlorine atom attack on the methyl substituent since there is apparently no chlorine addition on the ring [8, 9]; chlorine atoms were generated in the upstream part of the flow tube thanks to the following reaction of transfer:  $\text{F} + \text{Cl}_2 \rightarrow \text{FCl} + \text{Cl}$ . The LIF signals were obtained by exciting in the visible band of benzyl radicals ( $\lambda \approx 450/465 \text{ nm}$ ) and detected at maximum fluorescence intensity, around  $(480 \pm 10) \text{ nm}$  [10].

The experimental results are gathered in Tables 2 and 3.

**Table 2:** Rate constants (in  $10^{-12} \text{ cm}^3 \text{ s}^{-1}$ ) for benzyl-type radicals measured in this work.

Radical	O <sub>2</sub>	NO	NO <sub>2</sub>
benzyl	0.72	6.3	60
<i>p</i> -fluorobenzyl	0.78	8.9	50
<i>m</i> -fluorobenzyl	0.51	7.45	41
<i>o</i> -methylbenzyl	0.91	10.5	57
<i>m</i> -methylbenzyl	1.11	13	56

**Table 3:** Comparison between the room temperature values of the rate constant for (benzyl + O<sub>2</sub>) by various techniques.

$k / 10^{-12} \text{ cm}^3 \text{ s}^{-1}$	technique	pressure / Torr	reference
$0.99 \pm 0.07$	FP/UV Abs	N <sub>2</sub> , 160	[11]
$1.12 \pm 0.2$	LP/LIF	N <sub>2</sub> , 3/15	[12]
$0.74 \pm 0.2$	DF/MS	He, 0.75/3	[13]
1.2	FP/UV Abs	N <sub>2</sub> , 760	[14]
$1.5 \pm 0.2$	PR/UV Abs	Ar, 1013	[9]
$0.97 \pm 0.1$	LP/MS	He, 4	[15]
$0.72 \pm 0.14$	DF-LIF	He, 1	this work

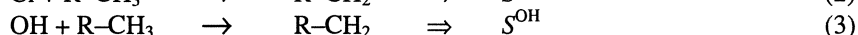
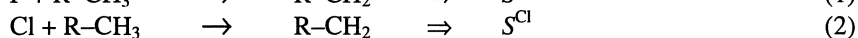
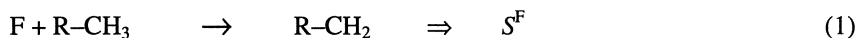
Our measurements are the first ones performed with the technique of discharge flow/LIF; also, concerning the reaction rates with  $\text{NO}_2$ , there are no other data with which our results can be compared. For the reaction rates with  $\text{O}_2$  and  $\text{NO}$ , our results are systematically below the results of other techniques (obtained at higher pressures) Although the uncertainty ranges usually overlap (Table 3); these minor discrepancies could be assigned (at least for the reaction rate with  $\text{O}_2$ ) to a fall-off behaviour [14].

Taking into account the experimental uncertainties and the small variations between the benzyl radicals, we propose the following generic values for the rate constants of a benzyl-type radical (in  $\text{cm}^3 \text{s}^{-1}$ ):  $\text{O}_2$ :  $0.9 \times 10^{-12}$ ;  $\text{NO}$ :  $8 \times 10^{-12}$ ;  $\text{NO}_2$ :  $5.8 \times 10^{-11}$ .

***Branching ratio measurements (R = abstraction/abstraction + addition) by a direct spectroscopic method***

The branching ratios have been measured with essentially the same set-up of discharge flow/LIF used for kinetic measurements. A double fluorescence cell allows simultaneous monitoring of the benzyl radical (by LIF) and OH (by resonance fluorescence).

The benzyl radicals are formed by attack of the suitable precursor  $\text{R-CH}_3$  in large excess by one of the three reactants: F, Cl or OH at the same concentration; with each reactant, the corresponding signal of the benzyl radical fluorescence:  $S^{\text{F}}$ ,  $S^{\text{Cl}}$ ,  $S^{\text{OH}}$  is probed by LIF:



Stoichiometric conversions between the three reactants are achieved thanks to the following rapid transfer reactions:



Since the branching ratio for reaction 2 is one at room temperature [8, 9, 14], the branching ratio for OH abstraction (*i.e.* in reaction 3) is simply  $R = S^{\text{OH}}/S^{\text{Cl}}$  (this is our so called direct method). Another indirect method can also been used if the branching ratio for reaction 1 is known:  $R'' = S^{\text{F}}/S^{\text{Cl}}$ ; this happened for toluene and *p*-xylene [16]. The results of both methods used in the present work are gathered in Table 4, together with available literature data from end product analysis.

The good agreement between our values (from a spectroscopic method monitoring the first abstraction step) and the values derived from smog chamber data (from intermediate or final products) confirms that the "missing" final products responsible for the imperfect mass balance are probably associated with the dominant addition path.

**Table 4:** Room temperature branching ratios (abstraction/total).

	this work (direct technique)		product analysis	ref
	first method	second method		
toluene	0.06 ± 0.02	0.07 ± 0.03	0.12 0.073 0.065	[3] [17] [18]
<i>o</i> -xylene	0.11 ± 0.03		0.11 0.059	[3] [19]
<i>m</i> -xylene	0.07 ± 0.01		0.04 0.04	[19] [3]
<i>p</i> -xylene	0.08 ± 0.01	0.07 ± 0.02	0.08 0.078 0.08	[3] [19] [20]

### Assessment of the achievement

Our work during the project is part of a concerted effort of various European groups to unravel the mechanism of tropospheric oxidation of aromatics. A lot of kinetic, mechanistic and analytic data have been produced, especially concerning (i) the first primary steps of the mechanism (abstraction and addition) (ii) the nature and the yield of intermediate or final oxidation products. Also, it appeared that "standard" reaction schemes for oxidation (*i.e.* like those for alkanes) are not applicable to aromatics; this specificity of the latter prevented us from presenting a clear picture of the oxidation mechanism and requires new investigations.

### Acknowledgements

We thank the French programs "grands cycles biogéochimiques" (PACB), "environment" and the organisations CNRS, "Ministère de l'Environnement" for their support. We thank the CEC for a grant (STEP).

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### 3.5 Laboratory Studies of the Formation of Hydroperoxides in Ozonolysis of Anthropogenic and Biogenic Alkenes

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#### Summary

An HPLC fluorescence method for quantitative and qualitative hydroperoxide analysis was improved, so as to determine linear hydroperoxides and hydroxy hydroperoxides up to a chainlength of seven carbon atoms.

The hydroperoxide products of ozonolysis of a number of alkenes were determined under three sets of ozonolysis conditions: 1. concentrations of 4 ppm in dry synthetic air, 2. concentrations of 140 ppm in synthetic air at 100 % relative humidity and 3. concentrations of 100 ppm in water.

The main products of ozonolysis in dry air were alkyl hydroperoxides, while in aqueous solution 1-hydroxyalkyl hydroperoxides were the only products observed. In humid air at the higher concentrations, both types of products were present, and similar results were obtained when ozone was bubbled through aqueous solutions of the alkenes.

A mechanism consistent with these results is postulated.

#### Aims of the research

Atmospheric ozonolysis is believed to be a major pathway for the degradation of the vast quantities of biogenic and anthropogenic alkenes emitted annually. Analysis of air and precipitation has indicated that H<sub>2</sub>O<sub>2</sub>, alkyl hydroperoxides and 1-hydroxyalkyl hydroperoxides (1-HAHPs) are present [1]. Since both ozonolysis and other oxidation processes can lead to hydroperoxides, it is of interest to know to what extent ozonolysis is involved in the formation of those hydroperoxides actually found in the atmosphere.

In continuation of a long-standing study, we set out under LACTOZ to determine the products of ozonolysis of 1-pentene, 1-hexene and 1-heptene at gas-phase concentrations of 140 ppm at 100 % relative humidity. It was necessary to develop our HPLC system further in order to do this. We later extended the study to the ozonolysis of lower alkenes and of some terpenes at ca. 4 ppm in dry air.

Ozonolysis in water was then examined in search of a method for distinguishing ozonolysis in atmospheric droplets from true reaction in the gas phase.

### **Principal scientific findings**

#### *The analytical system*

The first step within this project was to improve the HPLC-fluorescence method [1] in order to determine not only hydrophilic but also lipophilic hydroperoxides of up to seven carbon atoms. Among the aspects investigated were column length, mixed solvent and gradient elution and the use of microperoxidase instead of horseradish peroxidase in the detection system [2, 3]. The use of microperoxidase let us add secondary, tertiary and other branched hydroperoxides to the list of peroxide species we can determine. For full analysis a number of hydroperoxides were synthesised as standards for retention time and quantitation: methyl hydroperoxide (MHP), ethyl hydroperoxide (EHP), 1- and 2-propyl hydroperoxides (PHPs), 1-butyl hydroperoxide (1-BHP), hydroxymethyl hydroperoxide (HMHP), 1-hydroxyethyl hydroperoxide (1-HEHP), 2-hydroxyethyl hydroperoxide (2-HEHP), 1-hydroxypropyl hydroperoxide (1-HPHP), 1-hydroxybutyl hydroperoxide (1-HBHP), 1-hydroxypentyl hydroperoxide (1-HPentHP), 1-hydroxyhexyl hydroperoxide (1-HHHP), bis(hydroperoxy) methane (MBHP) and bis(hydroxy-methyl) peroxide (BHMP). We decided in the end not to use gradient elution, which brought baseline problems, but rather to use side-by-side HPLC systems: one with acidified water as eluent for the more hydrophilic hydroperoxides ( $\text{H}_2\text{O}_2$  and the lower alkyl hydroperoxides) and a second, with a mixture of water and acetonitrile as eluent, for more lipophilic compounds. Neutralisation of the sample before chromatography allowed us to distinguish between alkyl and 1-hydroxyalkyl hydroperoxides (1-HAHPs), since it converted the latter to  $\text{H}_2\text{O}_2$  and the corresponding aldehydes. The detection limit of the enhanced system is about 0.05 mmol/L for both linear and branched primary and about 1 mmol/L for secondary hydroperoxides.

#### *The role of the ozonolysis conditions*

Dry gas-phase ozonolysis was carried out on ethene, propene, isoprene, and a- and b-pinene [4] at concentrations of 4 ppb in a 1000 L reactor [5]. A certain volume of the resulting gas was drawn through acidified water, which was then examined for its hydroperoxide content. The results are shown in Table 1. Small amounts of  $\text{H}_2\text{O}_2$  and HMHP were found in all the dry gas-phase experiments; it is still not certain whether these are artefacts, though it is reasonable, in a reaction that appears to have a high radical component, that some  $\text{H}_2\text{O}_2$  be formed via  $\text{HO}_2$  radicals. The only significant hydroperoxide detected was methyl hydroperoxide from those olefins with a methyl group on the double bond. A trace of 2-HEHP,



readily distinguished from MHP by its retention time, must be attributed to reaction of OH radicals with ethene [6].

**Table 1:** Hydroperoxide distribution in dry gas-phase ozonolysis as % of alkene; a dash means "not detected".

	Ethene	Propene	Isoprene	$\alpha$ -Pinene	$\beta$ -Pinene
H <sub>2</sub> O <sub>2</sub>	0.4	0.3	0.7	0.3	0.6
HMHP	0.2	0.2	0.5	0.1	0.3
MHP	–	4.1	5.0	0.8	–
1-HEHP	–	–	–	–	–
2-HEHP	< 0.1	–	–	–	–
other HAHPs	–	–	–	–	–
total	0.6	4.6	6.2	1.2	0.9

The experiments at 100 % relative humidity were carried out on 1-pentene, 1-hexene and 1-heptene at concentrations of 140 ppm in a 20 L borosilicate glass flask [7]. After an hour's reaction time the gaseous contents of the flask were drawn through acidified water; the walls of the flask were then washed with the same water. Analysis of the resulting solution for hydroperoxides gave the results in Table 2. Significant yields of H<sub>2</sub>O<sub>2</sub>, alkyl hydroperoxides and 1-HAHPs were obtained.

**Table 2:** Hydroperoxide distribution in humid gas-phase ozonolysis as % of alkene.

	1-Pentene	1-Hexene	1-Heptene
H <sub>2</sub> O <sub>2</sub>	2.8	2.4	2.5
HMHP	2.5	2.2	2.4
BHMP	0.7	1.2	1.3
MBHP	1.0	0.7	0.9
MHP	0.6	0.4	0.4
EHP	2.7	0.4	0.1
1-PHP	5.0	0.5	0.1
1-BHP	–	1.4	0.1
1-HPentHP	–	0.1	–
1-PentHP	–	–	0.7
1-HHHP	–	–	0.2
unknown	0.5	0.2	0.6
total	15.8	9.5	9.5

Ozonolysis in water was carried out by mixing a solution of the alkene in water (water/acetonitrile in the case of isoprene and the pinenes) with an aqueous solution of ozone. The hydroperoxide yields are in Table 3. The only significant products were 1-HAHPs [4].

When the ozonolysis in water was carried out by bubbling ozone through an aqueous solution of the alkene, rather than by mixing prepared solutions of the two, the product distribution (not tabulated) resembled the "mixed-reaction" distribution seen in the humid gas-phase reactions.

**Table 3:** Hydroperoxide distribution in aqueous-phase ozonolysis as % of alkene.

	Ethene	Propene	Isoprene	$\alpha$ -Pinene	$\beta$ -Pinene
H <sub>2</sub> O <sub>2</sub>	–	–	< 0.1	< 0.1	< 0.1
HMHP	27.9	2.7	11.1	–	0.2
MHP	–	–	–	–	–
1-HEHP	–	11.1	–	–	–
2-HEHP	–	–	–	–	–
other HAHPs	–	–	13.1	11.3	16.0
total	27.9	13.8	24.2	11.3	16.2

The products are consistent with the idea, as is some of the literature [8], that the early stages of the reactions under all the conditions examined here proceed by the Criegee ozonolysis mechanism (Fig. 1). Thus a primary ozonide decomposes rather unselectively to two carbonyl compounds (aldehydes or ketones) and two thermally excited carbonyl oxides (**2** and **3**), whose fate depends on the reaction medium. In aqueous solution the carbonyl oxides are largely relaxed by collision, whereafter they undergo high yield bimolecular reactions with water to 1-HAHPs [4]. In the gas phase, by contradistinction, the excited carbonyl oxides fragment thermally to a large extent before they can undergo bimolecular reaction [9] (Fig. 2). The major peroxide products come from the reactions of the fragment radicals with oxygen, the largest alkyl hydroperoxide corresponding in each case to the alkyl chain of the original alkene. The alkyl radical apparently first forms a peroxy radical, which extracts hydrogen from HO<sub>2</sub>; either direct formation of smaller alkyl fragments from the carbonyl oxide or further fragmentation of the initial alkyl radical yields other alkyl hydroperoxides all the way down to MHP. The experiments described here were not designed to tell us anything about the possible intermediacy of complexes in the cleavage of primary ozonides in the gas phase, such as have been suggested by some others [10].

The products of ozonolysis in humid air indicate that the carbonyl oxide can react with water in the gas phase, when enough water is present. The course of this reaction is as yet unknown. The 1-HAHPs observed may result from the fraction of carbonyl oxide that is not relaxed by collision. Alternatively, they may come from bimolecular reaction of the excited state with water; in either case, the products observed or some intermediate complexes with water then undergo relaxation.

It seems as if part of the reaction takes place in the gas phase when ozone is bubbled through aqueous solutions of alkene. The alkenes examined here have a rather low Henry's Law constant, so that it should not be surprising if a considerable fraction enters the gas phase, where it reacts with ozone and whence polar products like hydroperoxides are absorbed into the water.

In general, the yields of hydroperoxides decrease as the starting alkene becomes larger. This may simply reflect the greater number of reaction pathways open to larger molecules: our analysis detects only hydroperoxides, and in some of the experiments only primary linear alkyl hydroperoxides.

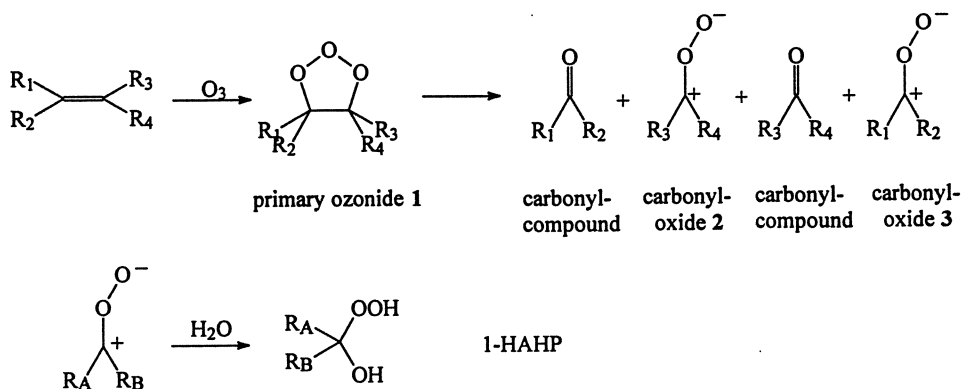


Fig. 1: Postulated mechanism for aqueous-phase ozonolysis.

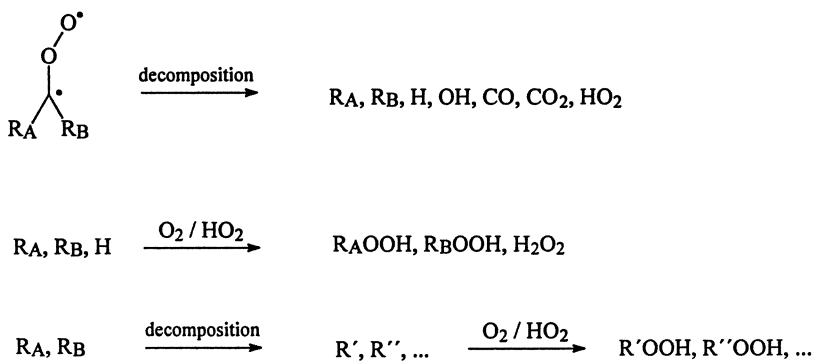


Fig. 2: Postulated mechanism of dry gas-phase ozonolysis.

### *The role of the alkene in ozonolysis*

Because ethene is symmetrical, a single carbonyl oxide,  $\text{CH}_2\text{OO}$ , is formed, along with formaldehyde. Addition of water to the carbonyl oxide gives HMHP, which was observed in all cases where water was present. The trace of HMHP observed from ozonolysis in dry air may, as noted above, be an artefact, but fragmentation of  $\text{CH}_2\text{OO}$  has been postulated by others to give H radicals; these would be expected to give  $\text{HO}_2$ , then  $\text{H}_2\text{O}_2$ .

Propene gives two carbonyl oxides,  $\text{CH}_2\text{OO}$  and  $\text{CH}_3\text{CHOO}$ , and accordingly the reaction in water gives HMHP and 1-HEHP; as observed by others, the carbonyl oxide is preferentially formed on that end of the olefin bond with the methyl substituent [9]. Fragmentation of  $\text{CH}_3\text{CHOO}$  to methyl radicals in the dry gas phase leads to MHP.

The ozonolysis of isoprene is complicated by the presence of two unlike double bonds. The 11.1 % yield of HMHP in water shows that a significant fraction of the primary ozonide cleaves to  $\text{CH}_2\text{OO}$ . No other hydroperoxide could be detected under the conditions used to analyse the products of this reaction, but we have indirect evidence that other HAHPs are indeed present in the sample. Thus neutralisation of the sample brought about a great increase in the yield of  $\text{H}_2\text{O}_2$ , which would arise from HAHPs too large to be eluted from the HPLC column by water. Normally, hydroxy C-4 hydroperoxides would be eluted by water, so we prefer not to speculate as yet about the nature of the "hidden" product, which we hope to detect by using the  $\text{H}_2\text{O}$ /methanol or  $\text{H}_2\text{O}$ /acetonitrile eluents. Ozonolysis of isoprene in the dry gas phase gives MHP in accordance with our scheme.

Either direction of cleavage of the primary ozonide from  $\alpha$ -pinene would produce a carbonyl oxide with ten carbon atoms. Fragmentation of this intermediate might well lead to a number of hydroperoxides we could detect, but only MHP was observed from gas-phase ozonolysis. As in the case of isoprene, neutralisation of the sample from aqueous ozonolysis before analysis indicates that significant amounts of HAHPs are formed in water. These are still under investigation.

$\beta$ -Pinene might in principle give  $\text{CH}_2\text{OO}$ , but the absence of HMHP from the products in water shows that the cleavage is very selective to the substituted carbonyl oxide. The nature of the larger HAHPs revealed by neutralisation is still unknown.

In all the cases here studied under both sets of limiting conditions, the yields on ozonolysis in water were much higher than those in dry air; this doubtless reflects the high stabilisation of the excited intermediates in the condensed phase.

The product in highest yield in the ozonolysis of 1-pentene in humid air (where the concentration is also considerably higher) is 1-PHP;. MHP and EHP are also seen, the yields decreasing with the chain length. The HMHP probably results from the reaction of water with  $\text{CH}_2\text{OO}$ , though some of it may come from reaction of formaldehyde with  $\text{H}_2\text{O}_2$ , while the BMHP observed must arise from addition of

H<sub>2</sub>O<sub>2</sub> to CH<sub>2</sub>OO. It is odd that no 1-HBHP was observed, since the corresponding 1-HAHPs had been observed in the ozonolysis of all the lower linear alkenes and were seen in the case of 1-hexene and 1-heptene as well. The ozonolysis of 1-hexene and 1-heptene also gave linear alkyl hydroperoxides. The reason the yields of these decrease with the chain length is uncertain, the energetics of the fragmentation of the carbonyl oxides not having been fully examined.

### Assessment

Ozonolysis in the gas phase leads to peroxide products and is especially interesting in that regard, because some of these peroxides can be formed even in the presence of NO<sub>x</sub>. The studies described here provide information about the yields and identity of hydroperoxide products in gas-phase ozonolysis under two sets of conditions highly relevant to the troposphere. These products must be part of any mechanism that purports to explain atmospheric ozonolysis. Since peroxides are a source of radicals and a reservoir of oxidising power, their concentrations must be considered in quantitative descriptions of the tropospheric ozone budget.

### Acknowledgements

Part of this work was carried out at the Institute of Ecological Chemistry, GSF-Gesellschaft für Gesundheits- und Umweltforschung, Freising/Attaching, Germany.

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### 3.6 Gas-Phase Reactions of Interest in Night-time Tropospheric Chemistry

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#### Summary

The nitrate radical,  $\text{NO}_3$ , is formed in the atmosphere by the reaction between  $\text{NO}_2$  and  $\text{O}_3$ . During the day  $\text{NO}_3$  is rapidly photolysed, but at night it builds up to several ppt. In recent years, the chemistry of  $\text{NO}_3$  in air has been studied extensively and found to play an important role in the troposphere [1]. This contribution to LACTOZ has been focused on certain aspects of  $\text{NO}_3$  chemistry: the identification of products and the understanding of mechanisms in the  $\text{NO}_3$  initiated degradation of some volatile organic compounds (VOC) and the role of  $\text{NO}_3$  in reactions leading to interconversion of  $\text{NO}_y$  species.

The organic compounds investigated were alkenes (propene, isobutene; *trans*- and *cis*-2-butene; 2-methyl-2-butene; 2,3-dimethyl-2-butene; isoprene [3–6], chlorinated butenes (2-chloro-1-butene; 3-chloro-1-butene; 1-chloro-2-butene; 2-chloro-2-butene) [7] and aromatics {benzene; *o*-xylene; *m*-xylene; *p*-xylene 4-fluorotoluene} [8]. The following main products were found for the reaction between  $\text{NO}_3$  and alkenes in air in the presence of  $\text{NO}_2$ : unsubstituted carbonyl compounds, nitroxycarbonyl compounds, nitroxy alcohols and dinitrates. For the reaction between  $\text{NO}_3$  and isoprene it was found that the main pathway, for the initial step, is an addition reaction to the  $\text{C}_1$ -carbon atom. From the study of the reactions between  $\text{NO}_3$  and chlorinated butenes the following conclusions were made: When a chlorine atom is attached to a double-bonded carbon, the channel leading to formation of carbonyl nitrates becomes less important while the one leading to non-nitrate carbonylic compounds becomes substantially more important. The reactions of  $\text{NO}_3$  with aromatic hydrocarbons formed aromatic aldehydes and aromatic nitrates as the main products.

The equilibrium constant for the reaction  $\text{N}_2\text{O}_5 + \text{M} \rightleftharpoons \text{NO}_3 + \text{NO}_2 + \text{M}$  was determined as  $2.8 \times 10^{10} \text{ molecule cm}^{-3}$  at 298 K [9] while the rate of the reaction  $\text{NO}_3 + \text{NO}_2 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2$  was determined as  $(5.1 \pm 1.8) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 296 K [10]. Results of model simulation of experimental data indicated that the rate constant of the reaction  $\text{HO}_2 + \text{NO}_3 \rightarrow \text{OH} + \text{NO}_2 + \text{O}_2$  should be below  $1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [11].

### Aims of the scientific research

The aims of this investigation was to provide mechanistic, product and kinetic data for  $\text{NO}_3$  reactions of atmospheric importance and to contribute to the background knowledge of the  $\text{NO}_3$  reaction mechanisms. These kind of investigations are needed to be able to perform a quantitative description of the tropospheric ozone budget in numerical models.

### Principal scientific findings during the project

#### Experimental setup

The product studies were performed by reacting the organic compounds with  $\text{NO}_3$  radicals in an  $\text{N}_2\text{O}_5/\text{NO}_2/\text{NO}_3$ /organic/air mixture at atmospheric pressure and at  $295 \pm 2$  K.

The experimental setup applied is shown in Fig. 1. The experiments were performed in a 480 L Teflon-coated evacuable reaction chamber as shown by Fig. 1. The chamber is equipped with multiple reflection mirror systems for on-line Fourier Transform Infrared Spectroscopy (FTIR) and on-line Tunable Diode Laser Spectroscopy (TDL) as well as UV/VIS spectroscopy. In addition, samples can be taken from the chamber and analysed by GC or by GC-MS.

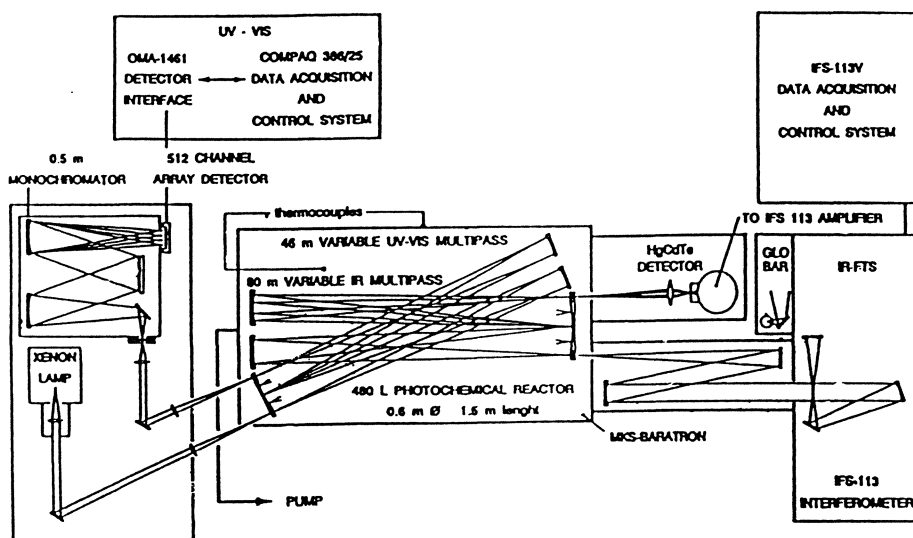
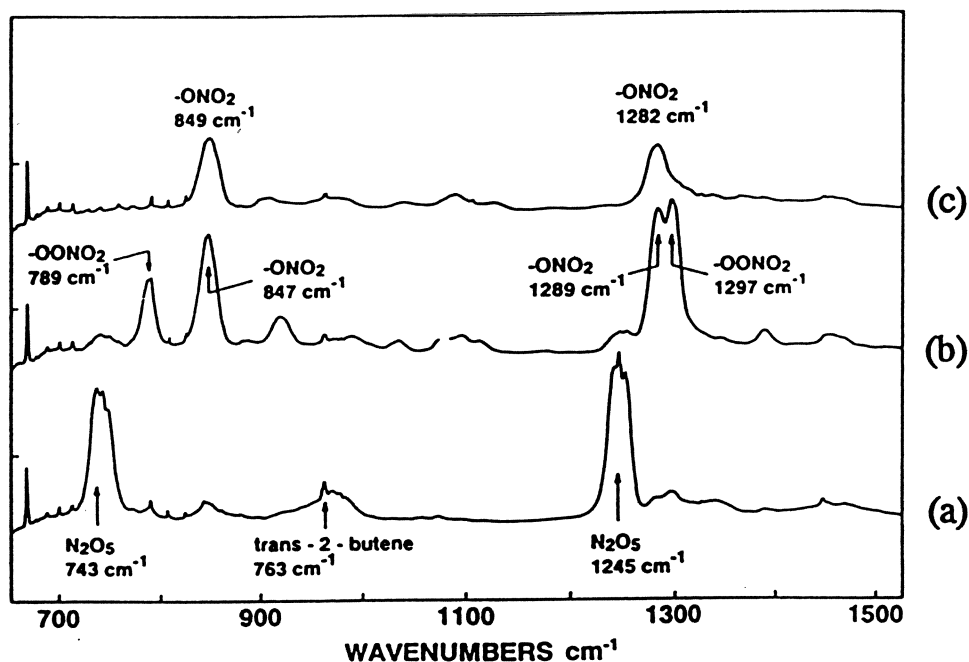


Fig. 1: Schematic picture of the experimental setup.

VOC + NO<sub>3</sub>

In the investigation of products and intermediates from the reactions between NO<sub>3</sub> and the alkenes (propene; isobutene; *trans*- and *cis* butene; 2-methyl-2-butene; 2,3-dimethyl-2-butene and isoprene) it was found that all of them followed a similar pattern. The build-up of organic nitrate bands (845, 1280 and 1667 cm<sup>-1</sup>) and peroxy-nitrate bands (790, 1300, 1725 cm<sup>-1</sup>) were observed in the IR-spectra as showed in Fig. 2. The subsequent decay of the peroxy-nitrate bands was accompanied by a build-up of spectral features attributed to stable products (see Fig. 2). These stable products were identified as aldehydes, alcohol nitrates, carbonyl nitrates and dinitrates [3, 4].



**Fig. 2:** Typical IR spectra recorded during the reaction of *trans*-2-butene with NO<sub>3</sub>, showing the build-up and decay of the nitroxy-nitroperoxy intermediate and the formation of stable organic nitrates. (a) Initial spectrum (N<sub>2</sub>O<sub>5</sub> is used as source of NO<sub>3</sub> radicals). (b) Spectrum recorded after 15 seconds reaction time. (c) Spectrum recorded after 1080 seconds reaction time.

Based on the end products identified and the intermediates observed in the IR spectra a reaction mechanism was proposed for these reactions [3, 4]. The reaction between NO<sub>3</sub> and isoprene was found to proceed mainly through a reaction pathway where NO<sub>3</sub> is added to the C<sub>1</sub>-carbon in an initial step (see Fig. 3).



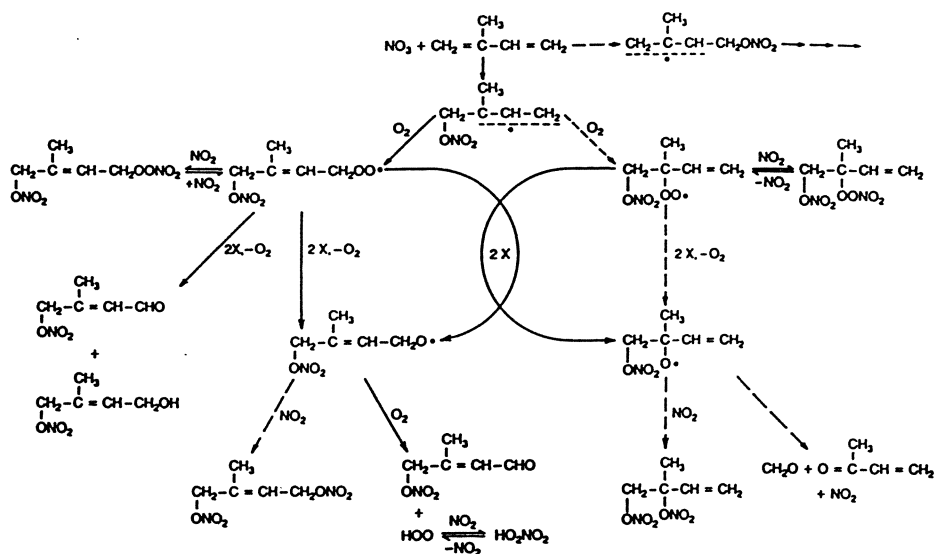


Fig. 3: Proposed reaction scheme for the reaction between  $\text{NO}_3$  and isoprene. Main reaction pathways are indicated by continuous arrows; minor reaction pathways are indicated by dashed arrows.

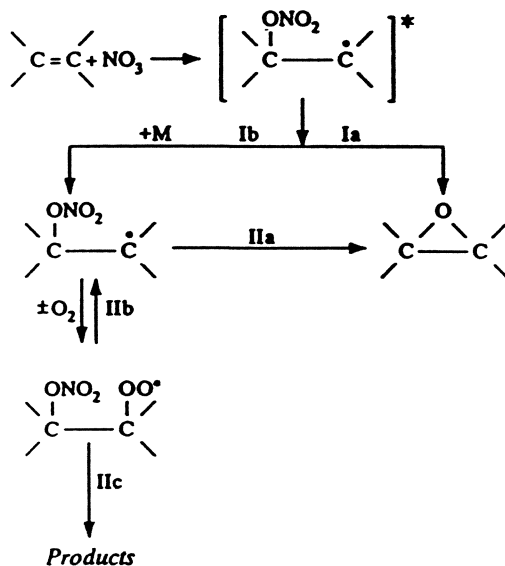


Fig. 4: Proposed scheme for the initial steps in the reaction between  $\text{NO}_3$  and 2,3-dimethyl-2-butene in the presence of  $\text{NO}_2$  and  $\text{O}_2$ .

In an investigation of the oxirane formation from the reaction between  $\text{NO}_3$  and alkenes [5, 6] it was found that at low pressures and at low  $\text{O}_2$  concentrations the oxirane formation pathway was the dominating pathway, but at atmospheric pressure (about 760 Torr) in air it was only a minor channel. The observations could be explained by the mechanism outlined in Fig. 4.

The reactions between the chlorinated butenes and the nitrate radical can be divided into two cases [7]:

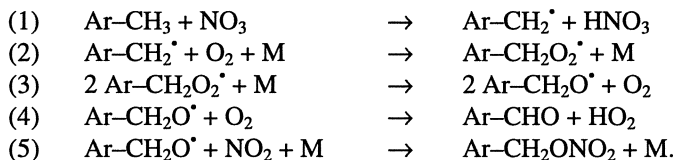
Case 1: The chlorine substitution is next to the double bond:

For the two investigated compounds with the chlorine atom substituted next to the double bond, the intensity of the nitroperoxy bands passed through a maximum while the nitroxy bands continued to increase during the course of the experiments. A carbonyl band at approximately  $1750\text{ cm}^{-1}$  was seen at the same time. This indicates that either a carbonyl nitrate compound or a nitrate and a carbonyl compound were formed through decomposition of the nitroperoxy nitrate intermediate. Small amounts of acetaldehyde and chloroacetaldehyde were found among the products formed from the reaction with 1-chloro-2-butene. In the reaction with 3-chloro-1-butene, significant amounts of formaldehyde were formed.

Case 2: The chlorine substitution is at the double bond:

In the experiments with 2-chloro-1-butene and 2-chloro-2-butene, the initial increase in absorption due to nitroxy and nitroperoxy groups were followed by a decrease and by a simultaneous formation of aldehydes and acid chlorides.

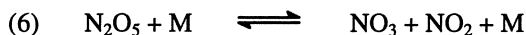
The yields of the main reaction products in reactions of aromatics with  $\text{NO}_3$  were determined by GC-MS after sampling on a carbon column or a XAD-2 trap [7]: For benzene only nitro-benzene was identified as a product, but benzene was essentially unconverted in the reaction with  $\text{NO}_3$ . Benzaldehyde and benzyl nitrate were identified in the reaction with toluene. For *ortho*-, *meta*-, *para*-xylene and 4-fluorotoluene the corresponding aldehydes and nitrates were identified as main products, which suggests that the below mechanism for toluene and the xylenes is the main reaction pathway [8]:



However, minor yields of aromatic nitroderivatives found in these reactions indicated that the nitrate radical may also react by addition to the aromatic ring.

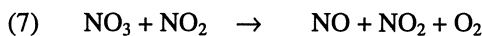
### Interconversion of NO<sub>y</sub> species

The rapidly established equilibrium between NO<sub>3</sub>, NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub>



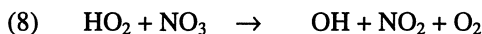
was investigated by direct measurement of all three components, by FTIR (NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub>) and UV/VIS (NO<sub>3</sub> and NO<sub>2</sub>). The equilibrium constant was found as  $(2.7 \pm 0.8) \times 10^{10}$  molecule cm<sup>-3</sup> at 298 K [9].

The rate constant of the reaction



was determined as  $(5.1 \pm 1.8) \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 296 K in a study where low concentrations of NO was measured by TDL spectroscopy [10].

The OH forming reaction



was studied by kinetic modelling of a complex chemical system at 750 and 50 Torr total pressure where HO<sub>2</sub> and NO<sub>3</sub> were formed by the thermal dissociation of HO<sub>2</sub>NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub>, respectively, and [OH] was estimated from the rate of co-oxidation. The best fits to the experimental data were obtained by applying values of *k*<sub>8</sub> below  $1 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [11].

### Atmospheric implications

The fast reaction of NO<sub>3</sub> radicals with alkenes was found to give substantial yields of bifunctional carbonyl-nitroxy products and the mechanism of their formation is expected to be relevant also for the conditions of the troposphere. Studies performed by other workers [12] have shown that such organic nitrates may contribute to the atmospheric transport of NO<sub>x</sub> by acting as reservoirs, releasing NO<sub>x</sub> by their degradation in the atmosphere, but bifunctional nitrates may also be subject to fast removal by wet deposition.

It is of particular relevance to atmospheric photochemistry that isoprene, a main naturally emitted hydrocarbon, was found to form bifunctional organic nitrates as the predominant products of its reaction with the NO<sub>3</sub> radical in air.

Although the OH initiated oxidation of aromatics is generally more important under atmospheric conditions than the reaction with NO<sub>3</sub> the latter type of reaction becomes more important with increasing alkyl-substitution and predominates for phenolic and heterocyclic aromatics [12]. Thus a basic understanding of the mechanism of these reactions is needed to investigate the role of aromatic species in tropospheric photochemistry.

## Acknowledgements

The authors gratefully acknowledge Mr. G. Ottobri for his help with the experimental setup and Prof. C. Lohse, Prof. B. Rindone, Prof. C.J. Nielsen and Dr. I. Wängberg for helpful discussions. This study has been supported by the CNR-ENEL project "Interaction of Energy Systems with Human Health and Environment", Rome, Italy.

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### 3.7 Laboratory Studies of Peroxy Radical Reactions of Importance for Tropospheric Chemistry

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#### Summary

Studies of the UV absorption spectra as well as the kinetics and products of reactions of the following organic peroxy radicals have been carried out:  $\text{CH}_3\text{O}_2$ ,  $\text{CH}_2=\text{CHCH}_2\text{O}_2$ ,  $\text{HOCH}_2\text{CH}_2\text{O}_2$ ,  $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}_2)\text{CH}_3$ ,  $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{O}_2$ ,  $(\text{CH}_3)_2\text{CH}(\text{OH})\text{CH}(\text{O}_2)(\text{CH}_3)_2$ ,  $\text{CH}_3\text{OCH}_2\text{O}_2$ ,  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$  and  $\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2$ . These radicals were chosen to be representative of those formed from the degradation of some classes of volatile organic compound (VOC) likely to be important in tropospheric chemistry (*i.e.* alkanes, alkenes, conjugated dienes, alcohols, ethers, aldehydes and ketones). Kinetic studies of the self reactions and reactions with  $\text{HO}_2$  were carried out using the molecular modulation technique and the laser flash photolysis technique, coupled with UV absorption spectroscopy. Product studies were carried out by long pathlength Fourier transform infra-red spectroscopy and UV-visible diode array spectroscopy. This work has also allowed investigation of a variety of laboratory sources of peroxy radicals.

The results have been used, along with those obtained by other LACTOZ participants, to establish trends of reactivity of peroxy radicals, and to assign rate coefficients to complex peroxy radicals, in particular those formed from the OH-initiated degradation of isoprene. A degradation mechanism of isoprene to first generation products has been assembled, incorporating these data, which gives a good description of the product yields measured in other laboratory studies.

#### Aims of the research

The reactions of organic peroxy radicals and  $\text{HO}_2$  are of interest for tropospheric chemistry, since they are chain carriers in VOC oxidation mechanisms, converting  $\text{NO}$  to  $\text{NO}_2$  and consequently producing  $\text{O}_3$ . The reactions of  $\text{RO}_2$  with  $\text{HO}_2$  and the permutation reactions of organic peroxy radicals ( $\text{RO}_2 + \text{RO}_2$  and  $\text{RO}_2 + \text{R}'\text{O}_2$ ) lead to radical termination, and may therefore significantly reduce  $\text{O}_3$  formation chain lengths, particularly at lower levels of  $\text{NO}_x$ .

Although some comparatively simple peroxy radicals of tropospheric importance can be readily generated and studied in laboratory systems, the majority are difficult to generate independently from isomeric species. Furthermore, the extreme diversity of emitted organic compounds implies the production of many hundreds of structurally different peroxy radicals which will never realistically be studied, but for which the rates and products of key reactions may need to be estimated. The main aims of the work presented in this report were:

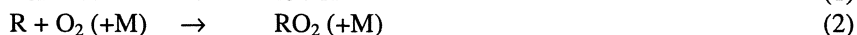
- To study the UV absorption spectra as well as the kinetics and products of the self-reactions and reactions with HO<sub>2</sub> for simple peroxy radicals derived from tropospherically abundant VOCs (*e.g.* CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>).
- To investigate novel methods for generating peroxy radicals in laboratory systems.
- To study the UV absorption spectra, and kinetics and products of the self-reactions and reactions with HO<sub>2</sub> for comparatively simple peroxy radicals containing structural features or functional groups representative of different classes of VOC.
- To identify and, where possible, rationalise the effect of the different functionalities on the UV absorption spectra and reactivity of organic peroxy radicals as a first step to defining structure-reactivity relationships.

### Principal scientific results

The work performed within the duration of the LACTOZ subproject has allowed laboratory data to be obtained on the UV absorption spectra, and kinetics and products of the self-reactions and reactions with HO<sub>2</sub> for a range of peroxy radicals. Some additional kinetic and mechanistic information related to other aspects of VOC degradation has also been obtained, particularly concerning the behaviour of some of the "oxy" radicals (RO) formed from reactions of the peroxy radicals. Much of this work has appeared in the open literature [1–12].

#### *Generation of peroxy radicals in laboratory systems*

The generation of peroxy radicals may be achieved in a number of ways, as recently discussed in detail [6]. In the present work programme, the photolysis of organic halides (RX, X = Br, I) has been considered as a novel method of generating specific peroxy radicals, independently of the isomeric species which would result in many cases from the general oxidation of a parent VOC:



Some success was achieved with this method, although certain complications were apparent which appear to arise from both the subsequent behaviour of the halogen atom X in the system, and from the generation of the organic fragment with a significant amount of excess energy. Both Br and I atoms were found to react with

RO<sub>2</sub> radicals to form ROOX adducts with very intense UV absorption spectra, peaking at *ca.* 265 and 295 nm respectively. This can cause significant complications in kinetics studies, owing to interfering UV absorptions and sequestration of the peroxy radical. However, it appears to be less of a problem in steady state systems (*e.g.* product studies) where the adduct acts as a comparatively short-lived intermediate in the RO<sub>2</sub> catalysed recombination of the halogen atoms, and does not accumulate significantly. In some systems, the generation of a "hot" organic fragment may complicate the subsequent chemistry, as was believed to be the case during the study of HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> formation from iodoethanol photolysis [4, 5].

### *UV absorption spectra*

The maximum UV absorption cross-sections and wavelengths of the maxima for all the peroxy radicals measured by this group are given in Table 1. For those radicals not containing a carbonyl group, the spectra at wavelengths longer than 200 nm have been found to consist of a single, unstructured UV band resulting from the "-OO" chromophore. The maximum absorption cross-sections for most of the species lie in the range *ca.*  $4\text{--}5 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ , suggesting that the presence of a range of functionalities on the organic group has only a comparatively minor influence on the intensity of the absorption spectra. The spectrum of the allyl peroxy radical (CH<sub>2</sub>=CHCH<sub>2</sub>O<sub>2</sub>) appears to be slightly more intense than that of the corresponding alkyl peroxy radical (*n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> [6]), and those for the  $\alpha$ -oxygenated radicals (HOCH<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub>) less intense than the corresponding alkyl peroxy radicals (CH<sub>3</sub>O<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>). The positions of the absorption maxima are also only influenced slightly by the presence of those functional groups investigated in the present work, although clear trends are emerging which apparently relate to the electron-donating ability of the organic group. All alkyl peroxy radical spectra appear to have maxima very close to 240 nm, which is some 35 nm to longer wavelength than that of HO<sub>2</sub>, presumably since organic groups are significantly more electron-donating than a hydrogen atom. The electron-withdrawing influence of the  $\alpha$ -oxygenated groups in HOCH<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> leads to a shift to shorter wavelengths by some 5–10 nm compared with the corresponding alkyl peroxy radicals. A similar effect is also observed for other peroxy radicals containing electron-withdrawing functionalities (*e.g.* halogen atoms)  $\alpha$  to the peroxy radical centre [6]. In contrast, the spectra of the  $\beta$ -oxygenated peroxy radicals (HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>CH(OH)CH(O<sub>2</sub>)CH<sub>3</sub> and (CH<sub>3</sub>)<sub>2</sub>CH(OH)CH(O<sub>2</sub>)(CH<sub>3</sub>)<sub>2</sub>) are shifted to longer wavelength by some 5 nm compared with alkyl peroxy radicals. This may be interpreted in terms of the effect of possible internal hydrogen bonding in these radicals, together with the reduced electron-withdrawing influence compared with the  $\alpha$ -substituted radicals.

Peroxy radicals containing carbonyl groups have been found to contain two maxima (*e.g.* CH<sub>3</sub>C(O)O<sub>2</sub> [6]). Collaborative studies with Risø [2] and Bordeaux

[11] have established that this is also the case for the acetyl peroxy radical ( $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$ ), although there is some disagreement concerning the precise positions and intensities of the absorption maxima.

**Table 1:** Maximum UV absorption cross-sections and positions of the maxima for a series organic peroxy radicals and  $\text{HO}_2$  measured in this laboratory.

Peroxy radical	$\lambda_{\text{max}} / \text{nm}$	$\sigma / 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$
$\text{HO}_2$	205	430
$\text{CH}_3\text{O}_2$	235–240	500
$\text{C}_2\text{H}_5\text{O}_2^{\text{a}}$	235–240	470
$\text{CH}_2=\text{CHCH}_2\text{O}_2$	235	620
$\text{HOCH}_2\text{O}_2^{\text{a}}$	230	340
$\text{HOCH}_2\text{CH}_2\text{O}_2$	245	510
$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}_2)\text{CH}_3$	245	420
$(\text{CH}_3)_2\text{CH}(\text{OH})\text{CH}(\text{O}_2)(\text{CH}_3)_2$	245	410
$\text{CH}_3\text{OCH}_2\text{O}_2$	230	400
$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2^{\text{b}}$	230	220
	290	250
$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2^{\text{c}}$	220	420
	300	150

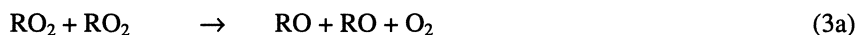
<sup>a</sup> Measured in this laboratory prior to LACTOZ. Displayed for comparison.

<sup>b</sup> Measured at University of Bordeaux in a collaborative study.

<sup>c</sup> Measured at Risø National Laboratory in a collaborative study.

### *Kinetics and branching ratios of self reactions*

Self-reaction rate coefficients ( $k_3$ ) and branching ratios (a) obtained in this laboratory for a series of peroxy radicals, are presented in Table 2, where a is defined as the fraction of the reaction proceeding via the propagating channel, *i.e.*  $k_{3a}/k_3$ :



It is apparent that rate coefficients for peroxy radical self reactions are strongly influenced by the structure of the radical. All peroxy radicals containing substituent functional groups have been found to be significantly more reactive than their unsubstituted alkyl peroxy counterparts: for example both  $\text{HOCH}_2\text{CH}_2\text{O}_2$  and  $\text{CH}_3\text{OCH}_2\text{O}_2$  are about 30 times more reactive than  $\text{C}_2\text{H}_5\text{O}_2$ . The work from this laboratory has concentrated particularly on the effect of the allyl group, and the  $\beta$ -hydroxy group, since the peroxy radicals derived from the OH-initiated oxidation of isoprene possess these functionalities. A trend of decreasing reactivity for the primary, secondary and tertiary  $\beta$ -hydroxy peroxy radicals  $\text{HOCH}_2\text{CH}_2\text{O}_2$ ,  $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}_2)\text{CH}_3$  and  $(\text{CH}_3)_2\text{CH}(\text{OH})\text{CH}(\text{O}_2)(\text{CH}_3)_2$  has been established, which is very similar to that observed for unsubstituted alkyl peroxy radicals [6].



**Table 2:** Summary of room temperature self-reaction parameters measured in this laboratory.

Peroxy radical	a	$k_4$	
		$10^{-12} \text{ cm}^3 \text{ s}^{-1}$	chemical system
CH <sub>3</sub> O <sub>2</sub>	0.33 <sup>b</sup>	0.36	Cl <sub>2</sub> / CH <sub>4</sub> / O <sub>2</sub>
		0.35	CH <sub>3</sub> I / O <sub>2</sub>
C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> <sup>c</sup>	0.63 <sup>b</sup>	0.080	Cl <sub>2</sub> / C <sub>2</sub> H <sub>6</sub> / O <sub>2</sub>
		0.072	azoethane / O <sub>2</sub>
		0.68	1,5-hexadiene / O <sub>2</sub>
CH <sub>2</sub> =CHCH <sub>2</sub> O <sub>2</sub>	0.61	0.68	1,5-hexadiene / O <sub>2</sub>
HOCH <sub>2</sub> O <sub>2</sub> <sup>c</sup>	0.89	6.1	HCHO / O <sub>2</sub>
HOCH <sub>2</sub> CH <sub>2</sub> O <sub>2</sub>	0.50 <sup>d</sup>	2.1	H <sub>2</sub> O <sub>2</sub> / C <sub>2</sub> H <sub>4</sub> / O <sub>2</sub>
		2.2	HOCH <sub>2</sub> CH <sub>2</sub> I / O <sub>2</sub>
CH <sub>3</sub> CH(OH)CH(O <sub>2</sub> )CH <sub>3</sub>	0.75 <sup>e</sup>	0.48	H <sub>2</sub> O <sub>2</sub> / <i>trans</i> 2-butene / O <sub>2</sub>
(CH <sub>3</sub> ) <sub>2</sub> CH(OH)CH(O <sub>2</sub> )(CH <sub>3</sub> ) <sub>2</sub>	1.0 <sup>f</sup>	0.0057	H <sub>2</sub> O <sub>2</sub> / 2,3-dimethyl 2-butene / O <sub>2</sub>
CH <sub>3</sub> OCH <sub>2</sub> O <sub>2</sub>	0.7	2.1	Cl <sub>2</sub> / CH <sub>3</sub> OCH <sub>3</sub> / O <sub>2</sub>
CH <sub>3</sub> C(O)CH <sub>2</sub> O <sub>2</sub> <sup>g</sup>	0.75	8.0	Cl <sub>2</sub> / CH <sub>3</sub> COCH <sub>3</sub> / O <sub>2</sub>

<sup>a</sup> Units  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

<sup>b</sup> Recommended by Lightfoot *et al.* [6].

<sup>c</sup> Measured in this laboratory prior to LACTOZ. Displayed for comparison.

<sup>d</sup> Measured by Barnes *et al.* [13].

<sup>e</sup> Estimated.

<sup>f</sup> By definition.

<sup>g</sup> Measured at University of Bordeaux in a collaborative study.

The values of *a* for primary peroxy radicals  $\geq \text{C}_2$  have been found to be remarkably insensitive to the nature of the organic group (lying in the range 0.5–0.75), despite rate coefficients ranging from  $0.08 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> to  $8.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for CH<sub>3</sub>C(O)CH<sub>2</sub>O<sub>2</sub>.

### Kinetics and branching ratios of reactions with HO<sub>2</sub>

Rate coefficients for the reactions of peroxy radicals with HO<sub>2</sub> (*k*<sub>4</sub>) measured in this laboratory are given in Table 3:



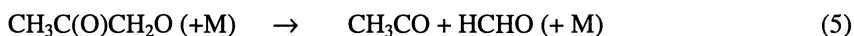
Although channel (4a) tends to dominate for most peroxy radicals, strong evidence for a significant contribution (*ca.* 40 %) from channel (4b) has been found for the reaction involving CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> [9] (collaborative study with Ford Motor Company, Dearborn), which is similar to that observed previously for the closely related radical HOCH<sub>2</sub>O<sub>2</sub> [6]. The kinetics studies indicate that the values of *k*<sub>4</sub> for primary secondary and tertiary  $\beta$ -hydroxy peroxy radicals are equivalent, within experimental error, suggesting that the rates of such reactions are insensitive to both the size and degree of substitution of the organic group. These data also indicate that the  $\beta$ -hydroxy group itself apparently has little influence on the reactivity of peroxy radicals with HO<sub>2</sub>. From the available data base, it appears that alkyl and  $\beta$ -hydroxy peroxy radicals  $\geq \text{C}_3$  have room temperature rate

coefficients in the region of  $1.5$  to  $2 \times 10^{-11}$   $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ , with no significant trend with increasing carbon number (see also data from University of Bordeaux).

In contrast, available information on the reactions of alkyl and  $\beta$ -hydroxy peroxy radicals with NO [6, 14, 15] indicate a progressive decrease in reactivity as the carbon number increases, suggesting that the reactions with  $\text{HO}_2$  become progressively more favoured over the reactions with NO, as the size of the organic group becomes larger.

### *Oxy radical reactions*

Some information was also obtained which relates to the behaviour of oxy radicals, formed from reactions of peroxy radicals. The thermal decomposition of acetonoxo radicals ( $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}$ ) was found to predominate over the reaction with  $\text{O}_2$  under tropospheric conditions (collaboration with MPI Mainz and University of Bordeaux [10, 11]):



**Table 3:** Room temperature  $\text{RO}_2 + \text{HO}_2$  rate coefficients measured in this laboratory.

Peroxy radical	$k_4$	pressure	chemical system
	$10^{-12} \text{ cm}^3 \text{ s}^{-1}$	Torr	
$\text{CH}_3\text{O}_2$	5.4	10	$\text{Cl}_2 / \text{CH}_4 / \text{H}_2\text{O}_2 / \text{O}_2$
	6.8	760	$\text{Cl}_2 / \text{CH}_4 / \text{H}_2 / \text{O}_2$
$\text{C}_2\text{H}_5\text{O}_2^{\text{a}}$	6.3	2	$\text{Cl}_2 / \text{C}_2\text{H}_6 / \text{CH}_3\text{OH} / \text{O}_2$
	9.5	760	$\text{Cl}_2 / \text{C}_2\text{H}_6 / \text{CH}_3\text{OH} / \text{O}_2$
$\text{HOCH}_2\text{O}_2^{\text{a}}$	12.0	2	$\text{HCHO} / \text{O}_2$
$\text{HOCH}_2\text{CH}_2\text{O}_2$	8.4	10	$\text{HOCH}_2\text{CH}_2\text{I} / \text{O}_2$
	12.0	760	$\text{HOCH}_2\text{CH}_2\text{Cl} / \text{O}_2$
	15.0	760	$\text{H}_2\text{O}_2 / \text{C}_2\text{H}_4 / \text{O}_2$
$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}_2)\text{CH}_3$	15.0	760	$\text{H}_2\text{O}_2 / \text{trans-2-butene} / \text{O}_2$
$(\text{CH}_3)_2\text{CH}(\text{OH})\text{CH}(\text{O}_2)(\text{CH}_3)_2$	~ 20	760	$\text{H}_2\text{O}_2 / 2,3\text{-dimethyl 2-butene} / \text{O}_2$
$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2^{\text{b}}$	9.0	760	$\text{Cl}_2 / \text{CH}_3\text{COCH}_3 / \text{CH}_3\text{OH} / \text{O}_2$

<sup>a</sup> Measured in this laboratory prior to LACTOZ. Displayed for comparison.

<sup>b</sup> Measured at University of Bordeaux in a collaborative study.

The methoxymethoxy radical ( $\text{CH}_3\text{OCH}_2\text{O}$ ) was found to decompose by a mechanism involving H-atom ejection, in competition with its reaction with  $\text{O}_2$  [8], thereby explaining complications in a previously published study [16] of the kinetics of  $\text{CH}_3\text{OCH}_2\text{O}_2$ :



## Achievements

The work performed on the UV spectra and kinetics of reactions of peroxy radicals at this laboratory, and by collaborating partners within LACTOZ, has significantly expanded the available data base and has consequently improved our understanding of some of the processes describing the degradation of VOCs in the troposphere. Consistent with the primary objective of this work, significant progress has been made in establishing the influence on peroxy radical reactivity, of a variety of functional groups likely to be prevalent in peroxy radicals involved in tropospheric chemistry. This is perhaps best illustrated by the detailed mechanism of the OH initiated degradation of isoprene to first generation products, which was constructed by this group [12] using information mainly obtained by collaborating partners within the LACTOZ subproject. Due to the complexity of the organic compound, the mechanism was defined on the basis of correlations and trends of reactivity of intermediates possessing similar functional groups. The resulting mechanism is able to give a good description of the yields of stable products measured in the laboratory in both the presence and absence of NO<sub>x</sub> [12], indicating a sound understanding of the detailed chemistry. The work performed to date provides, therefore, a sound basis for further systematic expansion of the data base on peroxy radical reactivity, and the future development of structure-reactivity rules which can be applied to peroxy radicals derived from many classes of VOC.

## Acknowledgements

The support of the European Commission, the Natural Environment Research Council and the UK Department of the Environment is gratefully acknowledged. We also wish to thank Geert Moortgat and John Crowley (MPI Mainz), Robert Lesclaux, Phil Lightfoot and Bernard Veyret (University of Bordeaux), Tim Wallington (Ford Motor Company) and Ole John Nielsen (Risø) for close collaboration on peroxy radicals studies during the past seven years.

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### 3.8 The Rates and Mechanisms for VOC Photo-oxidation Reactions under Simulated Tropospheric Conditions

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#### Summary

Laboratory kinetic studies of gas-phase elementary reactions of importance to tropospheric chemistry were initiated as part of the LACTOZ programme at the Swiss Federal Institute of Environmental Science and Technology (EAWAG) in October 1989. Two types of experiments have been carried out: (i) studies of the kinetics of competitive OH radical reactions with VOC in an atmospheric flow reactor and (ii) detailed end-product analyses of the OH radical initiated photo-oxidations of VOCs carried out in a static Teflon bag reactor.

The first type of experiment involves the application of a flow reactor designed to operate over the temperature range  $-25$  to  $80$  °C and over the pressure range 100 to 760 Torr. This reactor has been used to study competitive OH reactions with pairs of aliphatic ethers or with an ether plus 2,3-dimethylbutane as the reference compound. The temperature coefficients of the OH reactions with diethyl ether, methyl *n*-butyl ether, ethyl *n*-butyl ether and di-*n*-butyl ether have been determined. This system has also been used to study competitive OH reactions with pairs of aromatic compounds or with an aromatic compound plus a reference compound. The temperature coefficients of the OH reactions with benzene, toluene, phenol, benzaldehyde, *o*-cresol, *m*-cresol and *p*-cresol have been determined.

In the second series of experiments, the products from the photo-oxidation of diethyl ether, carried out in a Teflon bag reactor at ppm and ppb levels, have been determined by withdrawing vapour samples and monitoring by gas chromatography, HPLC and by chemiluminescence analysis. The major reaction products which have been measured are ethyl formate, ethyl acetate, acetaldehyde, formaldehyde, PAN, methyl nitrate and ethyl nitrate. The products observed arise from the decomposition reactions of the 1-ethoxyethoxy radical and from its reaction with oxygen. The data enable the establishment of a quantitative mechanism for the photo-oxidative reaction. In addition the rate of conversion of NO to NO<sub>2</sub>, determined by chemiluminescence analysis, shows that for each molecule of ether reacted only one molecule of NO is converted to NO<sub>2</sub>. In further end-product analyses experiments, the OH radical initiated photo-oxidation of *n*-hexane or the photolyses of 2- or 3-hexyl nitrites were studied to examine the

importance of alkoxy radicals undergoing isomerization versus unimolecular decomposition or reaction with oxygen. Based on the first observations of products arising from the isomerization of the hexoxy radicals in these systems, the fractions of alkoxy radicals undergoing isomerization were determined and are in good agreement with theoretical predictions.

### **Aims of the research**

The aims of the research project have been to obtain information on the rates and mechanisms for a range of VOC photo-oxidation reactions under simulated atmospheric conditions. By deriving detailed quantitative kinetic data on the reactions involved in the complex chemistry of the tropospheric photodegradations of VOC, we seek to provide key parameters required in tropospheric modelling. Such mathematical modelling studies will ultimately form the basis for drawing up scientifically sound control strategies for the release of VOC into the atmosphere.

### **Principal scientific findings**

#### *Kinetic studies*

The experiments were performed in an irradiated thermostated flow reactor over the temperature range 248–353 K. Assuming loss of the ether (ROR) and of the reference compound (REF) occurs only by OH attack via reactions (1) and (2):



then integration and combination of the rate expressions for reactions (1) and (2) leads to

$$\ln \frac{[\text{ROR}]_0}{[\text{ROR}]_i} = \frac{k_2}{k_1} \ln \frac{[\text{REF}]_0}{[\text{REF}]_i} \quad (i)$$

where the subscripts 0 and i refer to the concentrations measured in the dark and under reactor illumination respectively. Plots of the data according to equation (i) are linear with zero intercepts, confirming the general correctness of the treatment of the data. The rate coefficient ratios at a given temperature were then derived from such plots and relative Arrhenius parameters were obtained from measurements of the ratios over a range of temperatures. These were converted to absolute values from a knowledge of the temperature dependent rate coefficients of the reference reactions.

#### Rate coefficients for the reactions of OH radicals with ethers

The Arrhenius parameters of the reactions of hydroxyl radicals with aliphatic ethers, shown in Table 1, are based on the temperature independent value of

$k_1 = 6.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for OH + 2,3-dimethylbutane [1]. Previous discrepancies in the room temperature rate coefficients for the OH reactions with ethyl *n*-butyl ether and di-*n*-butyl ether, obtained in the flow and static experiments of Bennett and Kerr [2] have been resolved.

**Table 1:** Arrhenius parameters for OH radical reactions with ethers.

Ether	$(E_a/R) / \text{K}$	$A / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
Diethyl ether	$-262 \pm 150$	$5.2 \times 10^{-12}$
Methyl <i>n</i> -butyl ether	$-309 \pm 150$	$5.4 \times 10^{-12}$
Ethyl <i>n</i> -butyl ether	$-335 \pm 150$	$7.3 \times 10^{-12}$
Di- <i>n</i> -butyl ether	$-502 \pm 150$	$5.5 \times 10^{-12}$
Di- <i>n</i> -pentyl ether	$-417 \pm 150$	$8.5 \times 10^{-12}$

### Rate coefficients for the reactions of OH radicals with aromatic compounds

The Arrhenius parameters of the reactions of hydroxyl radicals with aromatic compounds, listed in Table 2, are based on the rate coefficients ( $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ) of the reference compounds taken from recent evaluations of OH radical reactions:  $k(\text{2,3-dimethylbutane}) = 6.2 \times 10^{-12}$  [1], independent of temperature;  $k(\text{diethyl ether}) = 7.3 \times 10^{-12} \exp(158 \text{ K} / T)$ , 242–440 K [3];  $k(\text{1,3-butadiene}) = 1.48 \times 10^{-11} \exp(448 \text{ K} / T)$ , 295–483 K [1];  $k(\text{phenol}) = 6.75 \times 10^{-12} \exp(405 \text{ K} / T)$ , 245–300 K [3]. Our results are in good agreement with existing literature data on OH + aromatic compounds and where possible evaluated rate coefficients have been deduced or updated.

**Table 2:** Arrhenius parameters for OH radical reactions with aromatic compounds.

Aromatic	$(E_a/R) / \text{K}$	$A / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
Benzene	$231 \pm 84$	$2.6 \times 10^{-12}$
Toluene	$-614 \pm 114$	$7.9 \times 10^{-13}$
<i>o</i> -Cresol	$-1170 \pm 248$	$9.8 \times 10^{-13}$
<i>m</i> -Cresol	$-686 \pm 231$	$5.2 \times 10^{-12}$
<i>p</i> -Cresol	$-943 \pm 449$	$2.2 \times 10^{-12}$
Phenol	$-1270 \pm 233$	$3.7 \times 10^{-13}$
Benzaldehyde	$-243 \pm 85$	$5.3 \times 10^{-12}$

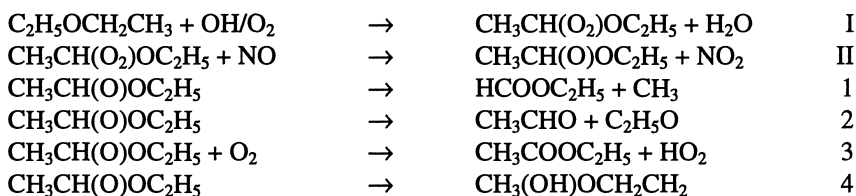
### Product studies

The experiments were carried out in 200 dm<sup>3</sup> Teflon bag reactors at room temperature ( $297 \pm 3 \text{ K}$ ) and at atmospheric pressure ( $725 \pm 5 \text{ Torr}$ ). The decay of the VOC concentration and build up of the product concentrations were monitored during the course of the experiment. The concentration of VOC was measured by GC-FID. The formation of organic nitrates and carbonyls were measured by GC with sample preconcentration using adsorption tubes filled with Tenax TA. Detection was performed with FID and ECD coupled in series. The carbonyl

products were determined by derivatisation with 2,4-dinitrophenylhydrazine (2,4-DNPH) followed by HPLC using a three-component gradient solvent programme and u.v. detection.

#### OH initiated photo-oxidation of diethyl ether

The major products were ethyl formate and formaldehyde and the minor products were ethyl acetate, acetaldehyde, peroxyacetyl nitrate, and methyl and ethyl nitrates. The products arise from the decomposition reactions of the 1-ethoxyethoxy radical and from its reaction with molecular oxygen:



The fractions of the 1-ethoxyethoxy radicals undergoing reactions 1–4 are shown in Table 3 and compared with previous FTIR studies and with theoretical estimates. Although diethyl ether is rapidly photo-oxidised, its contribution to tropospheric ozone formation is limited as one of the major products is ethyl formate which is relatively unreactive in the troposphere. This is also confirmed from the NO–NO<sub>2</sub> oxidation stoichiometry, *ca.* 1 mole NO is oxidised per mole diethyl ether reacted.

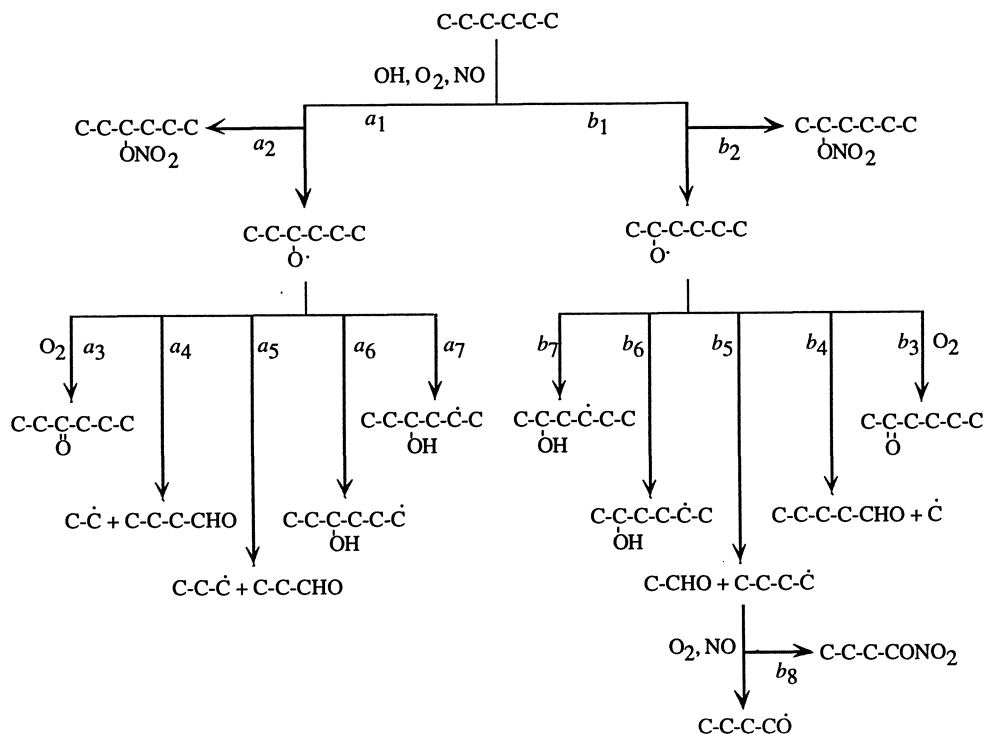
**Table 3:** Product formation from the alkoxy radical CH<sub>3</sub>CH(O)OC<sub>2</sub>H<sub>5</sub>.

Reference	f <sub>1</sub>	f <sub>2</sub>	f <sub>3</sub>	f <sub>4</sub>
This work	0.84 ± 0.05	0.06 ± 0.01	0.10 ± 0.03	0
[6]	0.92 ± 0.06	< 0.05	< 0.05	0
[7]	0.95	0	0.04	0.01

Alkoxy radicals from the photolyses of hexyl nitrites and the photo-oxidation of hexane.

The primary products which were quantified include 3-hexyl nitrate, 2-hexyl nitrate, *n*-butyl nitrate, 3-hexanone, 2-hexanone, formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde and 5-hydroxy-2-hexanone. 2,5-hexanedione was quantified but is thought to be a secondary product. and 5-nitrooxy-2-hexanol was detected but reliable quantification was not possible.





**Fig. 1:** General reaction scheme for the photo-oxidation of hexane.

A general reaction mechanism for the OH initiated photo-oxidation of hexane is shown in Fig. 1. For a quantitative assessment of the importance of each reaction channel for the reactions of the hexoxy radicals, the observed yields of the primary products were corrected for secondary photo-oxidation, and the fractions were calculated as described by Eberhard *et al.* [4]. As shown in Table 4 the derived fractions for the isomerization reaction channels  $a_6$  and  $b_6$  are in very good agreement with the theoretical predictions. These values indicate that the 2-hexoxy radical undergoes rapid isomerization by abstracting a secondary H-atom. In comparison the isomerization of the 3-hexoxy radical is significantly slower owing to the need to abstract a primary H-atom.

**Table 4:** Summary of derived fractions for hexoxy radical reactions.

Reaction channel <sup>a</sup>	Process	Fraction (%)	Estimation <sup>b,c</sup> (%)
<b>3-Hexoxy</b>			
<i>a</i> <sub>3</sub>	reaction with O <sub>2</sub>	6.7 ± 3.5	25.1
<i>a</i> <sub>4</sub>	decomposition	10.4 ± 7.3	2.5
<i>a</i> <sub>5</sub>	decomposition	9.1 ± 2.9	2.5
<i>a</i> <sub>6</sub>	1,5-H shift isomerization	73.8 ± 12.5 <sup>d</sup>	68.1
<i>a</i> <sub>7</sub>	1,4-H shift isomerization	0.0	1.8
<b>2-Hexoxy</b>			
<i>b</i> <sub>3</sub>	reaction with O <sub>2</sub>	0.8 ± 0.5	0.3
<i>b</i> <sub>4</sub>	decomposition	0.0	0.0
<i>b</i> <sub>5</sub>	decomposition	0.2 ± 0.1	0.0
<i>b</i> <sub>6</sub>	1,5-H shift isomerization	99.0 ± 0.5	99.6
<i>b</i> <sub>7</sub>	1,4-H shift isomerization	0.0	0.0

<sup>a</sup> See Fig. 1;

<sup>b</sup> Based on estimated rate coefficients by the method of Carter and Atkinson [5],

<sup>c</sup> Estimate for RO+O<sub>2</sub> reaction rate from Atkinson *et al.* [6],

<sup>d</sup> Calculated by difference.

### Achievements of the project

The project has resulted in a considerable extension of the kinetic data base for the reactions of OH radicals with the VOC classes of aliphatic ethers and of aromatic compounds. Such data are essential in the determination of tropospheric lifetimes of the VOC.

The detailed product studies of the atmospheric photo-oxidations of ethers have revealed much finer detail than hitherto reported and at the same time have been carried out under experimental conditions, with respect to mixing ratios of VOC, much closer to the real polluted atmosphere. Here the important conclusion is that data obtained from experiments carried out at VOC mixing ratios of ppm are consistent with those carried out at VOC mixing ratios much closer to tropospheric conditions, *i.e.* ~ ppb.

The highlight of the product studies has undoubtedly been the first observations and measurements of products arising from the isomerization reactions of alkoxy radicals in the photo-oxidations of hexane and hexyl nitrites. This is an important finding in directly confirming the occurrence of such isomerization reactions. Furthermore the quantitative agreement of the isomerization kinetic data with thermochemical kinetic estimates confirms that these estimation procedures can be used with confidence in the chemical mechanisms of modelling studies of the troposphere. The achievements of these projects have certainly matched and in many respects exceeded the original aims which were set out in initiating the research programme.

### Acknowledgement

This work was supported in part by a research grant from Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung.

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### 3.9 Laboratory Studies of NO<sub>3</sub> and OH Reactions of Tropospheric Relevance

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#### Summary

Kinetic studies have been performed on the individual steps occurring in the NO<sub>3</sub> and OH initiated oxidation of VOCs. The studied reactions include essentially reactions of NO<sub>3</sub> with alkenes, di-alkenes and dimethyl sulfide (DMS), reactions of NO<sub>3</sub> with intermediate peroxy radicals (HO<sub>2</sub>, CH<sub>3</sub>O<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>) and reactions of OH with methane and oxygenated VOCs (ethers, alcohols). The rate constants for these reactions have been measured, and mechanistic information has been determined. The experimental methods used were discharge-flow reactors coupled with mass spectrometry, electron paramagnetic resonance (EPR), laser-induced fluorescence (LIF) analysis and the laser photolysis associated with LIF analysis. The discharge-flow LIF and laser photolysis LIF experiments have been especially developed for these studies.

#### Aims of the research

The aims of the research were to provide kinetic and mechanistic data for NO<sub>3</sub> and OH reactions of potential atmospheric relevance. In particular, a large body of the studies aimed at improving the knowledge of the NO<sub>3</sub> initiated oxidation of VOCs during night-time in order to assess the contribution of the night-time processes to the overall atmospheric oxidation of VOCs and photo-oxidant formation.

#### Principal scientific findings

##### *NO<sub>3</sub> reactions in the night-time oxidation of VOCs*

Reactions of NO<sub>3</sub> with alkenes and di-alkenes

The kinetics of the reaction of NO<sub>3</sub> with the following molecules have been investigated using the discharge-flow mass spectrometry method: 2,3 dimethyl-2, butene ((CH<sub>3</sub>)<sub>2</sub>C=C(CH<sub>3</sub>)<sub>2</sub>), 1,3 butadiene (CH<sub>2</sub>=CH-CH=CH<sub>2</sub>), 2 methyl-1,3 butadiene (CH<sub>2</sub>=C(CH<sub>3</sub>)-CH=CH<sub>2</sub>, isoprene) and 2,3 dimethyl-1,3 butadiene (CH<sub>2</sub>=C(CH<sub>3</sub>)-C(CH<sub>3</sub>)=CH<sub>2</sub>).

The rate constants measured at 298 K (see Table III of the report) have contributed to extending the data base and to improving its quality. The data followed the same trend as for the similar electrophilic addition reaction of OH: the rate constant increases with the degree of methyl substitution of the butadiene.

Mass spectrometry analysis of the products provided some insight into the reaction mechanisms. Especially, the observations indicate that the NO<sub>3</sub> addition primarily occurs on both π bonds of the isoprene molecule.

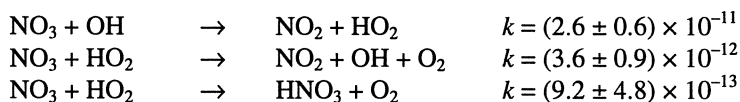
#### Reaction NO<sub>3</sub> + DMS

Although not directly relevant to LACTOZ, the study of the NO<sub>3</sub> + DMS reaction is mentioned since it has led to development of a method to study reaction mechanisms applicable to other VOCs. The method consisted of mass spectrometry chemical titration of the primary radicals produced (R), using Cl<sub>2</sub> or Br<sub>2</sub> as the titrant (R + Cl<sub>2</sub> → RCl + Cl and R + Br<sub>2</sub> → RBr + Br). The results showed that the reaction predominantly (≥ 98 %) proceeds to completion: NO<sub>3</sub> + CH<sub>3</sub>SCH<sub>3</sub> → CH<sub>3</sub>SCH<sub>2</sub> + HNO<sub>3</sub>, and hence converts NO<sub>x</sub> into HNO<sub>3</sub>. The peroxy radical, CH<sub>3</sub>SCH<sub>2</sub>O<sub>2</sub>, was observed by mass spectrometry upon addition of O<sub>2</sub> to the discharge-flow reactor.

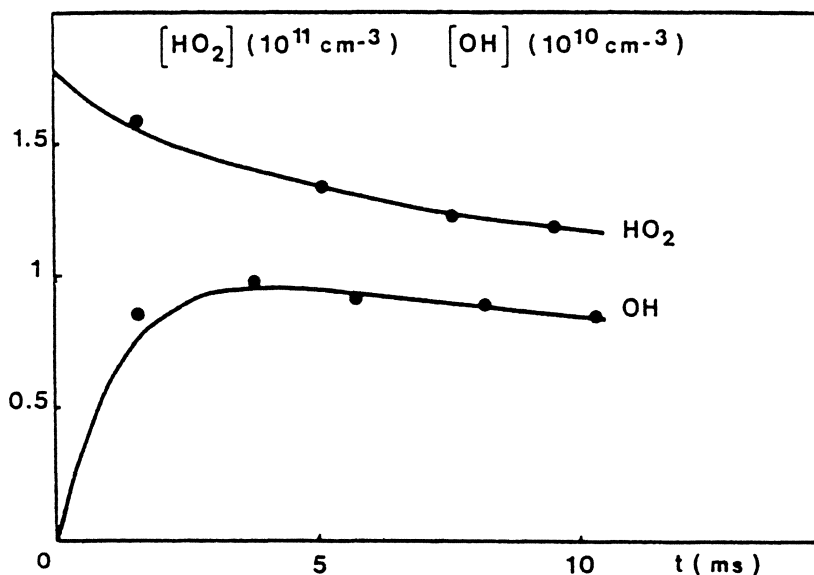
#### NO<sub>3</sub> reactions with peroxy radicals

##### Reaction of NO<sub>3</sub> with HO<sub>2</sub>

The reaction of NO<sub>3</sub> + HO<sub>2</sub> was considered of potential atmospheric relevance since both NO<sub>3</sub> and HO<sub>2</sub> radicals are present during night-time (PAN and PNA decomposition, reactions of NO<sub>3</sub> with H<sub>2</sub>CO and some hydrocarbons are sources of HO<sub>2</sub> radicals). The reaction of NO<sub>3</sub> + HO<sub>2</sub> was investigated together with the reaction of NO<sub>3</sub> + OH which interacted under the conditions of the flow-tube experiments. OH and HO<sub>2</sub> (after conversion into OH via NO + HO<sub>2</sub> → NO<sub>2</sub> + OH) were monitored by gas-phase EPR. The kinetic treatment of the OH and HO<sub>2</sub> decays (Fig. 1) yielded a rate constant at 298 K for the following reactions (units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>):



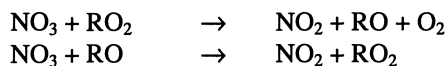
Thus, the NO<sub>3</sub> + HO<sub>2</sub> reaction was found to be a potentially significant source of OH radicals during night-time.



**Fig. 1:** Reactions of  $\text{NO}_3$  with  $\text{OH}$  and  $\text{HO}_2$ ; typical experimental (points) and calculated (solid lines) profiles of  $\text{OH}$  and  $\text{HO}_2$ ;  $[\text{NO}_3]_0 = 2.5 \times 10^{13} \text{ cm}^{-3}$ .

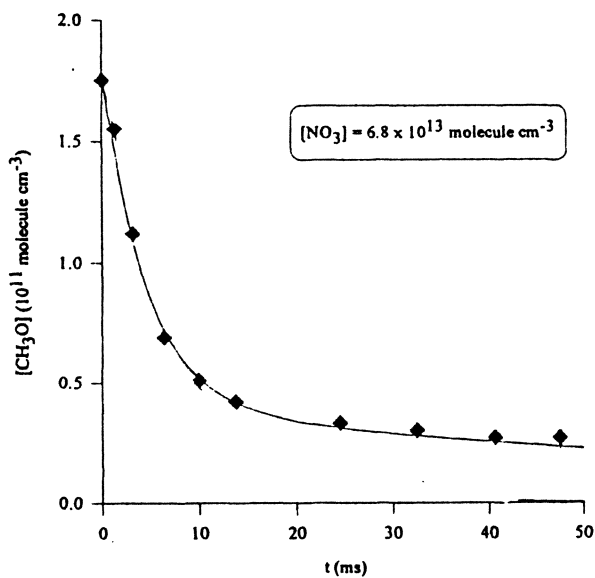
#### Reactions of $\text{NO}_3$ with $\text{CH}_3\text{O}_2$ and $\text{C}_2\text{H}_5\text{O}_2$

The reactions of  $\text{NO}_3$  with  $\text{RO}_2$  ( $\text{CH}_3\text{O}_2$ ,  $\text{C}_2\text{H}_5\text{O}_2$ ) have been investigated as potential conversion steps of  $\text{RO}_2$  into  $\text{RO}$  as the  $\text{NO}_3 + \text{HO}_2$  reaction converts  $\text{HO}_2$  into  $\text{OH}$ .  $\text{CH}_3\text{O}_2$  and  $\text{C}_2\text{H}_5\text{O}_2$  were chosen as models for peroxy radicals produced in the atmosphere as intermediates in the oxidation of hydrocarbons. The reactions of  $\text{NO}_3$  with  $\text{RO}_2$  ( $\text{CH}_3\text{O}_2$  and  $\text{C}_2\text{H}_5\text{O}_2$ ) were effectively found to be coupled with the reactions of  $\text{NO}_3$  and  $\text{RO}$  ( $\text{CH}_3\text{O}$  and  $\text{C}_2\text{H}_5\text{O}$ ) under laboratory conditions:

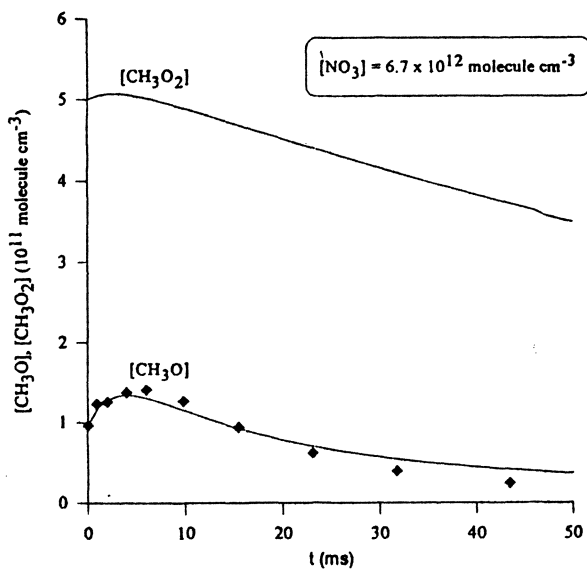


The rate constants of these reactions were determined in discharge-flow experiments from kinetic analysis of  $\text{RO}$  concentrations measured by LIF using as initial reactants  $\text{NO}_3$  and  $\text{RO}$  or  $\text{NO}_3$  and  $\text{RO}_2$  (Figs 2 and 3).

The data obtained at 298 K are summarised in Table 1 together with those for reactions of  $\text{NO}_3$  with  $\text{HO}_2$  and  $\text{OH}$ .



**Fig. 2:** Reaction of  $\text{NO}_3$  with  $\text{CH}_3\text{O}$  and  $\text{CH}_3\text{O}_2$ , with  $\text{NO}_3$  and  $\text{CH}_3\text{O}$  as initial reactants: experimental (points) and calculated (solid line) profiles of  $\text{CH}_3\text{O}$ .



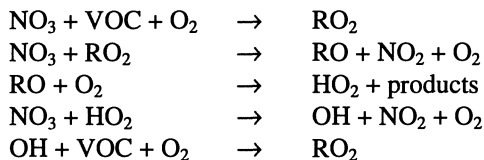
**Fig. 3:** Reaction of  $\text{NO}_3$  with  $\text{CH}_3\text{O}$  and  $\text{CH}_3\text{O}_2$ , with  $\text{NO}_3$  and  $\text{CH}_3\text{O}_2$  as initial reactants: experimental (points) of  $\text{CH}_3\text{O}$  and calculated (solid line) profiles of  $\text{CH}_3\text{O}$  and  $\text{CH}_3\text{O}_2$ .

**Table 1:** Rate constants in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K for the reactions of  $\text{NO}_3$  with RO and  $\text{RO}_2$ 

R	H	$\text{CH}_3$	$\text{C}_2\text{H}_5$
$\text{NO}_3 + \text{RO} \rightarrow \text{NO}_2 + \text{RO}_2$	$(2.6 \pm 0.6) \times 10^{-11}$	$(1.8 \pm 0.5) \times 10^{-12}$	$(3.3 \pm 0.8) \times 10^{-12}$
$\text{NO}_3 + \text{RO}_2 \rightarrow \text{NO}_2 + \text{RO} + \text{O}_2$	$(3.6 \pm 0.9) \times 10^{-12}$	$(1.2 \pm 0.6) \times 10^{-12}$	$(1.3 \pm 1.0) \times 10^{-12}$

### Mechanism for the $\text{NO}_3$ initiated oxidation of VOCs in the atmosphere

We suggested the following chain mechanism for the night-time oxidation of VOCs [1]:



The present results together with those obtained at PCL, Oxford and MPI, Mainz, indicate that reactions of  $\text{NO}_3$  with  $\text{HO}_2$  and  $\text{RO}_2$  ( $\text{CH}_3\text{O}_2$ ,  $\text{C}_2\text{H}_5\text{O}_2$ ) are potentially important chain propagation steps in the above mechanism: their rate constants are fairly high, and they convert  $\text{HO}_2$  into OH and  $\text{RO}_2$  into RO. Such mechanisms used in box modelling of  $\text{NO}_3$  – DMS interaction in semi-polluted coastal areas have been shown to produce high levels of peroxy radicals and related so-called photo-oxidants ( $\text{CH}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{CH}_3\text{OOH}$ ) during night-time [1,2]. Further kinetic and mechanistic data are indeed required for reactions of  $\text{NO}_3$  with other peroxy radicals before such a mechanism could be generalised.

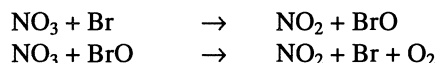
### *$\text{NO}_3$ reactions with inorganic species*

Reactions of  $\text{NO}_3$  with hydrogen halides, HX (X = Cl, Br, I)

The reactions of  $\text{NO}_3$  with HX have been studied by discharge-flow EPR, by monitoring the halogen atom (X) resulting from the sequence:  $\text{NO}_3 + \text{HX} \rightarrow \text{HNO}_3 + \text{X}$ ;  $\text{NO}_3 + \text{X} \rightarrow \text{NO}_2 + \text{XO}$ ;  $\text{NO} + \text{XO} \rightarrow \text{NO}_2 + \text{X}$ . No reactivity was observed at 298 K between  $\text{NO}_3$  and HCl and HBr. In contrast  $\text{NO}_3$  was found to react with HI:  $k = 1.3 \times 10^{-12} \exp\{(-1830 \pm 300) \text{ K} / T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 298–373 K. This reaction is nevertheless too slow to be of atmospheric significance.

Reactions of  $\text{NO}_3$  with Br and BrO

These reactions have been studied in a discharge-flow reactor by monitoring Br and BrO by gas-phase EPR. Similarly to the reactions of  $\text{NO}_3$  with OH and  $\text{HO}_2$ , these two reactions were found to interact under laboratory conditions:





The rate constants obtained at 298 K were:  $(1.6 \pm 0.7) \times 10^{-11}$  and  $0.3 \times 10^{-12} < k < 3 \times 10^{-12}$  ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ), respectively. These reactions have been recently postulated to possibly control both  $\text{NO}_3$  and active bromine in the atmosphere. It was suggested that the reaction of  $\text{NO}_3 + \text{BrO}$  could be the missing process responsible for the loss of  $\text{NO}_3$  in some field observations [3].

### **OH reactions with VOCs**

#### **Reaction of OH with $\text{CH}_4$**

The reaction  $\text{OH} + \text{CH}_4$  has been investigated subsequent to a study yielding a rate constant value 25 % lower than that recommended so far over the atmospheric temperature range [4]. The data obtained using both the discharge-flow EPR and LP-LIF methods are in excellent agreement with this determination. The LP-LIF value is  $k = (2.56 \pm 0.53) \times 10^{-12} \exp\{-(1765 \pm 146) / T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 233–343 K with  $k = (6.34 \pm 0.56) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K. These data illustrate the requirement of high precision measurements for key reactions such as the reaction  $\text{OH} + \text{CH}_4$  which controls the oxidative capacity of the troposphere and the atmospheric concentration of the greenhouse  $\text{CH}_4$  species.

#### **Reactions of OH with oxygenated VOCs (ethers, alcohols)**

Oxygenated VOCs such as ethers and alcohols are used as solvents or fuel additives. The rate constants for OH reactions with several ethers and alcohols have been measured over the temperature range 230–370 K, using the LP-LIF method. The studied ethers and alcohols are: dimethyl ether ( $(\text{CH}_3)_2\text{O}$ ), dipropyl ether ( $(\text{C}_3\text{H}_7)_2\text{O}$ ), ethyl butyl ether ( $\text{C}_2\text{H}_5\text{OC}_4\text{H}_9$ ), methyl *tert*-butyl ether ( $\text{C}_2\text{H}_5\text{OC}(\text{CH}_3)_3$ ), methyl *tert*-amyl ether ( $\text{CH}_3\text{OC}(\text{CH}_3)_2\text{C}_2\text{H}_5$ ) and *tert*-butanol ( $(\text{CH}_3)_3\text{COH}$ ). The Arrhenius plots  $\ln k = f(1 / T)$  are presented in Fig. 4 for the reactions of  $\text{OH} +$  ethers. The rate constant data are summarised in Chapter 2, Table 1. These measurements improve the existing data base for these reactions [5], especially by providing additional data at the lowest temperatures. Slight curvatures of the Arrhenius plot are observed for some reactions which were not previously considered.

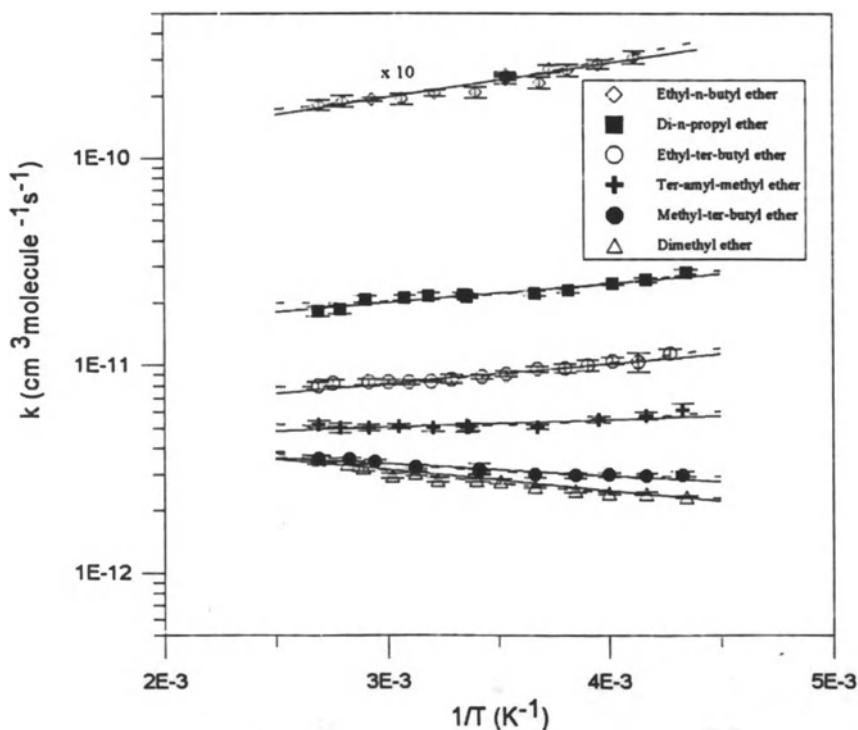


Fig. 4: Arrhenius plot for the reactions of OH with the studied oxygenated VOCs

### Achievements

Kinetic and mechanistic data have been provided for reactions involved in the  $\text{NO}_3$  and OH initiated oxidation mechanisms of VOCs. These data can be used, and some of them have already been used (*e.g.* [6]), in models for assessing the role of VOCs and  $\text{NO}_x$  precursors in ozone and other photo-oxidant formation.

### Acknowledgements

- J. P. Burrows, J. N. Crowley, C. Golz, G. Moortgat, U. Platt, R. Schindler, R. Singer and U. Ville for contributing to joint experiments or modelling calculations.
- EC (through Environment Programme), CNRS (Programme Environnement and CNRS / MPG agreement), Ministère de l'Environnement and Institut Français du Pétrole, for support.

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### 3.10 Peroxy Radical Reactions of Tropospheric Interest

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#### Summary

Our work during the LACTOZ project has essentially focused on the investigation of peroxy radical reactivity under atmospheric conditions, with the principal aim of providing data important in modelling ozone formation in the troposphere. A set of typical radicals have been studied in order to build structure-reactivity relationships for the principal reactions of atmospheric importance. Significant advances have been achieved for cross-reactions such as  $\text{RO}_2 + \text{HO}_2$ ,  $\text{RO}_2 + \text{CH}_3\text{O}_2$  and  $\text{RO}_2 + \text{CH}_3\text{C}(\text{O})\text{O}_2$ . Concerning self-reactions, a great deal of information has been collected, particularly about the influence of functional groups, but more work is necessary to ascertain relationships between structure and reactivity. It should be emphasised that the latter work has provided valuable information about the way alkoxy radicals react under tropospheric conditions.

In addition, the important reaction of PAN formation has been investigated in great detail.

#### Aims of the scientific research during the project

It is well recognised that peroxy radicals play a key role in the oxidation processes of hydrocarbons under the conditions of the atmosphere, leading to the formation of tropospheric ozone and other oxidised molecules, in the presence of nitrogen oxides. Their relative reaction rate with nitrogen oxides and with other radicals is one of the principal factors determining the ozone balance in the troposphere.

The principal aim of our work was to establish the general characteristics of the reactivity of peroxy radicals with the main atmospheric reactive trace species, *i.e.* nitrogen oxides and other peroxy radicals. Most of our work focused on the reactions of peroxy radicals with themselves, on reactions with  $\text{HO}_2$  and on their cross-reactions. The objective was to build structure-reactivity relationships by studying typical peroxy radicals. Collaboration with other groups within LACTOZ has resulted in significant progress in understanding the reactivity of peroxy radicals and in assessing their actual role in the chemical processes prevailing in the troposphere and leading to the formation of ozone. Note that in the course of our studies, important information has also been obtained on the reactions of several alkoxy radicals.

All radicals and their particular reactions investigated during the project are listed in Table 1.

**Table 1:** Peroxy radicals investigated during the project.

Radical	Spectrum	Self-reaction	$\alpha^a$	Reaction with HO <sub>2</sub>	Reaction with CH <sub>3</sub> O <sub>2</sub>	Reaction with NO <sub>2</sub>	Alkoxy <sup>b</sup>
HO <sub>2</sub>	+	+		+	+		
CH <sub>3</sub> O <sub>2</sub>	+	+	+	+	+	+	
C <sub>2</sub> H <sub>5</sub> O <sub>2</sub>	+	+		+	+		+
AllylO <sub>2</sub>		+		+	+		+
<i>t</i> -butylO <sub>2</sub>	+	+					+
neopentylO <sub>2</sub>	+	+	+	+	+		+
<i>c</i> -C <sub>5</sub> H <sub>9</sub> O <sub>2</sub>	+	+		+			+
<i>c</i> -C <sub>6</sub> H <sub>11</sub> O <sub>2</sub>	+	+	+	+	+		+
BenzylO <sub>2</sub>	+	+	+	+	+		+
CH <sub>3</sub> C(O)O <sub>2</sub>	+	+		+	+	+	
C <sub>2</sub> H <sub>5</sub> C(O)O <sub>2</sub>				+			
CH <sub>3</sub> C(O)CH <sub>2</sub> O <sub>2</sub>	+	+	+	+	+		+
HOCH <sub>2</sub> O <sub>2</sub>	+	+		+			+
HOC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> O <sub>2</sub>	+	+	+	+			+
CH <sub>2</sub> ClO <sub>2</sub>	+	+	+	+	+		+
CHCl <sub>2</sub> O <sub>2</sub>	+	+	+	+			+
CCl <sub>3</sub> O <sub>2</sub>	+	+		+	+		+
CH <sub>2</sub> BrO <sub>2</sub>	+	+		+			
CH <sub>3</sub> CHBrCH(O <sub>2</sub> )CH <sub>3</sub>	+	+					

<sup>a</sup> Branching ratio for the non-terminating channel in self-reaction.

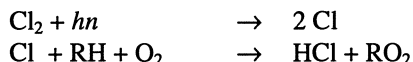
<sup>b</sup> Indicates information has been obtained on the reaction of the corresponding alkoxy radical.

## Principal scientific findings during the project

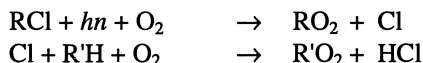
### *Experimental methods*

Most of our experiments were performed using the flash-photolysis technique with UV detection of peroxy radicals, in the spectral range extending from 190 to 300 nm. The temperature could be varied from 248 up to 600 K and the pressure from 30 to 760 Torr.

In most our studies, radicals were generated by photolysis of molecular chlorine in the presence of an appropriate precursor:



Laser photolysis was also utilised when the above method could not be applied, in particular when other precursors had to be used (for the allylperoxy radical, for example) or when two radicals had to be generated simultaneously in order to study their cross-reaction. For example, the following system was used to study the cross-reaction between  $\text{RO}_2$  and  $\text{R}'\text{O}_2$ :



Rate constants were obtained by numerically simulating decay traces, using the complete reaction mechanism and including all reactive and absorbing species. Thus, in most cases, the primary rate constant was obtained instead of the observed rate constant (which include secondary loss processes).

The reaction mechanism had to be determined in many instances by collaborating with other groups: Moortgat (Mainz), Zabel and Becker (Wuppertal), Cox, Hayman and Jenkin (Harwell), Wallington (Ford).

### *UV spectra of peroxy radicals*

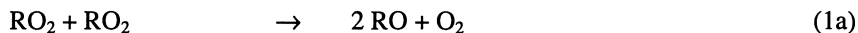
The most appropriate way of detecting peroxy radicals in studies of their reaction kinetics is the UV absorption spectrometry. The UV absorption spectra of 17 radicals have been determined in our group during the LACTOZ project, as indicated in Table 1. The radicals all have the characteristic broad absorption band peaking around 230–250 nm, with a maximum absorption cross-section of generally  $(4 \pm 1) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ . Halogen substitution apparently tends to lower the maximum absorption cross-section. For example, the absorption cross-section of chloromethyl peroxy radicals decreases regularly with chlorine substitution to reach the low value of  $1.6 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  for  $\text{CCl}_3\text{O}_2$ .

A second absorption band appearing at shorter wavelength (200–210 nm) can be seen when the C–O–O chromophore is conjugated with an unsaturated group. This second band has been well characterised in the case of acylperoxy radicals, bearing the O=C–O–O group. The start of a second band has also been seen for the benzylperoxy radical but not for allylperoxy. However, the spectrum of the latter has not been fully investigated at wavelength shorter than 230 nm. Spectra of peroxy radicals have been discussed in detail in the review on peroxy radicals written by LACTOZ contributors [1].

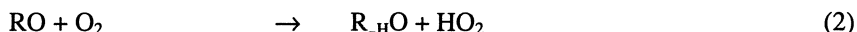
The acetylperoxy radical exhibits a distinctive spectrum having a second absorption band at longer wavelengths ( $\gg 300 \text{ nm}$ ). This band apparently corresponds to the  $n\text{-}\pi^*$  transition of the carbonyl group, which has been enhanced. However, the reason for this enhancement is not presently understood and has not been explained by semi-empirical calculations.

### Self-reactions of peroxy radicals

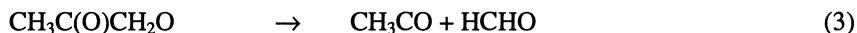
Self-reactions of peroxy radicals may occur in the atmosphere under low  $\text{NO}_x$  concentrations, particularly for the fastest cases, where rate constants may reach values as high as  $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . In addition, self-reactions must be well characterised before studying other reactions of peroxy radicals, particularly those with  $\text{HO}_2$  and  $\text{CH}_3\text{O}_2$ . The general mechanism for  $\text{RO}_2$  self-reactions is the following:



with  $\text{R}_{-H}\text{O}$  being an aldehyde or a ketone and  $\alpha$  the branching ratio of the non-terminating channel (1a):  $\alpha = k_{1a}/k_1$ . A possible third reaction channel, forming the peroxide  $\text{ROOR}$ , has never been observed. The non-terminating channel generates an alkoxy radical which is either converted into  $\text{HO}_2$  and a carbonyl compound by reaction with  $\text{O}_2$ :



or into new peroxy radical after decomposition, for example:



giving rise to new reaction routes for the initial  $\text{RO}_2$  radical ( $\text{RO}_2 + \text{HO}_2$  or  $\text{RO}_2 + \text{R}'\text{O}_2$ ). In most of our experiments, the determination of rate constants were performed by using the complete reaction mechanism in which the subsequent reactions of  $\text{RO}_2$  were included. This has necessitated the determination of  $\alpha$  and of the reaction mechanism when necessary, using the collaborations mentioned above.

All self-reactions investigated during the project are listed in Table 1 and rate constants values are reported in Chapter 2, Table 8. Also indicated in Table 1 are the radicals for which we have participated in the determination of both  $\alpha$  and of the reaction mechanism. The detailed analysis of each reaction has been presented in preceding reports and only general considerations regarding structure-reactivity relationships are considered here.

#### Primary peroxy radicals ( $\text{RCH}_2\text{O}_2$ )

The simplest alkyl peroxy radicals have rate constant values at 298 K of about  $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which may increase in the case of chain branching, *e.g.*  $1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for neopentylperoxy. Apparently, these values are roughly the lower and upper limits for primary alkylperoxy radicals and more data would be required to refine the relationship between structure and reactivity of such radicals.

The most striking feature of the results is the dramatic increase of the rate constant under substitution of an H atom in the alkyl peroxy radicals with halogen atom, an

OH radical or a particular functional group such as a carbonyl group, unsaturated bond or aromatic ring. Apparently, this effect is independent of the position of the substituent ( $\alpha$  or  $\beta$ ) relative to the peroxy function.

In the case of the methyl peroxy radical, for example, the presence of an F atom, Cl atom (s), or OH group, increases the rate constant by more than a factor of 10. The effect of bromine, on the contrary seems smaller. The enhancement is even larger with the presence of a carbonyl group (*e.g.* acetylperoxy) or an aromatic ring (*e.g.* benzylperoxy).

The acetylperoxy radical, and probably other acylperoxy radicals  $RC(O)O_2$ , exhibit even higher rate constants:  $1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Acylperoxy radicals are certainly the most reactive peroxy radicals, as seen below for other type of reactions.

A negative temperature dependence of the rate constant seems to be a general characteristic of self-reactions of primary alkylperoxy radicals.

#### Secondary peroxy radicals ( $RCHO_2R'$ )

Very few data are available for self-reactions of secondary alkylperoxy radicals. Our main contribution in this case is the study of cycloalkylperoxy radicals  $c\text{-C}_5\text{H}_9\text{O}_2$  and  $c\text{-C}_6\text{H}_{11}\text{O}_2$  radicals. The rate constants are 40 times larger than the only linear secondary peroxy radical studied so far,  $i\text{-C}_3\text{H}_7\text{O}_2$  and exhibit a slight positive temperature dependence. More data would be necessary for a better description of such reactions but, due to their relatively low rate constants ( $< 5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) their contribution to atmospheric chemistry is negligible.

It should be emphasised, however, that the presence of a functional group may result in a significant increase of the rate constant, up to nearly  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . We have confirmed this behaviour in the case of bromine substitution and shown that the temperature dependence has become negative. More data are needed to confirm if this spectacular effect occurs with other functional group substitution.

#### Tertiary peroxy radicals

We have confirmed that the rate constant of the *t*-butyl peroxy radical self-reaction is very slow, with a fairly high activation energy. However, as above, the effect of functional groups on the rate constant should be investigated.

#### ***Reactions of peroxy radicals with $HO_2$***

Due to the fairly high concentration of  $HO_2$  in the atmosphere,  $RO_2 + HO_2$  reactions play an important role under moderately low concentrations of  $NO_x$ . Investigations of such reactions have represented a significant part of our work during the project. The reactions that have been studied are listed in Table 1 and



the results are given in the Chapter 2, Table 5. Structure to reactivity rules are much easier to establish than in the case of self-reactions, as all rate constant values are restricted within a factor of about three.

There is no clear systematic effect of functional groups on the rate constants except, perhaps, for halogen substitution which seems to maintain the rate constant at the lower limit. Apparently, the main factor influencing the rate constant is the size of the radical. The lowest rate constants are those of  $\text{CH}_3\text{O}_2$  and of the corresponding halogen substituted radicals, around  $6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The rate constant increases rapidly, over  $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for bigger radicals and reaches values of  $1.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for *c*- $\text{C}_3\text{H}_9\text{O}_2$  and *c*- $\text{C}_6\text{H}_{11}\text{O}_2$ . A recommendation might be as follows (units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ):  $6 \times 10^{-12}$  for  $\text{CH}_3\text{O}_2$  and halogenated peroxy radicals,  $1.0 \times 10^{-11}$  for  $\text{C}_2$ – $\text{C}_3$  radicals and  $1.5 \times 10^{-11}$  for bigger radicals ( $> \text{C}_4$ ) and acyl peroxy radicals. All reactions exhibit strong negative temperature dependence with exponential factors varying from  $800 \text{ K} / T$  to  $1600 \text{ K} / T$ .

### *Reactions of peroxy radicals with $\text{CH}_3\text{O}_2$*

It has been shown that  $\text{CH}_3\text{O}_2$  is the most abundant alkylperoxy radical in the atmosphere and, under low  $\text{NO}_x$  level its concentration can be as high as that of  $\text{HO}_2$  [2]. Therefore, there is a possibility that reactions of the type  $\text{RO}_2 + \text{CH}_3\text{O}_2$  play a role in the chemistry of remote atmospheres, depending on the rate constants of such cross-reactions. We have investigated a series of this type of reaction. They are listed in Table 1 and the values of the rate constants are reported in Chapter 2, Table 5. It is observed that the rate constants for cross-reactions are generally intermediate between the rate constants for self-reactions of  $\text{RO}_2$  and  $\text{CH}_3\text{O}_2$ . A geometrical mean such as

$$k(\text{RO}_2 + \text{CH}_3\text{O}_2) = \sqrt{k(\text{RO}_2 + \text{RO}_2) \cdot k(\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2)}$$

might be a good estimate for the cross-reaction rate constant. However, it is observed that when the  $\text{RO}_2$  self-reactions is fast,  $k(\text{RO}_2 + \text{CH}_3\text{O}_2)$  is much closer to  $k(\text{RO}_2 + \text{RO}_2)$  than to  $k(\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2)$ . This is true, for example, for acetyl, acetonyl and chloromethylperoxy radicals. If this behaviour is indeed general, a better approximation would be to set  $k(\text{RO}_2 + \text{CH}_3\text{O}_2)$  equal to  $k(\text{RO}_2 + \text{RO}_2)$ . This would be wrong for slow reactions, but as far as atmospheric chemistry is concerned, slow reactions are unimportant.

### *Reactions of peroxy radicals with $\text{CH}_3\text{C}(\text{O})\text{O}_2$*

A few cross-reactions of  $\text{RO}_2$  radicals with the acetylperoxy radical have been investigated:  $\text{CH}_3\text{O}_2$ ,  $\text{C}_2\text{H}_5\text{O}_2$  and *c*- $\text{C}_6\text{H}_{11}\text{O}_2$ . The reactions are very fast, with rate constants equal to  $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This is even true for the secondary radical *c*- $\text{C}_6\text{H}_{11}\text{O}_2$ , in spite of the much lower rate constant observed for the self-reaction ( $4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). This may be important since the acetylperoxy radical is also an abundant radical in the atmosphere and, if all cross-

reactions of this type are as fast as those reported above, they should be taken into account in modelling the chemistry of remote atmospheres. Further experiments are in progress.

### ***Reactions of peroxy radicals with NO<sub>2</sub>***

The reaction of the acetylperoxy radical with NO<sub>2</sub>, forming PAN, is one of the most important reactions influencing the formation of ozone in the troposphere. We have performed a very detailed investigation of this reaction, in collaboration with the group from Wuppertal having considered the kinetics of the forward and reverse reaction, the equilibrium constant and thermodynamics, pressure and temperature effects and the interpretation of results using statistical theories [3]. This is obviously one of our most significant results and is now the reference work for this reaction. The equilibrated reaction of CH<sub>3</sub>O<sub>2</sub> with NO<sub>2</sub> has also been reinvestigated.

### ***Reactions of alkoxy radicals***

The analysis of peroxy radical self-reactions, including the complete reaction mechanism, has provided information on the way alkoxy radicals react either under tropospheric conditions or under the conditions of laboratory studies. CH<sub>3</sub>O, C<sub>2</sub>H<sub>5</sub>O, allylO and benzylO, all react with oxygen to yield HO<sub>2</sub> and an aldehyde. The same reaction occurs in the atmosphere for HOCH<sub>2</sub>O and CH<sub>2</sub>ClO, but these radicals may decompose at low oxygen partial pressure (by H elimination for HOCH<sub>2</sub>O and HCl elimination for CH<sub>2</sub>ClO). Competition between reaction with oxygen and decomposition has been observed for *c*-C<sub>6</sub>H<sub>11</sub>O under atmospheric conditions and for neopentylO at high O<sub>2</sub> partial pressure. Only decomposition was observed for all other radicals: *c*-C<sub>5</sub>H<sub>9</sub>O, CH<sub>3</sub>C(O)CH<sub>2</sub>O, CHCl<sub>2</sub>O, CCl<sub>3</sub>O and HOC(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>O.

It is certainly difficult, at the present time, to establish relationships between structure and reactivity for reactions of alkoxy radicals. More experimental and theoretical approaches are necessary to build a general picture of alkoxy radical reactivity.

### **Conclusions**

Various types of information have been obtained from our studies of kinetics and mechanisms of peroxy radical reactions. The principal achievements, relevant to tropospheric chemistry, are the following:

- Reactions with NO<sub>2</sub>: PAN formation and decomposition reactions have been studied in detail; pressure and temperature dependencies of the kinetics, thermodynamic properties and thermal parameters of the equilibrium constant have been measured.
- Self-reactions: significant information on relationships between structure and reactivity have been obtained, but more data are still necessary; we have shown

that substitution by functional groups in alkyl peroxy radicals may result in a dramatic increase of the rate constant.

- Reactions with HO<sub>2</sub>: the data obtained for this important type of reaction allow us to propose a fairly reliable structure-reactivity relationship.
- Cross-reactions of peroxy radicals: original data have been obtained on the kinetics of RO<sub>2</sub> reactions with CH<sub>3</sub>O<sub>2</sub> and CH<sub>3</sub>C(O)O<sub>2</sub>; some reactions with CH<sub>3</sub>O<sub>2</sub> are fast enough to play a role in the tropospheric chemistry and all reactions with CH<sub>3</sub>C(O)O<sub>2</sub> are apparently very fast and should be taken into account.

All the results obtained in this work are necessary for modelling the atmospheric oxidation of hydrocarbons and for mechanism reduction in complex oxidation processes.

### Acknowledgements

The authors wish to thank the European Commission for funding this work.

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### 3.11 Laboratory Studies of Some Thermal Reactions Involving NO<sub>y</sub> Species

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#### Summary

An investigation of the mechanism of heterogeneous PAN decomposition was made. It was found that the reactions of the acetylperoxy radical were influenced slightly by the presence of surfaces. The temperature dependence of the side-channel of the reaction between nitrate radicals and nitrogen dioxide, producing nitric oxide, nitrogen dioxide and molecular oxygen, was investigated. Monte Carlo simulation calculations of the photolysis of nitrogen dioxide were performed. Reaction products and in some cases also kinetic information were determined for several alkenes reacting with nitrate radicals. Structurally related, simple carbonyl compounds were among the more abundant products together with nitrooxy-substituted ketones and alcohols. A systematic investigation of reaction kinetics and product distributions from nitrate radical reaction with aliphatic esters, ethers and alcohols was made. The rate coefficients for ethers and alcohols were found to be substantially higher than expected from simple correlations, *e.g.* for alkanes. This is interpreted as an effect of the oxygen atom, weakening adjacent hydrogen-carbon bonds. The oxygen atom also has an additional influence, possibly via stabilisation of the transition complex. The nitrate radical is quite specific for abstraction of the weakest bonded hydrogen atom and reaction products can often be deduced from this information combined with common knowledge of atmospheric gas-phase reactions.

#### Aims of the research

This work was intended to give information about non-photochemical processes affecting species that are involved in hydrocarbon oxidation and ozone formation, such as the hydrocarbons themselves or the active nitrogen compounds. The main part of the work was concerned with rates and products in nitrate radical reactions with various hydrocarbons. Some interest was also taken in purely inorganic reactions.

## Principal scientific results

### *PAN decomposition*

The results show that reaction (I) is a gas-phase reaction that is not influenced by the surface / volume ( $S/V$ ) ratio [1].



The disappearance of the acetylperoxy radical is the rate controlling step for PAN destruction in a situation where equilibrium (I) is established. The peroxy radical disappearance is the result of at least two competing processes with different temperature dependencies and where at least one is heterogeneous. A mathematical model of the decomposition was set up and calculations were made for some realistic cases. The results show that the ambient concentration of PAN is unlikely to be influenced by heterogeneous decomposition on aerosol surfaces, nor can the aerosol composition be significantly changed due to deposition of PAN. Laboratory investigations involving PAN and which are made using equipment with a high  $S/V$  ratio could be sensitive to heterogeneous PAN decomposition. The stability of gas mixtures containing PAN for calibration of analytical systems and other laboratory work will benefit from containers having a low  $S/V$  ratio. The greatest gain in stability can be realised if some  $\text{NO}_2$  can be tolerated together with the PAN. The higher the  $\text{NO}_2/\text{PAN}$  ratio is, the better, since acetylperoxy radical formation is suppressed.

### *$\text{NO}_2$ photolysis*

An exception from the studies of non-photochemical processes is the theoretical work on  $\text{NO}_2$  photolysis [2]. Stochastic simulation of  $\text{NO}_2$  ( $X^2A_1$ ) @  $\text{O}(^3P_j)$  +  $\text{NO}$  ( $X^2\Pi_{g_2}$ ) photodissociation in the wavelength range between 348 and 379 nm lends no support to the hypothesis that vibrationally excited  $\text{NO}_2$  molecules should give a distinct contribution to the quantum yield in the vicinity of the nominal dissociation wavelength.

### *The reaction $\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{NO} + \text{NO}_2 + \text{O}_2$*

The temperature dependence of the reaction rate was investigated using FTIR and TDL spectroscopy [3]. The rate coefficient can be described by  $k = 5.4 \times 10^{-14} \exp(-1488 \text{ K} / T)$ .

### *Alkene- $\text{NO}_3$ reactions*

#### Halogenated compounds

The products formed in the reactions between the nitrate radical and 2-chloro-1-butene, 3-chloro-1-butene, 1-chloro-2-butene and 2-chloro-2-butene were investigated by FTIR spectroscopy [4]. The experiments were performed in

synthetic air and using  $N_2O_5$  as the  $NO_3$  source. The principal products formed from chloro-butenes, where the chlorine atom was substituted at a carbon participating in the double bond, were acid chlorides, aldehydes and  $NO_2$ . The products formed from chlorobutenes with the chlorine atom substituted at a carbon next to the double bond, were chlorinated carbonyl-nitrate compounds and  $NO_2$ .

The kinetic behaviour was investigated [5] in a collaboration with PCL, Oxford. Some of the observed rate coefficients are given in Table 1. Later this work was carried on to its full potential, by further experimental work and theoretical calculations by the Oxford group [6].

### Butenes

Nitrate radical-initiated oxidation of 2-butenes was investigated using long optical path FTIR-spectroscopy [7]. At 295 K, 1020 mbar and 21 %  $O_2$ , major products were 3-nitroxy-2-butanone, 3-nitroxy-2-butanol and acetaldehyde. The oxygen dependence of the product formation was investigated by varying the  $O_2$  concentration. The yield of 3-nitroxy-2-butanone increased and the formation of 3-nitroxy-2-butanol and acetaldehyde decreased with increasing oxygen concentration. At low  $O_2$  concentrations (< 0.01 %) and 1020 mbar pressure, large amounts of 3-nitro-2-butyl nitrate were formed together with small amounts of *trans*-2-butene-oxide.

### Cyclic alkenes

Cyclic alkenes have some structural resemblance with certain terpenes. Since compounds with a smaller molecular weight than the terpenes themselves, are easier to handle experimentally, they are interesting as model compounds.

Absolute rate coefficients for the reaction between  $NO_3$  and cyclopentene, cyclohexene and 1-methyl cyclohexene were determined using the fast flow-discharge technique [8] and are listed in Table 1. The simple cyclic alkenes react slightly faster than *cis*-2-butene which contains a similar active structural element. The rate coefficient for reaction with 1-methyl cyclohexene is close to that for  $D^3$  carene or 2-carene but significantly greater than that for  $\alpha$ -pinene.

Cyclohexene, cyclopentene and 1-methylcyclohexene were investigated concerning product formation [9]. The main products from these three cycloalkenes are likely to be di-carbonyls formed by ring opening. Thus, glutaric aldehyde was identified from cyclopentene experiments. The corresponding compounds from cyclohexene and 1-methylcyclohexene, *i.e.* adipic aldehyde and 6-oxo-heptanal were not positively identified due to the lack of reference compounds. However, the appearance of characteristic aldehyde bands in spectra from the experiments indicated the existence of such compounds. In addition, 2-nitrooxycyclopentanone, 2-nitrooxycyclopentanol and 1,2-cyclopentanedinitrate were identified in a molar relation of 4/2/1 from cyclopentene. From cyclohexene, 2-nitrooxycyclohexanone, 2-nitrooxycyclohexanol and 1,2-cyclohexanedinitrate were observed in a molar

relation of 4/2/1. In the case of 1-methyl-cyclohexene, 2-methyl-2-nitrooxycyclohexanone and 1-methyl-2-nitrooxycyclohexanol were found in a 1/1 relation. A detailed mechanism that accounts for the formation of these compounds is given in the original paper [9].

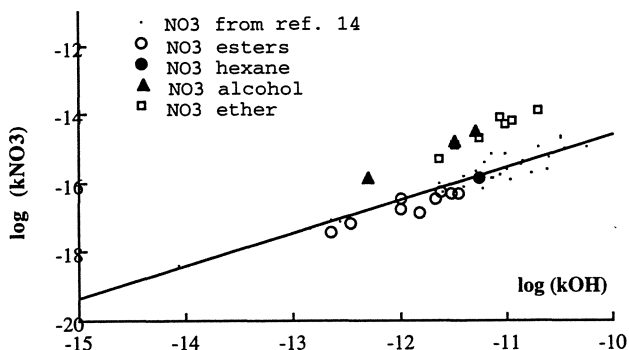
**Table 1:** Rate coefficients or rate coefficient expressions for nitrate radical reactions. When no temperature expression is given the value refers to room temperature.

compound	rate coefficient expression or $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	ref
2-chloro-1-butene	$7 \times 10^{-14}$	5
3-chloro-1-butene	$2.4 \times 10^{-12} \exp(-1992 \text{ K} / T)$	5
1-chloro-2-butene	$6.0 \times 10^{-13} \exp(-981 \text{ K} / T)$	5
2-chloro-2-butene	$11.0 \times 10^{-14}$	5
cyclopentene	$(5.9 \pm 1.1) \times 10^{-13}$	8
cyclohexene	$(6.3 \pm 1.3) \times 10^{-13}$ ( $E_a = 1 \pm 4 \text{ kJ mol}^{-1}$ )	8
1-methyl cyclohexene	$(1.5 \pm 0.5) \times 10^{-11}$ ( $E_a = 0 \pm 5 \text{ kJ mol}^{-1}$ )	8
methyl formate	$(0.36 \pm 0.08) \times 10^{-17}$	10
methyl acetate	$(0.7 \pm 0.2) \times 10^{-17}$	10
methyl propionate	$(3.3 \pm 0.8) \times 10^{-17}$	10
methyl butyrate	$(4.8 \pm 0.5) \times 10^{-17}$	10
ethyl formate	$(1.7 \pm 0.3) \times 10^{-17}$	10
ethyl acetate	$(1.3 \pm 0.3) \times 10^{-17}$ ( $E_a = 23 \pm 8 \text{ kJ mol}^{-1}$ )	10
ethyl propionate	$(3.3 \pm 0.4) \times 10^{-17}$	10
propyl formate	$(5.4 \pm 0.9) \times 10^{-17}$	10
propyl acetate	$(5 \pm 2) \times 10^{-17}$	10
dimethyl ether	$(1.40 \pm 0.42) \times 10^{-12} \exp(-2525 \pm 600 \text{ K} / T)$	11
diethyl ether	$(3.88 \pm 1.12) \times 10^{-12} \exp(-2065 \pm 480 \text{ K} / T)$	11
di- <i>n</i> -propyl ether	$(3.33 \pm 0.51) \times 10^{-12} \exp(-1870 \pm 250 \text{ K} / T)$	11
methyl <i>t</i> -butyl ether	$(2.40 \pm 0.29) \times 10^{-12} \exp(-2415 \pm 199 \text{ K} / T)$	11
ethyl <i>t</i> -butyl ether	$(2.48 \pm 0.78) \times 10^{-12} \exp(-1613 \pm 542 \text{ K} / T)$	12
diisopropyl ether	$(2.02 \pm 0.35) \times 10^{-12} \exp(-1759 \pm 301 \text{ K} / T)$	12
<i>t</i> -amyl methyl ether	$(1.21 \pm 0.22) \times 10^{-12} \exp(-1874 \pm 304 \text{ K} / T)$	12
methanol	$(1.06 \pm 0.51) \times 10^{-12} \exp(-2093 \pm 803 \text{ K} / T)$	13
ethanol	$(6.99 \pm 1.21) \times 10^{-13} \exp(-1815 \pm 419 \text{ K} / T)$	13
isopropanol	$(1.54 \pm 0.75) \times 10^{-12} \exp(-1743 \pm 1009 \text{ K} / T)$	13

### Oxygenated, aliphatic substances

A number of esters [10], ethers [11, 12] and alcohols [13] were investigated with respect to reactivity with nitrate radicals. Both absolute and relative rate methods were employed. Rate coefficients for the reaction of  $\text{NO}_3$  are given in Table 1. The rate coefficients for aliphatic esters may be predicted from available group reactivity factors for alkanes provided that formate carbonyl hydrogen atoms are treated as primary hydrogen atoms. The rate coefficients with temperature dependence for ethers and alcohols are valid between 268 to 363 K.

Fig. 1, adapted from Wayne *et al.* [14] shows that the rate coefficients for ethers and alcohols are high when the effect of the weakened carbon-hydrogen bonds in the vicinity of the oxygen atom is accounted for. This effect could arise from an increased stability of a transition complex, caused by interaction between the nitrate radical and the oxygen atom.



**Fig. 1:** Graph showing the correlation between the logarithms of rate coefficients for a certain organic substance, reacting by hydrogen abstraction, for reaction with nitrate and hydroxyl radicals. The straight line is the best fit to a number of compounds (dots), taken from [14]. The other symbols represent data from [10–13].

The product studies [11–13] show that the nitrate radical is quite selective for the weakest bonded hydrogen atom in these compounds. This knowledge, combined with common knowledge of atmospheric oxidation reactions makes possible a prediction of the products. For a detailed account of the branching of some competitive processes, the reader is referred to the original work.

### Acknowledgements

The work included in this report was supported financially by the Swedish Environmental Protection Agency (SNV), AB VOLVO Technological Development and the Swedish National Science Research Council (NFR).

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### 3.12 High-Resolution Measurements of the Absorption Cross-Sections for O<sub>3</sub> and NO<sub>2</sub>

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#### Summary

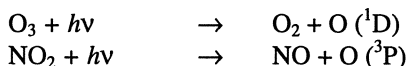
Two objectives have been achieved during these last years:

- the determination of the absorption cross-sections of O<sub>3</sub> and NO<sub>2</sub> in the UV and visible regions at different temperatures.
- the construction of a modulated photolysis apparatus for the study of atmospheric reactions initiated by photolysis.

#### Aims of the scientific research

The main work in this study is the determination of the absolute absorption cross-sections of the two important molecules, O<sub>3</sub> and NO<sub>2</sub>, involved in atmospheric chemistry.

These parameters are used in the UV-visible region by the ground-based and satellite networks to measure the total amount and the concentration profile of the two species in the atmosphere. They are also involved in the calculation of the photodissociation coefficients related to the processes:



These reactions are particularly important because the O (<sup>3</sup>P) and O (<sup>1</sup>D) atoms interact with molecules such as H<sub>2</sub>O, CH<sub>4</sub>, hydrocarbons and O<sub>2</sub>. Moreover, the absorption cross-sections of O<sub>3</sub> are of great importance to calculate the solar flux penetration especially in the UV wavelength range where ozone absorbs in the Huggins and Hartley bands.

In order to provide sets of data directly available for the modelling or for optical *in situ* concentration measurements, the laboratory experiments need to be made in pressure and temperature conditions similar to those in the atmosphere.

Thus ozone absorption spectrum has been studied in the UV (200–500 nm) and visible (450–700 nm) regions at ambient and low temperatures down to 218 K.

For  $\text{NO}_2$ , absorption data have been obtained with very low ( $\text{NO}_2 - \text{N}_2\text{O}_4$ ) pressures in the spectral region (300–500 nm) under similar temperature conditions.

## Principal scientific findings during the project

### $\text{O}_3$ spectroscopy

- i) In a first step, the Hartley and Huggins bands which play a very important role in the atmosphere since they are located in the critical UV region, 200–350 nm, have been studied under high resolution (0.01 nm). The first work was to test our apparatus and our calculation method for the determination of the ozone concentration during the experiments. From this work, cross-section values were obtained at ambient temperature [1]. Measurements were extended to low temperatures (273, 243, 228 and 218 K) corresponding to tropospheric and stratospheric conditions [2, 3].

The absorption spectrum consists of a large continuum from 200 to 350 nm with a maximum near 250 nm ( $\sigma(\text{O}_3) \gg 10^{-17} \text{ cm}^2$ ) which overlaps with small diffuse structures spaced by approximately  $200 \text{ cm}^{-1}$ . At higher wavelengths (310–350 nm) the spectrum is dominated by diffuse vibrational bands corresponding to the Huggins bands.

We have shown that the effect of temperature on the cross-section values is weak in the Hartley band ( $\lambda < 310 \text{ nm}$ ); at the mercury wavelength ( $\lambda < 253.6 \text{ nm}$ ), commonly used as reference, the cross-section value decreases from 1.0 % for a temperature variation from 218 to 295 K. Our results are in very good agreement ( $\Delta\sigma / \sigma = 0.5 \%$ ) with those determined by Barnes and Mauersberger [4] at the same temperatures.

On the other hand, in the Huggins bands, the temperature effect is important and increases progressively at increasing wavelengths where variations higher than 50 % can be observed.

Comparison with the most recent data [5–7] have been made, showing that our results are reliable.

- ii) In the continuation of this work, the study of the Chappuis band has been undertaken in the visible region (515–650 nm) at ambient and low (218 K) temperatures, since differences up to 10 % were observed between the results of previous data [8–13].

The comparison at ambient temperature shows that our results are very close to those of Hearn [11], Anderson and Mauersberger [13] determined at some fixed wavelengths, while the data of Amoruso *et al.* [12] and Inn and Tanaka [9] are 5 % and 10 % below, respectively. The temperature dependence has been found to be very small ( $< 1 \%$ ) in the whole spectral range, in agreement with the conclusions of Vigroux [8] and Amoruso *et al.* [12].

iii) In order to provide data required by the *in situ* O<sub>3</sub> concentration measurements (SANO/SOZ experiments) we have extended our cross-section determinations in the whole UV-visible region (200–820 nm) with the same conditions of resolution.

In the region located between the Huggins and the Chappuis bands, the cross-sections are very weak ( $10^{-22}$ – $10^{-23}$  cm<sup>2</sup>), and the data are either missing (390 nm <  $\lambda$  < 420 nm) or obtained under insufficient resolution (Johnston for  $\lambda$  > 420 nm and Wahner for  $\lambda$  > 390 nm). To measure such a weak absorption we have built a 1 metre multipass absorption cell, coolable down to –60 °C. The body of the cell, made of stainless steel, is well suited to being filled with corrosive gases such as pure ozone. Measurements are in progress; they concern the 440–515 nm and 650–720 nm ranges at ambient temperature.

### **NO<sub>2</sub> spectroscopy**

Before the beginning of our work, there were data for the NO<sub>2</sub> absorption in the UV visible region, but these data, obtained under various experimental conditions, exhibit differences up to 20 %.

In the 300–500 nm region, a new analysis was performed at three temperatures (293, 240 and 220 K) with long absorption paths (60 m) coupled with very low gas pressures. Under these conditions, the partial pressure of the dimer N<sub>2</sub>O<sub>4</sub> is negligible at ambient temperature. Therefore reliable NO<sub>2</sub> cross-sections have been obtained in the 300–500 nm region at high resolution (0.01 nm) [14].

On the other hand, at lower temperatures, the determinations below 400 nm are complicated by the contribution of the N<sub>2</sub>O<sub>4</sub> dimer that absorbs in this region which is also the photodissociation region of NO<sub>2</sub>. Nevertheless for wavelengths higher than 400 nm, owing to the low pressures used, we were able to obtain the NO<sub>2</sub> cross-sections which are now available at 0.01 nm intervals [15]. A temperature effect is clearly shown for this structured region (400–500 nm).

Below 400 nm, even with low pressures, N<sub>2</sub>O<sub>4</sub> shows a significant absorption compared to the total absorption, and it is necessary to make finer measurements at different pressures to separate the contribution of the two species. New experiments are necessary to improve the accuracy of our results.

Our values, acquired at ambient temperature in the 300–500 nm and at lower temperatures in the 400–500 nm, are an over previous ones [16–19]. With our experimental conditions, accuracies better than 3 %, 4 % and 6 % were obtained at ambient temperature, at 240 and 220 K. Our values provide a good set of data for the atmospheric purposes such as the modelling and the NO<sub>2</sub> concentration measurements by differential absorption techniques.

### **Kinetic studies**

Recently a modulated photolysis system was constructed in our laboratory in order to study the kinetics of some atmospheric reactions. It consists of a coolable multipass triple jacket cell (1 m long, 7 cm in diameter) in which the reactants are photolysed by 12 surrounding fluorescent "sun lamps". The absorption of the reactants can be controlled by means of a classical mounting with an absorption source, a monochromator and a photomultiplier. Absorption paths up to 40 m allow to detect the presence of low reactant concentrations, and measurements can be carried out in a wide range of experimental conditions: from 1 to 760 Torr and from  $-30\text{ }^{\circ}\text{C}$  to  $100\text{ }^{\circ}\text{C}$ , with frequencies varying up to 10 Hz.

Currently, the setup has been tested with simple peroxy radicals such as  $\text{C}_2\text{H}_5\text{O}_2$  and  $\text{HO}_2$ . The first results are in agreement with the published data.

### **Achievements of the project**

Our objective initially based on the determination of the absorption cross-sections of  $\text{O}_3$  in the Hartley and Huggins bands and of  $\text{NO}_2$  in the 300–500 nm region has been achieved. Additional regions towards the higher wavelengths have been studied to provide new data required by the extension of new *in situ* measurements.

Moreover a modulated photolysis apparatus has been set up for kinetic studies of atmospheric compounds.

### **Acknowledgements**

This project was supported by the French EUROTRAC committee. We gratefully acknowledge this help.

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### 3.13 Laboratory Studies of Peroxy Radicals, Carbonyl Compounds and Ozonolysis Reactions of Tropospheric Importance

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#### Summary

Spectroscopic, kinetic, photolytic and mechanistic studies have been carried out on simple peroxy radicals such as  $\text{HO}_2$ ,  $\text{CH}_3\text{O}_2$ ,  $\text{C}_2\text{H}_5\text{O}_2$  and  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  using a variety of laboratory techniques. The photo-oxidation studies of selected carbonyl compounds was performed and quantum yields established in order to assess their photolytic lifetime in the troposphere. The product distribution of the ozonolysis of selected alkenes was determined in the presence of water vapour.

#### Aims of the research

The objective of present research was to provide a better understanding of the chemical processes involved in production and loss of ozone in the troposphere. This was achieved by providing kinetic and mechanistic data for several reactions of peroxy radicals involved in the photo-oxidation of volatile organic compounds (VOC). Additional aims were to determine the product quantum yields in the photolysis of carbonyl compounds, and to investigate the mechanism in the ozonolysis of alkenes, especially in the presence of water vapour.

#### Principal scientific findings

##### *Studies of peroxy radical reactions of tropospheric importance*

UV Absorption spectra of  $\text{HO}_2$ ,  $\text{CH}_3\text{O}_2$ ,  $\text{C}_2\text{H}_5\text{O}_2$ ,  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  radicals

A vast majority of the kinetic measurements involving  $\text{RO}_2$  radicals has made use of the relatively intense UV absorption spectrum of these species in order to obtain time-concentration profiles. Moreover, for the study of peroxy radical self-reactions, absolute concentrations must be known in order to analyse second order decay profiles, indicating the importance of accurately measured absolute absorption cross sections. The cited peroxy radicals were generated by photolysis

of mixtures of molecular chlorine in the presence of appropriate precursors in air, and monitored by absorption spectroscopy. Specifically, the techniques of modulated photolysis, and laser flash photolysis was used for the determination of absorption cross sections. The spectra of  $\text{HO}_2$  [1],  $\text{CH}_3\text{O}_2$  [2],  $\text{C}_2\text{H}_5\text{O}_2$  [3] and  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  [4] are displayed in Fig. 1. The absorption cross sections of  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  were recently measured and found to be 30 % smaller than a previous determination [5].

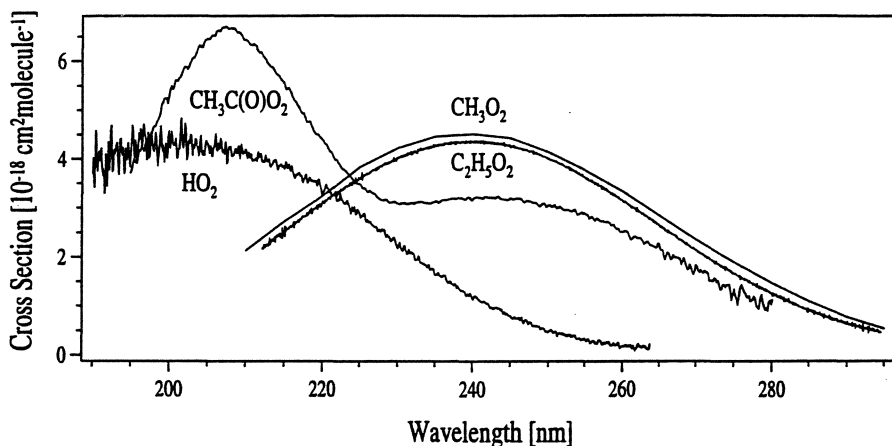
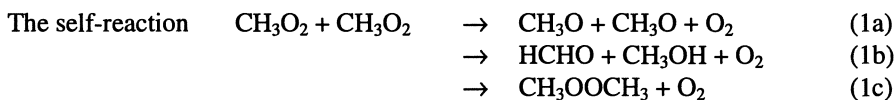


Fig. 1: Absorption spectra of  $\text{HO}_2$ ,  $\text{CH}_3\text{O}_2$ ,  $\text{C}_2\text{H}_5\text{O}_2$  and  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  radicals.

#### Kinetic studies of peroxy radicals



The rate constant of the self-reaction was obtained by the modulated photolysis technique combined with long path UV absorption spectroscopy. Absorption-time profiles, obtained at various wavelengths, were analysed with the help of computer simulation. The presence of  $\text{HO}_2$  radicals must be taken into account in the kinetics analysis, since they are generated by reaction (2) of  $\text{CH}_3\text{O}$  radicals with  $\text{O}_2$ , emphasising the importance of the knowledge about channel (1a):



The observed rate constant was measured as  $k_1(\text{obs}) = (1 + \alpha) k_1 = 4.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K, where  $k_1 = k_{1a} + k_{1b} + k_{1c}$  and  $\alpha = k_1/k_{1a} = 0.34$  [2].

The temperature dependence of the products  $\text{HCHO}$  and  $\text{CH}_3\text{OH}$ , generated in reactions (1b) and (2), was measured by making use of a matrix isolation technique combined with FTIR spectroscopy [6]. Here, in a novel reactor, aliquots of the



gaseous reaction mixture were deposited on a cold finger maintained at 7 K by liquid helium to form a cold matrix, which is then analysed by FTIR spectroscopy. In the temperature range 223 and 333 K, the branching ratio  $a$  is given by  $\alpha = 1 / \{1 + [\exp((1535 \pm 90) \text{ K} / T)] / (51 \pm 15)\}$ .

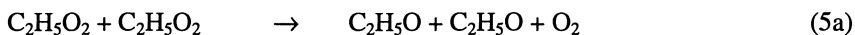


The kinetics of the reaction  $\text{CH}_3\text{O}_2 + \text{NO}_3$  was studied by modulated photolysis spectroscopy [7] and later in a discharge flow reactor combined with molecular beam mass spectrometry [8]. In the latter experiment, the  $\text{CD}_3\text{O}_2$  radicals were used instead of  $\text{CH}_3\text{O}_2$ , and their first order decay monitored in the presence of excess  $\text{NO}_3$  radicals. It was however observed that the first order decay of the methylperoxy radicals did not extrapolate to a common intercept and that the second order plot showed a large positive intercept. This is caused by the regeneration of  $\text{CH}_3\text{O}_2$  radicals via reaction



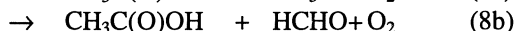
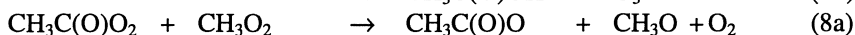
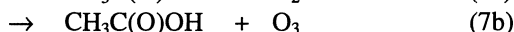
which was confirmed by direct kinetic measurements by the groups in Orléans and Oxford. Analysis of the data resulted in  $k_3 = (1.4 \pm 0.3) \times 10^{-12}$  and  $k_4 = (3.3 \pm 0.8) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [9].

#### *Ethylperoxy radicals* ( $\text{C}_2\text{H}_5\text{O}_2$ )



The kinetics of the self-reaction was investigated by modulated photolysis spectroscopy in the temperature range 220–330 K [3]. In this temperature range a curvature in the Arrhenius plot is observed. The rate constant  $k_5 = k_{5a} + k_{5b}$  is described by  $k_5 = 2.49 \times 10^{-13} \exp(-518 / T) + 9.39 \times 10^{-16} \exp(960 \text{ K} / T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and the branching ratio by  $k_{5a}/k_{5b} = 265 \exp(-1478 \text{ K} / T)$ . At 298 K  $k_5 = 6.7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , with  $k_{5a}/k_5 = 0.65$ . Substitution of an H atom by a Br atom at the  $\beta$ -carbon was also studied and found to enhance the rate constant for the self-reaction by a factor 60 [10].

#### *Acetylperoxy radicals* $\text{CH}_3\text{C}(\text{O})\text{O}_2$



The kinetics of the self-reaction (6) and the cross reactions (7) and (8) were studied by conventional flash photolysis [5, 11] and later by laser flash photolysis [4] combined with UV long path absorption spectroscopy. Rate constants for reaction (6) to (8) were obtained:

$$k_6 = (1.4 \pm 0.2) \times 10^{-11}, k_7 = (1.3 \pm 0.2) \times 10^{-11},$$

$$k_{8a} = (8.4 \pm 0.3) \times 10^{-12} \text{ cm}^3$$

and  $k_{8b} = (8.2 \pm 1.5) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

The temperature dependence of the branching ratio of the cross reactions (7) and (8) was obtained in a separate study [12], whereby biacetyl was photolysed in the presence of O<sub>2</sub>, as source of CH<sub>3</sub>C(O)O<sub>2</sub> radicals. The reaction products, arising from the set of reactions (6) to (8), were analysed by matrix isolation FTIR spectroscopy. The branching ratios were obtained in the temperature range 233–333 K are  $k_{7a}/k_{7b} = 330 \exp(-1430 \text{ K} / T)$  and  $k_{8a}/k_{8b} = 2.2 \times 10^6 \exp(-3870 \text{ K} / T)$ .

### *Photochemical studies of carbonyl compounds*

#### Photo-oxidation of HCHO

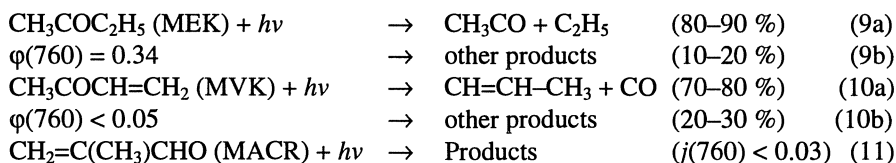
The photo-oxidation of both HCHO–O<sub>2</sub> and Cl<sub>2</sub>–HCHO–O<sub>2</sub> mixtures were investigated by modulated and flash photolysis [13, 14] and the spectrum and kinetics of the intermediate radical HOCH<sub>2</sub>O<sub>2</sub> determined, which is formed in the equilibrium of HO<sub>2</sub> and HCHO. Significant production of HCOOH was observed.

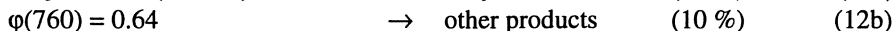
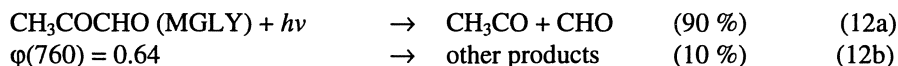
#### Photo-oxidation of CH<sub>3</sub>CHO

The kinetics of the radicals CH<sub>3</sub>O<sub>2</sub> and HO<sub>2</sub>, which are produced in the photo-oxidation of CH<sub>3</sub>CHO, were studied under variable O<sub>2</sub> concentrations [15]. Direct observation of both CH<sub>3</sub>O<sub>2</sub> and HO<sub>2</sub> radicals allowed the determination of  $k(\text{CH}_3\text{O}_2 + \text{HO}_2) = (6.7 \pm 2.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  in agreement with previous studies. From the products CH<sub>3</sub>OH, CO<sub>2</sub>, CH<sub>3</sub>OOH, CH<sub>3</sub>C(O)OH and CH<sub>3</sub>C(O)OOH, the kinetic parameters  $k_8 = (1.5 \pm 0.5) \times 10^{-11}$  and  $k(\text{CH}_3\text{O} + \text{CH}_3\text{CHO}) = (1.5 \pm 1) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  were determined.

#### Photo-oxidation of MEK, MVK, MACR and MGLY

The photo-oxidation of four carbonyl compounds, methylethyl ketone (MEK), methyl-vinyl ketone (MVK), methacrolein (MACR) and methyl glyoxal (MGLY), was studied by long path FTIR spectroscopy at 298 K [16, 17]. The absorption spectra were obtained using diode array spectroscopy [16–18]. Broad-band photolysis was performed using sun lamps (280–360 nm), and overall quantum yields of removal of reactants and formation of products were measured in the total pressure range 50 to 760 Torr. The main photolysis processes in the cited wavelength range are:





All photolytic systems showed a Stern-Volmer type pressure dependent behaviour. The photolytic lifetimes were calculated on the basis of the cited overall quantum yields: 4 day for MEK, 14 h for MVK, 22 h for MACR and 35 min for MGLY.

In a separate experiment the photolysis of MGLY was investigated and CO quantum yield measured as a function of wavelength at pressures ranging between 50 and 760 Torr [19].

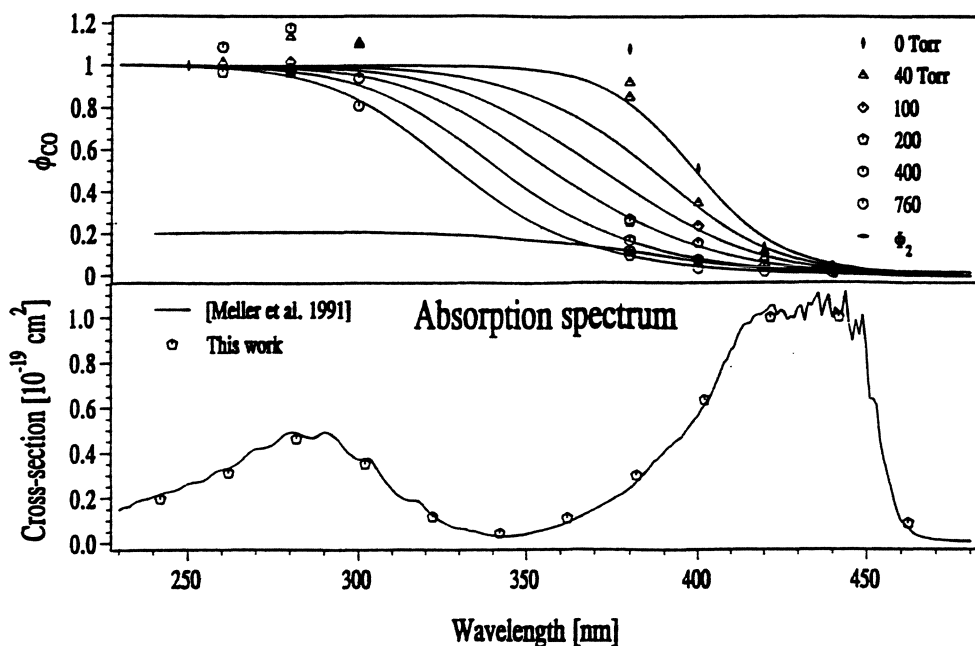


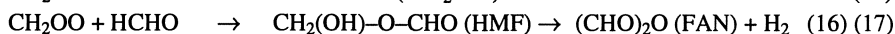
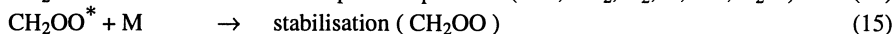
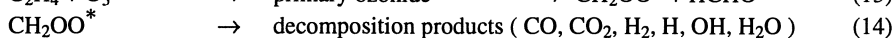
Fig. 2: Wavelength-dependent CO quantum yields of MGLY as a function of total pressure.

The pressure-dependent CO quantum yields are shown in Fig. 2 and can be represented by  $\phi(12a) = 1/(1 + a e^{-b/k} + c e^{-d/k} P)$  with  $a = 8.1 \times 10^{12}$ ,  $b = 1.2 \times 10^4 \text{ nm}$ ,  $c = 2.1 \times 10^4 \text{ Torr}^{-1}$  and  $d = 5.5 \times 10^3 \text{ nm}$ . The yield of the other minor channel  $\phi(12b)$  is pressure independent and contributes to about 20 %.

### Ozonolysis of alkenes. Influence of water vapour

The ozonolysis of simple alkenes was studied in two different apparatus: a 2 litre stirred tank reactor (for ethene, propene, *trans*-2-butene, butadiene, and isoprene) coupled *via* molecular beam sampling to a matrix isolation FTIR set-up [20, 21], and a 570 L spherical glass vessel "big sphere" (for ethene, 2-butene isomers, isobutene, and isoprene) where products were identified by FTIR spectroscopy, GC and a scrubber sampling unit for analysis with HPLC (for peroxides) and IC (for organic acids). In the latter system, two extreme humidity conditions, one with 0.5 ppm and the other with  $2 \times 10^4$  ppm (corresponding to *ca.* 60 % relative humidity at 298 K) were used, which are referred to as "dry" and "wet" conditions, respectively. Results of the studies performed in the "big sphere" are summarised here.

According to currently accepted Criegee mechanism [20], the formation of the reaction products in the ozonolysis of ethene is explained in terms of the formation of the excited Criegee intermediate  $\text{CH}_2\text{OO}^*$  and its subsequent decomposition and collisional stabilisation:



The following observations were made:

- Both compounds HMF and FAN were identified and their total yield  $\text{D(HMF)} + \text{D(FAN)}$  (relative to  $\text{O}_3$  converted) was estimated to *ca.* 0.2. Initially, the rate of HMF formation was found to increase linearly for low  $\text{O}_3$  conversions. However at larger  $\text{O}_3$  conversions, the rate of the HMF formation tended to decrease, while the FAN formation was accelerated. These results suggest that HMF is the precursor of FAN. Subsequent experiments with the added HCHO yielded  $\text{D(HMF)} + \text{D(FAN)}$  which was about 40 % lower than in the absence of HCHO addition. These observations imply either that HMF has different precursors or that the stabilised Criegee intermediate  $\text{CH}_2\text{OO}$  may not be formed [22]. The formation of trace amounts ( $< 0.05$ ) of HMF and FAN was also noted in the ozonolysis of isobutene. Analogous products to HMF were assigned in the ozonolysis of *cis*- and *trans*-2-butene isomers [23].
- Under wet conditions,  $\text{HCOOH}$  and  $\text{HOCH}_2\text{OOH}$  (HMHP) are formed in the ozonolysis of ethene [24]. However, the rate of the  $\text{HCOOH}$  formation increased with  $\text{O}_3$  conversion, indicating the secondary nature of the  $\text{HCOOH}$  formation [19]. This was also observed in the ozonolysis of propene, isobutene and isoprene under wet conditions.  $\text{CH}_3\text{COOH}$  was observed in the ozonolysis of *cis*- and *trans*-2-butene isomers. Noteworthy also is the observation an  $\text{CH}_3\text{CH}(\text{OH})\text{OOH}$  in the ozonolysis of *cis*- and *trans*-2-butene isomers, and the

formation of HOCH<sub>2</sub>OOH and higher (not identified) hydroperoxides in ozonolysis of isobutene in the presence of the water vapour.

The observation that these hydroperoxides decompose rapidly under the experimental conditions may be related to the increasing formation rates of HCOOH (and probably of CH<sub>3</sub>COOH) toward high O<sub>3</sub> conversion ranges, although further study is required. In view of these observations, both HCOOH and HMHP may be considered formed from the reaction of CH<sub>2</sub>OO\* intermediate with H<sub>2</sub>O vapour:



- c) The OH yield in the ozonolysis can be directly determined from the amount alkene converted per O<sub>3</sub> reacted. While in the C<sub>2</sub>H<sub>4</sub> ozonolysis, the OH yield is low,  $Y(\text{OH}) \gg 0.05$ ,  $Y(\text{OH})$  values for 2-butenes and isobutene were high;  $Y(\text{OH}) \gg 0.4$  for *cis*-2-butene, *ca.* 0.6 for *trans*-2-butene, and *ca.* 0.6 for isobutene. For isoprene,  $Y(\text{OH})$  was roughly in the range of 0.1 to 0.15.
- d) In the ozonolysis of isoprene, the main products were MVK, MACR, HCHO, CO, CO<sub>2</sub>, and FAN. Minor products included HMF, ketene, CH<sub>2</sub>=CO, and MGLY. The effect of water vapour addition on the relative yield of the two main carbonyl products,  $R = \text{MACR}/\text{MVK}$ , was investigated. Under dry conditions,  $R = 2.5$  and was not affected by the addition of the OH radical scavengers such as HCHO, cyclohexane, or CO. Under the wet conditions, D(MVK) increased while D(MACR) remained unchanged, resulting in the decrease in  $R$  to 1.8. The yield of HCOOH increased up to *ca.* 0.3 under the wet conditions.

### Assessment of achievements

The goals set with respect to the spectroscopy and kinetics of the simple peroxy radicals was mainly achieved. A detailed review on the chemistry and role of the peroxy radicals in the photo-oxidation of VOC was written within the LACTOZ project [25]. Further studies on quantum yields determination of photolabile carbonyl compounds and on the mechanism of the ozonolysis of alkenes are required.

### Acknowledgements

The work performed within LACTOZ was supported by the Max-Planck-Gesellschaft, the Sonderforschungsbereich 233 and various grants by the CEC. We acknowledge the close collaboration with Robert Lesclaux, Phil Lightfoot and Bernard Veyret (University of Bordeaux), Garry Hayman and Mike Jenkin (AEA, Culham), Tony Cox (Cambridge) and Georges Le Bras and Gilles Poulet (CNRS Orléans).

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### 3.14 Atmospheric Chemistry of Nitrogen-Containing Species

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#### Summary

The rate constants for the reactions of OH with a series of organic nitroalkanes, nitrites and nitrates and of NO with a series of peroxy radicals were measured at 298 K and a total pressure of 1 atm. The rate constants were obtained using the absolute technique of pulse radiolysis combined with time-resolved UV-VIS spectroscopy. The results are discussed in terms of reactivity trends and the atmospheric chemistry.

#### Aims of the research

The aim of this research is to provide new information on the kinetics and mechanisms for reactions of nitrogen species for use in atmospheric modelling.

#### Principal scientific findings during the project

Volatile organic nitrogen-containing compounds may act more or less as long-lived reservoirs for NO<sub>x</sub> in the troposphere. The reactions of OH radicals with three series of compounds have been studied: *n*-nitroalkanes, *n*-alkyl nitrates and *n*-alkyl nitrites. Nitroalkanes are employed as propellants and as industrial solvents leading to their potential release into the atmosphere. Alkyl nitrates can be formed in the oxidation of volatile organic compounds in the troposphere when peroxy radicals react with NO. Small amounts of alkyl nitrites may be formed in the urban atmosphere by reaction of alkoxy radicals with NO. The photodissociative lifetime of alkyl nitrites has been calculated to be around 2 min under typical atmospheric conditions. Thus alkyl nitrites can only be a temporary reservoir for NO<sub>x</sub> during night-time hours. Reaction of these organonitrogen compounds with hydroxyl radicals is an important factor in determining their atmospheric residence times. However, previously very little information concerning the kinetics and mechanisms for these reactions have been available. Results summarised in Table 1.

Peroxy radicals, RO<sub>2</sub>, are important intermediates in the atmospheric degradation of organic compounds emitted to the atmosphere. The alkyl radical, R, can be produced from emitted organic compounds in several ways, *e.g.*, by reactions with OH, or NO<sub>3</sub>, radicals, or by photolysis. Alkyl radicals will react rapidly with atmospheric O<sub>2</sub> to form peroxy radicals, RO<sub>2</sub>:

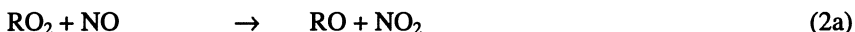


where M is a third body, N<sub>2</sub> and O<sub>2</sub>, in the atmosphere. The fate of RO<sub>2</sub> radicals in the atmosphere is determined by reaction with NO, NO<sub>2</sub>, HO<sub>2</sub>, or other RO<sub>2</sub> radicals:



The relative importance of reactions (2–5) depends on the NO, NO<sub>2</sub>, HO<sub>2</sub> and RO<sub>2</sub> concentrations and the values of the respective rate constants. In remote areas NO<sub>x</sub> concentrations as low as 1 ppt have been measured, decreasing the importance of reactions (2) and (3). However, in urban areas with higher NO<sub>x</sub> concentrations reaction (2) and (3) will be the major sink for RO<sub>2</sub> radicals.

The reaction of RO<sub>2</sub> radicals with NO proceeds through two channels:



In this work we have used the pulse radiolysis technique to investigate reaction 2 for a number of alkyl peroxy and halogenated alkyl peroxy radicals: CH<sub>3</sub>O<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>, (CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>O<sub>2</sub>, (CH<sub>3</sub>)<sub>3</sub>CC(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>O<sub>2</sub>, CH<sub>2</sub>FO<sub>2</sub>, CH<sub>2</sub>ClO<sub>2</sub>, CH<sub>2</sub>BrO<sub>2</sub>, CHF<sub>2</sub>O<sub>2</sub>, CF<sub>2</sub>ClO<sub>2</sub>, CHF<sub>2</sub>CF<sub>2</sub>O<sub>2</sub>, CF<sub>3</sub>CF<sub>2</sub>O<sub>2</sub>, CFCl<sub>2</sub>CH<sub>2</sub>O<sub>2</sub>, and CF<sub>2</sub>ClCH<sub>2</sub>O<sub>2</sub>.

## Experimental

The experimental set-up used, pulse radiolysis combined with kinetic spectroscopy in the visible wavelength region, has been described in detail previously [1] and will only be discussed briefly here. The experiments were carried out in a 1 litre stainless steel gas cell equipped with an internal White type mirror system adjusted to give an optical path-length of 120 cm. A pulsed xenon lamp delivers the analytical light, which is guided through the reaction cell to a detection system consisting of a 1 m McPherson grating UV-VIS monochromator and a Hamamatsu photomultiplier. The instrumental spectral resolution was 0.8 nm. A Biomation digitiser recorded the transmittance as function of time, and a PDP11 minicomputer handled and stored the data. A chromel/alumel thermocouple measured the temperature inside the reaction cell close to the centre. All experiments were carried out at 298 ± 2 K. The partial pressures of the different gases were measured with a Baratron absolute membrane manometer with a resolution down to 10<sup>-5</sup> bar.



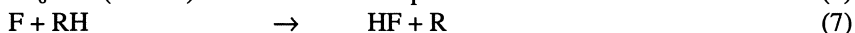
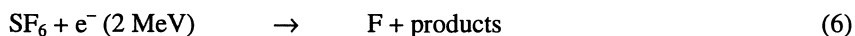
**Table 1:** Rate constants for the reaction of OH radicals and Cl atoms with  $\text{RNO}_x$  at 298 K.

Compound	$10^{13} k_{\text{Cl}}(\text{rel})$	$10^{13} k_{\text{OH}}(\text{rel})$	$10^{13} k_{\text{OH}}(\text{abs})$	Reference
$\text{CD}_3\text{NO}_2$	$0.02 \pm 0.0$	$0.9 \pm 0.1$	$1.0 \pm 0.2$	This work
			$0.09 \pm 0.004^{\text{a}}$	[1]
$\text{CH}_3\text{NO}_2$	$0.06 \pm 0.02$	$1.1 \pm 0.1$	$0.04^{\text{b}}$	[6]
			$1.6 \pm 0.5$	This work
$\text{C}_2\text{H}_5\text{NO}_2$	$1.7 \pm 0.1$	$1.5 \pm 0.1$	$0.14 \pm 0.01^{\text{a}}$	[1]
			$0.11^{\text{b}}$	[6]
$n\text{-C}_3\text{H}_7\text{NO}_2$	$99 \pm 6$	$5.5 \pm 0.8$	$1.5 \pm 0.5$	This work
			$0.72 \pm 0.08^{\text{a}}$	[1]
$n\text{-C}_4\text{H}_9\text{NO}_2$	$619 \pm 20$	$17.3 \pm 1.1$	$3.4 \pm 0.8$	This work
			$3.6 \pm 0.2^{\text{a}}$	[1]
$n\text{-C}_5\text{H}_{11}\text{NO}_2$	$1377 \pm 58$	$32.7 \pm 1.5$	$15.5 \pm 0.9$	This work
			$6.6 \pm 0.4^{\text{a}}$	[1]
			$13.5 \pm 1.8$	[7]
$\text{CH}_3\text{ONO}_2$	$2.62 \pm 0.02$	$33.3 \pm 0.5$	This work	
		$10.0 \pm 0.6^{\text{a}}$	[1]	
$\text{CH}_3\text{ONO}_2$	$2.62 \pm 0.02$	$3.4 \pm 0.7$	This work	
		$3.7 \pm 0.9$	[8]	
$\text{C}_2\text{H}_5\text{ONO}_2$	$42.7 \pm 1.6$	$0.34 \pm 0.04^{\text{c}}$	[9]	
		$4.6 \pm 0.3$	This work	
$n\text{-C}_3\text{H}_7\text{ONO}_2$	$247 \pm 15$	$4.8 \pm 2.0$	[8]	
		$7.7 \pm 0.8$	This work	
$n\text{-C}_4\text{H}_9\text{ONO}_2$	$924 \pm 2$	$7.0 \pm 2.2$	[8]	
		$6.2 \pm 1.0$	[7]	
		$16.2 \pm 0.8$	This work	
$n\text{-C}_5\text{H}_{11}\text{ONO}_2$	$1571 \pm 33$	$14.0 \pm 1.9$	[10]	
		$17.8 \pm 1.9$	[7]	
		$29.6 \pm 0.9$	This work	
$\text{CH}_3\text{ONO}$	$94.4 \pm 7.4$	$3.0 \pm 1.0$	This work	
		$14.1 \pm 1.9^{\text{d}}$	[11]	
		$10.9 \pm 1.7^{\text{d}}$	[12]	
		$2.1 \pm 0.4^{\text{f}}$	[13]	
		$1.2 \pm 0.3^{\text{g}}$	[13]	
		$10.0 \pm 1.5^{\text{e}}$	[14]	
$\text{C}_2\text{H}_5\text{ONO}$	$295 \pm 13$	$7.0 \pm 1.5$	This work	
		$17.7 \pm 2.8^{\text{d}}$	[12]	
$n\text{-C}_3\text{H}_7\text{ONO}$	$646 \pm 58$	$11.0 \pm 1.5$	This work	
		$24.0 \pm 4.5^{\text{d}}$	[12]	
$n\text{-C}_4\text{H}_9\text{ONO}$	$1370 \pm 58$	$23.1 \pm 3.4^{\text{e}}$	[14]	
		$22.7 \pm 0.8$	This work	
		$52.0 \pm 18^{\text{d}}$	[12]	
$n\text{-C}_5\text{H}_{11}\text{ONO}$	$2464 \pm 444$	$48.0 \pm 7.2^{\text{e}}$	[14]	
		$37.4 \pm 5.0$	This work	
			$42.5 \pm 8.0$	

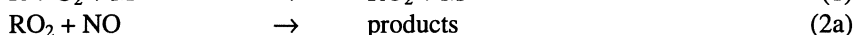
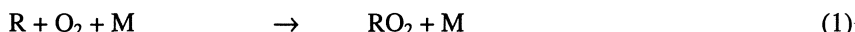
<sup>a</sup> FP-RF at 25–50 Torr; <sup>b</sup> LP-LIF at 100 Torr; <sup>c</sup> total pressure of 2–3 Torr;<sup>d</sup> at 100 Torr, <sup>e</sup> at 1–2 Torr; <sup>f</sup> relative to *n*-hexane; <sup>g</sup> relative to dimethyl ether.

The radical reactions were initiated by irradiation of the gas mixtures in the cell with a 30 ns pulse of 2 MeV electrons from a Febetron 705B field emission accelerator. The irradiation dose was varied by inserting stainless steel attenuators between the accelerator and the cell. The doses are given relative to the maximum dose, which is set to unity. SF<sub>6</sub> was used as diluent gas and the experiments were carried out at a total pressure of 1 bar. The pulsed irradiation is used to rapidly (<1 ms) produce a high concentration (10<sup>14</sup> – 3 × 10<sup>15</sup> cm<sup>-3</sup>) of radical species *e.g.* OH and F atoms.

For the RO<sub>2</sub> + NO investigation the first chemical step is reaction with fluorine atoms which produce the alkyl radical, R, by hydrogen abstraction from the compounds in question, RH,



The alkyl radical, R, reacts with O<sub>2</sub> to form RO<sub>2</sub>, which subsequently reacts with NO:



The formation of NO<sub>2</sub> was followed by its absorption of light at both 400 and 450 nm in order to assure that there was no interference from spectral features from other transient species in the system. All kinetic traces could be fitted using simple first-order formation kinetics.

## Results

The observed formation of NO<sub>2</sub> was always first order. No significant difference between experiments performed at 400 nm and 450 nm was detected. Hence the data from 400 nm and 450 nm have been treated together.

Before a value for *k*<sub>2</sub> can be extracted from the observed kinetics of the NO<sub>2</sub> formation the impact of potential secondary reactions needs to be considered. Peroxy radicals, RO<sub>2</sub>, are known to react with NO<sub>2</sub> to form peroxy nitrates [2, 3]. Hence, following the formation of NO<sub>2</sub> from reaction (2), there is a competition between reactions (2) and (3) for the available RO<sub>2</sub> radicals:



Similarly, alkoxy radicals produced in reaction (2) also react with both NO and NO<sub>2</sub>:



Reactions (3) and (9) remove  $\text{NO}_2$  from the system with an efficiency which increases at long reaction times. The removal decreases the time taken for the  $\text{NO}_2$  concentration to reach a maximum. Hence, reaction (3) and (9) lead to an increase in the apparent pseudo first order rate constant for  $\text{NO}_2$  formation. This effect is most pronounced under low  $[\text{NO}]_0$  concentrations leading to positive intercepts in plots of  $k^{\text{1st}}$  versus  $[\text{NO}]$ . Positive intercepts were observed for all the alkyl peroxy radicals studied here. Interestingly, similar plots for the halogenated peroxy radicals have intercepts which are zero, within the experimental uncertainty. To assess the impact of reactions (3), (8) and (9) and, hence, to compute corrections for such, detailed modelling of the experimental data was performed using the Acuchem chemical kinetic modelling program [4] with a mechanism consisting of reaction (2), (3), (8), and (9) (see publication for details).

**Table 2:** Summary of rate constants for  $\text{RO}_2 + \text{NO}$  products reactions.

Species	Technique	$10^{12} k_2$	Reference
$\text{CH}_3\text{O}_2$	FP-UV	$7.1 \pm 1.4$	[15]
	DF-MS	$6.5 \pm 2.0$	[16]
	FP-UV	$7.7 \pm 0.9$	[17]
	DF-MS	$8.6 \pm 2.0$	[18]
	LP-LIF	$7.8 \pm 1.2$	[19]
	LP-LA	$7.0 \pm 1.5$	[20]
$\text{C}_2\text{H}_5\text{O}_2$	PR-UV	$8.8 \pm 1.4$	This work
	DF-MS	$8.9 \pm 3.0$	[21]
<i>i</i> - $\text{C}_3\text{H}_7\text{O}_2$	PR-UV	$8.5 \pm 1.2$	This work
	FP-UV	$3.5 \pm 0.2$	[22]
<i>t</i> - $\text{C}_4\text{H}_9\text{O}_2$	DF-MS	$5.0 \pm 1.2$	[23]
	DF-MS	$4.0 \pm 1.1$	[14]
$(\text{CH}_3)_3\text{CCH}_2\text{O}_2$	PR-UV	$4.7 \pm 0.4$	This work
$(\text{CH}_3)_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{O}_2$	PR-UV	$1.8 \pm 0.2$	This work
$\text{CF}_3\text{CHFO}_2$	PR-UV	$12.8 \pm 3.6$	[24]
$\text{CHF}_2\text{CF}_2\text{O}_2$	PR-UV	$>9.7 \pm 1.3$	This work
$\text{CF}_3\text{CF}_2\text{O}_2$	PR-UV	$>10.7 \pm 1.5$	This work
$\text{CFCl}_2\text{CH}_2\text{O}_2$	PR-UV	$12.8 \pm 1.1$	This work
$\text{CF}_2\text{ClCH}_2\text{O}_2$	PR-UV	$11.8 \pm 1.0$	This work
$\text{CH}_2\text{FO}_2$	PR-UV	$12.5 \pm 1.3$	This work
$\text{CH}_2\text{ClO}_2$	PR-UV	$18.7 \pm 2.0$	This work
$\text{CH}_2\text{BrO}_2$	PR-UV	$10.7 \pm 1.1$	This work
$\text{CHF}_2\text{O}_2$	PR-UV	$12.6 \pm 1.6$	This work
$\text{CF}_3\text{O}_2$	DF-MS	$17.8 \pm 3.6$	[25]
	LP-MS	$14.5 \pm 2.0$	[26]
	PR-UV	$16.9 \pm 2.6$	[27]
$\text{CF}_2\text{ClO}_2$	LP-MS	$16.0 \pm 3$	[17]
	PR-UV	$13.1 \pm 1.2$	This work
$\text{CFCl}_2\text{O}_2$	LP-MS	$16.0 \pm 2.0$	[28]
	LP-MS	$14.5 \pm 2.0$	[17]
$\text{CCl}_3\text{O}_2$	DF-MS	$18.6 \pm 2.8$	[29]
	LP-MS	$17.0 \pm 2.0$	[17]

In view of the corrections applied to the data for  $\text{CH}_3\text{O}_2$ ,  $\text{C}_2\text{H}_5\text{O}_2$ ,  $(\text{CH}_3)_3\text{CCH}_2\text{O}_2$ , and  $(\text{CH}_3)_3\text{CC}(\text{CH}_3)_2\text{CH}_2\text{O}_2$  radicals, we choose to add an additional 10 % and 20 % uncertainty range to the measured rate constants of the reactions of  $\text{CH}_3\text{O}_2$  and  $\text{C}_2\text{H}_5\text{O}_2$  radicals, and  $(\text{CH}_3)_3\text{CCH}_2\text{O}_2$  and  $(\text{CH}_3)_3\text{CC}(\text{CH}_3)_2\text{CH}_2\text{O}_2$  radicals with  $\text{NO}$ , respectively. Values cited in Table 2 reflect these additional uncertainties. The absolute accuracy of the rate constants depends on the precision of reactant concentrations and possible unidentified systematic errors. The overall accuracy of the measured rate constants is estimated to be of the order  $\pm 25\%$ . In the case of experiments including neopentyl peroxy radicals two different total pressures were used; 1 and 0.5 bar. No effect of total pressure on  $k_2$  was evident.

## Discussion

In Table 2 we compare our results to those available in the literature. Also all data has been presented graphically in Fig. 1. For the reactions of  $\text{CF}_3\text{CF}_2\text{O}_2$  and  $\text{CHF}_2\text{CF}_2\text{O}_2$  radicals with  $\text{NO}$ , the alkoxy radicals formed decompose to give another fluorinated alkyl radical which can then react with  $\text{NO}$  to give more  $\text{NO}_2$ . The presence of additional processes forming  $\text{NO}_2$  subsequent to reaction (2) increases the time taken for the  $\text{NO}_2$  to reach a maximum. Hence, only lower limits can be established for the reaction of  $\text{CF}_3\text{CF}_2\text{O}_2$  and  $\text{CHF}_2\text{CF}_2\text{O}_2$  radicals with  $\text{NO}$ . In all cases the halogenated  $\text{C}_2$  peroxy radicals are significantly more reactive towards  $\text{NO}$  than ethyl peroxy radicals.

As shown in Fig. 1, the rate constants for  $\text{RO}_2 + \text{NO}$  reactions vary by one order of magnitude. Comparison of all the available data demonstrates two different trends. Firstly, the rate constants decrease with increasing alkyl chain length and branching going from  $\text{C}_1$  to  $\text{C}_8$ . Secondly, halogen substituents, especially chlorine, increase the  $\text{RO}_2 + \text{NO}$  rate constant.

It is possible to rationalise the first trend in terms of steric effects associated with the increasing alkyl chain length and branching. The same trend is observed in the peroxy radical self-reaction kinetics. The second trend is more difficult to explain but may reflect a decrease in the  $\text{RO-O}$  bond strength caused by the electron withdrawing halogen atom. *Ab initio* theoretical studies are needed to shed further light on the reactivity trends.

Finally we need to consider the implication of the results from the present work on our understanding of atmospheric chemistry of halogenated organic compounds. In all cases the peroxy radicals derived from haloalkanes were observed to react rapidly with  $\text{NO}$  with rate constants in the range of  $(9.7\text{--}18.7) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . A reasonable estimate for the global average tropospheric  $\text{NO}$  concentration is  $2.5 \times 10^8 \text{ cm}^{-3}$  [5]. Hence the lifetimes of halogenated peroxy radicals with respect to reaction with  $\text{NO}$  will be 4–7 minutes. In the atmosphere reaction (2) competes with reactions (3), (4) and (5) for available  $\text{RO}_2$  radicals. Kinetic data for reactions (4) and (5) are not available for the halogenated  $\text{RO}_2$  radicals studied here. Kinetic data are available for the reaction of  $\text{CF}_2\text{ClO}_2$ ,  $\text{CFCl}_2\text{O}_2$ ,  $\text{CCl}_3\text{O}_2$  and  $\text{CF}_3\text{O}_2$  with  $\text{NO}_2$ .

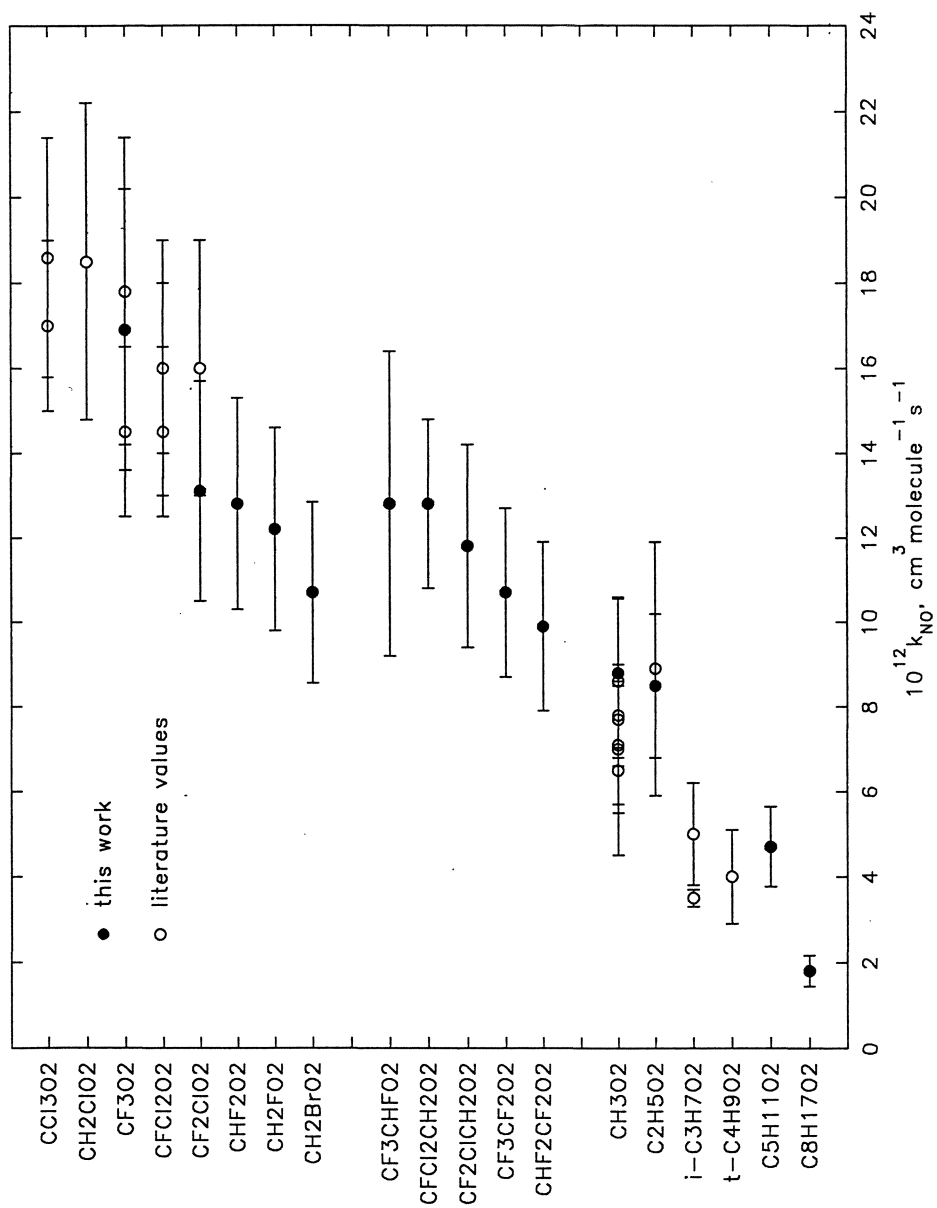


Fig 1: Rate constants for the reactions of NO with RO<sub>2</sub>.

At one atmosphere total pressure these reactions are at or close to the high pressure limit with rate constants of  $6.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Reasonable estimates of the global average tropospheric  $\text{NO}_2$ ,  $\text{HO}_2$ , and  $\text{RO}_2$  (represented by  $\text{CH}_3\text{O}_2$ ) are  $2.5 \times 10^8$ ,  $10^9$ , and  $1.3 \times 10^8 \text{ cm}^{-3}$  [5]. Based upon the data base for other peroxy radicals we estimate that the halogenated peroxy radicals studies have  $k_3 = 6 \times 10^{-12}$ ,  $k_4 = 6 \times 10^{-12}$ , and  $k_5 = 4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The atmospheric lifetimes of the halogenated  $\text{RO}_2$  radicals with respect to reactions (3), (4) and (5) are likely to be of the order of 11, 3, and 32 minutes, respectively.

Clearly reactions (2), (3), (4) and (5) could all play significant roles in the atmospheric degradation of halogenated organic compounds. Kinetic data for reactions (3), (4) and (5) are needed for a more complete understanding of the atmospheric chemistry for halogenated organic compounds.

### Acknowledgements

Thanks are due to all our collaborators during this 7 year project.

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### 3.15 Kinetic Studies of Reactions of Alkylperoxy and Haloalkylperoxy Radicals with NO. A Structure-Activity Relationship for Reactions of OH with Alkenes and Polyalkenes

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#### Summary

The kinetics of the reactions of higher alkylperoxy radicals and of H(C)FC-derived haloalkylperoxy radicals with NO have been studied at  $T = 290$  K and  $p = 2$  Torr He using the fast-flow technique combined with molecular-beam sampling mass spectrometry. The total rate constant of  $\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2 / \text{RONO}_2$  was determined from the shape of the  $\text{NO}_2$ -growth profile. The method was validated by measurements of  $k(\text{CF}_3\text{O}_2 + \text{NO}) = (1.51 \pm 0.4) 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  and of  $k(\text{C}_2\text{H}_5\text{O}_2 + \text{NO}) = (8.9 \pm 3.5) 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ . Thus, the first direct, validated measurements were made of  $k(\text{RO}_2 + \text{NO})$  for higher alkylperoxy radicals:  $k(i\text{-C}_3\text{H}_7\text{O}_2 + \text{NO}) = (5.0 \pm 1.2) 10^{-12}$ ,  $k(s\text{-C}_4\text{H}_9\text{O}_2 + \text{NO}) = (4.1 \pm 1.0) 10^{-12}$  and  $k(t\text{-C}_4\text{H}_9\text{O}_2 + \text{NO}) = (4.0 \pm 1.1) 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , showing a marked decrease of the rate coefficient with increasing  $\text{CH}_3$ -substitution, contrary to earlier assumptions. The  $k(\text{RO}_2 + \text{NO})$  rate constants for the peroxy radicals from H(C)FC's 134a, 143a, 142b and 123 were all found to be in the range  $1.2$  to  $1.6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ .

In a second part of the work, a Structure-Activity Relationship has been developed for the addition of OH to (poly)alkenes. It was shown that the total rate constants can be expressed in very good approximation by a sum of partial, site-specific rate constants for addition to a given (double-bonded) carbon atom, the values of these partial rate constants depending solely on the stability-type of the ensuing  $\beta$ -hydroxy radical. The SAR is particularly useful in that it also allows the prediction of the detailed primary product distributions of (poly)alkene + OH reactions. Therefore, the SAR is a powerful tool in the modeling of the tropospheric OH-initiated oxidation of biogenic VOC.

#### Aims of the project

The major aim of the research during the project was to gather kinetic and mechanistic information on reactions of VOC-derived peroxy radicals, in particular reactions with NO, in order to provide data relevant to the formation of tropospheric ozone. A secondary objective was to determine  $k(\text{RO}_2 + \text{NO})$



coefficients for H(C)FC-derived peroxy radicals and to gain information on the subsequent fate of the resulting oxy-radicals.

Finally, it was also aimed to obtain quantitative information on the primary-product distributions of reactions of OH with alkenes and polyalkenes.

## Principal scientific findings during the project

### A. Reactions of alkylperoxy- and haloalkylperoxy radicals with NO

#### Experimental and data analysis

The apparatus is a multi-stage fast-flow reactor, coupled to a molecular-beam sampling mass spectrometer (MBMS). The reactor consists of a 2.8 cm inner diameter quartz tube, with a side-arm equipped with a microwave cavity, and a set of two (or three) coaxial, movable injector tubes. To generate the specific alkyl radicals *i*-C<sub>3</sub>H<sub>7</sub>, *s*-C<sub>4</sub>H<sub>9</sub> and *t*-C<sub>4</sub>H<sub>9</sub>, hydrogen atoms created upstream in the microwave discharge side-arm were admixed to a large excess of an appropriate alkene admitted through the outer injector tubes; for the above alkyl radicals, the alkenes were respectively propene, 2-butene and isobutene, ensuring yields of the specific radical of 94 % [1], 99 % [2] and 100 % respectively. The radicals C<sub>2</sub>H<sub>5</sub>, CF<sub>3</sub> and the H(C)FC-derived haloalkyl radicals were produced by H-abstraction from C<sub>2</sub>H<sub>6</sub>, CF<sub>3</sub>H or the pertaining H(C)FC's (in large excess) by F-atoms, created from F<sub>2</sub> in the upstream microwave discharge. The concentration of the (halo)alkyl radicals R, produced in the constant-length "preparation region" of the flow reactor, was between 2 and 6 × 10<sup>12</sup> cm<sup>-3</sup>. A high amount of O<sub>2</sub> (~ 5 × 10<sup>15</sup> cm<sup>-3</sup>) together with a variable amount of NO (1 to 10 × 10<sup>13</sup> cm<sup>-3</sup>) was admixed to the (halo)alkyl radicals via the inner injector tube, resulting in their very fast conversion to RO<sub>2</sub> radicals, followed by the slow reaction thereof with NO (in at least a five-fold excess), yielding NO<sub>2</sub> and alkyl nitrates. The *i*(NO<sub>2</sub><sup>+</sup>)-versus-time growth profiles were recorded by moving the two coaxial injectors together, away from the sampling point. The NO<sub>2</sub><sup>+</sup> signals were monitored at an ionizing electron energy of 14 or 40 eV (depending on the presence or absence of *m/e* = 46 fragment ions from the R-precursor molecule). The NO<sub>2</sub>-growth method is preferred over the RO<sub>2</sub>-decay method since (for most of the cases at hand) there is no RO<sub>2</sub><sup>+</sup>-parent ion nor any interference-proof fragment ion. The experiments were carried out at total pressures of 2 and 0.7 torr (He bath gas) and at 290 K. Flow velocities were about 1800 cm s<sup>-1</sup>.

The determination of the *total* rate constant *k* of the process RO<sub>2</sub> + NO → RO + NO<sub>2</sub>/nitrate from the *shape* of *i*(NO<sub>2</sub><sup>+</sup>) is essentially based on the first-order law [NO<sub>2</sub>](*t*) = [NO<sub>2</sub>]<sub>∞</sub> [1 - exp(-*k* [NO] *t*)]. Corrections were made for the (slight) [NO]-decrease and for axial diffusion effects. Moreover, side-reactions such as RO<sub>2</sub> + NO<sub>2</sub> → pernitrate, RO + NO → nitrite, RO + NO<sub>2</sub> → nitrate, decomposition of RO and subsequent reactions, as well as contributions of nitrates and pernitrates to the total NO<sub>2</sub><sup>+</sup> signal, were duly taken into account by kinetic

modeling (resulting in corrections of 5 to 30 %). The  $k$ -values were obtained from plots of the corrected pseudo-first-order growth constants versus the  $[\text{NO}]$ -concentration.

## Results

The  $\text{NO}_2$ -growth method was validated by measurements of the rate constants of  $\text{CF}_3\text{O}_2 + \text{NO}$  and of  $\text{C}_2\text{H}_5\text{O}_2 + \text{NO}$ , for which we obtained respectively  $k = (1.51 \pm 0.4) \times 10^{-11}$  and  $k = (8.9 \pm 3.5) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , in good agreement with the literature values of these known reactions [3, 4, 6, 7, 12]. The validity of the method is further supported by our own measurement  $k(\text{CF}_3\text{O}_2 + \text{NO}) = 1.54 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  from the  $\text{CF}_3\text{O}_2$  decay as monitored by means of the specific  $\text{CF}_2\text{O}_2^+$  fragment ion.

Table 1 displays our results for alkylperoxy radicals together with literature values, when available.

**Table 1:** Rate constants of reactions between alkylperoxy radicals and  $\text{NO}$ ;  $T = 290 \text{ K}$ . Data of this work obtained at  $p(\text{He}) = 2 \text{ Torr}$  for  $\text{C}_2\text{H}_5$ ,  $i\text{-C}_3\text{H}_7$  and  $s\text{-C}_4\text{H}_9$ , and at both 0.7 and 2 Torr for  $t\text{-C}_4\text{H}_9$ .

$\text{RO}_2$	$k(\text{RO}_2 + \text{NO}) / 10^{-12} \text{ cm}^3 \text{ s}^{-1}$		
	this work	literature data	
$\text{C}_2\text{H}_5\text{O}_2$	$8.9 \pm 3.5$		
			$8.9 \pm 3.0$ [6]
			$7.2 \pm 1.3$ [7]
			$8.5 \pm 1.2$ [12]
$i\text{-C}_3\text{H}_7\text{O}_2$	$5.0 \pm 1.2$ [8, 9]		$2.7 \pm 0.2$ [5]
			$3.5 \pm 0.2$ [10]
$s\text{-C}_4\text{H}_9\text{O}_2$	$4.1 \pm 1.0$ [9]		
$t\text{-C}_4\text{H}_9\text{O}_2$	$4.0 \pm 1.1$ [8, 9]		

Our data, taken in combination with the well-known  $k(\text{CH}_3\text{O}_2 + \text{NO}) = (7.8 \pm 2) \times 10^{-12}$  and  $k(\text{HO}_2 + \text{NO}) = (8.5 \pm 2.0) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  [11] show a marked decrease of the kinetic coefficient for  $\text{RO}_2 + \text{NO}$  reactions with increasing  $\text{CH}_3$ -substitution on the  $\alpha$ -carbon atom. This pronounced trend is contrary to earlier assumptions and is observed for the first time. Adachi and Basco had already measured a low value for  $i\text{-C}_3\text{H}_7\text{O}_2$  [10], of  $3.5 \times 10^{-12}$ , but their results for  $\text{CH}_3\text{O}_2$  and  $\text{C}_2\text{H}_5\text{O}_2$ , using a similar method, are also only  $3.0$  and  $2.7 \times 10^{-12}$ . In later work, Nielsen *et al.* [12] confirmed the downward trend of  $k(\text{RO}_2 + \text{NO})$  with increasing size of the alkyl radical: for  $(\text{CH}_3)_3\text{CCH}_2\text{O}_2$  they obtained  $k = (4.7 \pm 0.4) \times 10^{-12}$  and for  $(\text{CH}_3)_3\text{CC}(\text{CH}_3)_2\text{CH}_2\text{O}_2$ :  $k = (1.8 \pm 0.2) \times 10^{-12}$ , while confirming also  $k = (8.5 \pm 1.2) \times 10^{-12}$  for  $\text{C}_2\text{H}_5\text{O}_2$ .

The following table lists our results for  $\text{CF}_3\text{O}_2$  and for several  $\text{H}(\text{C})\text{FC}$ -derived haloethylperoxy radicals.

**Table 2:** Rate constants of reactions of  $\text{CF}_3\text{O}_2$  and of haloethylperoxy radicals with NO;  $T = 290 \text{ K}$  (our results at a helium pressure  $p = 2 \text{ Torr}$ ).

$\text{RO}_2$	$k(\text{RO}_2 + \text{NO}) / 10^{-12} \text{ cm}^3 \text{ s}^{-1}$			
	this work		literature data	
$\text{CF}_3\text{O}_2$	$15.1 \pm 4.0$	[8]		
	$15.3 \pm 3.0^a$	[8]		
			$15.1 \pm 2.0$	[3]
		$17.8 \pm 3.6$	[4]	
		$16.9 \pm 2.6$	[14]	
$\text{CF}_3\text{CHFO}_2$ (from HFC 134a)	$15.6 \pm 4.1$	[13]	$12.8 \pm 3.6$	[15]
			$13.0 \pm 3.0$	[16]
$\text{CF}_3\text{CH}_2\text{O}_2$ (from HFC 143a)	$12.3 \pm 3.2$	[13]	$13.0 \pm 3.0$	[16]
$\text{CF}_2\text{ClCH}_2\text{O}_2$ (from HCFC 142b)	$11.8 \pm 3.0$	[13]	$11.8 \pm 1.0$	[17]
$\text{CF}_3\text{CCl}_2\text{O}_2$ (from HCFC 123)	$14.5 \pm 3.9$	[13]	$17.5 \pm 2.5$	[18]

<sup>a</sup> from  $\text{CF}_3\text{O}_2$  decays

Our results agree well with other recent data. For all the investigated haloethylperoxy radicals, our  $k(\text{RO}_2 + \text{NO})$  is in the range of  $11$  to  $16 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ . Our data indicate that the kinetic coefficient is highest for the radicals with one or more halogen atoms on the  $\alpha$ -carbon atom; yet, a  $\text{CX}_3$  substituent on the  $\alpha$ -carbon clearly also promotes the reaction. A combination of all the available data on reactions of peroxy radicals with NO confirms the view that  $e^-$  acceptors on the  $\alpha$ -carbon enhance the reactivity toward NO, whereas  $e^-$  donors (such as alkyl groups) lower the reactivity [8].

### B. Product distributions of reactions of OH with (poly)alkenes.

#### A structure-activity relationship for OH-addition

Existing SARs for OH + polyalkene reactions merely attribute a reactivity to a specific complete C=C structure or to a complete C=C-C=C structure for conjugated dienes. These SARs provide no information with relevance to the detailed product distribution of the various possible OH-adducts.

In the frame of the present project, a detailed analysis of known total rate constants  $k_{\text{OH}}$  for OH + alkene reactions was carried out, revealing that for monoalkenes and non-conjugated polyalkenes, the total rate constant can be expressed as a sum of independent, partial rate constants  $k_i$  for addition to a given double-bonded C-atom. These site-specific  $k_i$  depend only on the stability type of the ensuing hydroxyalkyl radical, which can be either primary, secondary or tertiary. Thus, there are only three such  $k_i$ , denoted here as  $k_{\text{prim}}$ ,  $k_{\text{sec}}$  and  $k_{\text{tert}}$  [19]. It should be

understood that for addition of OH to Carbon atom  $C_a$  of a  $C_a=C_b$  structure, it is the environment of Carbon atom  $C_b$  that determines the adduct stability type, and therefore the  $k_i$ . The values of the three  $k_i$  were determined from the total rate constants  $k_{OH}$  for the three symmetric alkenes ethene, 2-butene, and tetramethylethene:

$$\begin{aligned} k_{\text{prim}} &= 1/2 k_{OH}^{\infty} (\text{ethene}) &= 0.45 \times 10^{-11} \\ k_{\text{sec}} &= 1/2 k_{OH} (\text{2-butene}) &= 3.0 \times 10^{-11} \\ k_{\text{tert}} &= 1/2 k_{OH} (\text{tetramethylethene}) &= 5.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \end{aligned}$$

Using the above  $k_i$ , the additivity hypothesis  $k_{OH} = \sum k_i$  (the sum being made over all double-bonded C-atoms) was verified for the 28 alkenes and nonconjugated dialkenes for which  $k_{OH}$  data are available. All predicted  $k_{OH}$  are within 20 % of the experimental values, and the standard deviation is only 12.6 % (excepting  $\alpha$ -pinene, for which the deviation is 30 %, probably due to steric hindrance caused by the bridged 6-cycle) [19].

For conjugated dienes, one must take into account the resonance stabilisation for some of the possible adduct radicals. This is the case for OH addition to one of the terminal C-atoms of a  $C=C-C=C$  structure, because of the resulting allyl-like resonance between the "original"  $\beta$ -hydroxy radical and the resonant  $\delta$ -hydroxy structure. As an example, when the former is a secondary radical and the latter a tertiary one, the corresponding partial site-specific rate constant is denoted as  $k_{\text{sec/tert}}$ . Generally, for conjugated dienes there are six such additional partial rate constants (beside  $k_{\text{prim}}$ ,  $k_{\text{sec}}$  and  $k_{\text{tert}}$ ). They were evaluated from the known total  $k_{OH}$  for six conjugated dienes; they are listed below, in units of  $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ .

$$\begin{array}{lll} k_{\text{sec/prim}} = 3.0 & k_{\text{sec/sec}} = 3.75 & k_{\text{sec/tert}} = 5.05 \\ k_{\text{tert/prim}} = 5.65 & k_{\text{tert/sec}} = 8.35 & k_{\text{tert/tert}} = 9.85 \end{array}$$

One clearly sees the increase of the partial rate constant with increasing stability of the resonant structure. Again, the predicted total rate constants for other conjugated dienes,  $k_{OH} = \sum k_i$ , agree very well with the experimental values, with an average deviation of only 10 % (excepting for two cases, with exceptionally large measured  $k_{OH}$ ,  $\alpha$ -phallandrene and  $\alpha$ -terpinene) [19].

The present SAR is especially valuable for the prediction of the detailed product distribution of the primary OH-adducts. Since the total rate constant is a sum of independent partial rate constants for addition to specific sites, the yield of a given primary adduct arising from process  $i$  should indeed be:  $\text{yield}_i = k_i / \sum k_i$ . As an example, application to isoprene  $H_2C_a=C_b(\text{Me})-C_cH=C_dH_2$  results in the following prediction: addition to  $C_a$ : yield 60 %; addition to both  $C_b$  and  $C_c$ : yield 5 % each; addition to  $C_d$ : yield 30 %.

#### Measurement of the OH-adduct product distribution

In order to verify and validate the above SAR with respect to its product-distribution implications, measurements have been carried out aiming to quantify the

yields of the various possible primary products of the reactions of OH with various alkenes and dienes: propene; 1-butene; isobutene; 1,3-butadiene and isoprene. In discharge/flow-MBMS experiments, a small amount of OH (generated upstream by  $H + NO_2$ ) was reacted with a large excess of the (poly)alkene, and the resulting primary radicals were converted subsequently to stable bromide molecules by reaction with an excess  $Br_2$ . Quantitative analysis of the various  $R_iBr$  was undertaken by MBMS, on the basis of the fragment ion mass spectra. At present, the final quantitative results are not yet available; in order to determine the fragmentation spectra of the pure reference compounds, these bromoalcohols have to be synthesised, a process which is now in progress. Only an approximate result for 1,3-butadiene can be given now. The preliminary value for the yield ratio  $CH_2=CH-CH-CH_2OH / CH_2=CH-CHOH-CH_2$  is 4.5 with error margins of +2.5 and -1.5, whereas the above SAR predicts a ratio of 5. Generally, as far as can be assessed from estimated fragmentation spectra, the experimental results are broadly in line with the SAR predictions.

### Assessment in the light of the aims of LACTOZ

Our new finding that the kinetic coefficient of alkylperoxy + NO reactions decreases with increasing size (or  $CH_3$ -substitution) of the alkyl radical is of considerable importance with respect to tropospheric ozone formation from higher hydrocarbons, the more so since the rate constants of the competing alkylperoxy +  $HO_2$  reactions [20] increase significantly for larger R.

Our  $k(RO_2+NO)$  data, in combination with these provided by other LACTOZ groups are now serving as basis for Structure-Activity Relationships regarding peroxy radical + NO reactions [21]. Moreover, our result for *s*- $C_4H_9O_2$  [9] is currently incorporated in tropospheric chemistry models (where butane is a model NMHC alkane).

The major value of the new Structure-Activity Relationship presented and developed by us [19] for (poly)alkene + OH reactions resides in its inherent predictive potential regarding the detailed primary-product distributions of such reactions. This is especially useful for quantitative assessments of the various possible OH-initiated degradation pathways of biogenic VOC, of which there is such a diversity and multitude that one can realistically hope to perform detailed experimental studies on only a few of them.

### Acknowledgments

This research was carried out in the frame of the Belgian participation in the EUROTRAC programme, supported by the Belgian State – Prime Minister's Services – Science Policy Office, contract E7/01/01P. Support by the CEC is also acknowledged.

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### 3.16 Mechanism and Kinetics of the Reaction of OH with Volatile Organic Compounds

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#### Summary

Laser flash photolysis and discharge flow measurements of the reaction rates of OH with several VOC have been made in a project designed to provide data for the determination of the photochemical ozone creation potentials of the VOC. In related studies, the mechanisms of the atmospheric oxidation of a wide range of compounds have been developed. Finally, objective techniques for extensive mechanism reduction, first applied in combustion chemistry, have been applied to tropospheric mechanisms.

#### Aims of the research

The major aims of the research are the establishment of quantitative mechanisms of atmospheric oxidation of volatile organic compounds.

#### Principal scientific results

In order to assess the impact of volatile organic compounds (VOC) on ozone formation in the troposphere it is necessary to know:

- (i) The rate constant for the reaction between OH and the VOC. This reaction initiates the oxidation chain and determines the time (and distance) scales of ozone formation.
- (ii) The mechanism for the oxidation of the VOC. This aspect draws heavily on the work of the LACTOZ subproject.

In this component of the subproject, OH + VOC rate constants have been measured and oxidation mechanisms developed. In addition, work is continuing on the reduction of the mechanisms, so that they can be more feasibly incorporated in atmospheric transport models.

#### Experimental studies of OH + VOC

We have employed laser flash photolysis coupled with laser-induced fluorescence (LP) and discharge flow (DF) coupled with LIF to study the rates of reaction of OH with a range of VOC. The compounds studied have significant emission rates and data are needed to determine their photochemical ozone creation potentials.

The systems were tested on the reactions with methane (LP) and cyclohexane (DF) showing good agreement with literature data. The principal results are shown in Table 1. The rate constants were measured at pressures of 760 Torr (LP) and 2 Torr (DF) in a helium diluent.

**Table 1:** Results of rate constant measurements for reaction of OH with VOC at 295K.

VOC	$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Method
methane	$5.4 \times 10^{-15}$	LP
cyclohexane	$6.7 \times 10^{-12}$	DF
<i>i</i> -butanol	$9.0 \times 10^{-12}$	LP
<i>t</i> -butanol	$8.1 \times 10^{-13}$	DF
<i>n</i> -butanol	$8.4 \times 10^{-12}$	LP
<i>i</i> -amyl-alcohol	$1.3 \times 10^{-11}$	DF
1,2-butadiene	$1.9 \times 10^{-11}$	DF
<i>t</i> -amyl methyl ether	$5.0 \times 10^{-12}$	LP
<i>n</i> -propyl acetate	$2.9 \times 10^{-12}$	LP
methyl methacrylate	$2.6 \times 10^{-11}$	DF
cyclohexane	$4.3 \times 10^{-12}$	LP
vinyl acetate	$2.5 \times 10^{-11}$	DF
acrylonitrile	$3.2 \times 10^{-12}$	DF
cyclohexylamine	$3.0 \times 10^{-11}$	DF
1,2 dichloroethane	$2.0 \times 10^{-13}$	LP
<i>trans</i> -1,2 dichloroethane	$1.9 \times 10^{-12}$	DF

LP - laser flash photolysis/laser induced fluorescence.

DF - discharge flow/laser induced fluorescence.

### Mechanism development

A programme is in progress to develop, in collaboration with ME Jenkin (AEA Technology), detailed mechanisms for the atmospheric oxidation of 100 VOC of primary interest in the troposphere. The mechanisms draw on recent work, especially in the LACTOZ programme, and incorporate the following features in addition to the central OH initiated radical  $\rightarrow$  peroxy radical  $\rightarrow$  alkoxy radical chain:

- Reaction of alkenes with  $\text{NO}_3$
- Reaction of carbonyls, alkenes and aromatics with  $\text{NO}_3$ .
- Reaction of  $\text{RO}_2$  with  $\text{HO}_2$  and  $\text{R/O}_2$ .
- Reactions of alkoxy radicals, including isomerisation, decomposition and reaction with  $\text{O}_2$ .
- Photochemistry of carbonyls and hydroperoxides.
- PAN chemistry.

The mechanisms are fully documented and are also provided in a reduced format suitable for incorporation in a computer code.



### ***Mechanism reduction techniques***

The mechanisms generated by the process described above are very complex. For butane, for example, the overall mechanism describing the total oxidation process contains nearly six hundred reactions and over two hundred species. It is difficult to incorporate such mechanisms in atmospheric transport models, especially those based on Eulerian codes. This difficulty is discussed in a recent review of air pollution modelling by Zlatev *et al.* [1] Thus it is desirable to simplify the representation in some way, and since the bulk of the computing time is spent in solving the equations describing the chemical interactions of the components of the air mass, it is common to minimise the number of chemical species. Two of the chemical schemes most widely used for modelling ground-level ozone formation employ a lumped species (LCC - Lurmann *et al.* [2] ) or a lumped structure (CBM4 - Gery *et al.* [3] ) approach. In this way the number VOCs in the scheme is reduced by a factor of more than ten. Typically the chemical reactions of this reduced set of species are then derived by use of laboratory data on individual reactions and by comparison of the resulting scheme with a large number of environmental chamber experiments. In this work, we apply a suite of systematic reduction techniques, from the program package KINAL [4] developed to study combustion systems [5] to an extended lumped structure mechanism (CBMEX). We then compare the resulting smaller mechanism with a reduced version derived from considerations of typical ambient air conditions and environmental chamber results, CBM4.

### ***Method***

The reduction procedure used here has the following steps:

- (i) the important predictions from the model (*e.g.* ozone concentration) and the range of conditions (*e.g.* concentrations, temperature, humidity) of the air mass are chosen;
- (ii) a simulation using the full mechanism is performed and time points for further investigation are selected;
- (iii) the chemical species necessary for accurate prediction of the important variables are found by calculating the change in the rate of production of the important species as a function of a change in the concentration of each species in the mechanism at the selected time points, this is an iterative process;
- (iv) the necessary reactions are found by a rate coefficient sensitivity calculation, in which the resulting changes in rate production of necessary species as a function of change in each rate coefficient, are sorted using a principal component analysis;
- (v) fast reversible reactions are identified from the rates of production and loss, and removed from the scheme in pairs;

- (vi) quasi-steady-state species, are found from a comparison of the lifetimes of the remaining species and the calculated error in assuming the quasi-steady-state approximation for the group of species. This procedure replaces the ordinary differential rate equation by an algebraic equation by setting the rate to zero. The algebraic equation can then be solved to obtain explicit relationships between the fast species and the slower species.

The reduction procedure was applied to three sets of initial conditions which were taken from environmental chamber experiments, 134P, 136P and 137P of Hess *et al.* [6]. Without isoprene this gave initial VOC: NO<sub>x</sub> ratios of 3.5, 8.7 and 15.6 { $N(C) / N(NO_x)$ }. The concentrations of the species were simulated for a 48 hour period in which the temperature and solar flux were varied as for a typical diurnal cycle in July at a latitude of 50° N [7]. No further emission or deposition of species were included in the simulation. At each stage of the reduction the ozone profile calculated from the smaller mechanism was compared with that for the CBMEX profile.

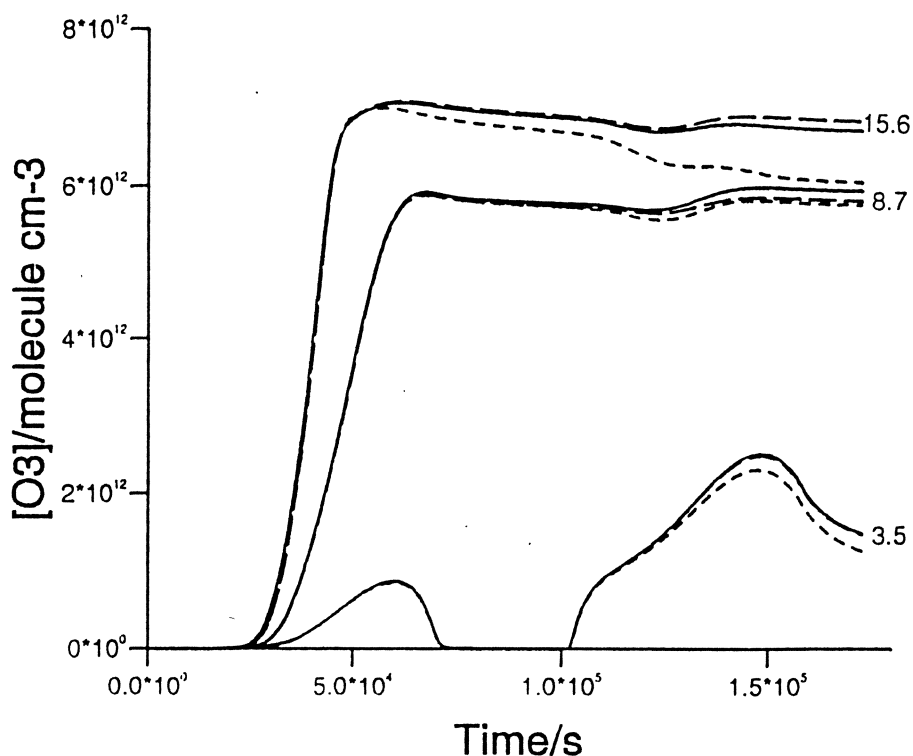
### Results and discussion

The CBMEX mechanism consists of 204 reactions and 90 species, CBM4 has 81 reactions and 33 species, whereas CBMKINAL, the mechanism derived in this work, has 55 reactions and 30 species. The ozone profiles for the three mechanisms at each of the VOC: NO<sub>x</sub> ratios are shown in Fig. 1. For each ratio there is less deviation from the CBMEX profile with CBMKINAL than with CBM4. The performance of the mechanism under more realistic atmospheric conditions has also been investigated. A trajectory model [8] was used in which a box of air is moved over a grid of emissions of VOC and NO<sub>x</sub> representative of those for Europe. The chemistry of the air parcel was simulated for a 5 day period in July, with the same diurnal variation in temperature, solar flux and humidity as previously. Dry deposition of the chemical species was also included. Two trajectories have been considered with a background VOC: NO<sub>x</sub> value in each case of 2.7. Trajectory (a) passes mostly over the sea and goes from East of Sweden to West of Scotland, whereas trajectory (b) travels overland and goes from Yugoslavia to Northern France. There was a large discrepancy in the ozone concentration for CBMKINAL compared with the full mechanism, most of which could be attributed to the elimination of the reaction between OH and methane, CH<sub>4</sub>. The concentrations of all organic surrogates (except FORM and KET) were about 10 times lower in the trajectory runs than in the environmental chamber simulations making CH<sub>4</sub> relatively more important. However, with CH<sub>4</sub> included in KINAL, for case (a) CBM4 deviates further from CBMEX than does CBMKINAL and in case (b) CBMKINAL agrees very well with CBMEX up until 83 hours after which time CBM4 has a better agreement.

From these results we conclude that the systematic reduction techniques discussed can be usefully applied to tropospheric chemical reaction schemes. The process is totally objective and easily accomplished. It is also clear from the results that the

reduction must be carried out under conditions closely related to those pertaining in the specific tropospheric scenario under investigation. This conclusion illustrates the need for an approach involving construction of a comprehensive mechanism incorporating all of the appropriate chemistry, followed by systematic reduction, of the type described here, under realistic conditions.

Work is in progress on the reduction of the comprehensive butane scheme. Substantial reductions have already been achieved. This methodology will then be applied to a range of compounds for a variety of conditions.



**Fig. 1:** Ozone concentrations *versus* time for three VOC : NO<sub>x</sub> ratios.  
(----- CBMEX;----- CBMIV, - - - - - CBMKINAL)

### Acknowledgements

Funding from the Department of the Environment and NERC is gratefully acknowledged.

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### 3.17 Reactions of *n*- and *s*-Butoxy Radicals in Oxygen. Importance of Isomerisation and Formation of Pollutants

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#### Summary

Reactions of  $C_4H_9O$  radicals have been investigated in mixtures of  $O_2/N_2$  under atmospheric pressure in the temperature range 313–503 K, for *s*- $C_4H_9O$ , and 343–503 K, for *n*- $C_4H_9O$  radicals. Flow and static experiments were performed in various vessels (quartz or Pyrex, different diameters, walls passivated or not towards reactions of radicals), and products were analysed by HPLC and GC/MS.

The main products formed by reactions of *s*-butoxy radicals  $CH_3CH(O)CH_2CH_3$  are: hydrogen peroxide and ethyl-hydroperoxide as peroxides, acetaldehyde, methylethylketone and traces of propionaldehyde as carbonyl compounds. The reaction of the *s*-butoxy radical with oxygen, (2)  $s-C_4H_9O + O_2 \rightarrow HO_2 + CH_3COC_2H_5$ , yielding  $HO_2$  radicals and methylethylketone, is by far the main channel from room temperature to about 393 K, whereas the decomposition reaction (3)  $s-C_4H_9O \rightarrow C_2H_5 + CH_3CHO$  plays the main role when the temperature is raised above 393 K. The rate constant ratio  $k_3/k_2[O_2]$  was obtained from the experimental values of  $[CH_3CHO]/[CH_3COC_2H_5]$ , and the decomposition rate constant  $k_3$  determined:

$$k_3 = 10^{13.8 \pm 0.2} \exp\{-15\,000 \pm 900 \text{ kcal mol}^{-1}/RT\}.$$

The main products formed by reactions of *n*-butoxy radicals  $CH_3CH_2CH_2CH_2O$  are butyraldehyde, hydroperoxide  $C_4H_8O_3$  of MW 104, 1-butanol, butyrolactone, *n*-propyl hydroperoxide. It is shown that transformation of these RO radicals occurs through two reaction pathways, H shift isomerization (forming  $C_4H_8OH$  radicals) and decomposition. A difference in activation energy  $\Delta E = (7.7 \pm 0.1)$  (σ) kcal/mol between these reactions is found, leading to an isomerization rate constant  $k_{\text{isom}}(n-C_4H_9O) = 4.4 \times 10^{11} \exp(-9\,700/RT)$  or  $4.4 \times 10^{11} \exp(-10\,700/RT)$ . Oxidation, producing butyraldehyde, would occur after isomerization, in parallel with an association reaction of  $C_4H_8OH$  radicals producing  $O_2C_4H_8OH$  radicals which, after isomerization lead to a main product, an hydroperoxide of molecular weight 104. The ratio of butyraldehyde/(butyraldehyde + isomerization products) =  $0.290 \pm 0.035$  (σ), studied from 448 to 496 K, is independent of oxygen concentration. Butyraldehyde would be mainly formed from the isomerised radical  $H-O-C-C-C-C^{\bullet} + O_2 \rightarrow H-O-C-C-C-CO_2 \rightarrow O=C-C-C-C + HO_2$ , because the addition of small quantities of NO has no

influence on butyraldehyde formation but decreases the concentration of the hydroperoxides (that of MW 104 and  $C_3H_7OOH$ ). By measuring the decay of [MW 104] as a function of [NO] added (0–22.5 ppm) at 487 K, an estimate of the isomerization rate constant  $O_2C_4H_8OH \rightarrow HO_2C_4H_7OH$  (5),  $k_5 \approx 10^{11} \exp(-17\,600/RT)$  is made. Implications of these results for atmospheric chemistry are discussed.

### Aims of the scientific research

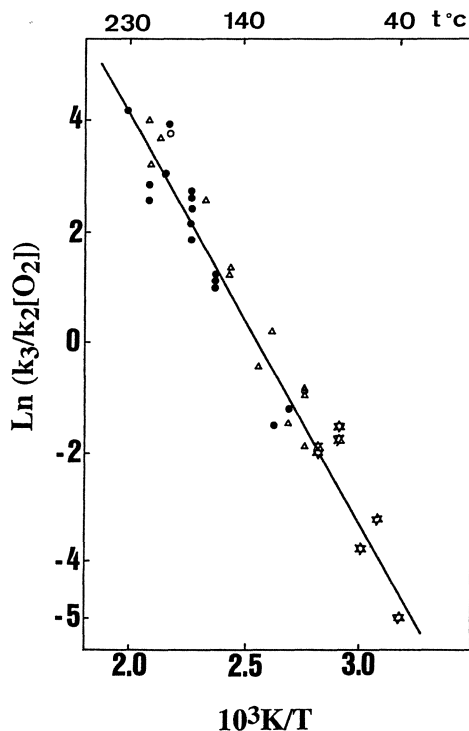
The reactions of RO radicals play a key role in the degradation of hydrocarbons in atmospheric chemistry. These reactions are numerous, depending upon the structure of the hydrocarbon, the temperature and the environment in which they occur. A lot of products are formed through their intermediate, and many of these products are atmospheric pollutants. For alkane hydrocarbons with a carbon number  $\geq C_4$ , estimations from smog chamber data made by Baldwin *et al.* [1] have shown, for instance, that the isomerization reaction of the *n*-butoxy radical is by far the main pathway under atmospheric conditions, the reactions with oxygen or that of decomposition contributing for less than 1 % to the global transformation. Experimental investigations [2–4] found contribution of the oxidation reaction amounting to 25–30 % at room temperature. From calculations about product distributions for more abundant alkanes representative of US emissions into the troposphere [5] it can be concluded that the 1,5-H shift isomerization of the *n*-butoxy radical accounts for about 73 % of the transformation of this radical at 300 K, the remainder being due to the reaction with oxygen (the decomposition reaction is negligible under these conditions). A recent study of Kerr *et al.* [6] involving 2- and 3- hexoxy radicals, showed that the 1,5-H shift isomerization could represent  $68 \pm 48$  % and even  $96 \pm 30$  % of the overall reaction. Studies carried out until now consisted mainly of making analyses of end-products present after combustion or after their transformation in the atmosphere. With regard to the formation mechanism of all these products, certainties are hard to achieve.

We have considered that *n*-butoxy radical is the smallest alkoxy radical we can experimentally study, for which isomerization occurs, generating mechanistic as well as kinetic complexities. Isomerization can play an important role from room to high temperatures, and analysis of the generated products enables us to understand what kind of chemical transformations occurs after this channel. For instance, the role of isomerization is especially interesting to analyse in the formation of pollutants, in combustion and in atmospheric chemistry, especially for tropospheric ozone. Experiments have been made with a variety of reactors (different treatments and diameters), with a wide range of oxygen concentrations and also by adding traces of NO in order to confirm certain aspects of the chemical mechanism; experimental results enable us to estimate not only the isomerization rate constants of *n*- $C_4H_9O$  radicals but also that of  $O_2C_4H_8OH$  radicals.

### Principal scientific findings

#### Reactions of *s*-butoxy radicals $\text{CH}_3\text{CH}(\text{O})\text{CH}_2\text{CH}_3$

The products analysed by HPLC chromatography were: *peroxides*  $\text{H}_2\text{O}_2$ ,  $\text{C}_2\text{H}_5\text{O}-\text{OH}$  and the remaining *s*- $\text{C}_4\text{H}_9\text{O}-\text{OC}_4\text{H}_9$ , *carbonyl compounds*  $\text{CH}_3\text{CHO}$ ,  $\text{CH}_3\text{COC}_2\text{H}_5$  and traces of  $\text{C}_2\text{H}_5\text{CHO}$ .

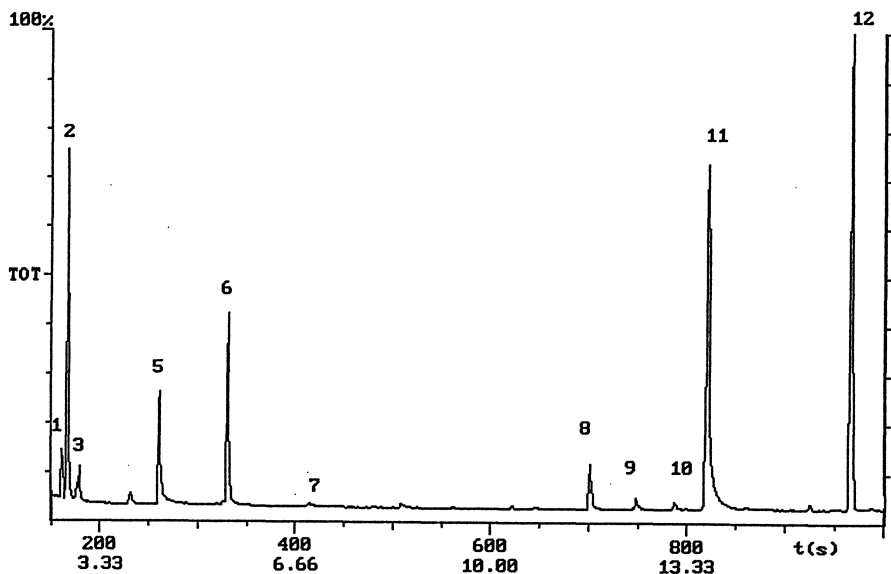


**Fig. 1:** Arrhenius plot,  $\ln(k_3/k_2[\text{O}_2])$  versus  $1/T$ , decomposition of *s*- $\text{C}_4\text{H}_9\text{O}-\text{OC}_4\text{H}_9$ , ● Pyrex vessel  $\Phi_1$  10 mm,  $\Delta$  quartz vessel  $\Phi_1$  20 mm, ★ quartz vessel  $\Phi_1$  30 mm (stopped-flow experiments in the temperature range 40–80 °C), the straight line is the least-squares fit [7].

The reaction of the *s*-butoxy radical with oxygen, (2)  $s\text{-C}_4\text{H}_9\text{O} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CH}_3\text{COC}_2\text{H}_5$ , yielding  $\text{HO}_2$  radicals and methylethylketone, is by far the main channel from room temperature to about 393 K, whereas the decomposition reaction (3)  $s\text{-C}_4\text{H}_9\text{O} \rightarrow \text{C}_2\text{H}_5 + \text{CH}_3\text{CHO}$  plays the main role when the temperature is raised above this last temperature. From the study of experimental ratios  $\text{CH}_3\text{CHO}/\text{CH}_3\text{COC}_2\text{H}_5$  the rate constant ratio  $k_3/k_2[\text{O}_2]$  versus  $1/T$  has been determined (Arrhenius plot of Fig. 1) by computer simulation according to a mechanism of 14 reactions [7a]. A difference in the activation energy  $E_3 - E_2 = 14.8 \pm 0.9$  kcal/mol has been found, and for  $s\text{-C}_4\text{H}_9\text{O} + \text{O}_2$ ,  $E_2 = 0.2$  kcal/mol, the decomposition rate constant  $k_3$  was determined:

$$k_3 = 10^{13.8 \pm 0.2} \exp\{(-15\,000 \pm 900) / RT\}$$

Static experiments were made in a treated quartz vessel [7b], at 353, 343, 333, 323 and 313 K, in full agreement with our previous extrapolation to atmospheric conditions [7a].



**Fig. 2:** GC/MS chromatogram, total ion current TIC vs elution time in s; capillary column HP-1, 25 m length, id 0.20 mm, film 0.50  $\mu\text{m}$ , carrier gas He 99.9999 %. 1) 2,3 dihydrofuran  $\text{C}_4\text{H}_6\text{O}$ , 2) butyraldehyde, 3) propene-methoxy  $\text{C}_4\text{H}_8\text{O}$ , 4) tetrahydrofuran  $\text{C}_4\text{H}_8\text{O}$ , 5) 1-butanol, 6) *n*-propyl hydroperoxide  $\text{CH}_3\text{CH}_2\text{CH}_2\text{O}-\text{OH}$  of MW 76, 7)  $\text{C}_3\text{H}_6\text{O}$ ?, 8) butyrolactone  $\text{C}_4\text{H}_6\text{O}_2$ , 9) tetrahydro-2,5-dimethoxy-furan  $\text{C}_6\text{H}_{12}\text{O}_3$ , 10) hydroperoxide  $\text{C}_4\text{H}_8\text{O}_3$  of MW 104, 11) hydroperoxide  $\text{C}_4\text{H}_8\text{O}_3$  of MW 104, 12) remaining di-*n*-butylperoxide  $\text{CH}_3(\text{CH}_2)_3\text{O}-\text{O}(\text{CH}_2)_3\text{CH}_3$  of MW 146.

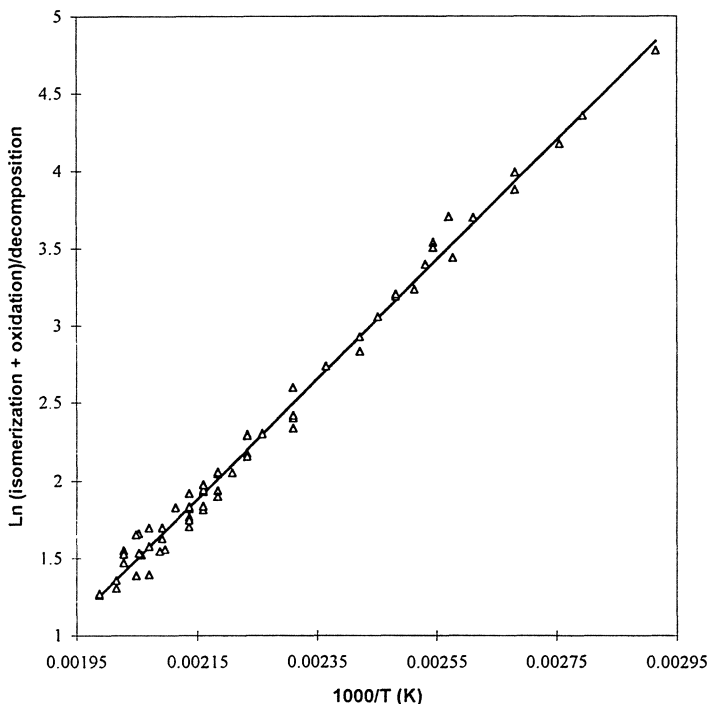
### Reactions of *n*-butoxy radicals $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$

The GC/MS chromatogram of Fig. 2 shows the products obtained in an experiment performed at 498 K, in a (boric acid coated and  $\text{H}_2/\text{O}_2$  treated) quartz reactor id. 10 mm,  $\text{O}_2/\text{N}_2$  1:1, residence time 1.6 s.

In the literature, it is commonly admitted that alkoxy radicals RO are involved in three types of reactions, oxidation, isomerization, decomposition, which occur according to parallel pathways. It is the reason for which, the products generated by the reactions of the *n*-butoxy radical have been analysed and separated in three different groups corresponding to each pathway (1-butanol apart, because it is likely produced by  $\text{RO} + \text{RH} \rightarrow \text{ROH} + \text{R}$ ): butyraldehyde (oxidation), other compounds in  $\text{C}_4$  resulting from the isomerization, and species in  $\text{C}_3$  formed by the



decomposition reaction. We tried to determine the logarithm of the following concentration ratios (butyraldehyde / decomposition products) and (isomerization products / decomposition products) as a function of  $1/T$ , but we observed a difference of activation energy of about 7–10 kcal/mol.



**Fig. 3:** Arrhenius plot of the logarithm of the ratio (isomerization products + butyraldehyde) / (decomposition products) versus reciprocal temperature.

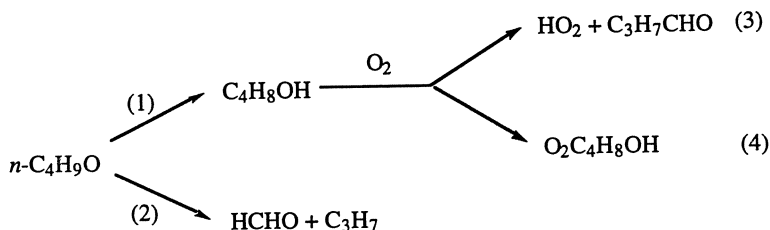
If the ratio  $R = (\text{butyraldehyde} + \text{isomerization products}) / (\text{decomposition products})$  were taken into account, the plot of its logarithm as a function of  $1/T$  led (with 66 points for temperatures ranging from 343 to 503 K and a least-mean-squares analysis) to the straight line of Fig. 3, correlation factor  $r^2 = 0.9953$ . For this ratio  $R$  we find a temperature dependence of 7.7 kcal/mol. This value would correspond to the difference of activation energies between the reactions of decomposition and isomerization of the ratio  $k_{\text{isom}}/k_{\text{decomp}}$ :

$$\Delta E = (7.7 \pm 0.1 (\sigma)) \text{ kcal/mol.}$$

If, for the decomposition rate constant of the *n*-butoxy radical, the values recommended by Carter *et al.* [3] and Altshuller [5]  $8 \times 10^{14} e^{-18\,400/RT}$  or  $8 \times 10^{14} e^{-17\,400/RT}$ , are used an activation energy for the isomerization reaction of 9.7 or 10.7 kcal/mol is found, in agreement with values for isomerisation [1, 3, 5, 8]. For 1 H atom, the pre-exponential factor  $A_{\text{isom}} = 4.4 \times 10^{11}$ . The isomerisation rate constant can then be written:

$$k_{\text{isom}}(n\text{-C}_4\text{H}_9\text{O}) = 4.4 \times 10^{11} \exp(-9\,700/RT) \text{ or } 4.4 \times 10^{11} \exp(-10\,700/RT).$$

To sum up our results for the *n*-butoxy radical in presence of O<sub>2</sub>, they are in favour of two reaction pathways, isomerization and decomposition, according to the following mechanism [9]:



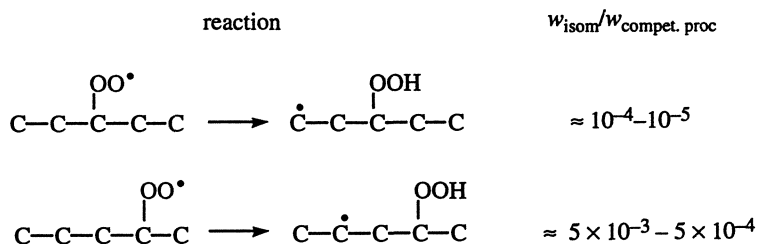
After isomerisation occurs either oxidation (with formation of C<sub>3</sub>H<sub>7</sub>CHO) or an addition reaction with oxygen, forming the radical O<sub>2</sub>C<sub>4</sub>H<sub>8</sub>OH which in turn can isomerise. It is obvious that this mechanism has to be checked for other alkoxy radicals.

The independence of the ratio butyraldehyde / (butyraldehyde + isomerization products) = 0.290 ± 0.035 (σ) towards O<sub>2</sub> (percentage of O<sub>2</sub> varied from 5 to 80 %), temperature range 448–496 K, agrees with the above mechanism (1–4). By measuring, at 487 K, the decay of hydroperoxides of MW 104 and 76 vs. [NO] added (0–22.5 ppm), a first estimation could be made for the isomerization rate constant O<sub>2</sub>C<sub>4</sub>H<sub>8</sub>OH → HO<sub>2</sub>C<sub>4</sub>H<sub>7</sub>OH (5), for which we found

$$k_5 \approx 10^{11} \exp(-17\,600/RT).$$

We observed, in flow experiments with untreated vessels of small internal diameter 10 mm (Pyrex or quartz for which the boric acid coating has been removed), that (i) hydroperoxides MW 104 and 76 totally disappear, (ii) when radicals are destroyed at the walls, almost all compounds were transformed into butyraldehyde. Particularly, it makes us wonder when the major product (reported in the literature) is an aldehyde or a ketone that its formation could be mainly *heterogeneous*.

For tropospheric ozone, the isomerisation of the RO radical, followed by the association with O<sub>2</sub>, can be important if it is followed by the isomerization of the O<sub>2</sub>R<sub>H</sub>OH radical, leading to a complex hydroperoxide bearing an aldehyde or epoxy function. The role played in atmosphere by the isomerisation of the RO<sub>2</sub> radical has been analysed by Carter *et al.* [3a]. They estimated the ratios of 1,5 H shift alkylperoxy isomerisation rate to rate of major competing processes under ambient conditions. Using a NO concentration of 0.1 ppm, they obtained the following values:



Measurements made by AIRPARIF [10] show that in rural areas the NO concentration is *ca.*  $3 \mu\text{g}/\text{m}^3$ , whereas it reaches  $30-60 \mu\text{g}/\text{m}^3$  in city areas; on the contrary,  $\text{O}_3$  concentration is about  $50-60 \mu\text{g}/\text{m}^3$  in rural areas and decreases to  $30-40 \mu\text{g}/\text{m}^3$  in cities.  $[\text{NO}]$  is *ca.*  $30-40$  favours the isomerization of the  $\text{O}_2\text{R}_{\text{-H}}\text{OH}$  radical. Ratios estimated for these reactions are therefore *ca.*  $30-40$  times higher and this has to be taken into account. Moreover, we have to add the case, for the  $\text{O}_2\text{R}_{\text{-H}}\text{OH}$  radical, for which the H atom abstraction is carried out from the carbon atom bearing the OH group. In this case,  $\Delta\text{H}$  can be  $4-5$  kcal/mol lower than that without O atoms [11]. This fact lowers the activation energy, and consequently increases the isomerization rate of the  $\text{O}_2\text{R}_{\text{-H}}\text{OH}$  radical and the formation rate of the peroxide in the atmosphere. This peroxide can constitute a complementary source of radicals, which at the end leads to an increase of tropospheric ozone. The reaction sequence, isomerization of the RO radical followed by that of the  $\text{O}_2\text{R}_{\text{-H}}\text{OH}$  radical, would lead to an increase of concentration of radicals because, one radical ( $n\text{-C}_4\text{H}_9\text{O}$ ) is replaced by an other ( $\text{C}_4\text{H}_8\text{OH}$ ), and also an hydroperoxide is generated which can be decomposed by light or thermally and produce two radicals RO and OH; in short, one radical is replaced by three. The rate constant that we have estimated  $k_5 \approx 10^{11} \exp(-17\ 600/RT)$  gives, indeed, a lifetime  $\tau = (1/k_1) \approx 50$  s at 300 K, and in the absence of termination reactions, a concentration rise (of radicals) of several orders of magnitude in about 10 min, could be reached. A realistic mechanism should be analysed in order to estimate the actual tropospheric impact. Particularly the competition between isomerization of the  $\text{O}_2\text{R}_{\text{-H}}\text{OH}$  radical and reactions with NO,  $\text{NO}_2$ ,  $\text{HO}_2$ , and the global  $\text{RO}_2$  radicals (such as  $\text{CH}_3\text{O}_2$  *etc.*), has to be taken into account, their probability ratio being given by the following expression {reaction (5) being in competition with reaction (9)  $\text{O}_2\text{C}_4\text{H}_8\text{OH} \rightarrow \text{HO}_2\text{C}_4\text{H}_7\text{OH}$  (5),  $\text{O}_2\text{C}_4\text{H}_8\text{OH} + \text{NO} \rightarrow \text{OC}_4\text{H}_8\text{OH} + \text{NO}_2$  (9)}:

$$(k_5 \cdot \text{RO}_2 / k_9 \cdot \text{NO} \cdot \text{RO}_2) = k_5 / k_9 \cdot \text{NO}$$

This short analysis points out how important it is to know the reactions in which different alkoxy radicals are involved, particularly their isomerization reactions and reactions ensuing from them, in order to better understand the formation and

transformation processes of many pollutants in the troposphere. In the field of combustion, the role of these reactions can be more complex, due to the large inhomogeneity of the medium, and still deeper investigations are therefore needed.

### Achievements of the project

In the framework of laboratory studies of elementary reactions relevant to tropospheric chemistry, we think that very interesting results have been achieved in the field of alkoxy radicals, in which exist a lot of theoretical speculations and estimations but only a few reliable experimental results. It seems to us that investigations on reactions of primary and secondary butoxy radicals can serve as models to understand the behaviour of higher RO radicals. Based on this assumption, investigations are in progress on reactions of  $n\text{-C}_5\text{H}_{11}\text{O}$  radicals in oxygen, which will soon, as we are convinced, lead to interesting conclusions.

### Acknowledgements

All this work has been carried out without the least financial support by either LACTOZ or by the French PROGRAMME ENVIRONNEMENT. In addition, thanks to the French CNRS support, a GC/MS Saturn (Varian) could be bought.

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### 3.18 Gas-Phase Ozonolysis of Alkenes and the Role of the Criegee Intermediate

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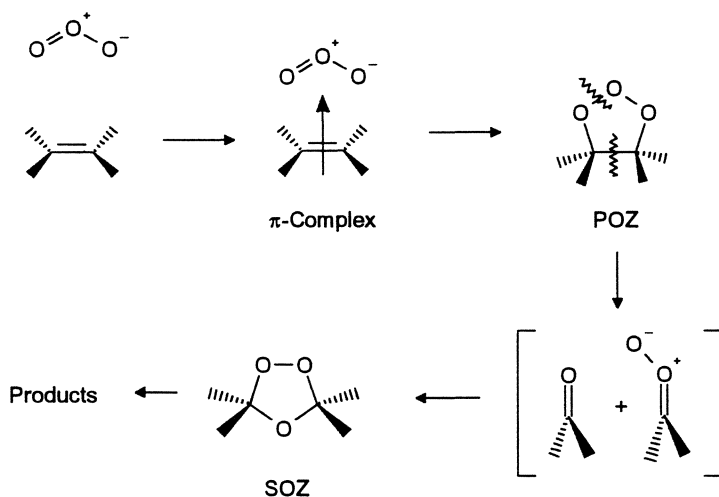
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#### Summary

The mechanism of the ozonolysis reaction of alkenes has been investigated in the gas phase and solid state using matrix isolation spectroscopy. While alkene/ozone  $\pi$ -complexes and the primary ozonides are readily observed by IR und UV/vis spectroscopy, there is no direct spectroscopic evidence for the *Criegee* intermediate (carbonyl O oxide) in these reactions. However, these elusive species can be synthesized and characterized via the carbene/oxygen route. Comparison of experimental and calculated spectroscopic data allows for the prediction of the spectroscopic properties of carbonyl oxides which are not accessible by this method.

#### Aims of the scientific research

Ozone plays a major role in the degradation of unsaturated VOCs in the troposphere, especially during night-time. The rate constants of the ozonolysis of a variety of alkenes have been reported [1]. However, in most instances the fate of the primary products of the ozonolysis is unknown, although the secondary reaction products are of crucial importance for the overall understanding of the alkene/ozone chemistry. The classical *Criegee* mechanism of the ozonolysis reaction involves the primary ozonide (POZ, 1,2,3-trioxolane), which cleaves to the *Criegee* intermediate (carbonyl O oxide) and a carbonyl compound [2, 3]. The secondary ozonide (SOZ, 1,2,4-trioxolane) is formed from these components in a [1,3]-dipolar cycloaddition reaction.

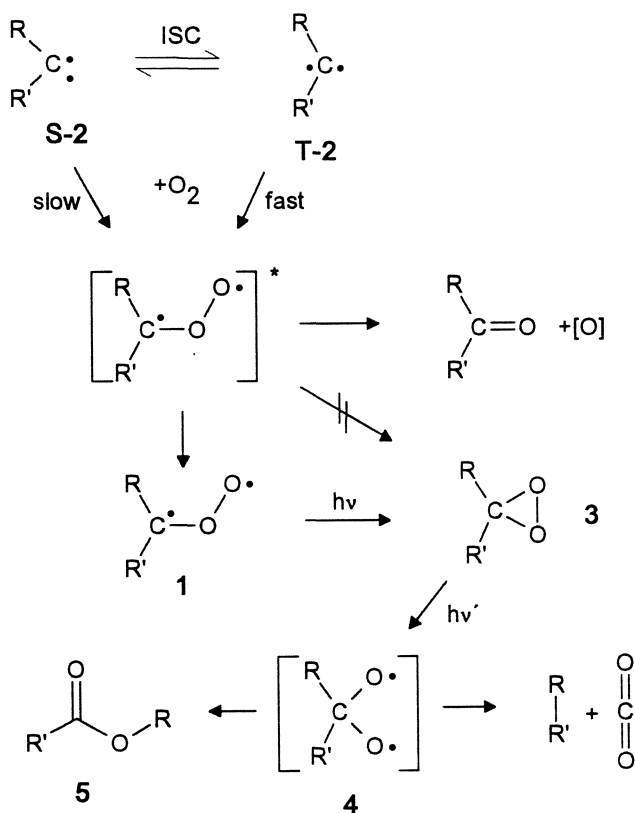


The *Criegee* intermediate has been claimed to be of importance in tropospheric chemistry [4] but never been observed by direct spectroscopic methods in the ozonolysis reaction. The aims of our research were therefore: (i) to provide spectroscopic (IR, UV/Vis) data of a variety of substituted carbonyl O oxides, (ii) to develop a theoretical model which allows the prediction of the spectra of carbonyl O oxides which are not accessible by laboratory studies, but might be of importance to tropospheric chemistry, and (iii) to elucidate the mechanism of the ozonolysis of alkenes and investigate the role of carbonyl O oxides in these reactions.

## Principal scientific findings

### *Spectroscopic properties of carbonyl oxides*

The only route to carbonyl O oxides **1** which is suitable for matrix isolation is the oxidation of free carbenes **2** with molecular oxygen  $^3\text{O}_2$  [5–7]. The carbenes are generated by photolysis of the corresponding diazo compounds or diazirines. Prerequisite for this method is that the carbenes are stable under the conditions of matrix isolation (solid rare gas at 10 K). This excludes simple alkyl substituents, because these carbenes rapidly undergo [1,2]-H shifts to yield alkenes in essentially quantitative yields. During the last years we were able to study the spectroscopy and chemistry of a number of carbonyl oxides (R and R' were H, Ph,  $\text{HC}\equiv\text{C}$ ,  $\text{CF}_3$ , cyclic systems *etc.*) [8–12] by IR and UV/vis spectroscopy.



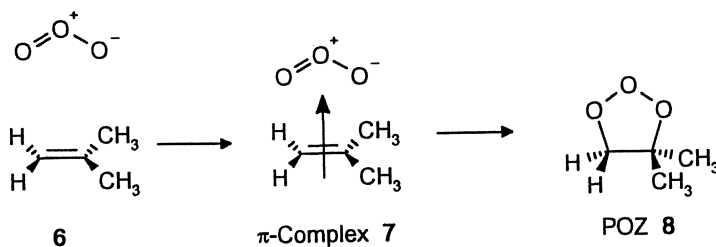
All carbonyl oxides proved to be highly photolabile, and on photolysis yield dioxiranes **3** or split off oxygen atoms to produce ketones. Oxygen atoms are also formed thermally from vibrationally excited **1**. Thus, if the large exothermicity of the ozonolysis reaction is taken into account, **1** might be a source of O atoms and OH radicals in the troposphere. The role of dioxiranes has not yet been discussed in context with atmospheric chemistry, although the formation of these species – in contrast to the isomeric carbonyl oxides – in ozone/alkene reactions has been unequivocally demonstrated [13].

Carbonyl oxides **1** exhibit two characteristic spectroscopic features: in the IR an intense absorption in the range  $900\text{--}1000\text{ cm}^{-1}$  is observed which is assigned to the O–O stretching mode. This assignment has been confirmed by isotopic labeling and *ab initio* calculations. The carbonyl oxides **1** are intensely colored yellow to red, and in the visible spectrum a strong and broad absorption near  $400\text{--}500\text{ nm}$  is found. This absorption is nicely reproduced by semiempirical CNDO/S calculations [14]. The influence of electron-withdrawing or -donating substituents can now be confidently estimated. These data should allow for the identification of carbonyl oxides in the troposphere.

### Ozonolysis of olefins

The gas-phase reaction of ozone and alkenes is very complex, particularly in the presence of excess oxygen, and even the simplest alkenes result in the formation of a large number of partially oxidized products. Some of these products are short-lived and require special techniques to be identified. Our approach was to combine gas-phase reactions at ambient temperature and matrix isolation at low temperature to gain insight into the mechanistic details. Two types of experiments have been performed: (i) Ozone and the alkene were mixed in a flow reactor, and the reaction products either analyzed by mass spectroscopy or trapped in argon at 10 K and analyzed by IR and UV/vis spectroscopy. This allows us to observe many of the secondary products of the ozonolysis. However, highly labile compounds, such as most free radicals, carbonyl oxides *etc.*, are not trapped under these conditions. (ii) Ozone and the alkene are co-deposited with a large excess of argon at 10–30 K. Due to the very low thermal energy accessible, only reactions with low activation barriers (< 5 kcal/mol) can proceed at these temperatures. Labile compounds, *e.g.*  $\pi$ -complexes, primary ozonides, are stable enough to be observed spectroscopically.

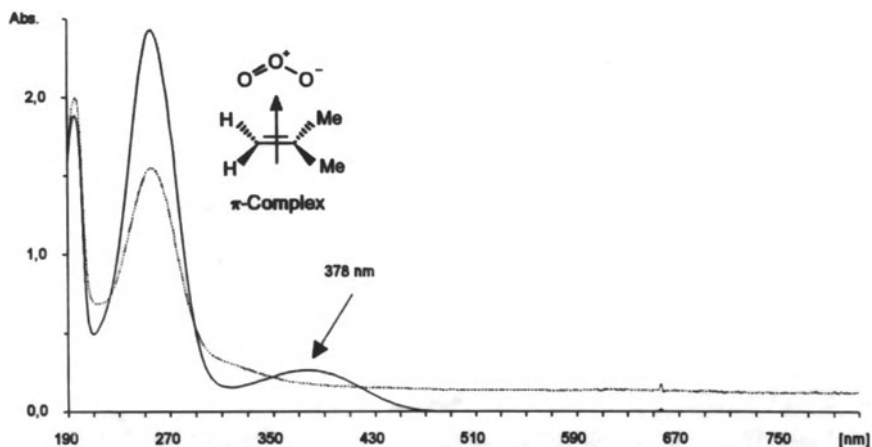
The olefins investigated were 1,1-diphenylethylene, stilbene, styrene, 2-methylpropene, 2,3-dimethyl-2-butene, butadiene, pentadiene, and isoprene. The phenyl-substituted alkenes were chosen because the spectra of the expected carbonyl oxides are well known, the alkyl-substituted because of their relevance in tropospheric chemistry.



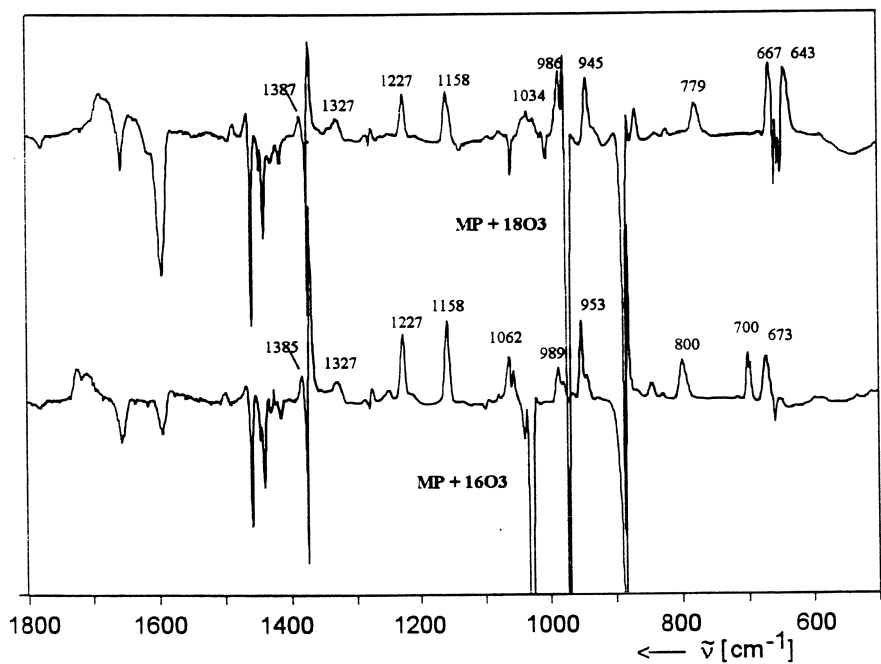
The main results of these experiments can be demonstrated with 2-methylpropene **6**. Codeposition of **6** and O<sub>3</sub> with excess Xe at 10 K produces a colorless matrix which turns yellow on warming to 35 K (Fig. 1). The yellow compound ( $\lambda_{\text{max}} = 378 \text{ nm}$ ) is assigned the structure of  $\pi$ -complex **7**.

Warming to 50–70 K results in the formation of POZ **8** and small amounts of acetone. The POZ **8** has been identified by comparison with other primary ozonides, and several bands could be assigned by <sup>18</sup>O labeling. Acetone O oxide or the SOZ are not formed under these conditions.



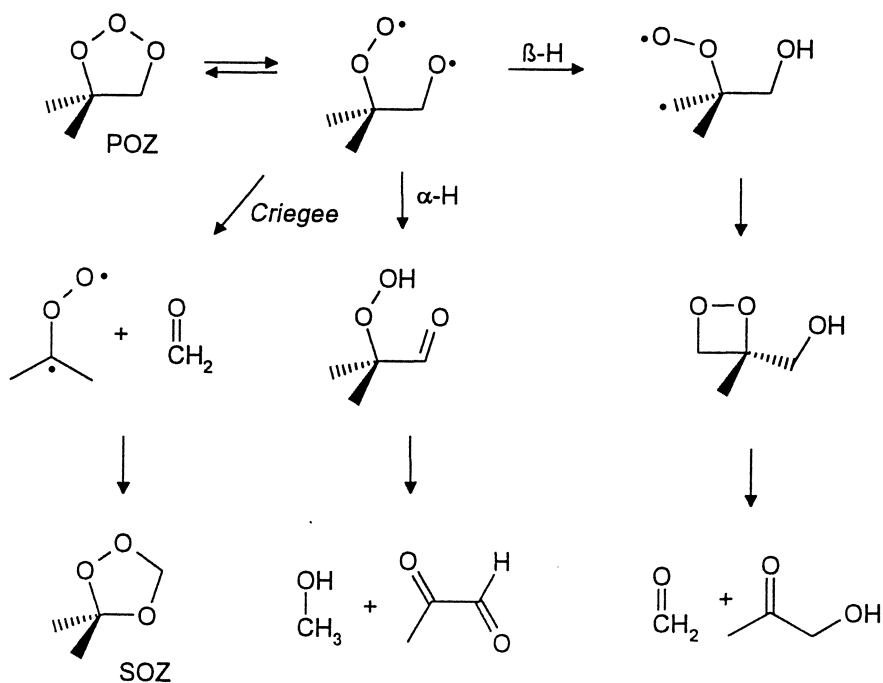


**Fig. 1:** UV/vis spectrum of 6 (dotted line) and the CT-complex of 6 and O<sub>3</sub> (solid line) in solid Xe.



**Fig. 2:** IR spectrum of the thermal reaction (Xe matrix, 60 K) of 6 and <sup>16</sup>O<sub>3</sub> or <sup>18</sup>O<sub>3</sub>, respectively. Top: absorptions growing in; bottom: absorptions disappearing, assigned to the primary ozonides.

The main products of the gas-phase ozonolysis of **6** are  $\text{CO}_2$ , formaldehyde, formic acid and acetone. Traces of acetic acid, hydroxy acetone, methanol, methylglyoxal and methane were also identified. Methyl acetate, the product of the rearrangement of acetone O oxide, is not formed. Under similar conditions tetramethylethylene produces methyl acetate, and thus we conclude that acetone O oxide is not a product of the ozonolysis of **6**. This is in contrast to the prediction of the preferred POZ cleavage and requests for an alternative mechanism to explain the formation of hydroxy acetone. The key step in this mechanism is the asynchronous ring opening of the POZ to yield a diradical. This diradical can be stabilized via cleavage to acetone O oxide and formaldehyde – the Criegee products – or by intramolecular abstraction of  $\alpha$ - or  $\beta$ -hydrogen atoms. This mechanism explains the formation of methylglyoxal, methanol, hydroxy acetone, and formaldehyde without recourse to acetone O oxide.



Dienes, such as butadiene or isoprene, react similarly with the formation of  $\pi$ -complexes as primary adducts. However, the subsequent chemistry is more complicated leading to methylvinylketone, methacrolein, formic acid, formaldehyde, and peroxidic species. The mechanistic details of these reactions are still not completely understood and under current investigation in our laboratory.

The main results of our investigations are: (i) The first step in the alkene/ozone reaction is the formation of a  $\pi$ -complex with absorptions in the near UV or visible range. (ii) At 50–70 K this complex reacts to the primary ozonide (POZ) and, depending on substituents, traces of the secondary ozonide (SOZ). (iii) No carbonyl oxide was observed under any conditions used in our ozonolysis experiments. (iv) Some of the partially oxidized products formed are not in accordance with the *Criegee* mechanism and thus alternative mechanisms have to be considered.

### Contribution to EUROTRAC and LACTOZ

The reaction of ozone and alkenes is sufficiently fast that it can compete with other removal processes and provide sinks for both ozone and alkenes in the troposphere. While kinetic data for a series of alkene/ozone reactions have been reported, not much is known about details of the reaction mechanisms, the role that carbonyl O oxides play, and the role that free radicals play in these processes. Our laboratory experiments provide the spectroscopic data (both infrared and UV/visible) that are important for the spectroscopic identification of Criegee intermediates in the troposphere. In addition, we were able to characterize secondary partially oxidized products (aldehydes, peroxides *etc.*) that are produced during the gas-phase ozonolysis. These products might lead to a net increase of ozone, if oxygen atoms are formed during their decomposition.

### Acknowledgment

This research was supported by the *Bundesminister of Forschung and Technologie* (07EU761), the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*.

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### 3.19 Mechanistic and Kinetic Studies of Selected Oxidation Steps of Tropospheric Interest

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#### Summary

Reaction mechanisms and the kinetics of selected steps in the tropospheric oxidation of simple radical intermediates and of unsaturated organic compounds have been studied. As oxidants the nitrate radical  $\text{NO}_3$ , ozone  $\text{O}_3$  and the peroxy radical  $\text{CH}_3\text{O}_2$  were employed.

The primary interaction of  $\text{NO}_3$  with radical species X at ambient temperatures yields rovibrationally excited products  $\text{XONO}_2$  which in the gas phase immediately decompose to yield XO and  $\text{NO}_2$ . This way X = H,  $\text{CH}_3$ , HO, NO,  $\text{HO}_2$ ,  $\text{CH}_3\text{O}_2$ , Cl and ClO are oxidised by  $\text{NO}_3$  with high efficiency. This mechanism has been verified for X = H, HO and  $\text{CH}_3$  by *ab initio* calculations on MP2-level of theory. Interaction of  $\text{NO}_3$  with unsaturated organics starts through an electrophilic radical attack at the double bond forming a rovibrationally excited adduct radical with free rotation at the attacked bond. The adduct radical either spontaneously eliminates  $\text{NO}_2$  to form a stable epoxide or becomes stabilised in air by formation of a nitroalkyl-peroxy radical.

$\text{O}_3$  alkene systems under atmospheric conditions were found to be a source for OH radicals. From experiments with an excess of CO added, source strengths of  $0.50 \pm 0.1$ , 0.37 and  $0.24 \pm 0.2$  were obtained for TME, *trans*-2-butene and isoprene, respectively. Elucidation of the mechanism for OH generation is attempted by following intrinsic reaction pathways of the intermediates by model calculations.

A very sensitive and specific method of  $\text{CH}_3\text{O}_2$  detection has been developed in the project. It is based on REMPI-MS techniques employing laser irradiation at two wavelengths. In EI-MS studies radical reaction of  $\text{CH}_3\text{O}_2$  with other radicals were investigated including the species  $\text{NO}_3$ , halogen atoms, ClO and BrO.

#### Aims of the scientific research during the project

The activities of the Kiel group within LACTOZ concentrated on investigations of secondary atmospheric oxidation processes. The processes selected constitute elementary steps in reaction sequences leading to transformation and degradation of VOCs in the troposphere. The oxidants employed in our studies were the nitrate radical  $\text{NO}_3$ , ozone  $\text{O}_3$ , and in recent experiments the  $\text{CH}_3\text{O}_2$  radical. It was the aim of the scientific research to elucidate reaction mechanisms operating in the

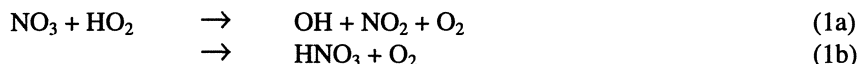
transformation/degradation of unsaturated organic compounds as well as of short-lived species and to provide elementary kinetic data of the reactions studied for modelling purposes.

### Principal scientific findings during the project

The principal findings shall be presented in three sections:

#### *Investigations of NO<sub>3</sub> radical reactions*

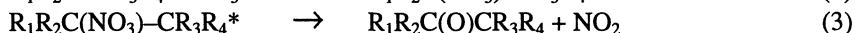
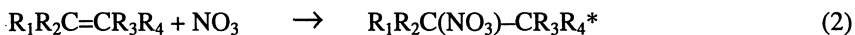
In kinetic investigations under flow conditions NO<sub>3</sub> radicals were generated preferentially by F atoms abstracting the hydrogen from HNO<sub>3</sub>. Although this NO<sub>3</sub> source is very convenient and generally accepted by now, it must be handled with care, because of the fast secondary reactions between F and NO<sub>3</sub> in the system. The FO formed can lead to secondary side reactions which repeatedly offset the kinetic analysis. The kinetics of the NO<sub>3</sub> source has been dealt with in two contributions [1, 2]. Secondary oxidation reactions of NO<sub>3</sub> radicals with atomic and simple inorganic species, including the NO<sub>3</sub> self-reaction, have been reported [1–7]. The most tropospherically relevant of these studies was the investigation of reaction (1) which might serve as night-time OH source:



The branching ratio in (1) was determined by us to be  $k(1\text{a}) / k(1\text{b}) \gg 4.4 \pm 0.8$  at low pressures, in reasonable agreement with two other low pressure studies. For a recent investigation of the reaction  $\text{NO}_3 + \text{CH}_3\text{O}_2$  see below.

The majority of the kinetic investigations have dealt with the electrophilic attack of NO<sub>3</sub> on unsaturated organics [8–21]. A strong influence of methyl-substitutions at the double bond on reactivity became apparent in these studies.

Product analysis based on a new digital method of MS-data evaluation and mechanistic studies (see below) revealed that at low pressures epoxides are a predominant product of the reactions with NO<sub>3</sub> for all alkenes and dienes studied [10, 12, 14–18]. Besides the epoxides the corresponding NO<sub>2</sub> formed has also been identified by REMPI-MS [15, 19, 20]. It was found that the reaction sequence (2)–(3) is operative up to atmospheric pressure in all cases with large values of  $k(2)$ .



Statistical rate theory calculations were performed to quantitatively describe the observed pressure dependence [21]. Finally, epoxides formation with selected alkenes and isoprene was observed by FTIR spectroscopy. Under atmospheric conditions for tetramethylethylene an epoxide yield of ~20 % was observed [19].

This environmentally relevant finding is supported by recent results obtained by others. For unreactive alkenes only small epoxide yields were found.

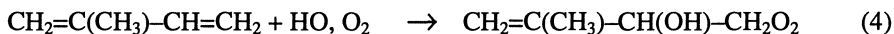
### *Investigations of O<sub>3</sub> alkene reactions*

The ozonolysis of isoprene and of selected butenes has been studied at 1 atm total pressure to quantify the strength of this night-time source in generating OH radicals and O as well as H atoms in the troposphere. In an earlier report from the Seinfeld group at Caltech, source strengths of  $0.68 \pm 0.15$  and  $0.45 \pm 0.25$  for OH and O atoms, respectively, were reported for each O<sub>3</sub> molecule consumed.

Experiments were carried out in the absence and in the presence of up to 20 % O<sub>2</sub>. An excess of CO was used as scavenger. Model calculations indicated that the CO<sub>2</sub> formed in the reaction can be equated to the OH source strength. A value of  $0.24 \pm 0.02$  was obtained in isoprene ozonolysis. In TME - ozonolysis this value was  $0.50 \pm 0.1$  and in *trans*-2-butene 0.37 [22].] In the absence of O<sub>2</sub> the O atom source strength could be determined from oxirane formation to be  $\leq 0.05$  in all systems studied [23].

The OH radicals formed in ozonolysis are suggested to result in part from unimolecular decomposition of the intermediate Criegee radicals. *Ab initio* model calculations using G-2 theory have shown that for its decomposition thermodynamically accessible intrinsic reaction pathways can be plotted leading to the products HO and RCO. This reaction path is qualitatively supported by the detection of corresponding amounts of CO as product of the reaction. A different way to generate the Criegee radical CH<sub>2</sub>O<sub>2</sub> is described in the next section (see below).

In the presence of O<sub>2</sub> there appear to exist also other routes of OH radical formation in ozonolysis. Here unimolecular decomposition of secondary alkoxy-peroxy radicals seem to be involved. For isoprene a sequence as given by (4)–(6) may be considered:



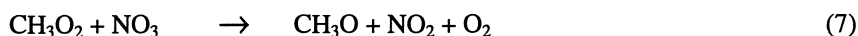
The primary attack can also occur at the substituted double bond. In this case methylvinylketone (MVK) would result instead of methacrolein.

### *Investigations of CH<sub>3</sub>O<sub>2</sub> reactions*

Peroxy radicals are rather unreactive radicals and thus in the troposphere they are an abundant species. At ambient temperatures only their interaction with other open shell species needs to be considered. With NO they are easily converted to alkoxy radicals.

In PI-MS using ns lasers neither HO<sub>2</sub> nor CH<sub>3</sub>O<sub>2</sub> yielded a characteristic parent ion signal. However, two-colour REMPI experiments make CH<sub>3</sub>O<sub>2</sub> indirectly detectable through its photolysis product CH<sub>3</sub> generated at  $\lambda = 248$  nm in the ion source [24, 25]. Photoionisation of CH<sub>3</sub> is carried out as a (2 + 1) process at  $\lambda = 333$  nm. The spectrum shows rovibrational structures. This REMPI-detection is highly specific and also extremely sensitive. The detection limit is estimated to be  $< 10^9$  cm<sup>-3</sup>. Detection of HO<sub>2</sub> through its photolysis product H was also possible.

In recent experiments on the kinetics of the tropospherically relevant reaction (7) good agreement was found



with data reported by other groups [26]. Together with the consumption of CH<sub>3</sub>O<sub>2</sub> formation of CH<sub>3</sub>O could be followed. Step (7) appears to be analogous to reaction (1) described above.

The reaction of CH<sub>3</sub>O<sub>2</sub> with halogen atoms X (X = F, Cl, Br) constitutes an interesting source of Criegee radical formation in flow systems.



The exothermicity of this reaction varies from  $\Delta H_{\text{R}} = -58.1$  kcal mol<sup>-1</sup> for X = F to  $\Delta H_{\text{R}} = -9.7$  kcal mol<sup>-1</sup> for X = Br. The radical CH<sub>2</sub>O<sub>2</sub> decomposes at low pressure spontaneously to yield predominantly CO<sub>2</sub> [27]. It appears that CH<sub>2</sub>O<sub>2</sub> formed chemically activated – as in ozonolysis – follows a different decomposition pattern than CH<sub>2</sub>O<sub>2</sub> formed kinetically hot in the abstraction process (8).

The peroxy radical CH<sub>3</sub>O<sub>2</sub> is able to oxidise ClO to form ClOO. *Ab initio* calculations suggest that this reaction proceeds through direct dissociation of an intermediate CH<sub>3</sub>OOCl collision complex [27]. The mechanism of CH<sub>3</sub>OCl formation, which has been observed by several groups, is still not clear. A bimolecular substitution process can computationally be formulated employing the functional density approach.

## Conclusions

Although not fully exploited because of the high diversity and complexity of laser experiments the introduction of multiphoton ionisation into mass spectrometry significantly expanded the applicability of this tool in the analysis of complex gas mixtures as the polluted atmosphere. Molecular specificity as obtained in high resolution vibrational spectroscopy combined with high sensitivity as known for ion counting methods makes this new technique unique in untangling reaction mechanisms [15, 19, 20, 24].



### Acknowledgements

The work was supported through project 07 EU 709 4 of the BMBF, Bonn, and through project EV5V-CT93-0038 of the EC, Brussels.

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## 3.20 Reactions of OH Radicals with Organic Nitrogen-Containing Compounds

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### Summary

Rate constants for the reactions of OH radicals with *n*-nitroalkanes, *n*-alkyl nitrates and *n*-alkyl nitrites have been determined at 298 K and 1 atmosphere total pressure using both pulse radiolysis combined with kinetic spectroscopy and a conventional relative rate method. In order to provide more mechanistic information for these reactions, rate constants for the reaction of Cl atoms with these compounds were determined using the relative rate method. The data indicate that the reaction of OH radicals with these nitrogen-containing compounds involves both an abstraction and an addition channel. These results are discussed in terms of reactivity trends and compared with the data from the literature.

### Aims of the research

The purpose of this research was to obtain kinetic data for the reaction of OH radicals with nitrogen-containing organic compounds under atmospheric conditions. The results give tropospheric lifetimes for these species and indicate their role in the long-range transport of odd nitrogen.

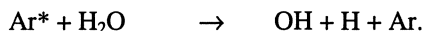
### Principal scientific results

#### *Introduction*

Volatile organic nitrogen-containing compounds may act as more or less long-lived reservoirs for NO<sub>x</sub> in the troposphere. Nitroalkanes are employed as propellants and industrial solvents leading to their potential release in the troposphere [1]. Alkyl nitrates can be formed in the oxidation of volatile organic compounds in the troposphere when peroxy radicals react with NO [2]. Small amounts of alkyl nitrites may be formed in the urban atmosphere by reaction of alkoxy with NO or via direct emission from the burning of alcohol-based fuels [3, 4]. The major atmospheric removal processes for these nitrogen-containing compounds are expected to be by photolysis or via reaction with OH radicals. Previously very little information concerning the kinetics and mechanisms for the reactions of these compounds with OH radicals has been available.

### Experimental

Absolute experiments were performed in which a 30 ns pulse of 2 MeV electrons from an accelerator irradiated the gas mixtures to initiate the radical reactions. The decay of the radicals was recorded by use of transient UV spectroscopy, for OH at 309 nm. Hydroxyl radicals were produced by irradiation of 11 Torr H<sub>2</sub>O mixed with 749 Torr Ar. Initially excited argon atoms, Ar\*, are formed, and OH radicals are produced through the reaction:



Formation of OH is rapid relative to the time scale of the OH decay. When adding up to 7.6 Torr of a substrate compound, RH, the OH decay obeys pseudo-first-order kinetics due to the reaction: RH + OH → products. A plot of the logarithm of the absorbency versus time is therefore linear. Plotting the slopes of these log plots,  $k'$ , versus the RH concentrations gave linear plots with slopes equal to  $k(\text{OH} + \text{RH})$ .

Relative rate experiments were carried out in a 50 litre FEP Teflon reaction chamber. The chamber was surrounded by blacklamps and sunlamps. Temperature was maintained at 298 K. Hydroxyl radicals were produced by photolysis of methyl nitrite in air with NO added or by the dark reaction of hydrazine with O<sub>3</sub>. The generated OH radicals react with the substrate compound, RH, and the reference compound, REF:



and



Providing the substrate compound and the reference compound are consumed only by reaction with OH,  $k_1$  can be determined from the expression:

$$\ln \left( \frac{[\text{RH}]_0}{[\text{RH}]_t} \right) = \frac{k_1}{k_2} \ln \left( \frac{[\text{REF}]_0}{[\text{REF}]_t} \right)$$

Chlorine atom rate constants can be derived analogously from the above equation. Chlorine atoms were generated directly from the photolysis of molecular chlorine. Gas chromatography (FID) was employed to carry out the quantitative analysis of the concentrations of substrate and reference compounds.

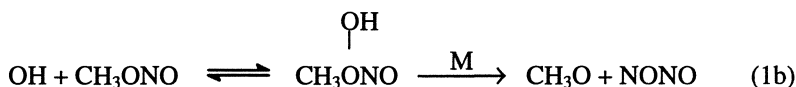
### Results and discussion

The available kinetic data for the reactions of OH radicals and Cl atoms with *n*-nitroalkanes, *n*-alkyl nitrates and *n*-alkyl nitrites are given in Table 1 (section 3.14). Rate constant data derived in this work from pulse radiolysis and relative rate experiments for the reaction of OH radicals with these nitrogen-containing organics at atmospheric pressure and 298 K agree within experimental error.

Where comparisons are possible, agreement with other reported data for the reactions of both Cl atoms and OH radicals under these experimental conditions is, in general, also satisfactory.

It is of interest to compare the rate constants for the reaction of OH radicals and Cl atoms with *n*-nitroalkanes, *n*-alkyl nitrates and *n*-alkyl nitrites. It is apparent from the data that there is quite a dramatic difference in the deactivating effect of the  $-\text{NO}_2$ ,  $-\text{ONO}_2$  and  $-\text{ONO}$  groups with respect to reaction with Cl atoms. Thus the reactivity of  $\text{CH}_3\text{NO}_2$  is about 4 orders of magnitude less than that observed for the  $\text{CH}_3$  group in  $\text{C}_2\text{H}_6$  whilst in  $\text{CH}_3\text{ONO}$  the reduction in reactivity is only about a factor of 3. The reaction of Cl atoms with each of the three compounds presumably involves direct H atom abstraction, and the effect of the various functional groups on the observed reactivity is likely to be due to polar effects in the transition states for the reactions rather than changes in the overall enthalpy. Since Cl atoms are electrophilic the electron withdrawing abilities would appear to be in the order  $-\text{NO}_2 > -\text{ONO}_2 > -\text{ONO}$ . In all cases the deactivating effect of the functional group appears to extend to at least the  $\beta$  carbon atom. Obviously as the chain length increases the rate constant values begin to approach each other. For the reaction of OH radicals with *n*-nitroalkanes, *n*-alkyl nitrates and *n*-alkyl nitrites the reactivity trend is quite different from that found for the corresponding reactions with Cl atoms. In this case for all three functional groups the rate constants for reaction with the methyl compounds show relatively little variation, all falling within the range  $(1.44\text{--}3.3) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and also indicating that these compounds have about the same level of reactivity as  $\text{C}_2\text{H}_6$  with respect to OH radical attack. The result is surprising, since if the reaction of OH radicals with these compounds involved mainly hydrogen atom abstraction, the presence of the strongly electron-withdrawing functional groups would be expected to considerably decrease the rate constants for abstraction by the electrophilic OH radical, as shown for the corresponding Cl atom reactions. These results indicate that there may be mechanistic differences between the reactions of OH radicals and Cl atoms with these compounds.

Reaction between the OH radical and  $\text{CH}_3\text{NO}_2$ ,  $\text{CH}_3\text{ONO}_2$  and  $\text{CH}_3\text{ONO}$  may involve both hydrogen atom abstraction and OH radical addition followed by the decomposition of the adduct, for example:



It is suggested that the enhanced reactivity of these species with OH radicals relative to that shown for the reaction of Cl atoms is due to the importance of the addition channel at 1 atm pressure. Some support for this argument comes from the

low values of the rate constants for reactions of OH radicals at low pressures. It is proposed that under low pressure conditions, reactions of OH radicals with  $\text{CH}_3\text{NO}_2$ ,  $\text{CH}_3\text{ONO}_2$  and  $\text{CH}_3\text{ONO}$  involve mainly abstraction, whereas at higher pressures the addition channel is the major reaction pathway. As the length of the side chain increases, the addition pathway becomes relatively less important as the deactivating effect of the functional groups on the abstraction process become less significant.

### Conclusions

The atmospheric lifetimes of the *n*-nitroalkanes, *n*-alkyl-nitrates and *n*-alkyl nitrites due to loss by reaction with OH radicals can be estimated from the rate constant data determined in this work. Taking a tropospheric concentration of  $1 \times 10^6$  molecules  $\text{cm}^{-3}$  for OH radicals in moderately polluted atmospheres, the rate constant data give lifetimes of approximately 1 month for  $\text{CH}_3\text{NO}_2$ ,  $\text{CH}_3\text{ONO}_2$  and  $\text{CH}_3\text{ONO}$  to around a few days for the *n*- $\text{C}_5\text{H}_{11}$  derivatives. Estimates of the photodissociative lifetimes for alkyl nitrates of approximately 1 week have been reported [5], and hence these compounds could act as temporary reservoirs for nitrogen in the troposphere and may be important in long-range transport of odd nitrogen. Based on absorption cross-sectional data, photolysis lifetimes for nitroalkanes of several hours and for *n*-alkyl nitrites of a few minutes have been calculated [5]. Hence their atmospheric lifetimes will be dominated by photolysis and they will be rapidly removed during daylight hours.

### Acknowledgements

We gratefully acknowledge financial support from the Commission of the European Communities.

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## 3.21 Kinetics and Mechanism for the Reaction of Ozone with Cycloalkenes

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### Summary

Rate constants for the reaction of O<sub>3</sub> with a series of cycloalkenes have been investigated over the atmospherically important temperature range 240–324 K and 1 atmosphere total pressure. The rate data obtained in the present study are discussed in terms of substituent effects and ring strain for these cyclic systems. Hydroxyl radical formation yields were determined for the reactions of O<sub>3</sub> with cycloalkenes at 298 ± 2 K in an atmosphere of air. The results indicate that the OH yields are close to that obtained for the structurally similar molecule *cis*-2-butene providing support for the suggestion that OH radical yields in O<sub>3</sub>-alkene systems depend largely on the degree of alkyl group substitution at the double bond site.

### Aims of the research

The purpose of this research was to obtain kinetic data for the reaction of ozone with cycloalkenes and to determine the formation yields of hydroxyl radicals in these reactions under atmospheric conditions.

### Principal scientific results

#### *Introduction*

In general the dominant loss process in the troposphere for organic compounds is through reaction with hydroxyl radicals. However, ozone also plays an important role in the chemistry of the Earth's atmosphere, its importance in the stratosphere and troposphere being particularly well documented [1–3]. Among the various classes of compounds present in the troposphere, unsaturated hydrocarbons are unusual in exhibiting significant reactivity with ozone as well as towards hydroxyl radical and nitrate radicals. Numerous potentially important roles of the ozone-alkene reaction have been recognised since these reactions can provide mutual sinks for both ozone and alkenes and concomitantly serve as sources of partially oxidised compounds and free radicals.

Rate constants for the reactions of O<sub>3</sub> with a large number of both anthropogenic and biogenic alkenes have been reported, mainly at room temperature. Kinetic

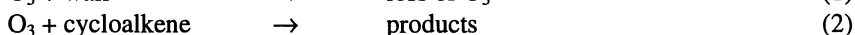
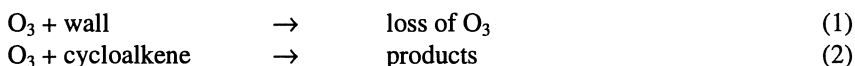
studies on the gas-phase reactions of  $O_3$  with cycloalkenes have been the subject of a number of studies although the effect of temperature on the rate constants has received little attention. Various kinetic and product studies have provided evidence that the gas-phase reactions of  $O_3$  with alkenes lead to the formation of OH radicals [4–16], however, little quantitative data are available for cycloalkenes [15].

As part of an investigation into the reaction of ozone with alkenes, the temperature dependence of the rate constants for the reaction of  $O_3$  with a series of cycloalkenes and the formation yields for OH radicals in these reactions have been obtained in the present work.

### *Experimental and results*

All reactions were carried out in a 60 dm<sup>3</sup> Teflon reaction chamber housed in a commercial deep-freeze cabinet. Sub-ambient temperatures were obtained using a modified temperature control unit, while higher temperatures were obtained using hot air blowers. Reactants entered the chamber through a ¼" o.d. Teflon tube, placed along the centre of the bag, which was plugged at one end and perforated along its length. This allowed for rapid mixing of reactants ( $\leq 1$  min) as determined by gas chromatographic analysis of a test hydrocarbon. Ozone was prepared by passing zero grade oxygen (BOC) through an ozone generator (Monitor Labs) directly into the bag. Accurate concentrations of the hydrocarbons were added by placing known pressures into a calibrated volume and sweeping the reactants into the bag with zero grade  $N_2$  (Air Products). Ozone concentrations were continuously monitored during the reaction by a Monitor Labs Model 8410 chemiluminescent ozone analyser. The signal was fed into a potentiometric chart recorder and to a microcomputer for data analysis. Quantitative analyses of hydrocarbons were carried out by gas chromatography (Shimadzu GC-8A) with flame ionisation detection. A 0.6 m  $\times$  6 mm o.d. Porapak Q column was used for analysis of ethene, *cis*-2-butene and 2-methyl-2-butene. Analyses of all other alkenes in the kinetic experiments were carried out on a 15 m  $\times$  0.54 mm i.d. SE-54 capillary column. In the OH radical formation yield experiments cyclohexanone was analysed on a 30 m  $\times$  0.54 mm i.d. carbowax column. The cycloalkenes and cyclohexane were quantitatively monitored using a 30 m  $\times$  0.54 mm i.d. SE-54 column.

Second-order rate constants were obtained by monitoring the increased rate of ozone decay in the presence of known excess concentrations of the alkene. In the presence of a cycloalkene, the processes for removing ozone are:



hence

$$-d[O_3] / dt \quad = \quad (k_1 + k_2 [\text{cycloalkene}]) [O_3] \quad (i)$$

$$-d(\ln[O_3]) / dt \quad = \quad k_2 [\text{cycloalkene}] + k_1 \quad (ii)$$



**Table 1:** Rate constants and Arrhenius parameters for the reaction of O<sub>3</sub> with cycloalkenes.

Alkene	$\frac{10^{15} A}{\text{cm}^3 \text{s}^{-1}}$	$\frac{E}{\text{cal mol}^{-1}}$	$\frac{10^{18} k^a}{\text{cm}^3 \text{s}^{-1}}$	Reference
<i>cis</i> -2-butene	—	—	141	17
	—	—	161 ± 7	18
	3.11	1900 ± 107	126 <sup>b</sup>	19
	—	—	138 ± 16	20
	3.52 <sup>+1.79</sup> <sub>-1.19</sub>	1953 ± 229	130 ± 39	3
	—	—	129 ± 9	21
	3.4 ± 0.7	1945 ± 43	123 ± 18	22
3.06 ± 0.15	1868 ± 83	131 ± 5	this work	
2-methyl-2-butene	—	—	793	17
	—	—	493 ± 16	18
	6.34	1641 ± 155	397 <sup>d</sup>	19
	6.17 <sup>+6.45</sup> <sub>-3.16</sub>	1586 ± 389	423 ± 169 <sup>d</sup>	3
	6.5 ± 1.3	1652 ± 86	425 ± 29	21
	5.21 ± 0.50	1459 ± 270	397 ± 12	22
—	—	450 ± 15	this work	
cyclopentene	—	—	813 ± 79	18
	50	2300	969	23
	—	—	275 ± 33	20
	—	—	497 ± 30	24
	—	—	624 ± 35	25
	—	—	655 ± 44	21
1.6 ± 0.3	693 ± 87	491 ± 40	this work	
1-methyl-1-cyclopentene	—	—	673 ± 99	this work
1-chloro-1-cyclopentene	0.443 ± 0.022	2005 ± 126	15 ± 0.5	this work
cyclohexene	—	—	160 ± 15	18
	12.6	2400	204	23
	—	—	104 ± 14	20
	—	—	151 ± 10	24
	—	—	78 ± 5	25
	—	—	75 ± 5	21
	2.6 ± 0.40	2113 ± 529	85 ± 8	this work
1-methyl-1-cyclohexene	5.25 ± 0.50	2066 ± 272	166 ± 12	this work
4-methyl-1-cyclohexene	2.16 ± 0.40	1892 ± 88	82 ± 3	this work
1-nitro-1-cyclohexene	—	—	1.2 ± 0.1	this work
cycloheptene	—	—	319 ± 36	20
	—	—	283 ± 15	25
	1.28 ± 0.40	981 ± 209	237 ± 21	this work
<i>cis</i> -cyclooctene	0.78 ± 0.03	432 ± 100	374 ± 11	this work
<i>cis</i> -cyclodecene	1.08 ± 0.57	2148 ± 338	29 ± 2	this work

a) 298 ± 4 K;

b) calculated from the Arrhenius expression.

Plots of the resulting pseudo-first-order rate constants against cycloalkene concentration were linear as expected. The Arrhenius parameters and measured room temperature rate constants obtained in this work are shown in Table 1.

In order to determine the OH formation yields from the reaction of O<sub>3</sub> with the cycloalkenes two different sets of experiments were carried out. Firstly, the loss of O<sub>3</sub> and the cycloalkene were monitored in experiments where [O<sub>3</sub>]<sub>0</sub> and [cycloalkene]<sub>0</sub> were in the range 1 to 6 ppm. The results provided values for the stoichiometry of the reactions, Δ[cycloalkene] / Δ[O<sub>3</sub>]. In a second series of experiments, sufficient cyclohexane was added to the reaction system in order to scavenge OH radicals formed in the ozone-cycloalkene reactions. In these experiments the loss of cycloalkene, O<sub>3</sub> and the yield of cyclohexanone, formed by the reaction of OH with cyclohexane were monitored. In order to determine the yield of cyclohexanone resulting from the reaction of OH with cyclohexane under the reaction conditions employed for the O<sub>3</sub>/cycloalkene/cyclohexane experiments, a series of experiments was carried out in which the cyclohexane concentrations employed were such that the OH radicals react both with the cycloalkene and cyclohexane. Under these conditions the loss of cyclohexane due to reaction with OH and the formation of cyclohexanone could be determined. The results from these studies showed that Δ[cyclohexanone] / Δ[cyclohexane] = 0.26 ± 0.04 for all the alkenes investigated.

**Table 2:** Hydroxyl radical formation yields from the gas-phase reactions of O<sub>3</sub> with ethene and a series of cycloalkenes at 298 ± 2 K in 1 atmosphere of air.

Alkene	[alkene] <sub>0</sub> ppm	[O <sub>3</sub> ] <sub>0</sub> ppm	[c-C <sub>6</sub> H <sub>12</sub> ] <sub>0</sub> ppm	$\frac{\Delta[\text{alkene}]}{\Delta[\text{O}_3]}$	$\frac{\Delta[\text{c-C}_6\text{H}_{12}]}{\Delta[\text{alkene}]}$	OH radical yield
Ethene	0.7–2.5	1.6–6.1	0	1.0 ± 0.1	—	< 0.1 <sup>a</sup>
	0.7–2.5	1.6–2.1	500–1000	1.0 ± 0.1	< 0.01	< 0.05 <sup>b</sup>
Cyclopentene	1.0–6.0	2.0	0	1.46 ± 0.05	—	0.46 ± 0.05 <sup>a</sup>
	1.0–6.0	2.0	500–1000	1.0 ± 0.1	0.16 ± 0.02	0.62 ± 0.20 <sup>b</sup>
Cyclohexene	1.3–6.7	2.3	0	1.39 ± 0.02	—	0.39 ± 0.02 <sup>a</sup>
	1.3–6.7	2.3	500–1000	1.0 ± 0.1	0.10 ± 0.01	0.38 ± 0.11 <sup>b</sup>
Cycloheptene	1.0–6.4	3.1	0	1.44 ± 0.05	—	0.44 ± 0.05 <sup>a</sup>
	1.0–6.4	3.1	500–1000	1.0 ± 0.1	0.12 ± 0.01	0.46 ± 0.14 <sup>b</sup>
<i>cis</i> - cyclooctene	1.5–4.2	2.5	0	1.39 ± 0.05	—	0.39 ± 0.05 <sup>a</sup>
	1.5–4.2	2.5	500–1000	Δ1.0 ± 0.1	0.09 ± 0.01	0.35 ± 0.10 <sup>b</sup>
<i>cis</i> - cyclodecene	1.1	1.3–2.3	0	1.40 ± 0.05	—	0.40 ± 0.05 <sup>a</sup>
	1.1	1.3–2.3	500–1000	1.0 ± 0.1	0.09 ± 0.01	0.35 ± 0.10 <sup>b</sup>

<sup>a</sup> based on reaction stoichiometry,

<sup>b</sup> based on (c-C<sub>6</sub>H<sub>10</sub>O formed) / (c-C<sub>6</sub>H<sub>12</sub> reacted) = 0.26 ± 0.04, (determined experimentally (see text)).

This value can be used in conjunction with the data from experiments where the loss of cycloalkene and yields of cyclohexanone were determined in experiments where cyclohexane was present in high enough concentrations to scavenge all the OH radicals produced in the O<sub>3</sub>-cycloalkene reactions. The OH formation yields were derived from both the reaction stoichiometries and from the amounts of cyclohexanone detected, and are shown in Table 2.

### Discussion

Room temperature rate constants and Arrhenius parameters for the gas-phase reactions of ozone with *cis*-2-butene, 2-methyl-2-butene and a number of cycloalkenes are shown in Table 1 together with the literature values. The rate coefficients for *cis*-2-butene and 2-methyl-2-butene are in excellent agreement with the data evaluation of Atkinson and Carter [3]. The reported room temperature rate constants for the reaction of ozone with cyclopentene and cyclohexene show a considerable degree of scatter. The present results for cyclopentene provide support for the recent determinations by Bennett *et al.* [24], Nolting *et al.* [25], and Green and Atkinson [21], while the value for cycloheptene is slightly lower than the reported values [20] and [25]. No previous kinetic studies have been carried out on the reactions of O<sub>3</sub> with *cis*-cyclooctene and *cis*-cyclodecene.

Atkinson *et al.* [20] have previously suggested that variations in the room temperature rate constants for reaction with ozone with cycloalkenes, could at least in part, be due to differences in the ring-strain energies of the cycloalkenes. The initial step in the reaction of O<sub>3</sub> with an alkene is the formation of an ozonide in which the carbon-carbon double bond is replaced by a single bond. Presumably the stability of the transition state relative to the reactants depends to a certain extent on the difference in ring-strain in the two structures. The Arrhenius parameters determined in the present work provide support for this suggestion. The cyclohexene ring contains very little strain energy [26] and as expected, the Arrhenius parameters are very close to those observed for the structurally similar molecule *cis*-2-butene. In contrast cyclopentene is considerably more reactive and the data show that the increase in reactivity is largely due to the significant reduction in activation energy. This result indicates that the reduction in ring-strain in the transition state is a factor in determining the reaction rate. Presumably the increased reactivity of cycloheptene and *cis*-cyclooctene relative to that of cyclohexene is also the result of ring-strain, both of these species having about the same ring-strain as cyclopentene [26].

Rate constants for the reaction of O<sub>3</sub> with a number of substituted cycloalkenes were also determined in this work. From the results, the magnitude of the rate constant depends on the nature of the substituent and its position on the ring. As expected, substitution of a hydrogen atom attached at the 1 position in cyclopentene by an electron-withdrawing chlorine atom decreases the reactivity for reaction with the electrophilic ozone molecule. This would appear to be due to both a decrease in the pre-exponential factor and an increase in activation energy.

A similar large reduction in rate was observed in going from cyclohexene to 1-nitro-1-cyclohexene. Similarly, substituting a hydrogen atom by an electron-donating methyl group at the double bond site in cyclopentene and cyclohexene enhances the reactivity in comparison to the unsubstituted cycloalkene. The presence of substituents at sites remote from the double bond has little effect on the reactivity as can be seen by comparing the Arrhenius parameters for cyclohexene and 4-methyl-1-cyclohexene.

The reactions of  $O_3$  with ethene and a series of cycloalkenes were investigated at  $298 \pm 2$  K in air at atmospheric pressure in the presence of cyclohexane. The added concentrations of cyclohexane were sufficient to totally scavenge any OH radicals generated in the  $O_3$ -radical reactions. The OH radical formation yields were derived from both the reaction stoichiometries and from the amounts of cyclohexanone produced from the reaction of OH with cyclohexane, Table 2. The values of  $D[\text{alkene}] / D[O_3]$  are close to unity for experiments carried out in excess cyclohexane indicating that OH radicals are efficiently scavenged by cyclohexane. In the absence of cyclohexane, the ratio  $D[\text{alkene}] / D[O_3]$  is  $1.42 \pm 0.04$  for all the cycloalkenes studied and is unity within experimental error for ethene. Based on the yields of cyclohexanone formed in experiments in which cyclohexane was present in high concentration, the OH radical formation yields for the cycloalkenes investigated are  $0.43 \pm 0.08$ . The yield of OH determined for the reaction of  $O_3$  with ethene is  $< 0.1$ . Hence from the measured stoichiometries and the cyclohexanone yields the derived OH formation yields, are equal within experimental error. The OH radical formation yields obtained in this work are lower than those previously obtained by Atkinson *et al.* [12,15] for ethene (0.12) and cyclohexene (0.68), who also used cyclohexane to scavenge OH radicals. Atkinson *et al.* [12,15] determined the OH yields from measurements of the sum of the cyclohexanone and cyclohexanol products formed, whereas, in this work a product of the  $O_3$ -alkene reaction was shown to interfere with the cyclohexanol measurements and hence OH yields were monitored using only the cyclohexanone product. The OH formation yields for reaction of  $O_3$  with cycloalkenes are close to the value of around 0.4 found by Atkinson and Aschmann [15] and by Horie *et al.* [16] for the structurally similar molecule *cis*-2-butene providing support for the suggestion that OH radical formation yields in  $O_3$ -alkene systems depend largely on the degree of alkyl group substitution at the double bond site [15].

## Conclusions

Kinetic studies on the gas-phase reactions of  $O_3$  with cycloalkenes as a function of temperature have provided a reliable kinetic database for these reactions which may be used as an important input into chemical models for the reactions of  $O_3$  with alkenes under atmospheric conditions. The relatively high hydroxyl radical formation yields from the  $O_3$ -cyclohexene reactions indicate that reactions of  $O_3$  with alkenes lead to the generation of OH radicals at night and hence allow the

OH-radical initiated oxidation of organic compounds to continue in the absence of sunlight.

### Acknowledgements

We gratefully acknowledge financial support from the Commission of the European Communities.

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### 3.22 Mechanisms for the Oxidation of C<sub>5</sub>-C<sub>7</sub> Hydrocarbons

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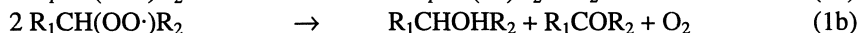
#### Summary

Product distributions resulting from the OH radical induced oxidation of the following hydrocarbons have been determined: 2-methyl-propane, 2,3-dimethyl-butane, 2-methyl-butane, *n*-pentane, cyclohexane, methylsubstituted 1-butenes, isoprene, toluene. Whenever possible, branching ratios for the self-reactions of alkylperoxy radicals and decomposition rate coefficients for alkoxy radicals were derived.

#### Aims of research

Previous laboratory studies of the gas-phase oxidation of hydrocarbons, mainly in the C<sub>1</sub>-C<sub>4</sub> size range, have established a general reaction mechanism involving alkylperoxy and alkoxy radicals [1]. The present project was to determine for a number of hydrocarbons in the C<sub>4</sub>-C<sub>7</sub> size range the distribution of products resulting from the OH radical-initiated oxidation, to establish the prevailing reaction mechanisms and to obtain branching ratios for reactions of alkylperoxy and alkoxy radicals. Reactions were carried out in bulbs of two or ten liter capacity filled with air at atmospheric pressure. The hydrocarbon content was 100 – 1000 ppm. Hydroxyl radicals were generated by photodecomposition of hydrogen peroxide at 254 nm wavelength using a mercury lamp placed in a quartz finger in the centre of the bulb. Products were separated and quantified by means of gas chromatography. Although a substantial effort was made to obtain a complete product identification for each hydrocarbon, this goal has not been accomplished in all cases.

The reaction of OH radicals with alkanes results in the abstraction of a hydrogen atom followed by addition of oxygen whereby an alkylperoxy radical is formed; In the reaction with alkenes OH is added to the double bond followed by addition of oxygen, generally at the neighbouring carbon atom. The peroxy radicals then enter into a reaction sequence of the type



followed by further reactions of the radicals produced in the decomposition and intramolecular hydrogen abstraction of the alkoxy radical, reactions (2b) and (2c), respectively. Because these reactions produce new alkylperoxy radicals, they will enter into cross combination reactions with other peroxy radicals present in the reaction mixture. Higher hydrocarbons also allow hydrogen abstraction at more than one site of the carbon chain, so that several different primary alkylperoxy radical are produced and interact with each other. The complete reaction mechanism thus can be considerably more complex than the above simplified scheme indicates. Computer simulations were used as far as possible to assist in the evaluation of experimental data.

### Principal scientific findings of the project

Detailed oxidation mechanisms for the individual hydrocarbons cannot be discussed for the lack of space. We state here mainly the product distributions observed (mole fraction unless otherwise indicated) and the principal conclusions derived for each substance studied.

#### *2-Methyl-propane (isobutane)*

*Percent product distribution:* acetone  $24.5 \pm 5.1$ , 2-methyl-2-propanol  $18.8 \pm 4.0$ , 2-methyl-2-hydroperoxypropane  $36.7 \pm 7.5$ , 2-methyl-propanal  $14.0 \pm 3.9$ , 2-methyl-propanol  $4.4 \pm 1.3$ , tertiary butylperoxide  $\leq 1.7$ . The peroxy radicals involved are primary 2-methyl-1-propylperoxy, primary methylperoxy and tertiary 2-methyl-2-propylperoxy. The relatively large yield of tertiary butanol is due to the interaction between  $\text{CH}_3\text{OO}$  and tertiary butylperoxy radicals. Computer simulations based on the known rate coefficients for the self-reactions of these radicals [2] gave  $k_{1\text{pt}} = 3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the cross combination reaction. To simulate the observed ratio of primary alcohol and aldehyde requires a rate coefficient  $k_{1\text{pt}} \mu 3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the interaction between 2-methyl-1-propylperoxy and tertiary 2-methyl-2-propyl-peroxy radicals. The oxidation mechanism is quantitatively well understood.

#### *2,3-Dimethylbutane*

*Percent product distribution:* acetone  $46.8 \pm 2.1$ , 2-propanol  $7.5 \pm 0.8$ , 2,3-dimethyl-2-hydroperoxybutane  $29.3 \pm 3.0$ , 2,3-dimethyl-2-butanol  $2.2 \pm 0.2$ , 2,3-dimethylbutanal  $8.7 \pm 0.8$ , 2,3-dimethyl-1-butanol  $3.4 \pm 0.5$ , unidentified  $2.2 \pm 0.2$ . The ratio of tertiary to primary hydrogen atom abstraction is 83:17. The reaction involves primary 2,3-dimethyl-butylperoxy, secondary 2-propylperoxy and tertiary 2,3-dimethyl-2-butylperoxy radicals. Large amounts of tertiary hydroperoxide are again formed due to the relatively rapid rate of the reaction between hydroperoxy and tertiary peroxy radicals compared to that of their self-reaction. Computer simulations of the product distribution allowed to estimate rate coefficients for the cross combination reactions of tertiary with primary and

secondary alkylperoxy radicals,  $k_{1pt} = 2 \times 10^{-16}$  and  $k_{1st} = 1.7 \times 10^{-17}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$ , respectively. The branching ratios determined for the alkylperoxy radical self-reactions are shown in Table 1. These results have been published [3].

**Table 1:** Branching ratios  $\hat{A} = k_{1a}/k_1$  for self-reactions of several alkylperoxy radicals.

Alkyl radical	Source	$k_{1a}/k_1$
2-propyl	2,3-dimethylbutane	$0.39 \pm 0.08$
2,3-dimethyl-1-butyl	2,3-dimethylbutane	$0.44 \pm 0.07$
2-pentyl	2-pentyl iodide	$0.47 \pm 0.07$
3-methyl-2-butyl	2-methylbutane	$0.51 \pm 0.08$
3-pentyl	3-pentyl iodide	$0.38 \pm 0.06$
cyclo-hexyl	cyclohexane	$0.42 \pm 0.02$
1-hydroxy-2-butyl	1-butene	$0.75 \pm 0.02$
1-hydroxy-3-methyl-2-butyl	3-methyl-1-butene	$0.83 \pm 0.01$
benzyl	toluene	$0.76 \pm 0.05$

### 2-Methylbutane (isopentane)

*Percent product distribution:* acetone  $27.6 \pm 1.9$ , acetaldehyde  $27.9 \pm 1.9$ , ethanol  $3.3 \pm 0.3$ , 2-methyl-2-hydroperoxybutane  $14.6 \pm 1.1$ , 2-methyl-2-butanol  $14.1 \pm 1.7$ , 3-methyl-2-butanone  $9.1 \pm 0.8$ , 3-methyl-2-butanol  $3.3 \pm 0.3$ . Another product expected, 2-propanol, could not be quantified because its signal was overlapped by that of the parent hydro-carbon. Analysis of the product distribution suggests that the ratio of hydrogen abstraction probabilities at the primary, secondary and tertiary sites is 13:17:70. The production of ethanol indicates that ethylperoxy radicals are produced in addition to the initial primary 2-methyl-1-butylperoxy and 3-methyl-1-butylperoxy, secondary 3-methyl-2-butylperoxy and tertiary 2-methyl-2-butylperoxy radicals; and acetone can be produced from the decomposition of 2-methyl-2-butoxy as well as of 2-propylperoxy radicals generated by decomposition of the 3-methyl-2-butoxy radical. Computer simulations were performed to explore the effect of cross combination reactions between primary and tertiary peroxy radicals on the yield of 2-methyl-2-butanol. The same rate coefficient was applied for the reactions of all primary peroxy radicals. Good agreement with the experimental product distribution was obtained with  $k_{1pt} = 3 \times 10^{-15}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$ . The branching ratio  $\hat{A} = k_{1a}/k_1$  estimated for the self-reaction of 3-methyl-2-butylperoxy radicals is shown in Table 1.

### n-Pentane

*Percent product distribution:* pentanal  $3.4 \pm 1.3$ , 1-pentanol  $0.72 \pm 0.06$ , 2-pentanone  $21.6 \pm 4.1$ , 2-pentanol  $11.97 \pm 0.39$ , 3-pentanone  $20.7 \pm 3.9$ , 3-pentanol  $6.7 \pm 0.39$ , butanal  $0.2 \pm 0.1$ , propanal  $3.3 \pm 0.8$ , acetaldehyde  $5.2 \pm 1.1$ , bifunctional products, not separated,  $26.2 \pm 4.8$ . Bifunctional products



are expected to be formed as a result of intramolecular hydrogen abstraction, which the 1-pentoxyl and the 2-pentoxyl radicals are capable of undergoing. The probabilities for formation of 1-pentylperoxy, 2-pentyl-peroxy and 3-pentylperoxy radicals due to hydrogen abstraction by OH radicals are approximately 10:60:30. The corresponding C<sub>5</sub>-alcohols are formed in the ratios 3.9%, 62.8% and 33.4%. The yield of 1-pentanol is significantly smaller than expected, particularly in relation to the yield of pentanal. The photolysis of 1-pentyl iodide was used to prepare 1-pentylperoxy radicals directly. The product distribution in this case was pentanal  $1.13 \pm 0.1$ , 1-pentanol  $1.0 \pm 0.1$ , and at least two unidentified isomerization products  $0.5 \pm 0.05$ . These results show that in the self-reaction of 1-pentylperoxy radicals pentanal and 1-pentanol are formed in roughly equimolar amounts, and that the 1-pentoxyl radical formed in reaction (1a) largely isomerizes. In the oxidation of *n*-pentane, cross combination reactions with 2-pentylperoxy and 3-pentyl-peroxy radicals predominate. Computer simulations showed that a smaller branching ratio for 1-pentanol formation in the cross combination reactions, and a larger one for pentanal formation, can to some extent explain the lower yield of 1-pentanol and the higher yield of pentanal.

The product distribution obtained in the photolysis of 3-pentyl iodide provided the branching ratio for the self-reaction of 3-pentylperoxy radicals and an estimate for the decomposition rate constant of the 3-pentoxyl radical (see Tables 1 and 2). Photolysis of 2-pentyl iodide indicated considerable isomerization of the 2-pentoxyl radical. The 1,4-diols expected were not observed, however. Instead a complex spectrum of smaller fragments appeared, which proved difficult to analyze. The system obviously involves a greater number of different peroxy radicals that can interact with 2-pentylperoxy, which makes it difficult to isolate the self-reaction of this radical. The branching ratio given in Table 1 thus must be considered tentative. The ratios of pentanones/pentanol observed in the pentyl iodide experiments differ considerably from those observed in the oxidation of *n*-pentane. Cross combination reactions of pentylperoxy radicals must largely be responsible for the differences. Further work is necessary to resolve these inconsistencies.

Table 2: Rate coefficients for the decomposition and isomerization of alkoxy radicals.

<sup>a</sup> The first pathway ( $k_{2b} = k_{dec}$ ) yields aldehyde and an alkyl or hydroxyalkyl radical, the second pathway ( $k_{2c} = k_{isom}$ ) yields a hydroxyalkyl radical.

alkoxy radical	source	$k_{dec} / s^{-1}$	$k_{isom} / s^{-1}$
1-pentoxyl	1-pentyl iodide	—	$1.7 \times 10^5$
2-pentoxyl	2-pentyl iodide	$8.9 \times 10^3$	$9.3 \times 10^4$ <sup>b</sup>
3-pentoxyl	3-pentyl iodide	$2.7 \times 10^4$	—
cyclo-hexoxyl	cyclohexane	$4.2 \times 10^3$	—
1-hydroxy-2-butoxyl	1-butene	$1.1 \times 10^5$	—
1-hydroxy-3-methyl-2-butoxyl	3-methyl-1-butene	$6.8 \times 10^4$	—

<sup>a</sup> relative to reaction with oxygen,  $k(O_2) = k_{2a} = 8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ; <sup>b</sup> lower limit.

### **Cyclohexane**

*Percent product distribution:* cyclo-hexanone  $67.0 \pm 1.2$ , cyclo-hexanol  $29.2 \pm 0.5$ , unidentified bifunctional compounds  $3.8 \pm 1.2$ . The cyclo-hexoxyl radical undergoes remarkably little ring cleavage. Values for the branching ratio of the cyclo-hexylperoxy radical self-reaction and for the decomposition rate coefficient of the cyclo-hexoxyl radical are shown in Tables 1 and 2.

### **Methyl-substituted 1-butenes**

The OH radical-induced oxidations of 1-butene, 3-methyl-1-butene and 2-methyl-1-butene were studied in order to quantify the 1,2-diols and 1-hydroxy-2-ketones expected to be formed as products.

#### **1-Butene**

*Percent product distribution:* propanal  $50.6 \pm 1.2$ , 2-hydroxy-butanal  $7.0 \pm 0.3$ , 1-hydroxy-butan-2-one  $24.2 \pm 0.7$ , 1,2-dihydroxybutane  $18.2 \pm 0.7$ . Computer assisted analysis of the product distribution showed that addition of the OH radical occurs to 26 % at the inner and to 74% at the outer position of the double bond. These reactions produced the corresponding primary and secondary hydroxy-alkylperoxy radicals. The branching ratio for the radical propagating channel of the self-reaction of the secondary peroxy radicals was determined to be  $k_{1ssa}/k_{1ss} = 0.75 \pm 0.02$ ; 28 % of the hydroxy-alkoxyl radical thus formed reacted with oxygen to produce hydroxyketone. If it is assumed that the rate coefficient for the reaction of the hydroxy-alkoxyl radical with oxygen is  $8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , the rate coefficient for the decomposition of this radical to produce propanal is  $1 \times 10^5 \text{ s}^{-1}$ .

#### **3-methyl-1-butene**

*Percent product distribution:* 2-methyl-propanal  $48.1 \pm 1.1$ , 2-hydroxy-3-methyl-butanal  $6.9 \pm 0.34$ , 1-hydroxy-3-methyl-2-butanone  $29.5 \pm 0.61$ , 1,2-dihydroxy-3-methyl-butane  $15.5 \pm 1.1$ . Data evaluation in a manner similar to that for 1-butene showed 24 % of OH addition to occur at the inner and 76 % at the outer position of the double bond,  $k_{1ssa}/k_{1ss} = 0.82 \pm 0.02$ , and 38% reaction of the hydroxy-alkoxyl radical with oxygen compared with decomposition. The rate coefficient for decomposition of 1-hydroxy-3-methyl-2-butoxyl was estimated to be  $6.3 \times 10^4 \text{ s}^{-1}$ .

#### **2-methyl-1-butene**

*Percent product distribution:* butanone  $80.8 \pm 1.46$ , 2-hydroxy-2-methyl-butanal  $4.6 \pm 0.1$ , 1,2-dihydroxy-2-methyl-butane  $14.3 \pm 0.3$ . The addition of OH at the double bond of 2-methyl-1-butene occurs to 10.5 % at the inner and to 89.5 % at the outer position. This results mainly in the formation of a tertiary hydroxyalkyl peroxy radical, which carries no abstractable hydrogen at the

2-position. The formation of 1,2-diols thus results entirely from addition of OH at the inner position of the double bond.

### *Isoprene*

*Percent product distribution* : Methylvinylketone (MVK)  $49.0 \pm 1.1$ , methacroleine (MAC)  $44.3 \pm 1.6$ , 3-methyl-furan (MFU)  $6.7 \pm 0.6$  for isoprene mole fractions 400 ppm. The ratio of MVK to MAC under these conditions was  $1.1 \pm 0.6$ . In the presence of NO the ratio is close to 1.4 [4]. Computer simulations based on our results for methylsubstituted 1-butenes showed that the observed [MVK]/[MAC] ratios are obtained with essentially equal probabilities for OH attack at the two double bonds of isoprene. This result contradicts predictions based on OH reaction rate coefficients for various methylsubstituted butenes [5]. Similar to results obtained for the 1-butenes, diols and hydroxycarbonyl compounds were found in small yields among the products. These are not included in the above product distribution because they are difficult to quantify .

### *Toluene*

*Product distribution* (percent reacted carbon): benzaldehyde  $4.9 \pm 1.1$ , benzylalcohol  $2.3 \pm 0.5$ , *o*-cresol  $30.6 \pm 6.5$ , *p*-cresol  $11.1 \pm 2.4$ , *m*-cresol  $\leq 0.4$ , methyl-*p*-benzoquin-one  $3.9 \pm 0.8$ , unidentified  $3.1 \pm 0.6$ , formaldehyde  $2.1 \pm 0.7$ , acetaldehyde  $1.1 \pm 0.4$ , glyoxal  $3.9 \pm 1.3$ , methylglyoxal  $4.9 \pm 1.6$ , carbon monoxide  $4.0 \pm 1.0$ , carbon dioxide  $8.9 \pm 2.2$ . The total product yield was  $81 \pm 20$  %; 56 % were ring-retaining products, 25 % resulted from ring cleavage. The distribution of ring cleavage products observed here under NO<sub>x</sub> free conditions was similar to that reported previously in the presence of NO<sub>x</sub>. The yield of cresols was higher. In particular, in comparison with previous results more *p*-cresol and less *m*-cresol was found. The self-reaction of hydroxy-methyl-cyclohexadienyl-peroxy (HMCHP) radicals is expected to produce dihydroxytoluenes; these compounds were not observed, however. A computer simulation indicated that internal rearrangement of the HMCHP radical must be rapid relative to reactions with other peroxy radicals. The branching ratio for the self-reaction of the benzylperoxy radical,  $k_{1ppa}/k_{1pp} = 0.76 \pm 0.05$  was determined by using chlorine atoms as reagent to produce the benzyl radical. In the oxidation of toluene induced by OH a smaller  $\bar{A}$  value was obtained, which indicated that the branching ratio is influenced by reactions of benzylperoxy with other peroxy radicals.

### **Conclusions**

Oxidation mechanisms for 2-methyl-propane, 2,3-dimethyl-butane, 2-methyl-butane, cyclohexane and methyl substituted 1-butenes have been fully delineated. The mechanism for *n*-pentane is understood although not entirely quantified. Progress has been made in deriving the mechanisms for the oxidation of isoprene

and toluene, but in these cases a complete identification of all products has not been possible.

### Acknowledgements

Financial support by the German Federal Ministry of Research and Technology is gratefully acknowledged. We thank Dr. Böge from the Institut für Troposphärenforschung, Leipzig, for the preparation of several compounds.

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### 3.23 Studies of the Kinetics and Mechanisms of Interactions of Nitrate and Peroxy Radicals of Tropospheric Interest

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#### Summary

This report describes research conducted in Oxford during the years 1988–1994 aimed at improving understanding of the reactivity of the nitrate and peroxy radicals through laboratory investigations of kinetics and mechanisms. Methods utilised included conventional discharge-flow and laser-flash photolysis techniques, and a new stopped-flow system was devised to allow investigations of slow reactions of the  $\text{NO}_3$  radical. Reactions of  $\text{NO}_3$  with a variety of closed-shell molecules (alkanes, alkenes, aldehydes, *etc.*) were investigated, and the room-temperature rate coefficients and, where possible, Arrhenius parameters are reported here. Investigations of reactions with inorganic open-shell species included those with atomic I and the self-reaction of  $\text{NO}_3$ . In addition, a new reaction of  $\text{NO}_3$  with molecular  $\text{I}_2$  was discovered. Much effort was addressed towards the direct study of the reactions between organic radicals and  $\text{NO}_3$ , with the ultimate objective of understanding the products and kinetics of the interaction between  $\text{CH}_3\text{O}_2$ ,  $\text{C}_2\text{H}_5\text{O}_2$  (and other  $\text{RO}_2$  species) and  $\text{NO}_3$ . A laser-induced fluorescence method was used to detect the RO species. The experiments make it clear that  $\text{RO}_2$  does indeed react with  $\text{NO}_3$ , that one of the products is RO and that RO in turn reacts with  $\text{NO}_3$  (in the laboratory system) to regenerate  $\text{RO}_2$ . Indirect studies, which involved examination of secondary reactions following H abstraction from organic substrates in the presence of  $\text{O}_2$  supplemented the direct investigations. Reactions of acylperoxy radicals such as  $\text{CH}_3\text{CO}\cdot\text{O}_2$  were examined in this way (using aldehydes as starting materials); a more direct method of following these reactions was devised in which peroxyacetyl nitrate (PAN) was pyrolysed in the presence of  $\text{NO}_3$ . The research on  $\text{RO}_2$  radicals has been extended to measurements of the kinetics of the self-reactions of several substituted methylperoxy species. The experimental work on reaction kinetics has been supplemented by attempts to interpret the reactivity of  $\text{NO}_3$  towards organic species using the framework of frontier orbital theory; calculations of orbital energies has permitted a variety of correlations to be evaluated and has provided further insight into the factors affecting reactivity.

### **Aims of the research**

The primary aim of this project is the investigation of the kinetics and mechanisms of reactions of  $\text{NO}_3$  with both radical and non-radical species. One objective is to gain an understanding of the reaction rates and product channels of the processes. The studies not only form a direct part of our interest in the physical chemistry of radical-radical interactions, as well as in the general aspects of atmospheric chemistry, but also help to identify patterns of reactivity that may have diagnostic and predictive value. In terms of the EUROTRAC project, the most important of the radical-radical reactions are likely to be those with organic peroxy radicals; included in this category are both alkylperoxy and acylperoxy species. Laboratory investigations need to encompass studies of R and RO radicals in addition to  $\text{RO}_2$ . Other problems in  $\text{NO}_3$  chemistry that were aims of this research include possible interactions that are too slow to study by 'conventional' time-resolved techniques; in this category fall the self-reaction of  $\text{NO}_3$ , which inevitably occurs in any experiment, reactions with some alkanes, and heterogeneous and thermal loss processes.

### **Principal scientific findings**

#### *Experimental methods*

Most of the experiments reported here were conducted using conventional discharge-flow methods; linear flow velocities were typically of the order of  $1$  to  $20 \text{ m s}^{-1}$ . Reaction of F with  $\text{HNO}_3$  was used to generate the  $\text{NO}_3$  radicals. In the great majority of experiments, multiple-pass optical absorption at  $\lambda = 662 \text{ nm}$  was used to monitor the radicals, although LIF was employed in a few instances.  $\text{CH}_3\text{O}$  and  $\text{C}_2\text{H}_5\text{O}$  radicals were monitored by LIF. One method for monitoring the  $\text{RO}_2$  radicals involved conversion to the corresponding RO species, followed by LIF detection of the RO. Another technique that we employed was based on LIF or MS determination of the  $\text{NO}_2$  generated on addition of excess NO to the gas flow.

In addition to the continuous-flow reactors, we developed a stopped-flow apparatus to study slow reactions of the  $\text{NO}_3$  radical. In this apparatus, a series of solenoid valves is used to divert and isolate a flow of gas that contains the reaction mixture. These valves were designed and fabricated in this laboratory by the PI, and ensure that only glass is in contact with the flow. Concentrations of  $\text{NO}_3$  are then followed as a function of time after the flow is cut off, the data being captured by computer. Figure 1 shows the apparatus in schematic form, while Fig. 2 illustrates decay curves for  $[\text{NO}_3]$  in the absence and presence of  $\text{C}_2\text{H}_4$ .

A modification to laser-flash photolysis was made in order to study the self-reaction of  $\text{NO}_3$  radicals. Photolysis of  $\text{F}_2$  in the presence of  $\text{HNO}_3$  was used to generate  $\text{NO}_3$ . Laser pulses were repeated until a suitable amount of  $\text{NO}_3$  had built up in the cell; irradiation was then terminated, and the decay of  $\text{NO}_3$  followed in real time.

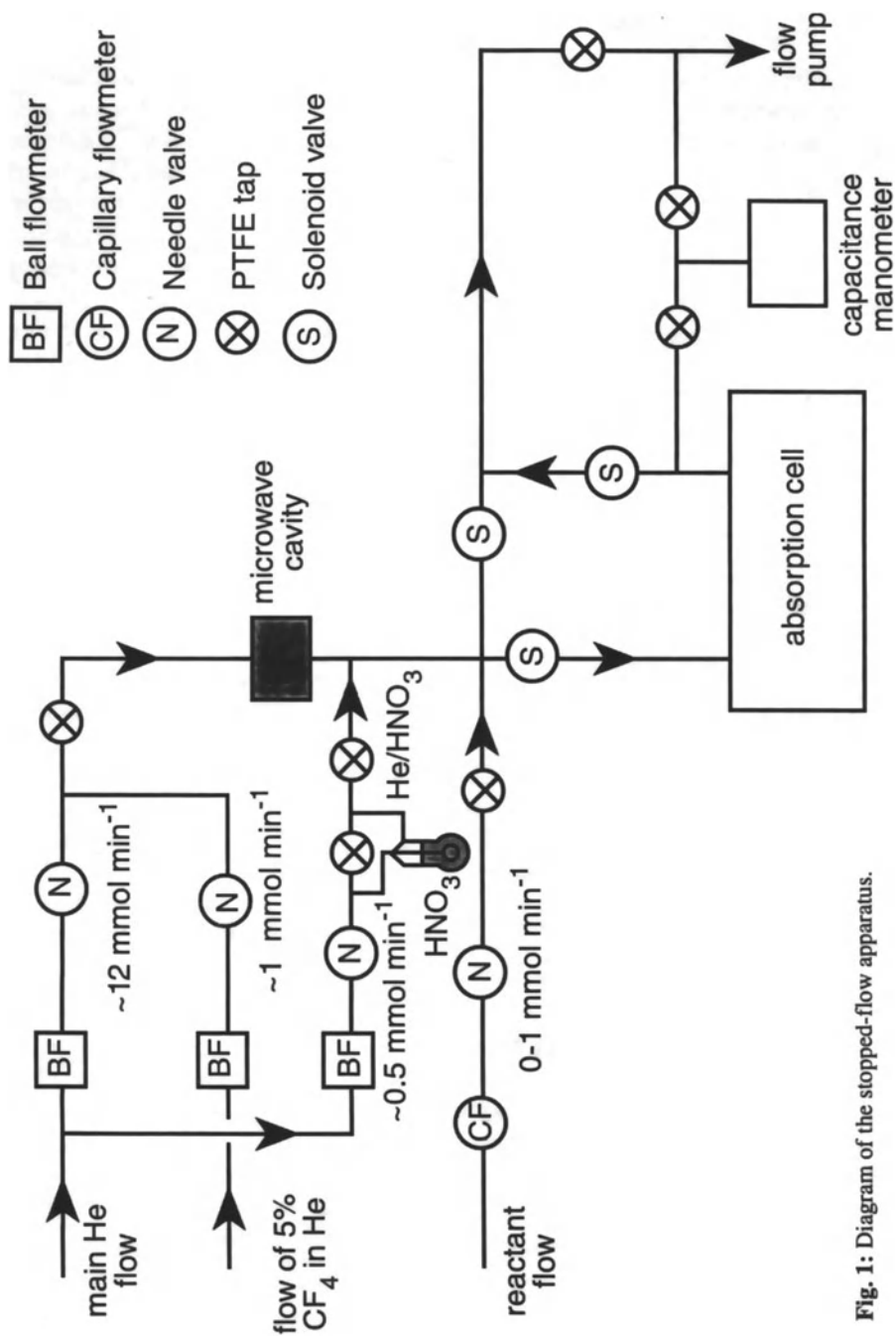
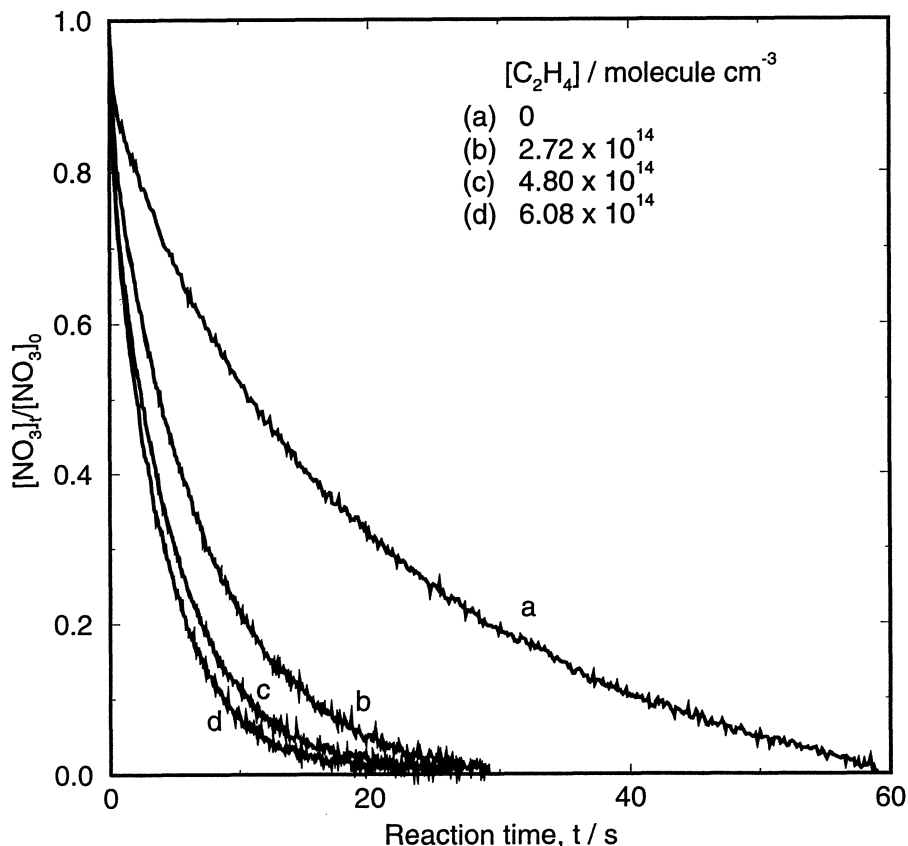


Fig. 1: Diagram of the stopped-flow apparatus.



**Fig. 2:** Decay of  $\text{NO}_3$  in the presence of  $\text{C}_2\text{H}_4$ .

### *Reactions of $\text{NO}_3$ with closed-shell organic species*

Table 1 summarises the rate data obtained during the course of this project. Although there have been previous determinations of the rate of reaction of alkanes with  $\text{NO}_3$  at room temperature, our work appears to be the first in which the temperature dependence of the reactions was studied. Our new measurements indicate that the reactions studied are not the major loss processes for alkanes in the atmosphere. They are, however, significant in the production of night-time nitric acid; the reaction with *i*-pentane makes this molecule the most important atmospheric alkane in terms of  $\text{HNO}_3$  generation.

Since many urban areas contain relatively high concentrations of a wide range of alkanes and alkenes, it is desirable that structure–reactivity relationships be found that assist understanding of the urban night-time troposphere. These new data provide some of the necessary information for uncovering such relationships; a later section explores the work that we have done in this respect.



**Table 1:** Rate parameters for selected reactions of NO<sub>3</sub> investigated in this laboratory.

Compound	$k(298\text{ K})$	$A$	$E_a$	Technique
	cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	kJ mol <sup>-1</sup>	
CH <sub>4</sub>	$< 4 \times 10^{-19}$			SF
C <sub>2</sub> H <sub>6</sub>	$8.3 \times 10^{-19}$	$1.7 \times 10^{-11}$	$41.8 \pm 1.4$	DF 373–553 K
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	$0.45 \pm 0.06 \times 10^{-16}$	$2.5 \pm 0.6 \times 10^{-12}$	$27.0 \pm 0.7$	DF 298–523 K
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	$1.1 \pm 0.2 \times 10^{-16}$	$2.3 \pm 0.6 \times 10^{-12}$	$24.6 \pm 0.7$	DF 298–523 K
CH <sub>2</sub> Cl <sub>2</sub>	$4.8 \pm 1.0 \times 10^{-18}$			SF
CHCl <sub>3</sub>	$6.0 \pm 0.5 \times 10^{-17}$			SF
CH <sub>3</sub> COCH <sub>3</sub>	$8.5 \pm 2.5 \times 10^{-18}$			SF
CH <sub>3</sub> CHO	$2.5 \pm 0.4 \times 10^{-15}$	$4.2 \pm 0.5 \times 10^{-12}$	$14.9 \pm 0.1$	DF 298–473 K
CH <sub>2</sub> ClCHO	$< 10^{-15}; > 6 \times 10^{-16}$		$16 \pm 3$	SF, DF 293–473 K
CHCl <sub>2</sub> CHO	$4 \pm 1 \times 10^{-17}$		$23 \pm 4$	SF, DF 298–473 K
CCl <sub>3</sub> CHO	$3 \pm 1 \times 10^{-18}$			SF
C <sub>2</sub> H <sub>4</sub>	$1.7 \pm 0.5 \times 10^{-16}$			SF
1,1-C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	$1.2 \pm 0.3 \times 10^{-15}$	$4.7 \pm 2.4 \times 10^{-13}$	$15.0 \pm 2.0$	DF
1,2-C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	$1.2 \pm 0.5 \times 10^{-16}$	$4.5 \pm 0.5 \times 10^{-13}$	$19.9 \pm 0.3$	DF
1-C <sub>4</sub> H <sub>8</sub>	$1.1 \pm 0.2 \times 10^{-14}$	$2.5 \times 10^{-13}$	$7.8 \pm 0.8$	DF 298–473 K
ClCH <sub>2</sub> CHCHCH <sub>3</sub>	$2.0 \pm 0.7 \times 10^{-14}$	$6.0 \times 10^{-13}$	$8.2 \pm 2.9$	DF 298–473 K
ClCHCHCH <sub>2</sub> CH <sub>3</sub>	$1.2 \pm 0.4 \times 10^{-14}$			DF
CH <sub>2</sub> CClCH <sub>2</sub> CH <sub>3</sub>	$1.7 \pm 0.3 \times 10^{-14}$			DF
CH <sub>2</sub> CHCHClCH <sub>3</sub>	$3.0 \pm 0.7 \times 10^{-15}$	$2.4 \times 10^{-12}$	$16.6 \pm 2.0$	DF 298–473 K
CH <sub>3</sub> CClCHCH <sub>3</sub>	$1.1 \pm 0.4 \times 10^{-13}$			DF
CH <sub>2</sub> C(CH <sub>3</sub> )CH <sub>2</sub> Cl	$9.0 \pm 2.3 \times 10^{-14}$			DF
CHClC(CH <sub>3</sub> ) <sub>2</sub>	$2.5 \pm 0.4 \times 10^{-14}$	$1.6 \times 10^{-12}$	$10.5 \pm 1.7$	DF 298–473 K
CH <sub>2</sub> CHCHBrCH <sub>3</sub>	$4 \pm 1 \times 10^{-15}$			DF
CH <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> Br	$5 \pm 1 \times 10^{-15}$			DF
CH <sub>3</sub> CHBrCHCH <sub>3</sub>	$1.3 \pm 0.1 \times 10^{-13}$			DF
1-C <sub>5</sub> H <sub>10</sub>	$(1.8 \pm 0.1) \times 10^{-14}$	$9.1 \times 10^{-13}$	$10.2 \pm 1.1$	DF 298–523 K
1-C <sub>6</sub> H <sub>12</sub>	$(1.5 \pm 0.1) \times 10^{-14}$	$1.13 \times 10^{-13}$	$10.9 \pm 0.6$	DF 298–523 K
I	$4.5 \pm 1.9 \times 10^{-10}$			DF
I <sub>2</sub>	$1.5 \pm 0.5 \times 10^{-12}$			DF
O <sub>3</sub>	$< 0.6 - 1 \times 10^{-19}$			SF
NO <sub>3</sub>	$2.3 \pm 0.8 \times 10^{-16}$			LP
CH <sub>3</sub>	$3.5 \pm 1.0 \times 10^{-11}$			DF
CH <sub>3</sub> O	$2.3 \pm 0.7 \times 10^{-12}$			DF
CH <sub>3</sub> O <sub>2</sub>	$1.0 \pm 0.6 \times 10^{-12}$			DF
C <sub>2</sub> H <sub>5</sub>	$4.0 \pm 1.0 \times 10^{-11}$			DF
C <sub>2</sub> H <sub>5</sub> O	$3.5 \pm 1.0 \times 10^{-12}$			DF
C <sub>2</sub> H <sub>5</sub> O <sub>2</sub>	$2.5 \pm 1.5 \times 10^{-12}$			DF
CH <sub>3</sub> CO.O <sub>2</sub>	$\sim 2 \times 10^{-11}$			DF

SF = stopped flow; DF = discharge flow; LP = laser photolysis

In analysing the results of the kinetic experiments, we paid considerable attention to the possible occurrence of secondary reactions. In the primary interaction of  $\text{NO}_3$  with alkanes, RH, hydrogen abstraction yields the radical R. Thus, if oxygen is deliberately added to the reaction mixture, a source of  $\text{RO}_2$  is available in the presence of the  $\text{NO}_3$ , so that information about interactions between the two radicals can be inferred from the detailed kinetic behaviour.

The data obtained in this way complements the information gained by the direct studies to be discussed later. In a converse manner, the data from the direct studies can be used to aid in the interpretation of secondary chemistry. Note that the experiments with  $\text{CH}_3\text{CHO}$  allow generation of  $\text{CH}_3\text{CO}\cdot\text{O}_2$  radicals.

### *Reaction of $\text{NO}_3$ with inorganic species*

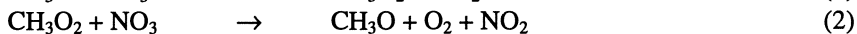
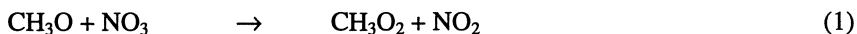
Data for four reactions are reported in Table 1. They are for the reactions with I,  $\text{I}_2$ ,  $\text{O}_3$ , and the self-reaction with  $\text{NO}_3$  itself. There is a possibility that iodine species could play a role in atmospheric chemistry close to the surface of oceans and in the emissions from nuclear power stations. The products of the reaction with I are thought to be  $\text{IO} + \text{NO}_2$ ; the rate coefficient is surprisingly large, and the mechanism may be different from those for the reactions with the other halogens. Reaction of  $\text{NO}_3$  with  $\text{I}_2$  appears not to have been observed previously; the products seem to be  $\text{I} + \text{IONO}_2$ .

We have previously considered the possibility of an interaction between  $\text{NO}_3$  and  $\text{O}_3$ . Detailed analysis of stopped-flow experiments yielded a value for the rate coefficient of between  $0.6$  and  $1.0 \times 10^{-19} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ . However, this process might be heterogeneous, and we therefore suggest the upper limit given in the table. It seems unlikely that the reaction could be of atmospheric importance during the time during which substantial concentrations of  $\text{NO}_3$  and  $\text{O}_3$  coexist.

Studies of the self-reaction between  $\text{NO}_3$  radicals have been conducted using both the stopped-flow and the 'slow' laser-flash photolysis system. We prefer the results from the photochemical system, and these are reported in the table. The data are of importance in the analysis of laboratory data, especially for the slower reactions of  $\text{NO}_3$ .

### *Reactions of $\text{NO}_3$ with organic radicals*

The prime requirement from the point of view of atmospheric chemistry is to discover the reaction channels and rates for the interaction of  $\text{RO}_2$  with  $\text{NO}_3$ . However, for laboratory study, we also need equivalent information on the reaction of the related R and RO radicals. We discovered that R ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ ) reacts with  $\text{NO}_3$  to yield RO; this process thus provides a convenient source for our studies of the RO radical. The peroxy radical,  $\text{RO}_2$ , can of course be generated by the addition of R to  $\text{O}_2$ ; however, we also discovered that RO reacts with  $\text{NO}_3$  to yield  $\text{RO}_2$ . Indeed, it turns out that  $\text{RO}_2$  in turn reacts with  $\text{NO}_3$  to regenerate RO, so that a cyclic process, represented for  $\text{R} = \text{CH}_3$  by the equations



operates. This finding is of critical importance to the interpretation of the observed concentration-time profiles, because there is a tendency for [RO] to approach a steady-state value at long contact times. Full numerical modelling of the reaction systems, using different sources of RO and RO<sub>2</sub> provides the rate coefficients reported in Table 1.

Because of the rapidity of the self-reaction of RCO.O<sub>2</sub> radicals and because RCO.O radicals are generally unstable, it is not possible to use a similar approach for the study of acyl peroxy radicals. Instead, we have used the thermal decomposition of PAN, CH<sub>3</sub>CO.O<sub>2</sub>NO<sub>2</sub>, as an *in situ* source of CH<sub>3</sub>CO.O<sub>2</sub>. In our experiments, concentrations of PAN were measured by FTIR spectroscopy, and the decay of NO<sub>3</sub> in a (slow) flow system provides the kinetic information. It is clear that radical reactions, and not direct reaction with PAN, are responsible for the losses of NO<sub>3</sub>. The current best fits to the experimental data were obtained with the rate coefficient given in Table 1 for the reaction



and the value appears to be independent of temperature over the range  $T = 300\text{--}423$  K.

The key conclusions from our studies of the reactions of RO<sub>2</sub> with NO<sub>3</sub> are:

- (i) the interconversion of oxy (RO) and peroxy (RO<sub>2</sub>) species through their reaction with NO<sub>3</sub> is critically necessary for the interpretation of the laboratory studies; and
- (ii) the rate constants for the reaction of RO<sub>2</sub> with NO<sub>3</sub> are large enough to make this process a possible source of HO<sub>2</sub> and OH radicals in the troposphere at night. Since, in the presence of O<sub>2</sub>, CH<sub>3</sub>CO.O radicals will be largely converted to CH<sub>3</sub>O<sub>2</sub>, this conclusion holds also for the acetyl peroxy radicals converted in reaction (3).

### *The self-reaction of RO<sub>2</sub> radicals*

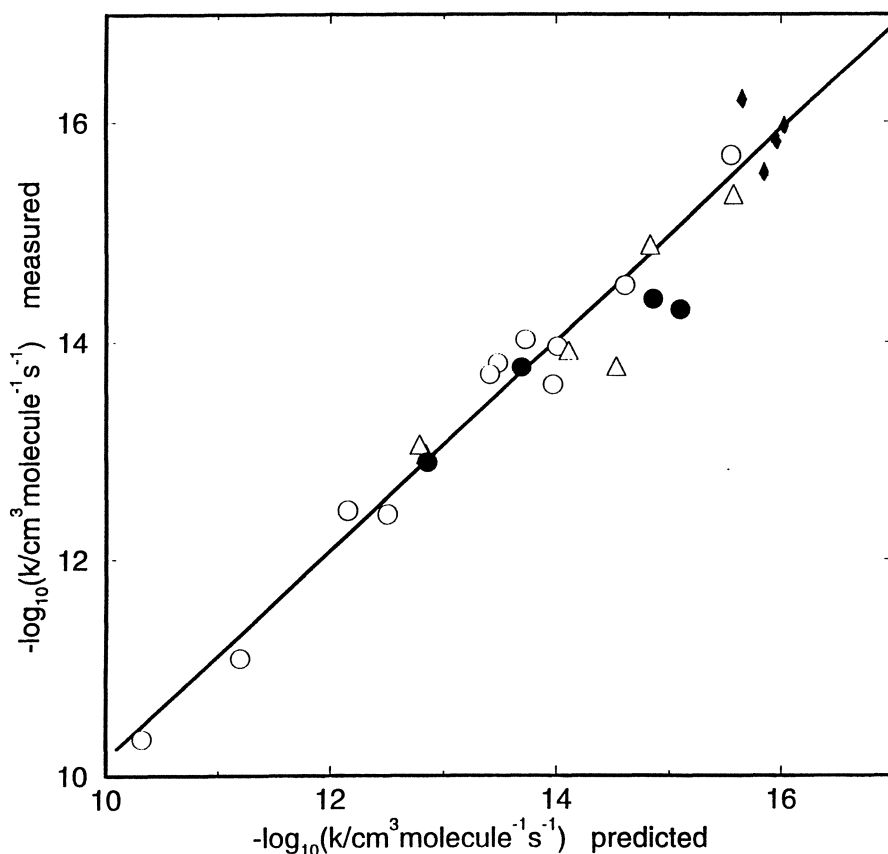
To complement the studies of the interaction between RO<sub>2</sub> and NO<sub>3</sub> radicals, we have carried out some studies on RO<sub>2</sub> + RO<sub>2</sub> systems, because this reaction, at least, must always compete with the reaction RO<sub>2</sub> + NO<sub>3</sub>. We have probed the processes by following the second-order decays of RO<sub>2</sub> for several partially and fully halogenated methyl peroxy radicals. Allowance is made in the analysis for the reaction RO<sub>2</sub> + HO<sub>2</sub> in those cases where HO<sub>2</sub> is a secondary product. The preliminary rate coefficients obtained are displayed in Table 2.

**Table 2:** Rate coefficients for the self-reaction of selected RO<sub>2</sub> radicals.

RO <sub>2</sub>	CH <sub>2</sub> BrO <sub>2</sub>	CHBr <sub>2</sub> O <sub>2</sub>	CH <sub>2</sub> ClO <sub>2</sub>	CHCl <sub>2</sub> O <sub>2</sub>	CF <sub>3</sub> O <sub>2</sub>
10 <sup>12</sup> k(298 K) / cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	2.0	2.5	1.0	4.0	2.1

### *Patterns of reactivity of the NO<sub>3</sub> radical*

Work on correlations of rate coefficients with ionisation potentials for the reactions of NO<sub>3</sub> with a series of alkenes has been extended. Ionisation potentials are determined using a semi-empirical molecular orbital package (MOPAC 5.0). We are now able to estimate both room-temperature rate coefficients and Arrhenius parameters for the reaction of NO<sub>3</sub> with a wide range of alkenes, including those containing vinylic chlorine atoms (which we earlier found difficult to handle). In an effort to improve our understanding of the physical basis of our observations, *ab initio* calculations have been performed on a limited number of compounds. Such calculations should overcome some of the limitations of the semi-empirical methods when applied to elements such as chlorine and bromine.



**Fig. 3:** Correlation for room-temperature rate coefficients in terms of *IP*.

○ alkenes and non-vinylic Cl-alkenes; ● Br-alkenes; △ Cl-alkenes with Cl at one end of double bond; ◆ Cl-alkenes with Cl at both ends of double bond.

**Assessment of achievement of project**

The work carried out within this project has provided answers to many of the questions posed at the outset. The data base for the kinetics of the reactions of  $\text{NO}_3$  has been extended considerably, new reactions of  $\text{NO}_3$  have been discovered, and correlations between reactivity and calculable molecular parameters have been found. The laboratory information required to evaluate the contribution of  $\text{NO}_3$  chemistry to night-time chemical transformation in the troposphere, including both oxidation and formation of  $\text{HNO}_3$ , is now on a firmer footing in several respects. These objectives were included in those of LACTOZ, which itself conformed with the overall aims of EUROTRAC. EUROTRAC also seeks to foster international co-operation. We have actively sought collaboration with other groups within Europe, and have worked most successfully with teams from Bordeaux, Castilla La Mancha, Dublin, Gothenburg, Kiel, Mainz, Orléans, Risø and Wuppertal.

**Acknowledgements to funding agencies**

We gratefully acknowledge the support received from the Natural Environment Research Council, the Department of the Environment, the Commission of the European Communities, and the Institut Français du Pétrole, as well as the University of Oxford.

### 3.24 Time-Resolved Studies of the NO<sub>2</sub> and OH Formation in the Integrated Oxidation Chain of Hydrocarbons

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#### Summary

The oxidation of alkanes, alkenes and simple aromatics at 293 K under NO<sub>x</sub> rich tropospheric conditions has been studied using laser pulse initiation combined with cw laser long path absorption/LIF for the detection of OH and NO<sub>2</sub>. In the case of aliphatic hydrocarbons the absolute yield and the kinetics of the formation of these products have been found to be sensitive indicators for the reaction behaviour of the oxy radicals RO. In combination with mechanistic simulations rate constants for individual reactions as well as branching ratios have been derived, which permit the evaluation of the compound specific NO/NO<sub>2</sub> conversion factors (NOCON - factors) for the first oxidation steps. In the case of benzene and toluene oxidation the results indicate that reaction of the primary formed X cyclohexadienyl radical (X = Cl, OH) with O<sub>2</sub> is the dominant pathway, although the rate coefficients were found to be lower than  $2 \times 10^{-16} \text{ cm}^3/\text{s}$ .

#### Aims of the research

As has been shown in various experimental studies the excimer laser photolysis/laser long path absorption/cw LIF technique developed in our laboratory within the LACTOZ program provides reliable information on branching ratios and rate coefficients in hydrocarbon oxidation under simulated NO<sub>x</sub> rich tropospheric conditions. As a systematic extension of our previous work on the alkane series C<sub>1</sub> – C<sub>6</sub> in the present period it was aimed to study:

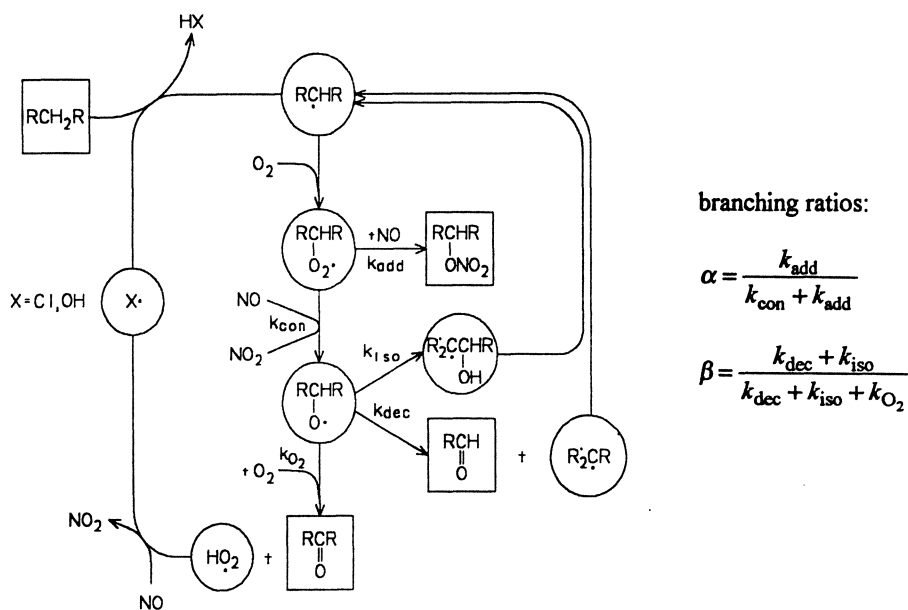
- the oxidation of long chain hydrocarbons (C<sub>7</sub>, C<sub>8</sub>) and selected isomers (*iso*-butane) and cyclic alkanes (*c*-hexane) to refine our understanding of oxy radical reaction pathways and possibly identify mechanistic characteristics. Moreover, branching ratios and integrated rate coefficients for oxy radical decomposition/isomerisation reactions were to be determined to extract substance specific NO/NO<sub>2</sub> conversion factors from this information.
- the oxidation of simple alkenes (ethene, propene and isoprene), in order to derive characteristic NOCON factors for this class of substances.
- the oxidation mechanism of simple aromatics including the addition/abstraction ratio in the initial oxidation step, as well as rate coefficients and branching ratios in the consecutive reactions of O<sub>2</sub> with the X cyclohexadienyl-adduct (X = Cl, OH)

### Principal experimental results

The oxidation of the hydrocarbons has been studied by observing the temporal evolution of OH and NO<sub>2</sub> following the pulse initiation of the oxidation chain using Cl atoms generated via excimer laser photolysis of Cl<sub>2</sub> at  $\lambda = 351$  nm. A detailed description of the experimental technique can be found elsewhere [1] and is not repeated here.

The temporal behaviour of the formation of NO<sub>2</sub> and OH reflects the time constant of the rate determining steps of their formation. Together with a complete chemical model and suitable adjustments of modelled and observed profiles individual rate constants were extracted. This data corresponds to an overall NO<sub>2</sub> (and therefore O<sub>3</sub>) yield per RH molecule entering the oxidation process.

The significance of NO<sub>2</sub> and OH profile measurement in the oxidation of selected alkanes and alkenes may be seen from consideration of the generalised reaction scheme as presented in Fig. 1.



**Fig. 1:** Generalised oxidation scheme for aliphatic hydrocarbons.

Decomposition or isomerization of the oxy radicals leads to the formation of another alkyl radical, followed by additional NO to NO<sub>2</sub> conversion. The generation of OH radicals is coupled with the formation of HO<sub>2</sub> radicals in the course of the reaction of the oxy radicals with O<sub>2</sub> and, therefore, reflects the

significance of this pathway. The experiments have been performed at  $p = 50$  mbar and  $T = 293$  K under different conditions characterised by a variation of NO  $\{(0.5\text{--}2.0) \times 10^{14} \text{ cm}^{-3}\}$  and O<sub>2</sub>  $\{(3.0\text{--}12.0) \times 10^{17} \text{ cm}^{-3}\}$  concentration.

### Alkanes

In Table 1 the experimental results for the alkanes investigated are summarised together with the branching ratio  $a$  and  $b$  (as defined in Fig. 1) and the ratios DNO<sub>2</sub> / DOH and DNO<sub>2</sub> / ΔRH (equivalent to the NOCON factor) extrapolated to lower tropospheric conditions. The NOCON factors have been determined neglecting the pressure dependence of the decomposition/isomerisation rate constants. C<sub>1</sub> to C<sub>6</sub>-alkanes have been investigated within LACTOZ I.

**Table 1:** Summary of results obtained for the oxidation of alkanes

C <sub>n</sub> H <sub>n+2</sub>	$\frac{k_{dec} + k_{iso}}{s^{-1}}$	$a^*$	$b$	DNO <sub>2</sub> / DOH $p(\text{O}_2) = 0.2 \text{ bar}$	DNO <sub>2</sub> / DRH $p(\text{O}_2) = 0.2 \text{ bar}$
CH <sub>4</sub>	—	—	—	2.0	2.0
C <sub>2</sub> H <sub>6</sub>	$\leq 1 \times 10^2$	0.0	$\leq 0.01$	2.0	2.0
C <sub>3</sub> H <sub>8</sub>	$\leq 4 \times 10^2$	0.02	$\leq 0.01$	2.01	1.96
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	$3.8 \times 10^3$	0.04	0.10	2.10	2.01
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	$1.1 \times 10^3$	0.09	0.03	2.03	1.85
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	$7.1 \times 10^3$	0.06	0.17	2.17	2.04
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	$3.3 \times 10^4$	0.12	0.49	2.49	2.19
<i>c</i> -C <sub>6</sub> H <sub>12</sub>	$3.0 \times 10^3$	0.07	0.07	2.07	1.92
<i>n</i> -C <sub>7</sub> H <sub>16</sub>	$4.5 \times 10^4$	0.24	0.54	2.54	1.93
<i>n</i> -C <sub>8</sub> H <sub>18</sub>	$4.7 \times 10^4$	0.37	0.56	2.56	1.61

\* weighted average value for all different oxy radicals

The branching ratio  $\beta$  generally increases with the chain length of the aliphatic hydrocarbon. The rate constants for the reactions of the oxy radicals with O<sub>2</sub> appear to be independent of the nature of the oxy radical (excl. CH<sub>3</sub>O) with  $k(\text{O}_2) = (8 \pm 2) \times 10^{-15} \text{ cm}^3/\text{s}$ , whereas the overall rates of decomposition and isomerisation depend both on the chain length and the structure of the radical.

### Alkenes

As can be seen from Fig. 1 the oxidation of alkenes generally corresponds to the alkane oxidation. However, it has to be considered that in this case the chlorine atom, which is used as a primary oxidant, predominantly adds to the double bond. Therefore, chlorine containing intermediates are formed. However, as a consequence of the oxidation mechanism only *b*-Cl oxy radicals are formed which are not expected to show significant deviations from the reactivity of their non-substituted analogues. In Table 2 the experimental results for alkenes are summarised when  $k(\text{O}_2)$  is fixed to  $8 \times 10^{-15} \text{ cm}^3/\text{s}$ .

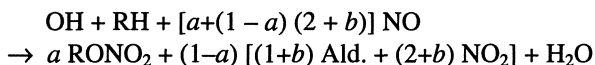


**Table 2:** Summary of results obtained for the oxidation of alkenes.

$C_nH_m$	$\frac{k_{dec} + k_{iso}}{s^{-1}}$	$a^*$	$b$	$DNO_2 / DOH$ $p(O_2) = 0.2 \text{ bar}$	$DNO_2 / DRH$ $p(O_2) = 0.2 \text{ bar}$
$C_2H_4$	$\leq 2 \times 10^3$	0.0	$\leq 0.05$	2.0	2.0
$C_3H_6$	$\leq 2 \times 10^3$	0.024	$\leq 0.05$	2.0	1.96
Isoprene	$1.2 \times 10^4$	0.061	0.34	2.34	1.91

\* weighted average value for all different oxy radicals

Based on the values for the parameters  $a$  and  $b$  for any aliphatic hydrocarbon, its oxidation to the primary carbonyl compound may be summarised by the overall mechanistic equation

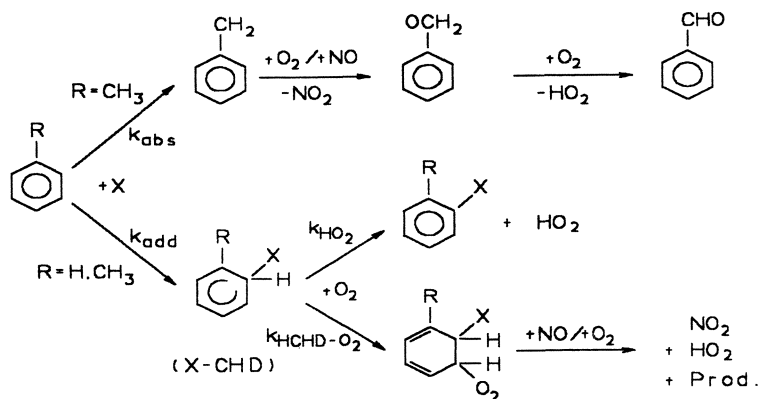


which may be a useful approach to a condensed oxidation mechanism in tropospheric modelling. In general, the results obtained

- are in agreement with literature data [3–5] concerning the fact, that the significance of decomposition and/or isomerisation reactions of the oxy radicals increases with the number of C atoms;
- show, that the relation  $DNO_2 / DRH$ , which is related to the ozone formation potential lies below 2.2 for all hydrocarbons investigated when the results are extrapolated to lower tropospheric conditions.

### Aromatics

The oxidation of benzene and toluene has been studied on the basis of a simplified reaction scheme presented in Fig. 2. The specific results obtained are collected in Table 3.



**Fig. 2:** Generalised oxidation scheme for simple aromatic hydrocarbons.

**Table 3:** Summary of results obtained for the oxidation of aromatic hydrocarbons.

aromatic	initiating radical	initiation reactions		X-CHD reactions	
		$k_{\text{add}}/k_{\text{abs}}$	$\frac{\sum k(\text{O}_2)}{10^{-16} \text{ cm}^3 \text{ s}^{-1}}$	$\frac{k(\text{HO}_2)}{k(\text{XCHD}-\text{O}_2)}$	
benzene	Cl	—	$1.2 \pm 0.6$	$0.50 \pm 0.25$	
toluene	OH	$\geq 6$	0.4–2.0	insensitive	

The results for the rate coefficients and the branching ratio for the initial addition/abstraction reactions of toluene with OH are in agreement with previous measurements [7]. For benzene and toluene the values for the rate coefficients of the reactions of X-CHD with O<sub>2</sub> tend to be lower than previously reported by Zetzsch *et al.* [7]. However, it has to be recognised that the data of the Cl atom initiated oxidation of benzene is based on the investigation of chlorine and hydroxyl containing hexadienyl radicals. A separation of the O<sub>2</sub> reactions of the different radicals was not possible.

In the OH initiated oxidation of toluene a rough determination of the rate coefficient of  $k(\text{O}_2)$  was possible. The biexponential decay profiles of OH and the extend of NO<sub>2</sub> formation appeared to be sensitive to the overall X CHD loss. However, the relatively fast recycling of OH due to formation of HO<sub>2</sub> during both degradation pathways made it impossible to deduce a branching ratio for these reactions.

## Conclusions

The present experiments were aimed at a quantification of NO/NO<sub>2</sub> conversion factors in the first oxidation step of a series of alkanes, alkenes and aromatics. Moreover, the experimental approach, namely time-resolved measurement of OH and NO<sub>2</sub> evolution together with numerical simulation permitted the extraction of individual rate coefficients for the decomposition/isomerisation of oxy radicals. It has been shown that these rate coefficients increase with the size of the molecule up to a limiting value of  $\sim 10^5 \text{ s}^{-1}$  at 298 K. The NOCON factors derived may be used to extract condensed mechanistic equations for the primary oxidation steps of hydrocarbons. The values derived in this work are integrated quantities comprising weighted averages of all fractional yields of detailed mechanisms as initiated by the attack of the primary oxidant to the various positions of the parent compound.

Together with the rate coefficients of primary oxidant attack ( which correspond to the lifetime of the parent compound) NOCON factors may be used in atmospheric chemical - dynamic modelling to derive photochemical ozone creation potentials (POCP - values) for the individual hydrocarbons. POCP- values are expected to be the primary assessment factors in photochemical smog abatement strategies.

### Acknowledgement

Support of this work by the "Bundesministerium für Forschung und Technologie" within the EUROTRAC subproject LACTOZ is gratefully acknowledged.

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### 3.25 Adduct Formation of OH with Aromatics and Unsaturated Hydrocarbons and Consecutive Reactions with O<sub>2</sub> and NO<sub>x</sub> to Regenerate OH

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#### Summary

Using time-resolved resonance fluorescence detection of OH, rate constants for the removal of aromatic<sup>•</sup>-OH adducts from the thermal equilibrium between OH and adduct were measured [1–4] for the aromatics benzene, toluene, *m*- and *p*-xylene, phenol, *m*-cresol, aniline and naphthalene. In the case of O<sub>2</sub> as scavenger, the rate constants (cm<sup>3</sup>/s) fall into two ranges depending on whether the aromatic is hydroxyl-substituted (phenol:  $3 \times 10^{-14}$ , *m*-cresol:  $8 \times 10^{-14}$ ) or not ( $2 \times 10^{-16}$  to  $2 \times 10^{-15}$ ). In additional smog chamber studies [5] on benzene, toluene, and *p*-xylene at low O<sub>2</sub> concentrations the FP/RF results were confirmed. Although the reactions with NO<sub>2</sub> as scavenger are fast ( $2.5$  to  $5 \times 10^{-11}$ ), they are unimportant at atmospheric conditions (based on our results, however, high-NO<sub>x</sub> smog-chamber studies had to be reinterpreted [6]). NO turned out to be unreactive against aromatic<sup>•</sup>-OH adducts, and upper limits (of a few  $10^{-14}$ ) were obtained.

Cycling experiments (FP/RF measurements in the systems OH/unsaturated HC/O<sub>2</sub>/NO) with some of the aromatics [3, 7] (at temperatures, where the back-decomposition of the adduct is slow) and also with isoprene, showed that the O<sub>2</sub> reactions of the adducts lead to the formation HO<sub>2</sub> (detected by conversion to OH: HO<sub>2</sub> + NO → OH + NO<sub>2</sub>) with high yield and without detectable delay (< 50 ms). Cycling of OH with acetylene [8–10] is rapid in the absence of NO.

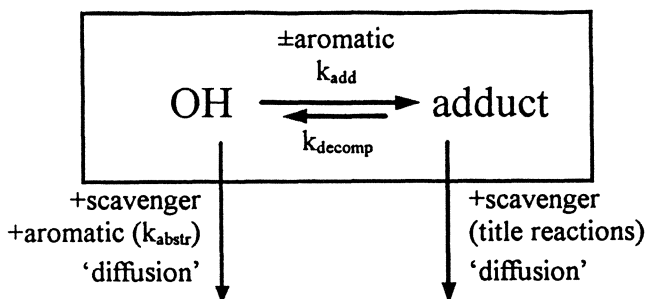
#### Aims of the research

For most unsaturated hydrocarbons, addition of OH is the first and rate-limiting step of the photochemical reaction chain. In the case of aromatics, which are emitted from automobiles, forest fires and fuel wood burning [11], the addition reaction is reversible at atmospheric temperatures. The effective rate constant for removal of the aromatic depends on consecutive reactions of the adduct. Prior to LACTOZ, consecutive reactions with O<sub>2</sub> had not been detected for benzene<sup>•</sup>-OH ([12],  $k < 2 \times 10^{-16}$  cm<sup>3</sup>/s) and toluene<sup>•</sup>-OH ([13]  $k < 10^{-15}$  cm<sup>3</sup>/s), so that Atkinson *et al.* concluded from their product studies [14, 15] that the corresponding NO<sub>2</sub> reactions [12, 16] dominate under their experimental conditions and possibly even in the troposphere. The project was undertaken to decide what is the second

reaction step under tropospheric conditions and to gain further insight into the mechanism. From the products of aromatic oxidation and their properties one may eventually explain the high ozone formation potential of aromatics found in smog chambers and extrapolate it to tropospheric conditions.

## Results

The method of flash photolysis/resonance fluorescence (FP/RF) and the details of our setup have been described elsewhere [17]. Reactions of the adduct aromatic-OH are determined from biexponential time profiles of OH, monitored by resonance fluorescence on a 1-to-600 ms timescale. The slope of the first exponential is dominated by the back and forth reaction between OH and the adduct, whereas the title reactions add to the final decay rate, common to OH and the adduct. The reaction mechanism is given in Fig. 1.



**Fig. 1:** The title reactions, adduct + scavenger, are studied by evaluating biexponential time profiles of OH. The structure of the adduct resembles cyclohexadienyl.

A set of decays recorded at constant temperature and pressure and various concentrations of hydrocarbon, R, and scavenger, S, is evaluated as a whole by fitting to them simulated decays calculated according to the 2nd order differential equation:

$$\begin{aligned} d[\text{OH}]/dt &= -a[\text{OH}] + b[\text{adduct}] \\ d[\text{adduct}]/dt &= c[\text{OH}] - d[\text{adduct}] \end{aligned}$$

with concentration-dependent coefficients parameterised as follows

$$\begin{aligned} a &= a_0 + (k_{\text{abstr}} + k_{\text{add}}) [\text{R}] + a_S [\text{S}] \\ b \cdot c &= k_{\text{decomp}} \cdot k_{\text{add}} [\text{R}] \\ d &= k_{\text{adduct-diff}} + k_{\text{decomp}} + d_R [\text{R}] + d_S [\text{S}] \end{aligned}$$

(inspection of the OH-part of the solution [1] shows that two of the four coefficients  $a$  to  $d$  occur always as product  $bc$ , *i.e.*, only three parameters are obtainable from a single biexponential decay of OH – plus its absolute intensity, which has no significance in pseudo-first-order kinetics). The fit parameters  $a_S$  and  $d_S$  are the rate constants for reactions of OH and adduct with the scavenger. The parameter  $d_R$ , denoting a reaction of the adduct with the aromatic reactant was never found to be of significance. The three remaining fit parameters,  $a_R$ ,  $bc_R$  and  $d_0$ , are combinations of four rate constants: abstraction, adduct formation and decomposition and a loss of the adduct not leading back to OH, slightly faster than adduct diffusion alone (4 to 10 s<sup>-1</sup> instead of < 1 s<sup>-1</sup>). Especially at the lower temperatures, where  $k_{\text{decomp}}$  is slow, this degeneracy leads to increased uncertainties for the rate constants involved, but it does not influence the evaluation of the title reactions.

### Pure aromatics

Rate constants for adduct formation and decomposition and for the abstraction pathway were obtained from experiments in the absence of NO<sub>x</sub> and O<sub>2</sub>. Values for the sum of both pathways ( $k_{\text{abstr}} + k_{\text{add}}$ , unaffected by the degeneracy) are given in Table 1. They are in good agreement with literature data [18]. The rate constants  $k_{\text{decomp}}$  are very similar for the studied aromatics, in the range 1 to 10 s<sup>-1</sup> at 298 K, with activation energies of 8000 to 9000 K, except for naphthalene–OH ( $k_{\text{decomp}} = 14$  s<sup>-1</sup> at 400 K). Earlier estimates of  $k_{\text{decomp}}$  [18] based on the observation of non-exponential decays of OH at faster timescales, *i.e.*, higher temperatures, are in reasonable agreement with our results. Our branching ratios for the abstraction pathway (see also Table 1) tend to be somewhat lower than is extrapolated from high-temperature data [18] and, if combined with them, extrapolate to room temperature values in agreement with branching ratios derived from product studies [14, 15, 19, 20].

**Table 1:** Rate constants at room temperature and formal activation energies for the total OH reactivity of aromatics,  $k_{\text{OH}} = k_{\text{abstr}} + k_{\text{add}}$ , obtained from measurements in 130 mbar Ar (slightly below the high-pressure limit) and within the indicated temperature range. Rate constants for the abstraction pathway are given at temperatures where the observed losses are not dominated by the unresolved loss of adduct not leading back to OH.

	$\frac{k_{\text{OH}}(298 \text{ K})}{10^{-12} \text{ cm}^3 \text{ s}^{-1}}$	$\frac{E/R}{\text{K}}$	$\frac{T - \text{range}}{\text{K}}$	$\frac{k_{\text{abstr}}}{10^{-13} \text{ cm}^3 \text{ s}^{-1}}$	$\frac{T}{\text{K}}$
benzene	1.05	-150	298–353	< 0.3	340
naphthalene	27.1	-630	295–352	< 2	420
toluene	6.38	-900	299–339	5.7 ± 1	340
<i>p</i> -xylene	15.8	-590	274–334	24 ± 3	390
<i>m</i> -xylene	21.1	-470	303–357	20 ± 2	380
phenol	24.7	-530	245–353	55 ± 7	340
<i>m</i> -cresol	56	-500	264–353	51 ± 5	380
aniline	100	-680	277–344	–	

We also studied the reaction of OH with isoprene [7] (250 to 440 K) and with acetylene [9] (294 to 353 K). For isoprene we obtained the expression  $k_{\text{OH}} = 0.97 \times 10^{-10} (T/298 \text{ K})^{-1.36} \text{ cm}^3/\text{s}$ . The decays were monoexponential up to 440 K, *i.e.*, no indication for decomposition of the adduct. For acetylene we obtained the Arrhenius expression  $k_{\text{OH}} = 1.2 \times 10^{-12} e^{-204 \text{ K}/T} \text{ cm}^3/\text{s}$  and confirmed the pressure dependence in good agreement with literature data

### Adduct + NO<sub>2</sub>

In the case of NO<sub>2</sub> as scavenger the differential equation is supplemented by a source term of OH due to the conversion of H atoms (from the H<sub>2</sub>O photolysis) by  $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$  leading to triexponential decays. Fig. 2 shows the measurements on *p*-xylene. While the determination of three exponentials from individual decays is too unstable, the use of the analytical solution [M. Siese in ref. 1] in a global fit leads to the rate constants given in Table 16, Chapter 2 of the general introduction. The reactions are fast – several  $10^{-11} \text{ cm}^3/\text{s}$  – and show a weak dependence on type of aromatic and temperature. Literature values on benzene [12, 21, 22] are considerably scattered, whereas the single literature value on toluene [23] is in reasonable agreement with our results.

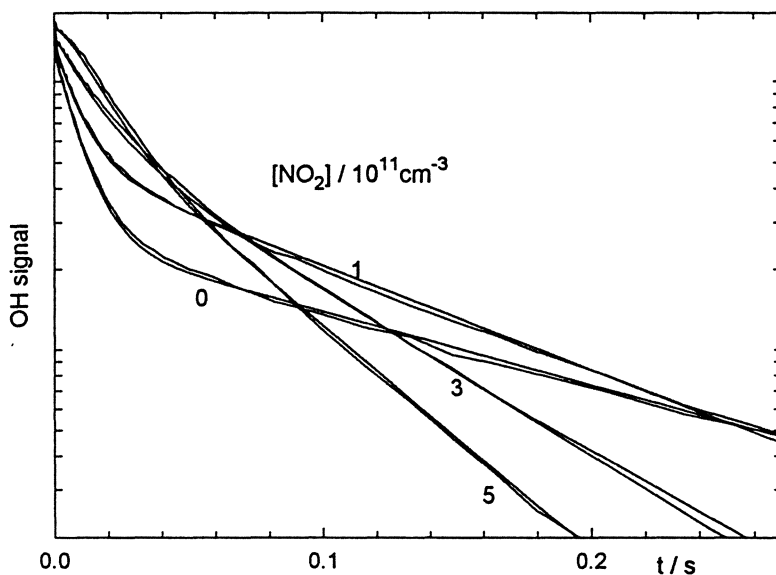


Fig. 2: Decays of OH in the presence of *p*-xylene ( $5.1 \times 10^{12} \text{ cm}^{-3}$ ) and increasing amounts of NO<sub>2</sub> at 317 K and 130 mbar of Ar. The continuous lines indicate the result of a triexponential global fit according to the mechanism of Fig. 1 plus an OH source due to conversion of H atoms by NO<sub>2</sub>. A minor discrepancy at  $t < 50 \text{ ms}$  has been reduced by allowing  $[\text{H}]_0 \neq [\text{OH}]_0$ : 20 % extra H atoms are assumed to stem from the photolysis of *p*-xylene. This degree of freedom has virtually no influence on the value of the target reaction  $-k(p\text{-xylene} - \text{OH} + \text{NO}_2) = (3.5 \pm 0.5) \times 10^{-11} \text{ cm}^3/\text{s}$ .

### Adduct + NO

This reaction was found to be slow compared to NO reactions with other organic radicals: Upper limits between 0.3 and  $1 \times 10^{-13}$  cm<sup>3</sup>/s were obtained by careful consideration of interfering reactions: NO<sub>2</sub> impurities in the NO are undesirable for two reasons. (i) The fast reaction adduct + NO<sub>2</sub> mimics a NO reactivity – probably the cause for a higher rate constant in the literature [12],  $k(\text{benzene-OH} + \text{NO}) = 1 \times 10^{-12}$  cm<sup>3</sup>/s. We successfully purified the NO with FeSO<sub>4</sub>. (ii) Although the concentration of NO<sub>2</sub> was measured (in the absence of aromatic) to be at most 10<sup>-4</sup> relative to NO, *i.e.*, well below [OH]<sub>0</sub>, the effect of the OH source term (H + NO<sub>2</sub>) may still be important in the presence of aromatic, because of the lower level of OH during the late part of the biexponential decays. Model calculations with [NO<sub>2</sub>] = 10<sup>-4</sup> [NO] showed that the final slope of the decays may even *decrease* with NO. Finally, the unavoidable reaction OH + NO + M → HONO + M (~ 10<sup>-12</sup> cm<sup>3</sup>/s at our pressure and temperature) is formally independent (see above *a*S and *d*S), but increases the uncertainty.

### Adduct + O<sub>2</sub>

In order to measure these low rate constants (with [O<sub>2</sub>] limited to below 10<sup>17</sup> cm<sup>-3</sup> because of quenching of the OH fluorescence) slow decays in the absence of O<sub>2</sub> are required, *i.e.*, a clean set-up, pure inert gas, a low level of radicals to avoid radical-radical reactions (here: S/N > 100 at 10<sup>10</sup> cm<sup>-3</sup>) and a non-reactive source of OH (here: flash photolysis of H<sub>2</sub>O). In the absence of reactants the decay rate of OH is as low as 3 to 4 s<sup>-1</sup>, with a stability of ±0.2 s<sup>-1</sup>.

Up to some 10<sup>17</sup> cm<sup>-3</sup> of O<sub>2</sub> has been applied to considerably steepen the final exponential curve. The loss of fluorescence intensity due to quenching was compensated by averaging several hundred shots. An initial concentration of O atoms (about ten times the OH concentration at 10<sup>17</sup> cm<sup>-3</sup> O<sub>2</sub>) is estimated by comparing the absorption cross sections of H<sub>2</sub>O and O<sub>2</sub>. Because of the low flash energy, ‘O + radical’ reactions are still unimportant, but a possible OH formation by ‘O + aromatic’ would lead to triexponential decays with the rate of the third exponential, up to 100 s<sup>-1</sup>, dominated by the competing three-body reaction with O<sub>2</sub> (forming the less reactive ozone). Since the observed decays do not deviate significantly from the model, upper limits are estimated for that OH forming reaction: 0.2, 1, 8, and 10 × 10<sup>-14</sup> cm<sup>3</sup>/s for benzene, toluene, *p*-xylene, and aniline, respectively, and about collision frequency for phenol and *m*-cresol (the trend being due to the concentrations of aromatic and O<sub>2</sub> applied when measuring the title reactions).

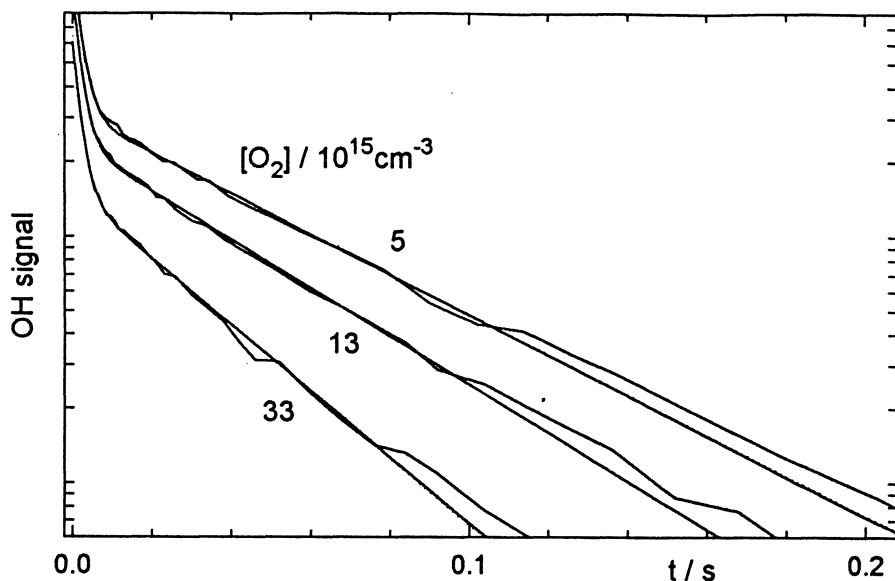
Fig. 3 shows decays in the presence of 3 × 10<sup>13</sup> cm<sup>-3</sup> of toluene and increasing amounts of O<sub>2</sub> together with the results of individual fits (broken lines) and of the global fit (full lines) according to the mechanism of Fig. 1.

The obtained rate constants for the O<sub>2</sub> reaction of the adducts divide into two ranges depending on whether the aromatic is hydroxyl-substituted or not



(Table 16, Chapter 2). At tropospheric conditions, the  $O_2$  reaction dominates – even in the case of benzene.

The competition with the thermal back-decomposition of the adduct,  $k_{\text{decomp}}$ , was studied by lowering the  $O_2$  concentration in chamber experiments on benzene, toluene, and *p*-xylene (with photolysis of  $H_2O_2$  as  $NO_x$ -free source of OH) [5]. At low levels of  $O_2$ , the removal of the aromatics (observed by cryo-focusing/GC/FID) corresponds to the abstraction channel, and increases to the sum of abstraction and addition in the limit of high  $O_2$ . In Table 2, ratios  $k_{\text{decomp}} / k(O_2)$  obtained from such measurements are compared to those calculated from our absolute rate constants. That an earlier chamber study on toluene and *p*-xylene [24] shows much less  $O_2$  dependence, has been attributed [19] to rather high concentrations of hydrocarbons,  $H_2O_2$ , and thus radicals in their experiments leading to further loss processes of the adduct.



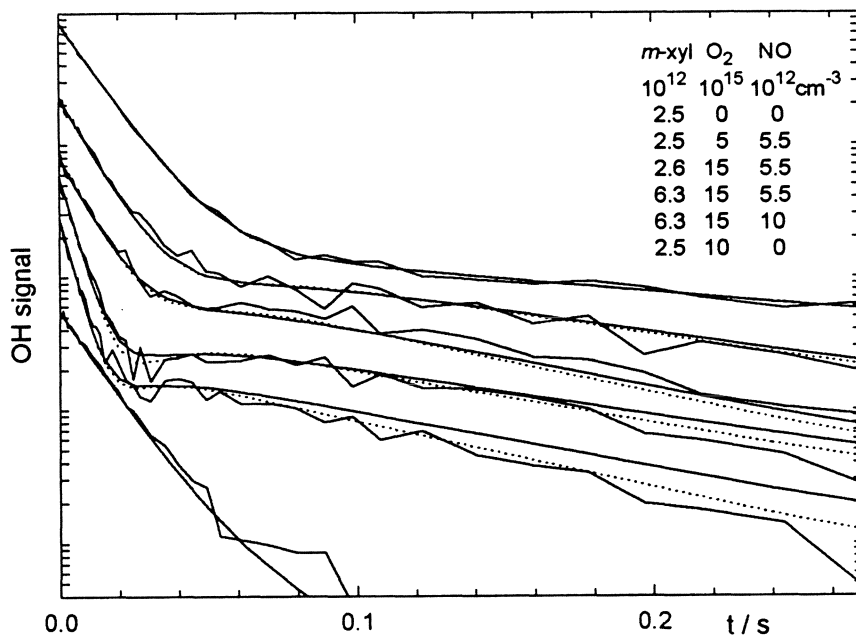
**Fig. 3:** Decays of OH in the presence of toluene ( $85 \times 10^{12} \text{ cm}^{-3}$ ) and increasing amounts of  $O_2$  at 339 K and 134 mbar of Ar. The biexponential individual fits (dotted lines) and the global fit according to the mechanism in Fig. 1 (continuous lines) yield the identical result,  $k(\text{toluene} + \text{OH} + O_2) = (5.6 \pm 0.6) \times 10^{-16} \text{ cm}^3/\text{s}$ .

**Table 2:** Ratios  $k_{\text{decomp}} / (k(\text{O}_2) \cdot 10^{16} \text{ cm}^{-3})$  obtained from smog chamber data [5] compared to those calculated with our absolute rate constants (300 K).

	FP/RF	smog chamber
benzene	2.3	1.8
toluene	1.1	1.2
<i>p</i> -xylene	0.52	0.36

Cycling experiments product of the reaction of  $\text{O}_2$  with the adduct. The resulting cycle of odd-hydrogen species allows us

- to measure  $k_{\text{add} + \text{O}_2}$  at temperatures too low for the direct regeneration of OH by thermal decomposition of the adduct,
- to determine the yield of  $\text{HO}_2$  (a possible loss reaction would be  $\text{ROO} + \text{NO} \rightarrow \text{RONO}_2$  instead of the chain propagation step  $\rightarrow \text{RO} + \text{NO}_2$ , see the case of isoprene below),
- to detect delays in the formation of  $\text{HO}_2$ .



**Fig. 4:** Cycling of OH in the presence of varying concentrations of *m*-xylene,  $\text{O}_2$ , and NO at 286 K and 255 mbar of He. The curves are arbitrarily shifted for clarity. The weak second exponential in the absence of  $\text{O}_2$  (topmost curve) is due to the thermal decomposition of the adduct – which is scavenged by the addition of  $\text{O}_2$  (lowest curve). With the addition of NO the signal comes up again (to about 4 times the level without  $\text{O}_2$ ; compare curves 1 and 3 at  $t = 0.1 \text{ s}$  respective to their initial intensities). The full and dotted lines are calculated by two alternative global models (see text).

Fig. 4 shows recent measurements with *m*-xylene. As with benzene and toluene, the measurements are fairly well reproduced by a model including only the prompt formation of HO<sub>2</sub> with unit yield. Based on the depth and width of the dip between the initial and final exponential decay, we can state that, if HO<sub>2</sub> is not formed *via* the prompt path, any further reaction steps should cause delays not larger than 20 ms (based on our experimental conditions), *i.e.*,

- any unimolecular step should be faster than 50 s<sup>-1</sup>
- any reaction step with NO should be faster than  $k(\text{HO}_2 + \text{NO})$
- any reaction step with O<sub>2</sub> should be faster than  $k(\text{add} + \text{O}_2)$ .

In the case of *m*-xylene, however, the dependence of the final signal level on NO concentration could be fitted only by either allowing the rate constant of HO<sub>2</sub> + NO → OH + NO<sub>2</sub> to settle at half the literature value (full lines in Fig. 4) or by inserting a further reaction with NO into the cycle: RO<sub>2</sub> + NO → RO + NO<sub>2</sub> (followed by the fast step RO + O<sub>2</sub> → HO<sub>2</sub>). The latter alternative allows us to slightly improve the modelling of the final decay rates by introducing the loss reaction RO<sub>2</sub> + NO → RONO<sub>2</sub> (dotted lines in Fig. 4).

The results for  $k_{\text{add} + \text{O}_2}$  obtained from cycling experiments are summarised in Table 3. They are in good agreement with those obtained by thermal decomposition of the adduct (at slightly higher temperatures).

**Table 3:** Rate constants  $k(\text{adduct} + \text{O}_2)$  derived from cycling experiments.

	<i>T</i> / K	$k(\text{add} + \text{O}_2)$ 10 <sup>-16</sup> cm <sup>3</sup> s <sup>-1</sup>
benzene	290	2.3 ± 0.3
	273	2.0 ± 0.3
toluene	295	6 ± 1
	258	5 ± 1
<i>m</i> -xylene	286	20 ± 4
naphthalene	336	0.8 ± 0.3
	298	8 ± 3
isoprene	345	0.6 × 10 <sup>4</sup>
	300	2.0 × 10 <sup>4</sup>
acetylene	296	(4.6 ± 0.4) × 10 <sup>4</sup>

First cycling experiments with isoprene [8] showed that the reaction of the adduct with O<sub>2</sub> is on the order of 10<sup>-12</sup> cm<sup>3</sup>/s, that HO<sub>2</sub> is a delayed product and that a chain-terminating reaction with NO is in competition (at experimental NO concentrations) with a chain-propagating reaction with O<sub>2</sub>.

In case of acetylene, OH is regenerated directly in a reaction of the adduct with O<sub>2</sub> [25]. We reinvestigated this reaction using FP/RF [8,9] and obtained a slightly negative temperature coefficient (294–353 K) and no pressure dependence (16–260 mbar Argon). The OH regeneration yield was found to be 86 % at room temperature and 260 mbar. However, at oxygen mixing ratios exceeding 1 % (studied by laser photolysis/cw uv laser long-path absorption [10]) this yield

decreases markedly – from 82 % at 6 mbar O<sub>2</sub> (in 1 bar N<sub>2</sub>) to 70 % in synthetic air to 57 % in pure oxygen. The measurements are in accord with a model where the OH yield is lower in the reaction of O<sub>2</sub> with not fully thermalised adducts.

### Achievements

In the atmosphere the reactions of the adducts aromatic-OH with O<sub>2</sub> dominate over their NO<sub>2</sub> reactions (and the reactions with NO are totally unimportant). However, this competition is at work in smog chamber experiments in the presence of NO<sub>x</sub>. Product studies from benzene, toluene [14] and the xylene isomers [15,6] show a dependence on NO<sub>2</sub> of the nitroaromatic yields in rough agreement with our absolute rate data.

### Acknowledgements

Support from the BMBF (grant 07 EU 705 A/O) and the CEC (grants STEP 0007-C and EV5V-CT93-0309) is gratefully acknowledged.

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# Subject Index

## A

- absorption cross-sections
  - carbonyl compounds 59, 60
  - formaldehyde 59
  - NO<sub>2</sub> 59, 158
  - organic nitrates 62
  - ozone 57, 158
  - PAN 62
- adducts
  - aromatic OH 247
- alkanes 243
- alkenes 29, 167, 203, 243
- alkoxy radical 54, 149
  - production from oxidation of hexyl nitrites and hexane 131
- alkylperoxy radical 225
- aniline 247
- Arrhenius parameters
  - nitrate radical reactions 236
  - ozone with cycloalkenes 220
  - reaction of OH radical with aromatic compounds 130, 249
  - reaction of OH radical with ethers 130

## B

- benzene 102, 244, 247
- benzyl radical
  - reaction with NO 102
  - reaction with NO<sub>2</sub> 102
  - reaction with O<sub>2</sub> 102
- biogenic compounds 68
- branching ratios
  - nitrate radical formation 49
  - OH radical reaction with alkanes and alkenes 82
  - OH radical with aromatics 249
  - oxidation of alkanes 243

- oxidation of alkenes 244
- peroxy radical reactions 36
- self-reactions of alkylperoxy radicals 227
- toluene 104
- xylene 104
- butane
  - photo-oxidation 76

## C

- carbonyl compounds 59, 165
- carbonyl O oxides 201
- CH<sub>3</sub>O<sub>2</sub> (methyl peroxy radical) reactions 210
- Cl atom
  - reaction with alkyl nitrates 215
  - reaction with alkyl nitrites 215
  - reaction with nitroalkanes 215
- continuous-flow reactor 233
- Criegee radicals 201, 210

## E

- ethene 83
- experimental techniques
  - chemical amplification 94
  - continuous-flow reactor 233
  - cycling experiment 253
  - detection of 1-hydroxy-hydroperoxides 75
  - determination of hydroperoxides 74
  - discharge flow method 186
  - enrichment of hydroperoxides 75
  - GC/MS determination of hydroperoxides 76
  - HPLC fluorescence 107
  - laser flash photolysis 186, 233
  - laser-induced fluorescence 186
  - matrix isolation 203

photolysis system 160  
 pulse radiolysis 171, 214  
 stopped-flow apparatus 233  
 time-resolved resonance fluorescence  
 247  
 tuneable diode laser absorption  
 spectroscopy 94  
 UV absorption spectrometry 145,  
 171

## F

formaldehyde 59

## H

HNO<sub>3</sub>  
   liquid-phase decomposition 92  
 hydrogen atom abstraction 225  
 hydroperoxide  
   formation in ozonolysis of alkenes  
   106  
 hydroperoxide distribution  
   ozonolysis of alkenes 108  
 hydroperoxide formation yields 33

## I

isomerisation 192  
 isoprene 70, 116  
   oxidation 68, 84  
   oxidation products 86  
   reaction with OH radical 84  
   reaction with ozone 85

## M

*m*-cresol 247  
 mechanism reduction techniques 188

## N

N<sub>2</sub>O  
   sources 93  
 naphthalene 247  
*n*-butoxy radical 192  
   decomposition 196

isomerisation 196  
 oxidation 197  
 nitrate radical 20, 61  
   atmospheric significance 93  
   reaction with alcohols 154  
   reaction with alkanes 235  
   reaction with alkenes 24, 115, 152  
   reaction with aromatic compounds  
   25  
   reaction with DMS 136  
   reaction with esters 154  
   reaction with ethers 154  
   reaction with inorganic radicals 237  
   reaction with inorganic species 28,  
   139  
   reaction with isoprene 116  
   reaction with organic compounds  
   114  
   reaction with peroxy radicals 26, 92,  
   136, 164  
   reactions 209  
   reactions with inorganic species 237  
   reactions with unsaturated  
   hydrocarbons 80  
   self-reactions 237  
   temperature dependence of reactions  
   235

## NO

  reaction with peroxy radical 170  
 NO<sub>2</sub> photolysis 152  
 NO<sub>y</sub> species  
   equilibrium 118

## O

OH radical 13  
   reaction with alcohols 140  
   reaction with alkanes 225  
   reaction with alkyl nitrates 215  
   reaction with alkyl nitrites 215  
   reaction with aromatic compounds  
   130  
   reaction with benzene 101  
   reaction with CH<sub>4</sub> 140

- reaction with diethyl ether (products) 131
  - reaction with ethers 129, 140
  - reaction with isoprene 84
  - reaction with nitrates 170
  - reaction with nitrites 170
  - reaction with nitroalkanes 170, 215
  - reaction with nitrogen-containing compounds 170
  - reaction with organic ketonitrates and dinitrates 82
  - reaction with *p*-xylene 64, 86
  - reaction with toluene 64, 86, 101
  - reaction with unsaturated carbonyl compounds 88
  - reaction with VOC 186
  - reaction with saturated hydrocarbons 80
  - OH radical formation yield 31, 222
  - ozone reactions 32
  - reaction of ozone with ethene and cycloalkenes 221
  - OH radical reaction products
    - reaction with *p*-xylene 87
    - reaction with toluene 87
  - organic radical
    - self-reactions 238
  - oxidation
    - alkanes 243
    - alkenes 243
    - aromatic compounds 63
    - benzene 244
    - biogenic compounds 68
    - isoprene 68
    - p*-xylene 67
    - toluene 67, 244
  - oxidation (nitrate radical-induced)
    - isoprene 70
  - oxidation (OH radical-induced)
    - 2,3-dimethylbutane product distribution 226
    - cyclohexane product distribution 229
    - isobutane product distribution 226
    - isopentane product distribution 227
    - isoprene 69
    - isoprene product distribution 230
    - methyl-substituted 1-butenes product distributions 229
    - n*-pentane product distribution 227
    - toluene product distribution 230
  - oxy radical 53
    - reactions 125
  - ozone
    - absorption cross-section 57
  - ozonolysis 200
    - alkenes 29, 33, 111, 167, 203
    - butenes 210
    - ethene 83, 107
    - isoprene 71, 107, 210
    - isoprene (product yields) 33
    - pinenes 107
    - propene 107
    - reaction with butenes 222
    - reaction with cycloalkenes 222
- ## P
- PAN decomposition 152
  - peroxide formation 32
  - peroxy radical 34, 164
    - absorption spectra 162
    - branching ratios 123
    - generation 121
    - reaction with  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  148
    - reaction with  $\text{CH}_3\text{O}_2$  46, 148
    - reaction with  $\text{HO}_2$  35, 124
    - reaction with nitrate radical 26, 92, 164
    - reaction with NO 46
    - reaction with  $\text{NO}_2$  149
    - reactions 120
    - reaction with  $\text{HO}_2$  147
    - self-reactions 44, 123, 146, 163
    - UV absorption spectra 122, 145
  - peroxynitrates 51, 52, 81
  - phenol 247
  - photolysis
    - alkanes 76
    - alkenes 77

- aromatic hydrocarbons 77
  - butane 76
  - carbonyl compounds 165
  - chlorinated hydrocarbons 78
  - ketones 77
  - photolysis frequencies 60
  - p*-xylene 86
  - pyruvic acid 62
- Q**
- quantum yields 59
- R**
- rate constant
    - alkoxy radical with O<sub>2</sub> 55
    - alkoxy radicals 54, 228
    - Cl atom with RNO<sub>x</sub> 172
    - from cycling experiments 254
    - nitrate radical reactions 154, 236
    - nitrate radical with inorganic species 28
    - nitrate radical with peroxy radicals 26
    - nitrate radical with VOC 22
    - NO with RO<sub>2</sub> 174
    - OH radical with aromatic compounds 130
    - OH radical with aromatics 249
    - OH radical with ethers 129
    - OH radical with RNO<sub>x</sub> 172
    - OH radical with VOC 15, 18, 187
    - organic radical self-reactions 238
    - ozone (temperature dependence) 31
    - ozone reactions 31
    - ozone with cycloalkenes 220
    - peroxy radical reactions 36
    - peroxy radical with HO<sub>2</sub> 124
    - radicals derived from aromatic VOCs 65
    - RO<sub>2</sub> radical with NO<sub>x</sub> 47
  - relative rate experiment 215
  - RO<sub>x</sub>
    - measurement campaigns 95
- S**
- s*-butoxy radical 192
  - reactions 194
  - structure-reactivity relationship 235
  - peroxy radical 35
- T**
- terpenes 68
  - toluene 86, 101, 102, 244, 247
- U**
- UV absorption spectra
    - peroxy radicals 162
- X**
- xylene 102, 247