

Springer Atmospheric Sciences

Hajime Akimoto

# Atmospheric Reaction Chemistry

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# Atmospheric Reaction Chemistry

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# Preface

Twenty-five years have passed since atmospheric chemistry was established as one of the fundamental sciences deeply relevant to global change. During this period, atmospheric chemistry has been grappling with many important atmospheric environmental issues such as ozone depletion, ozone/oxidant pollution, aerosol/PM<sub>2.5</sub> pollution, atmosphere–climate interaction, and others from a fundamental point of view of biogeochemical cycles of atmospheric trace components. Giving a “meaning” to academic studies targeting such environmental issues is an integrated point of view for interpreting a cause–effect relationship including human activities, and atmospheric chemistry has been developed with such a holistic aspect of view. Based on this view, many excellent textbooks on atmospheric chemistry have been published in the last 10 years or so.

Meanwhile, what is necessary to get a feeling that a system composed of various elements is “fully understood” and to reliably predict the future? In the field of atmospheric chemistry, a phenomenon would be felt “fully understood” when the controlling chemistry and physics are resolved in terms of their fundamental principles. Therefore, those who learn atmospheric chemistry have to learn fundamental chemistry and physics, which constructs the basis of the discipline. Reaction chemistry, which is a branch of physical chemistry, is one such area of the fundamentals of atmospheric chemistry. In reaction chemistry, it may be implied that the reaction is “understood” when a chemical reaction is fully explained by spectroscopy, photochemistry, and chemical kinetics that have bases in quantum chemistry. This book specializes in atmospheric reaction chemistry, skipping the vast fertile discussion of comprehensive atmospheric chemistry. For overall atmospheric chemistry, readers can refer to the existing textbooks complementarily.

This book is written with the aim of providing fundamental knowledge, and particularly the fundamental way of thinking, about atmospheric chemical reactions for undergraduate and graduate students who wish to learn atmospheric chemistry. Another aim is for it to be used as reference on individual photochemical and thermal reactions. In particular, it is hoped that students in chemistry majors would

more deeply understand the science hidden in each atmospheric reaction as being anchored to physical chemistry and quantum chemistry. It is also hoped that students in physics and meteorology majors would understand the principles and ways of thinking about chemical reactions.

Most small molecules which play an important role in atmospheric chemistry can be described accurately in terms of spectroscopy, chemical kinetics, photochemistry, and thermochemistry. Their photolysis and gas-phase homogeneous reactions have mostly been established systematically and understood fundamentally. On the contrary, among the chemical reactions covered in this book, those which do not fall into this category are the oxidation reactions of complex volatile organic compounds (VOCs) such as anthropogenic aromatics and biogenic hydrocarbons, organic aerosol formation processes from high boiling point oxidation products and surface reactions on atmospheric particles (aerosols). There are many aspects that are not yet resolved based on physical and quantum chemistry for those processes. It may be premature to cover these topics in a textbook in the sense that decisive interpretation and/or reliable values are not necessarily obtained yet. In these fields, the description of this book is not necessarily systematic and remains as an introduction of the results of the present research. These fields, however, are now attracting atmospheric scientists the most, so that a part of them were covered under the assumption that they will need to be revised in the near future.

Because this book originally was written as a textbook, the correct amounts of references are not necessarily cited. Although the best effort was made to cite the most important references, when there were too many relevant papers, references were selected arbitrarily to some extent. Apologies are in order for those authors who have been omitted from the citation list. Also, observed concentrations and their variability of the atmospheric species are taken from cited books without quoting original references. Absorption cross sections and rate constants are fully dependent on evaluations of the NASA/JPL Panel and the IUPAC subcommittee for kinetic and photochemical data for atmospheric chemistry and are updated for important findings thereafter. Among the textbooks on atmospheric chemistry, Finlayson-Pitts and Pitts (2000), Brasseur and Solomon (2005), and Seinfeld and Pandis (2006) are often referred to particularly for tropospheric chemistry, stratospheric chemistry, and both fields, respectively, because they contain more detailed chemistry than other textbooks. Also, the book *Photochemistry of Small Molecules* written by Hideo Okabe in 1978 was considered for constituting the chapters.

This book is dedicated to Prof. Ikuzo Tanaka, who was my Ph.D. supervisor in physical chemistry at the Tokyo Institute of Technology; the late Prof. James N. Pitts, Jr., who was my postdoctoral supervisor in chemistry of the atmosphere at the University of California, Riverside; and Prof. Barbara Finlayson-Pitts, at the University of California, Irvine, a friend of mine with whom I worked together on lab kinetics in the Pitts group at that time. Prof. Tanaka opened my eyes to research on photochemistry and molecular science from an international perspective in the then still economically poor and scientifically isolated country of Japan in the 1960s. Prof. Pitts led me to the study of chemistry on photochemical oxidants and tropospheric ozone, and I have been much affected by his pioneering stance to

tackle science and policy. As I gradually changed my research field from physical chemistry to atmospheric chemistry, Barbara has been providing me a fixed coordinate like a polar star as an atmospheric scientist anchored to physical chemistry. Also, I wish to dedicate this book to my wife, Yoko, who has been with me supporting my long career apart from the platform of science. Prof. Pitts passed away in June 2014, just before the publication of this book, and it is a major regret that its publication was not in time.

Furthermore, I would like to express appreciation to Drs. Eiji Akiyoshi, Jun Hirokawa, Takashi Imamura, Yoshizumi Kajii, Yugo Kanaya, Yutaka Matsumi, Fumikazu Taketani, and Hiroshi Tanimoto, who read the manuscript in their respective parts and gave me valuable comments. Particularly, I owe Prof. Hirokawa, who kindly checked all equations relevant to heterogeneous kinetics and proposed an alternative easy-to-understand form. I also would like to express appreciation to the Asia Center for Air Pollution Research and its staff, who provided me an opportunity to write this book besides the task as director general, and helping me in several aspects including obtaining references, drawing of figures, etc. Finally, I would like to express my thanks to the editorial staff members of Asakura Publishing Co., who made tremendous efforts for the completion of this book to be published.

Tsukuba, Ibaraki, Japan  
July 2014

Hajime Akimoto





## Preface to the English Edition

It is my great pleasure that my book *Atmospheric Reaction Chemistry*, which was originally published in Japanese in 2014, is now published in an English edition. As I wrote in the preface of the Japanese edition, in order to “fully understand” system science like atmospheric chemistry, one has to learn underlying chemistry and physics as fundamentals for gaining confidence in interpretation of atmospheric phenomena and particularly in future prediction. Reaction chemistry and kinetics, which is a branch of physical chemistry, is one such fundamental of atmospheric chemistry, and this book specializes in this area, skipping vast fertile discussion of comprehensive atmospheric chemistry. For overall atmospheric chemistry, readers can refer complementarily to the cited textbooks.

This book was written with the aim of providing a fundamental way of thinking about chemical reactions in the atmosphere for undergraduate and graduate students who wish to learn atmospheric chemistry. In particular, it is hoped that students in chemistry majors would understand more deeply the science hidden in each atmospheric reaction which is anchored to physical chemistry and quantum chemistry. It is also hoped that students in physics and meteorology majors would understand the fundamental principles of chemical reactions and kinetics. It is also hoped that it will be useful for research scientists in these fields as a reference book for consulting photochemical and thermal reaction pathways, absorption spectrum, and rate constants.

This book covers homogeneous gas-phase kinetics important in the atmosphere, which has been almost established, and provides the solid scientific bases of oxidation of trace gases and oxidant formation. Nevertheless, unresolved problems remain, for example, unsatisfactory reproduction of observed OH/HO<sub>2</sub> mixing ratio by model simulation under certain conditions, and oxidation mechanisms involving isoprene, terpenes and other biogenic hydrocarbons, and anthropogenic aromatic hydrocarbons. Therefore, descriptions of these topics are not completed in the book. Heterogeneous reaction chemistry is not covered well except for the chemistry on polar stratospheric clouds (PSCs) and reactive uptake coefficients of selected

inorganic gases on sea salt and other particle surfaces in the troposphere. Heterogeneous organic chemistry related to secondary organic aerosol is now developing fast, and we hope that it will be established in the next decades.

Most of photochemical and kinetic data useful for atmospheric chemistry have been compiled in excellent evaluations by the NASA Panel for Data Evaluation and IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, which have been frequently referred to in the book. Meanwhile, when they are referred to, I tried to quote selected original papers to be devoted to individual experimental and quantum chemists who actually obtained the data. This book is also an homage to the books *Photochemistry* by J. G. Calvert and J. N. Pitts, Jr (1966) and *Photochemistry of Small Molecules* by H. Okabe (1978), which were my desk-side books in my early career.

This book is dedicated to the late Prof. Ikuzo Tanaka, who was my Ph.D. supervisor in physical chemistry at the Tokyo Institute of Technology; the late Prof. James N. Pitts, Jr., who was my postdoctoral supervisor in chemistry of the atmosphere then at the University of California, Riverside; and Prof. Barbara Finlayson-Pitts, at the University of California, Irvine, a friend of mine with whom I worked together on lab kinetics in the Pitts' group at the beginning of the 1970s. Prof. Pitts and Prof. Tanaka passed away recently, in June 2014 and February 2015, respectively, just before and after the publication of the Japanese Edition. It is my wish that the fundamental photochemistry and reaction kinetics related to atmospheric chemistry will be inherited by the next generation through this book.

Tsukuba, Ibaraki, Japan  
August 2015

Hajime Akimoto

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# Chapter 1

## Introduction to Atmospheric Chemistry

This chapter serves as an introduction to atmospheric chemistry. It provides an overview of the development of the field, from the dawn of modern chemistry to the birth of atmospheric chemistry. Section 1.3 lists the textbooks on chemistry of the atmosphere and atmospheric chemistry that have been published to date. In addition, the literature that served as reference in the writing of this chapter is also listed at the end of this chapter under the bibliography.

### 1.1 The Dawn of Modern Chemistry and Chemistry of the Atmosphere

The birth of modern chemistry and chemistry of the atmosphere have an inseparable relationship. Chemistry of the atmosphere has its roots in the second half of the 18th century in England, when it first generated much interest as “air chemistry.” This also signified the dawn of modern chemistry. Black discovered carbon dioxide in 1755, while Cavendish discovered hydrogen in 1766. Thereafter, nitrogen was discovered in 1772 by Rutherford, and oxygen in 1774 by Priestley. Furthermore, many of the components of air that are known today as air pollutant gases, such as nitrogen monoxide, nitrogen dioxide, sulfur dioxide, hydrogen chloride, ammonia, and nitrous oxide (dinitrogen monoxide), were discovered successively during the same period.

The second half of the 18th century was also the exact period when the transition from alchemy to modern chemistry took place. Incidentally, although the Japanese word for alchemy (*renkinjutsu*, which originates in Chinese word and translates as “hermetic arts”) seems to have occult connotations, the English counterpart “alchemy” takes its “al” from the Arabic article for “the,” suggesting a more natural sense of continuity between “alchemy” and “chemistry.”

Furthermore, this was also the period when the phlogiston theory was propounded, and eventually refuted. This theory, which took the world by storm, hypothesized that combustion was the result of the loss of phlogiston in combustible materials. Today, we know that combustion is the result of a violent exothermic reaction that arises as a result of binding with oxygen in the air. However, according to the phlogiston theory from that time, combustion was thought to be a phenomenon that occurred when phlogiston rose violently from the combusting substance along with the flames, and was released into the air. The phlogiston theory was the mainstream theory propounded in academic circles then, and, for a relatively long time, was believed to be accurate. The inaccuracy of this theory was only acknowledged when Lavoisier formulated the law of conservation of mass in 1774, and it became known that the ashes that remain after the combustion of a substance are not lighter, but rather heavier, than the original substance. In this way, “air chemistry” is also related to the phlogiston theory, and formed a part of the prologue to modern chemistry. At the same time, this period also became the prologue to chemistry of the atmosphere, although no one had been conscious at that time.

The relationship between the ozone layer and the atmosphere triggered a growing awareness for chemists about chemistry of the atmosphere. Ozone molecules, which would later be recognized as a key species in the chemistry of the Earth’s atmosphere, were discovered by the German/Swiss chemist Schönbein in his laboratory in the nineteenth century, in 1839. Ozone was discovered in the atmosphere near the surface of the Earth in 1860, about 20 years after the discovery of ozone in the form of molecules, and the relevance of ozone with the atmosphere was uncovered. After that, it became a trend to measure the amount of ozone present in the atmosphere, and activities to measure the amount of ozone near the surface of the Earth began to take place at numerous locations in Europe. Thanks to this trend, records of ozone density at the end of the nineteenth century were preserved as numerical data. These data have taken on great importance, serving as reference values in the study of the increase in tropospheric ozone in the twentieth century. Incidentally, the ozone measurement method at the time involved exposing filter paper soaked in potassium iodide (KI) solution to the air, and measuring the density of the purplish-brown color that is produced when the solution undergoes oxidation. This was known as the Schönbein method. The wet chemical automatized oxidant analyzer, which had also been used in Japan until recently, operates based on this same principle.

On the other hand, ozone was synthesized in laboratories during this time, and an Irish chemist, Hartley, came up with a method for measuring absorption spectrum. As a result, it was found that ozone absorbs ultraviolet light most strongly at 200–320 nm, and this absorption band was therefore named the “Hartley band” after the chemist. Today, a standard method to measure ambient ozone concentration is to use an UV absorption instrument, which is based on the Hartley band. Data on the absorption spectrum of ozone took on even greater significance for chemistry of the atmosphere when it led to the discovery of the ozone layer in the stratosphere. Prior to this, scientists had measured the solar spectrum and learned that ultraviolet

rays with wavelengths shorter than 300 nm do not reach the surface of the Earth at all. As the limits of the wavelengths of these ultraviolet rays were consistent with the rising wavelengths of the ozone's absorption spectrum measured in the laboratory, in around 1880, Hartley concluded that this was definitely the result of the presence of a high density of ozone in the atmosphere. Even further on after that, it was inferred that an even larger amount of ozone was present in the upper air since the measurement data for ozone density near the surface of the Earth at the time could not provide an explanation for this degree of attenuation of solar ultraviolet rays at that density. The existence of the ozone layer in the stratosphere was validated 20–30 years after that in 1913, by two French physicists, Fabry and Buisson.

However, prior to that, the presence of the stratosphere, where temperature increases with altitude, was discovered in 1902 by the French meteorologist Teisserenc de Bort. Partly due to fact that the stratosphere was discovered before the ozone layer, it is common to say that the ozone layer exists in the stratosphere. In actual fact, the ozone layer had formed first in the Earth's atmosphere, and the stratosphere was formed as a consequence of the ozone layer. As ozone absorbs sunlight efficiently, the temperature of the atmosphere rises where there is a high density of ozone, resulting in the temperature reversal phenomenon where temperature rises with higher altitudes, and bringing about the formation of the stratosphere. Against the current concentration of oxygen in the Earth's atmosphere, ozone density is the highest at places between 20 and 25 km above the surface of the Earth. However, as air density falls and heat capacity becomes smaller as the stratum becomes higher, temperature in the stratosphere reaches its peak at an altitude of about 50 km, and not at the center of the ozone layer.

The minds researching chemistry of the atmosphere later turned their attention to chemical reactions in the atmosphere. Research on chemical reactions in the atmosphere stems from two broad streams—one from the perspective of geophysics, and another from the perspective of environmental science and geochemistry. Research from the perspective of geophysics has its roots in research on the chemistry of atmospheric ozone, which seeks to elucidate why the ozone layer was formed in the stratosphere. Chapman, a British geophysicist, was the first to elucidate that the ozone layer is formed through a photochemical reaction when oxygen in the Earth's atmosphere is irradiated by sunlight. This was known as the Chapman mechanism (theory), and was published in 1930. Chapman's theory was also known as "the pure oxygen theory", as it took only oxygen into consideration as the component in the Earth's atmosphere that absorbs sunlight. Oxygen is photolyzed into two oxygen atoms, and these atoms combine with other oxygen molecules to create ozone. If only this simple process operates, all oxygen will eventually be converted to ozone over time. However, this does not happen because the ozone that is produced undergoes photolysis in sunlight and also reacts with oxygen atom, and return to its original form of oxygen molecules. Through this process, oxygen and ozone are repeatedly generated and destroyed in sunlight, resulting in a state of photochemical equilibrium. Based on the absorption spectrum of oxygen and ozone, radiation intensity of sunlight, rate constant of the reaction of

oxygen atom with ozone and oxygen, and the altitude distribution of oxygen molecular density in the Earth's atmosphere, Chapman calculated the amount of ozone that was produced in different altitude, and succeeded in explaining the formation of the ozone layer at an altitude of 20–25 km. As for the density of the ozone, that as calculated by Chapman ignored the chemical reactions of trace gases other than oxygen, the values that he obtained were overestimated by about a factor of two as compared to the observed values that we have obtained today. However, the altitude distribution of ozone that he obtained was successfully reproduced in the observed profile.

Thereafter, research on chemical reactions in the stratosphere from the 1960s to the 1970s took into consideration chemical reactions that included trace components in the atmosphere, such as  $\text{H}_2\text{O}/\text{CH}_4$ ,  $\text{N}_2\text{O}$ , and  $\text{CH}_3\text{Cl}$ . This brought about significant academic advancements, contributing to the schematization of an important chain reaction theory for the atmosphere known as the “ $\text{HO}_x$ ,  $\text{NO}_x$ , and  $\text{ClO}_x$  cycle,” and at the same time, eliminating the aforementioned inconsistency of results with observations of ozone density in the stratosphere. This developed further in 1974 when Molina and Rowland propounded the theory that predicted the depletion of the ozone layer through chlorofluorocarbon (CFC), which contributed to solving an important environmental problem.

Meanwhile, research on the chemistry of the troposphere from the perspective of environmental science dates back to air pollution arising from coal combustion during the industrial revolution, and has its beginnings in the measurement of the chemical composition of rainfall and snowfall in England in the second half of the 18th century. The term “acid rain” was coined by the 19th century Scottish chemist, Angus Smith, and it was found at the time that rainfall in urban, suburban and unpolluted remote areas typically contained sulfuric acid/ammonium sulfate, ammonium sulfate, and ammonium carbonate, respectively. Such examples of early air pollution research have continued in the academic field of geochemistry in the form of research on precipitation chemistry and gas-aerosol chemistry. However, air chemistry in the field of geochemistry has remained low-key in comparison with other areas of study, such as marine chemistry and mineral chemistry. Furthermore, environmental science and geochemistry research on trace components in the atmosphere focus on research from the perspective of analytical chemistry, and did not contribute significantly to the development of research on chemical reactions in the atmosphere. One of the reasons was that compared to the stratosphere, the troposphere was in general considered to be a chemically static field.

Air pollution research only began to play a significant role in developing research on chemical reactions in the atmosphere during the late of 1940s, when photochemical smog emerged in South California, United States. The Los Angeles basin was shrouded in white smog in summer, and cases of health problems such as eye irritation and respiratory disorders were reported, in addition to reports of crop damage as leaves turned brown and the crops died (necrosis). These problems continued to appear successively into the 1950s, but the cause of the problems remained a mystery for a long period of time. This is because the main air pollutants

in this area, which include hydrocarbons and oxides of nitrogen in automobile exhaust gas, do not directly cause health problems and crop damage such as those observed in Southern California. This mystery was solved by Haagen-Smit, then professor at the California Institute of Technology. Haagen-Smit conducted experiments such as exposing automobile exhaust gas to ultraviolet rays, and proved the formation of oxidizing substances (oxidants) including ozone through photochemical reactions in polluted air, which caused damage to human health and plants. Ozone and most of the other oxidants are colorless gases and do not reduce visibility. However, particulate matter (aerosol) is generated as secondary products simultaneously when ozone is generated, and this particulate matter causes the “white smog” that reduces visibility.

Research on chemical reactions in the troposphere devolved by leaps and bounds after that, founded upon the research on the elucidation of mechanism of photochemical smog that was conducted from the 1960s through the 1970s. It began to be addressed in the academic circles as a part of the chemistry of the troposphere, including the free troposphere. The most significant example of that was the OH radical chain reaction theory in the troposphere, which was formulated in the early part of the 1970s. This established the reaction mechanism of photochemical air pollution as an unshakable fact, and at the same time, provided a fundamental theory of troposphere chemistry for the next generation that had greater universality due to its direct relationship with global environmental issues.

## 1.2 Development into Atmospheric Chemistry

In this way, chemistry of the atmosphere, which has been regarded mainly as chemistry of the ozone layer and chemistry of photochemical smog, entered a significant period of transition in the 1980s. This was its evolution from “chemistry of the atmosphere” to “atmospheric chemistry.” Until the 1980s, the chemistry of the stratosphere has been treated as fundamental knowledge constituting a part of geophysics. Conversely, chemistry of the troposphere was regarded as an applied field of chemistry related to air pollution, and was not treated as fundamental science. However, in the mid-1980s, chemistry of the troposphere, which had never historically been treated as a form of science, experienced a dramatic reversal and became widely regarded as a academic research field for the first time. At the same time, atmospheric chemistry, which encompasses chemistry of the troposphere and the stratosphere, came to be established as a new fundamental discipline that constitutes a part of Earth science. While the previous “chemistry of the atmosphere” focused on the analytical and reaction chemistry of atmospheric components, “atmospheric chemistry” sought to elucidate the series of processes related to global material cycle and balance—the process of emissions of atmospheric trace components from anthropogenic and natural sources including the biosphere, the transport processes in atmosphere and the accompanying chemical transformation processes, and the process of the removal of atmospheric

components from the atmosphere through wet and dry deposition. By doing so, atmospheric chemistry became a new academic field that had a system science aspect, which sought to elucidate the spatial distribution and temporal variation of atmospheric trace species on a global, regional and urban scale, as well as the biogeochemical cycling of these components. The second half of the 1980s coincided exactly with the dawn of the global environment era, and atmospheric chemistry, together with atmospheric physics, physical and chemical oceanography, as well as terrestrial and marine ecology, gained recognition as fundamental disciplines that were useful for understanding global changes that were brought about by human activities. These global changes included global warming, depletion of the ozone layer, and acid rain.

Atmospheric chemistry is an interdisciplinary academic field that brings together the conventional academic subjects of physical chemistry, analytical chemistry, geophysics, meteorology, and ecosystem science. In order to establish such a holistic academic field in a systematic manner, it is necessary to ensure that the respective elements of science that constitute the field are well organized.

In this context, this textbook focuses on “atmospheric reaction chemistry” as one of key elements of atmospheric chemistry, which is based on gas-phase chemical kinetics and photochemistry that is an aspect of the conventional research field of physical chemistry. A number of excellent textbooks on the subject of atmospheric chemistry as a systems science are listed after this, so please refer to these books for more information on the total subject.

### 1.3 Textbooks of Atmospheric Chemistry

Two of the textbooks on the chemistry of the atmosphere written in the 1960s are;

- Leighton, P. A., *Photochemistry of Air Pollution*, Academic Press, 300 pp, 1961, which was born out of photochemical air pollution research, and another,
- Junge, C. E., *Air Chemistry and Radioactivity*, Academic Press, 382 pp, 1963, which was born from the stream of geochemistry. These books may be called the atmospheric chemist’s bibles.

Textbooks written in the 1970s–1980s are:

- Phillips, L. F. and M. J. McEwan, *Chemistry of the Atmosphere*, 301 pp, Wiley & Sons, 1975.
- Heicklen, J., *Atmospheric Chemistry*, 406 pp, Academic Press, 1976.
- Shimazaki, T., *Minor Constituents in the Middle Atmosphere*, 444 pp. D. Reidel, 1985.
- Wayne, R. P., *Chemistry of Atmospheres*, 355 pp, Clarendon Press, 1985.
- Finlayson-Pitts, B. J., J. N. Pitts, Jr., *Atmospheric Chemistry*, 1098 pp, John Wiley & Sons, 1986.

- Seinfeld, J. H., *Atmospheric Chemistry and Physics of Air Pollution*, 738 pp, John Wiley & Sons, 1986.
- Warneck, P., *Chemistry of the Natural Atmosphere*, 753 pp, Academic Press, 1988.
- Ogawa, T., *Physics and Chemistry of the Atmosphere*, 224 pp., Tokyodo Shuppan (in Japanese).

These publications served as pioneering textbooks in an era when the study of the chemistry of the atmosphere was not yet so common. Although it is not a textbook on the chemistry of the atmosphere, a textbook on photochemistry that was also useful for a long time for atmospheric chemists, and the style of chapters was referred in writing the present textbook is;

- Okabe, H., *Photochemistry of Small Molecules*, 431 pp, John Wiley & Sons, 1978.

Textbooks in the era of “atmospheric chemistry” starting in 1990s when a strong consciousness of global environmental issues emerged and a viewpoint of system science was strengthened are as follows;

- Graedel, T. E., P. J. Crutzen, *Atmospheric Change*, 446 pp, W. H. Freeman and Company, 1993.

A textbook mainly for undergraduate students to understand various phenomena in the atmosphere, geosphere, hydrosphere, and biosphere in the perspective of one earth system.

- Brasseur, G. P., J. J. Orlando, G. S. Tyndall, Eds., *Atmospheric Chemistry and Global Change*, 654 pp, Oxford University Press, 1999.

From the viewpoint of the relevance of atmospheric chemistry with global environmental issues, processes, chemical compounds, ozone variability, climate change, and so on are discussed in each chapter by experts in each field. It is unique as it includes essays by senior scientists in atmospheric research at the end of each chapter.

- Warneck, P., *Chemistry of the Natural Atmosphere*, 2nd Edition, 927 pp, Academic Press, 1999.

It is the 2nd edition of the original book published in 1988. It covers chemical reactions, natural and anthropogenic emission sources, removal processes in the gas phase, and in aerosol, clouds and precipitation as well as global distribution and biogeochemical cycles of atmospheric constituents.

- Jacob, D., *Introduction to Atmospheric Chemistry*, 264 pp, Princeton University Press, 1999.

It is based on a lecture at Harvard University by the author. It is a compact textbook including fundamentals of atmospheric chemistry that can be learned in



one semester. The theme of environmental problems which are thought to be important for undergraduate students are selected.

- Finlayson-Pitts, B. J. and J. N. Pitts, Jr., *Chemistry of the Upper and Lower Atmosphere*, Academic Press, 969 pp, 2000.

Detailed description on the fundamentals of physical chemistry, such as descriptions of spectroscopy, photochemistry, reaction kinetics, homogeneous and heterogeneous reactions are given. The destruction of the ozone layer, photochemical oxidants, acid deposition, hazardous air pollutants, indoor pollution, and so on are widely covered, and their countermeasures are explained based on atmospheric chemistry.

- Wayne, R., *Chemistry of Atmospheres*, 3rd ed., 775 pp, Oxford University Press, 2000.

In addition to stratospheric and tropospheric chemistry, ions and atmospheric glow in the mesosphere and the chemistry of planetary atmosphere are included. The descriptions on chemical processes in cloud water and heterogeneous reactions as their basis are added in the chapter on photochemistry and reaction kinetics in the third edition.

- Hobbs, P. V., *Basic Physical Chemistry for the Atmospheric Sciences*, 2nd Edition, 208 pp, Cambridge University Press, 2000.

Principles of chemistry necessary for students learning atmospheric science and planetary science such as chemical equilibrium, thermochemistry, chemical kinetics, photochemistry, and others are concisely described, and it is paired with the following textbook on atmospheric chemistry for students.

- Hobbs, P. V., *Introduction to Atmospheric Chemistry*, 276 pp, Cambridge University Press, 2000.

A textbook briefly summed up for students on fundamental aspects of atmospheric chemistry including air pollution, ozone hole, global warming. Many problems and answers are provided.

- Akimoto, H, K. Kawamura, K. Nakazawa, and N. Washida eds., *Chemistry of the troposphere and Global Change*, 223 pp, Gakkai Shuppan Center, 2002. (in Japanese)

A book based on a research project on “tropospheric chemistry global dynamics,” which is the first big project in this field funded by Grant-in-Aid in Japan. Greenhouse gases, tropospheric photochemistry and reactive trace constituents, atmospheric homogeneous and heterogeneous reactions, and aerosols and their precursors are covered.

- McElroy, M. B., *The Atmospheric Environment: Effects of Human Activities*, 326 pp, Princeton University Press, 2002.

A textbook used at Harvard University for a fundamental course for global environmental issues for students of environmental science and social policy science major. Fundamental physics and chemistry of the atmosphere, carbon, nitrogen and sulfur cycles, tropospheric chemistry and rain chemistry, climate change, and other topics are explained in an accessible manner.

- Brasseur, G. P and S. Solomon, *Aeronomy of the Middle Atmosphere: Chemistry and Physics of the Stratosphere and Mesosphere*, 3rd ed., 644 pp, Springer, 2005.

A unique textbook focused on physics and chemistry in the stratosphere and mesosphere. Dynamics, transport, radiation, and chemical composition are explained in each chapter. Particularly regarding the ozone layer, data from models and observations are explained in detail including gas phase and heterogeneous reactions on PSCs in the chapters of chemical composition and ozone perturbation.

- Seinfeld, J. H. and S. N. Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 2nd ed., 1,203 pp, John Wiley and Sons, 2006.

In addition to homogeneous reactions in the stratosphere and troposphere, characteristics, fluid dynamics, thermodynamics, nucleation, deposition processes, organic aerosols, climate effect regarding aerosols are expounded. In particular, efforts are made to explain each process starting from basic principles.

- Holloway, A. M. and R. P. Wayne, *Atmospheric Chemistry*, 271 pp, The Royal Society of Chemistry Publishing, Cambridge, 2010.

A textbook for students majoring in chemistry and learning atmospheric chemistry. It is more compact than the above cited “Chemistry of Atmosphere (2000)” although it is written by one of the authors (Wayne). The special feature of this textbook is that the concept of sources and sinks, and atmospheric lifetimes are explained in separate chapters.

## 1.4 Literatures

General literatures consulted for Chapter 1 are given below:

- Brock, W. H., *The Fontana History of Chemistry*, 780 pp, Harper Collins Publishers, New York, 1992.
- Cowling, E. B., *Acid precipitation in historical perspective*, *Environ. Sci. Technol.*, 16, 110A–123A, 1982.
- Ihde, J., A., *The Development of Modern Chemistry*, 851 pp, Harper & Row Publishers, New York, 1964.
- Warneck, P., *Chemistry of the Natural Atmosphere*, 2nd Edition, 927 pp, Academic Press, San Diego, 1999.

## Chapter 2

# Fundamentals of Chemical Reactions

The chemical reaction system in the atmosphere is composed of photolysis and homogeneous reactions in the gas phase, and multiphase processes including heterogeneous reactions on particle surfaces. In this chapter, photochemistry and the chemical kinetics of homogeneous and multiphase reactions are described based on the principles of physical chemistry.

The fundamentals of most chemical reactions are already well established and several textbooks are cited at the end of this chapter. However, the multiphase heterogeneous reactions given in Sect. 2.4 have attracted more interest in recent years, and as fields of research, they are still developing, so it should be noted that their treatment is not necessarily standardized yet.

## 2.1 Photochemistry and Photolytic Reactions

### 2.1.1 *The First and Second Principle of Photochemistry*

The first principle of photochemistry is the Grotthuss-Draper law which states “only the light absorbed by chemical species can cause photochemical reactions,” or in other words “without light absorption there is no photochemical reaction.” The first principle of photochemistry states that if a molecule does not have absorption spectrum in the wavelength region of light irradiation, photochemical reaction cannot occur even if the strong light is irradiated or the quantum energy of the irradiated light is larger than the bond dissociation energy of the irradiated molecule. This means that the first step to understand photochemical reactions is to grasp the absorption spectrum of molecules, and the starting point of the discussion in atmospheric chemistry should be to understand the overlapping of wavelength range of the absorption spectrum of atmospheric species and solar radiation.

The second principle of photochemistry is called the photochemical equivalence law, or the Stark-Einstein law, which states “the absorption of light occurs in the quantum unit of photon” or “one molecule absorbs one photon, and one or less molecule can be photolyzed accordingly.”

Quantum energy of light  $E$  is expressed as

$$E = h\nu = \frac{hc}{\lambda} \quad (2.1)$$

where  $h$  is the Planck constant,  $6.6262 \times 10^{-34}$  J s,  $c$  is the velocity of light in vacuum,  $2.9979 \times 10^8$  m s<sup>-1</sup>,  $\nu$  is the frequency of light (s<sup>-1</sup>), and  $\lambda$  is the wavelength of light. The wavelength of visible and ultraviolet light that appears in atmospheric chemistry is usually expressed in nanometers (1 nm =  $10^{-9}$  m), but historically angstroms or ångstroms (1 Å =  $10^{-10}$  m) were also frequently used. Also, in the infrared region, wavenumber  $\omega$  (cm<sup>-1</sup>) is in common use, which is the reciprocal of wavelength  $\lambda$  expressed in cm. The meaning of the second principle of photochemistry is that a molecule absorbs the light by the quantized energy corresponding to each wavelength as given in Eq. (2.1).

Instead of molecule, moles (1 mol =  $6.022 \times 10^{23}$  molecules; Avogadro number) are often used in experimental chemistry. The unit of photon energy referenced to one mole is called an einstein. Photon energy per 1 einstein of light with wavelength  $\lambda$  (nm) is expressed as

$$\begin{aligned} E &= (6.022 \times 10^{23}) \times \frac{hc}{\lambda} \\ &= \frac{1.196 \times 10^5}{\lambda} \text{ kJ einstein}^{-1} \\ &= \frac{2.859 \times 10^4}{\lambda} \text{ kcal einstein}^{-1} \\ &= \frac{1.240 \times 10^3}{\lambda} \text{ eV} \end{aligned} \quad (2.2)$$

The values of physical constants which appear in this book are given in Table 2.1. Table 2.2 gives energy conversion table for energy units often used in chemistry, kJ (kilojoule), kcal (kilocalorie), and eV (electron volt). Also, conversion table of photon energy of 1 einstein with corresponding wavelengths of visible and ultraviolet light is given in Table 2.3. The energy threshold values for which different photolytic processes are energetically possible are given in the case studies described in Chap. 4.

**Table 2.1** Physical constants

Constants	Values
Boltzmann constant ( $k$ )	$1.3807 \times 10^{-23} \text{ J K}^{-1}$
Plank constants ( $h$ )	$6.6261 \times 10^{-34} \text{ J s}^{-1}$
Light velocity (in vacuum) ( $c$ )	$2.9979 \times 10^8 \text{ m s}^{-1}$
Avogadro number ( $N$ )	$6.0221 \times 10^{23} \text{ mol}^{-1}$
Gas constant ( $R$ )	$8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$ $=0.082058 \text{ L atm K}^{-1} \text{ mol}^{-1}$

**Table 2.2** Energy conversion table

	$\text{kJ mol}^{-1}$	$\text{kcal mol}^{-1}$	eV
$\text{kJ mol}^{-1} =$	1	$\times 0.2390$	$\times 0.01036$
$\text{kcal mol}^{-1} =$	$\times 4.184$	1	$\times 0.04337$
eV =	$\times 96.49$	$\times 23.06$	1

**Table 2.3** Photon energy per mole for UV-visible light of typical wavelengths

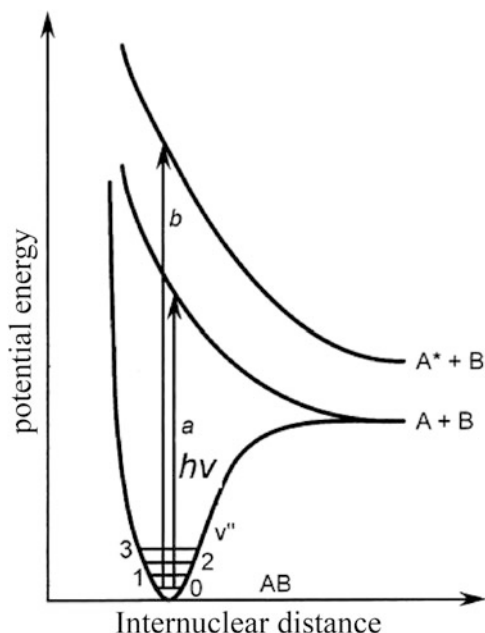
Wavelength ( $\lambda$ ) nm	Photon energy per mole (E)		
	$\text{kJ einstein}^{-1}$	$\text{kcal einstein}^{-1}$	eV
600	199	47.7	2.07
500	239	57.2	2.48
400	299	71.5	3.10
300	399	95.3	4.13
200	598	143.0	6.20
100	1196	285.9	12.40

$$\lambda \text{ (nm)} = 119600/E \text{ (kJ einstein}^{-1}\text{)} = 28590/E \text{ (kcal einstein}^{-1}\text{)} = 1240/E \text{ (eV)}$$

### 2.1.2 Photolytic Quantum Yields

Even if light with enough energy for photodissociation is irradiated to a molecule fulfilling the first principle of photochemistry, the molecule is not necessarily photolyzed. That is, fulfilling the first principle is a necessary condition for photolysis, not necessarily a sufficient condition. A molecule that absorbs the light in the visible or ultraviolet region reaches to the electronically excited state. Figures 2.1 and 2.2 illustrate the potential energy curve of the simplest case of a diatomic molecule. The abscissa of each of these figures is interatomic distance in a molecule, and the ordinate is the potential energy. The most stable, lowest energy state of an atom or molecule is called the ground state, and the higher energy state is called the excited state. The case of Fig. 2.1 is an example where the excited states are in a repulsive state that does not have a potential minimum. In this case, an excited molecule  $AB^*$  (an atom and molecule in their electronically excited state are expressed with an asterisk on the right shoulder) reached by the photo-absorption dissociates into  $A + B$  or  $A^* + B$  immediately. Figure 2.1 illustrates that the dissociation to the channel forming an excited atom,  $A^* + B$ , generally happens when the

**Fig. 2.1** Potential energy curves for a diatomic molecule showing excitations to repulsive electronic states

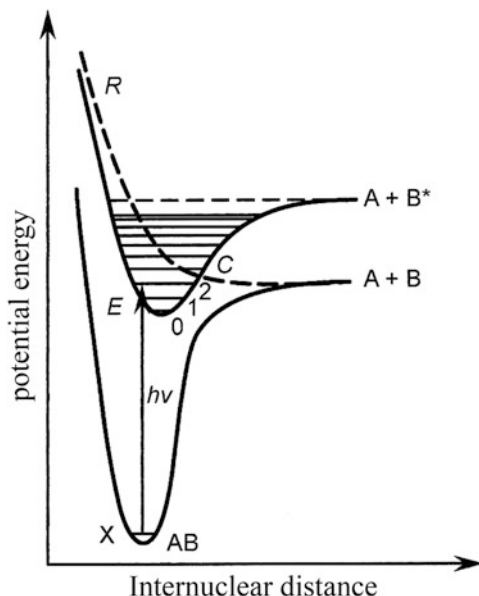


molecules absorb shorter wavelength light with higher photon energy. The horizontal lines drawn in the energy curve of the ground state designate vibrational energy levels ( $v''$ ).

Figure 2.2 is an example of a molecule with a bound excited state having a minimum on the potential energy curve. The horizontal lines in the bound excited state designate vibrational levels in the excited state ( $v'$ ). In this case, an excited molecule cannot dissociate immediately even though the potential energy in the excited state is higher than the dissociation energy, and it stays in the excited state for a certain period of time. During this period, the molecule may emit light and return to the ground state with a natural radiative lifetime. In such cases, photodissociation does not occur. However, an energy curve of the bound excited state is often crossed with a repulsive potential curve that leads to dissociation into A + B as illustrated in Fig. 2.2 by a broken line. When the absorbed photon energy is higher than the crossing point, traversing from the bound excited state to the repulsive state can occur, leading to dissociation into A + B. Dissociation in this form is called "predissociation." Further, when a bound state is reached by an excitation with higher energy than the dissociation energy of A\* + B, a molecule dissociates into A\* + B immediately.

To which case of Figs. 2.1 or 2.2, the photo-excitation is applicable, can be judged by the appearance of an absorption spectrum whether it is a continuum or has a band structure. In the case of Fig. 2.2, since the absorption occurs to the vibrational energy levels in the bound excited state, absorption spectrum reveals band structure. As an example, absorption spectra of chlorine ( $\text{Cl}_2$ ) (Maric et al. 1993)

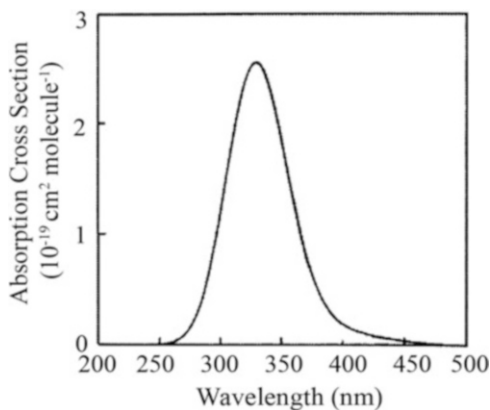
**Fig. 2.2** Potential energy curves for a diatomic molecule showing excitation to a bound electronic state that crosses with a repulsive state



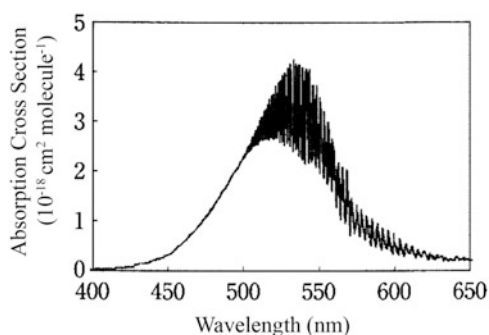
and Iodine ( $I_2$ ) (Saiz-Lopez et al. 2004) are shown in Figs. 2.3 and 2.4, respectively. Absorption spectrum of  $Cl_2$  in the wavelength region of 250–450 nm is a real continuum, which implies that the potential energy curve in the excited state corresponding to the photo-absorption in this region is repulsive. It is known that a  $Cl_2$  molecule photo-excited in this wavelength region dissociates into two ground state chlorine atoms  $Cl$  ( $^2P_{3/2}$ ) immediately. On the other hand, the absorption spectrum of  $I_2$  shows a band structure in the 500–650 nm domains overlapping with a continuum spectrum extending from 400 to 500 nm. The band spectrum corresponds to the transition to a quasi-stable state of the potential curve. In general, the probability of photodissociation when a molecule is excited into such a state has to be verified by experiments. The case of Fig. 2.4, showing the band structure overlapping with a continuum, in general corresponds to the predissociation mentioned above. Another example of absorption spectrum corresponding to an excitation to a pure bound potential curve without predissociation is given in Fig. 2.5 for the case of carbon monoxide ( $CO$ ) (Myer and Samson 1970). In such a case, the spectrum shows perfectly discrete bands, and the excited molecule does not photodissociate, but rather returns to the ground state emitting fluorescence or being deactivated by a collision with another molecules, that is also called quenching.

So far, the explanation was for an example of diatomic molecules. For the polyatomic molecules composed of  $n$ -pieces of atoms, the idea of the correspondence of the appearance of the absorption spectrum and the photo-excitation is the same, but the potential surfaces are in  $n-1$  dimensions. Since photodissociation can occur with multiple processes such as  $ABC \rightarrow AB + C$ ,  $A + BC$ , multi-dimensional potential surfaces for each dissociating inter-atomic distance must be considered.

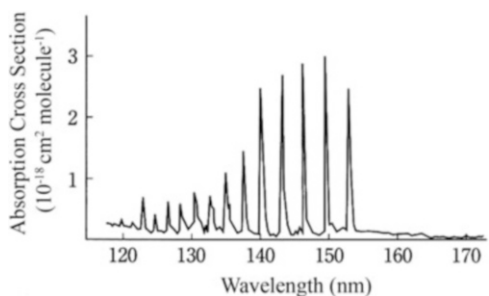
**Fig. 2.3** Absorption spectrum of  $\text{Cl}_2$  (Adapted from Maric et al. 1993)



**Fig. 2.4** Absorption spectrum of  $\text{I}_2$ . Resolution: 0.1 nm for 500–630 nm, 1 nm for other region (Adapted from Saiz-Lopez et al. 2004)



**Fig. 2.5** Absorption spectrum of  $\text{CO}$ . Resolution: 0.025 nm (Adapted from Myer and Samson 1970)



A probability of dissociation of a molecular per absorbed photon is called the photolytic quantum yield. Thus, the photolytic quantum yield  $\Phi$  is defined by

$$\Phi = \frac{\text{Number of dissociated molecules}}{\text{Number of absorbed photons}}. \quad (2.3)$$

By this definition, the maximum and minimum photolysis quantum yield is 1 and 0, respectively.



From the relationship between the photo-excitation and absorption spectrum, photodissociation quantum yields are in general unity when a molecule is excited to the repulsive potential curve as shown in Fig. 2.1. On the other hand, when an absorption spectrum has a band structure and a molecule is excited to a bound state as shown in Fig. 2.2, photodissociation quantum yields are in general  $0 \leq \Phi \leq 1$  and the value has to be determined experimentally.

When a certain wavelength light excites a molecule, photodissociation can occur in energetically permissible multi-pathways, and the photolytic quantum yield for each process has to be determined experimentally. For example, the photodissociation pathways of ozone ( $O_3$ ) by solar ultraviolet radiation,



are very important in tropospheric chemistry, and many experiments have been done to determine the wavelength dependence of photolytic quantum yields of each process (see Sect. 4.2.1).

### 2.1.3 The Beer-Lambert Law

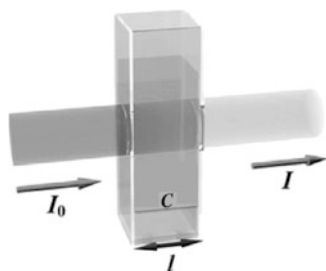
As shown in Fig. 2.6, when a parallel monochromatic light of wavelength  $\lambda$  with an intensity  $I_0$  (energy or number of photons) irradiates and passes through media with concentration  $C$  ( $\text{mol L}^{-1}$ ) and length  $l$  (cm), the intensity of the light after the passing can be expressed as

$$\ln \frac{I}{I_0} = -kCl \quad (2.6)$$

$$\frac{I}{I_0} = \exp(-kCl) \quad (2.7)$$

This relationship is called the Beer-Lambert law. The proportionality coefficient  $k$  is generally referred to absorption coefficient ( $\text{L mol}^{-1} \text{cm}^{-1}$ ).

**Fig. 2.6** Schematic diagram of Beer-Lambert Law



The Beer-Lambert law is also often expressed taking the base 10 of the logarithm as

$$\log \frac{I}{I_0} = -\epsilon Cl \quad (2.8)$$

$$\frac{I}{I_0} = 10^{-\epsilon Cl}, \quad (2.9)$$

where the proportional coefficient  $\epsilon$  ( $\text{L mol}^{-1} \text{cm}^{-1}$ ) is called the molar extinction coefficient. The  $\log(I/I_0)$  in Eq. 2.8 is called absorbance  $A$  and related to transmittance  $T$  with the following relationship,

$$A = -\log\left(\frac{I}{I_0}\right) = -\log T \quad (2.10)$$

The concentration unit of the media is usually taken as molecular number density  $n$  ( $\text{molecules cm}^{-3}$ ) in atmospheric chemistry, and in this case the Beer-Lambert law is customarily expressed with the natural logarithm as,

$$\ln \frac{I}{I_0} = -\sigma nl \quad (2.11)$$

$$\frac{I}{I_0} = \exp(-\sigma nl) \quad (2.12)$$

Here, the proportionality coefficient,  $\sigma$  ( $\text{cm}^2 \text{molecule}^{-1}$ ) has the dimension of area and is called the absorption cross section. Also, the dimensionless number in the above equation  $\sigma nl$  is denoted by  $\tau$  and is called optical depth,

$$\tau = \ln(I_0/I) = \sigma nl. \quad (2.13)$$

Absorption cross sections of many molecules in the atmosphere are given in the tables in Chap. 4. For example, the absorption cross section of the strong Hartley band of  $\text{O}_3$  at around 254 nm is  $\approx 1 \times 10^{-17} \text{cm}^2$  (c.f. Fig. 3.6, Table 4.1). Cross sections of important absorption of  $\text{O}_3$  at 308 nm and  $\text{NO}_2$  at 360 nm are  $\approx 1 \times 10^{-19}$ ,  $\approx 5 \times 10^{-19} \text{cm}^2$  (c.f. Fig. 3.6, Table 4.1; Fig. 4.9, Table 4.5), respectively, and that of CFC-11 ( $\text{CFCl}_3$ ) at around 200 nm which is important for ozone layer depletion, is  $\approx 6 \times 10^{-19} \text{cm}^2$  (c.f. Fig. 4.33, Table 4.26). Conceptually, if the molecular diameter is the order of  $10^{-8} \text{cm}$  and the light is absorbed 100% by the geometric surface area, the absorption cross section is in the order of  $\approx 10^{-16} \text{cm}^2$ . Generally speaking, when absorption cross section  $\sigma$  is larger than  $10^{-20} \text{cm}^2$ , it is thought to be strong enough, which can be important in the atmosphere.

When calculating the photolysis rate in atmospheric chemistry, it is desirable to use an absorption cross section as the concentration unit. However, it is sometimes necessary to convert an absorption coefficient in different unit given in literatures to

**Table 2.4** Conversion table of absorption coefficients in different units

Absorption cross section			
Absorption coefficient	$\text{cm}^2 \text{ molecule}^{-1}$	$\text{L mol}^{-1} \text{ cm}^{-1}$	$\text{atm}^{-1} \text{ cm}^{-1}, 273 \text{ K}$
$\text{cm}^2 \text{ molecule}^{-1}$ (base e) =	1	$\times 1.66 \times 10^{-21}$	$\times 3.72 \times 10^{-20}$
$\text{L mol}^{-1} \text{ cm}^{-1}$ (base 10) =	$\times 2.62 \times 10^{20}$	1	$\times 2.24 \times 10$
$\text{atm}^{-1} \text{ cm}^{-1}$ (base e, 273 K) =	$\times 2.69 \times 10^{19}$	$\times 4.46 \times 10^{-2}$	1

cross sections. Particularly, absorption spectra of gases in old literatures are often given in the natural logarithm base extinction coefficients in atm unit  $k$  ( $\text{atm}^{-1} \text{ cm}^{-1}$ ). In this case molecular density in the atm unit depends on temperature, and the temperature is usually defined at 273 K or 298 K so that the proper temperature should be used to convert from the extinction coefficient to the cross section. Table 2.4 gives conversion factors between absorption coefficients. In addition,  $k$  ( $\text{atm}^{-1} \text{ cm}^{-1}, 273 \text{ K}$ ) =  $1.09 k$  ( $\text{atm}^{-1} \text{ cm}^{-1}, 298 \text{ K}$ ), and  $k$  (base e) =  $2.303 \times k$  (base 10).

### 2.1.4 Photolysis Rate Constants

When a molecule A absorbs light and is photolyzed as



the photolysis rate is expressed by the first order reaction rate,

$$d[\text{A}]/dt = -k_p[\text{A}]. \quad (2.15)$$

Here,  $h$  and  $\nu$  in the left-hand side of Eq. (2.14) are the Plank constant and frequency of light appeared in Eq. (2.1) in origin, the  $[h\nu]$  here is customarily used as a symbol designating photon in a photochemical reaction formula. Photolysis rate constant  $k_p$  ( $\text{s}^{-1}$ ) is calculated practically by using the irradiating light intensity  $I$  (photons  $\text{cm}^{-2} \text{ s}^{-1}$ ), absorption cross section  $\sigma$  ( $\text{cm}^2 \text{ molecule}^{-1}$ , base e), and photolytic quantum yield  $\phi$ . When the irradiation is monochromatic light with wavelength  $\lambda$ ,  $k_p$  is given as,

$$k_p(\lambda) = \sigma(\lambda)\Phi(\lambda)I(\lambda). \quad (2.16)$$

When the photolysis occurs by the wide range wavelength light as in the atmospheric photochemical reactions, the photolysis rate is obtained by integrating the value at each wavelength,

$$k_p = \int_{\lambda} \sigma(\lambda) \Phi(\lambda) I(\lambda) d\lambda. \quad (2.17)$$

In the calculation for atmospheric photodissociation reactions, how to calculate the effective solar intensity is a major issue, because not only direct irradiation from the sun, but light from all directions reflected and scattered by the ground surface, clouds, atmospheric molecules, and aerosols can contribute to photolysis. Furthermore, in the troposphere for example, only solar radiation that has not been absorbed by atmospheric molecules in the higher atmosphere, the stratosphere and above, can cause photolytic reactions. The spherically integrated solar intensity after considering those many atmospheric processes is called the actinic flux  $F(\lambda)$  (photons  $\text{cm}^{-2} \text{s}^{-1}$ ), which means solar irradiation valid for photochemical effect. In atmospheric chemistry,  $j_p$  is often used instead of  $k_p$  for representing photolysis rate constant. Photodissociation rate constant in the atmosphere can be expressed using these parameters as

$$j_p = k_p = \int_{\lambda} \sigma(\lambda) \Phi(\lambda) F(\lambda) d\lambda. \quad (2.18)$$

Detailed method of calculation of  $F(\lambda)$  will be treated later in Chap. 3.

### 2.1.5 Spectroscopic Terms and Selection Rules

In chemical equations for the reactions in the atmosphere, atoms and molecules are sometimes denoted with symbols in a parenthesis, e.g.  $\text{O}({}^3\text{P})$ ,  $\text{O}({}^1\text{D})$ ,  $\text{O}_2({}^3\Sigma_g^-)$ ,  $\text{O}_2({}^3\Pi_u)$ , etc. These notation are called spectroscopic terms differentiating electronic states by the symmetry of angular momentum wave functions. Here, we do not enter into the theory of quantum chemistry, the meaning and usefulness of the symbols and selection rules which is important for the discussion of photo-absorption and photolysis reactions are remarked.

**Spectroscopic Terms** Spectroscopic terms for atoms are in general expressed as  ${}^{2S+1}L_J$ . Here,  $S$  and  $L$  is the electron spin and orbital angular momentum, corresponding rotation and revolution of electrons, respectively.  $J$  is the total angular momentum, which is the vectorial sum of spin and orbital angular momentum. Orbital angular momentum  $L$  is designated by S, P, D, etc. for  $L=0, 1, 2$ , etc. Spin angular momentum  $S$  is denoted by using the values of spin multiplicity,  $2S+1$ , i.e. 1, 2, 3 for  $S=1/2, 1, 3/2$ , respectively. Total angular momentum  $J$  is the synthetic vector given by  $J=|L+S|, |L+S-1|, |L+S-2|, \dots, |L-S+2|, |L-S+1|, |L-S|$ . Namely, for example, for the  ${}^3\text{P}$  state ( $S=1, L=1$ ),  $J$  can take the values of 0, 1, 2, giving three different electronic states,  ${}^3\text{P}_0, {}^3\text{P}_1, {}^3\text{P}_2$ . When these spin-orbit states are not differentiated, it is denoted simply by  ${}^3\text{P}$  omitting the  $J$  values. In atmospheric chemistry, ground and excited states of oxygen atoms are usually denoted as  $\text{O}({}^3\text{P})$ ,

O(<sup>1</sup>D) omitting  $J$  values. In the case of halogen atoms, however, discussions are sometimes made for Cl(<sup>2</sup>P<sub>3/2</sub>), Cl(<sup>2</sup>P<sub>1/2</sub>), I(<sup>2</sup>P<sub>3/2</sub>), I(<sup>2</sup>P<sub>1/2</sub>), etc. differentiating the electronic states with different  $J$  values (Sects. 4.3.8 and 4.4.1).

Spectroscopic symbols for diatomic molecules are in general denoted by <sup>2S+1</sup>Λ. Here, the spin angular momentum is the same as in the case of atoms. Orbital angular momentum Λ is the angular momentum around the molecular axis, and designated by Σ, Π, Δ, etc. corresponding to the values of Λ = 0, 1, 2, etc. Further, for homonuclear diatomic molecules such as O<sub>2</sub> and N<sub>2</sub>, another symbol is added representing another molecular symmetry of wave functions. Thus, the initial character, g and u of the German words, gerade and ungerade meaning even and odd, is put after Λ as a subscript to represent a wave function which does not change or change its sign for the inversion at the center of symmetry, respectively, e.g. O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) and O<sub>2</sub>(<sup>3</sup>Π<sub>u</sub>). Further, for the Σ state, the superscript + or - is put after Σ corresponding to the wave function which does not change or change the sign for the inversion at the plane including the molecular axis. According to these rules, the ground state of oxygen is denoted as O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>), and the excited states are denoted with variety e.g. O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>), O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>), O<sub>2</sub>(<sup>3</sup>Σ<sub>u</sub><sup>+</sup>), O<sub>2</sub>(<sup>3</sup>Π<sub>u</sub>), O<sub>2</sub>(<sup>3</sup>Σ<sub>u</sub><sup>-</sup>) (see Fig. 3.5). For a molecule, which is not a homonuclear diatomic molecule, g or u symbols are not put since it does not have the center of symmetry. For example, nitric oxide (NO) molecule has the ground state, NO(<sup>2</sup>Π), and the excited states, e.g. NO(<sup>2</sup>Σ<sup>+</sup>), NO(<sup>4</sup>Π), NO(<sup>2</sup>Δ) (see Fig. 4.28).

For general non-linear polyatomic molecules, symbols A', A'', A<sub>1</sub>, A<sub>2</sub>, B<sub>1</sub>, B<sub>2</sub> etc. are used depending on whether the sign of wave function is changed or not for the symmetric operation at the symmetric axis or plane. However, they seldom appear in the discussion of atmospheric chemistry.

Furthermore, it is customary to put X in front of the spectroscopic terms representing the ground state, and put A, B, C., etc., and a, b, c, etc. for the excited states with the same and different spin multiplicity as the ground state, respectively. For example, O<sub>2</sub>(X<sup>3</sup>Σ<sub>g</sub><sup>-</sup>), O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>), O<sub>2</sub>(b<sup>1</sup>Σ<sub>g</sub><sup>+</sup>), O<sub>2</sub>(A<sup>3</sup>Σ<sub>u</sub><sup>+</sup>), O<sub>2</sub>(B<sup>3</sup>Π<sub>u</sub>) will appear for O<sub>2</sub> (see Fig. 3.5), and NO(X<sup>2</sup>Π), NO(A<sup>2</sup>Σ<sup>+</sup>), NO(a<sup>4</sup>Π), NO(B<sup>2</sup>Π), NO(C<sup>2</sup>Π) for NO (see Fig. 4.28).

**Selection Rules** The intensity of photo-absorption for transition from a lower to higher energy state can be determined by the transition probability |**R**|<sup>2</sup>, where **R** expresses

$$\mathbf{R} = \int \psi'^* \mu \psi'' dv, \quad (2.19)$$

and **R** is called a dipole moment. Here, ψ'' and ψ' is the wave function, or eigenfunction, for the initial (ground) and final (excited) state, respectively, and μ is the electric dipole moment vector. The \* on the right shoulder of ψ'\* represents a so-called conjugated complex function, in which an imaginary part of the wave function, i is replaced by -i. An eigenfunction of a molecule is generally expressed by

$$\psi = \psi_e \psi_v \psi_r, \quad (2.20)$$

where  $\psi_e, \psi_v, \psi_r$  are eigenfunctions of electronic, vibrational and rotational motion, respectively. Using an Eq. (2.20),  $\mathbf{R}$  is written as

$$\mathbf{R} = \int \psi_e'^* \boldsymbol{\mu} \psi_e'' dv_e \int \psi_v'^* \psi_v'' dv_v \int \psi_r'^* \psi_r'' \cos \alpha dv_r. \quad (2.21)$$

Transition probability is determined only by electronic eigenfunctions for atoms, since there is no vibrational or rotational motion.

In order for the absorption and emission of light to occur, above the transition moment has to have non-zero value, and rules to fulfill this are called selection rules. The selection rule for the electric dipole transition of an atom is

$$\Delta L = 0, \pm 1 \text{ (excluding } L = 0 \rightarrow 0) \quad (2.22)$$

for the orbital angular moment and

$$\Delta J = 0, \pm 1 \text{ (excluding } J = 0 \rightarrow 0) \quad (2.23)$$

for the total angular momentum. The case where the total angular momentum  $\mathbf{J}$  is expressed as  $J = |L + S|, |L + S - 1|, |L + S - 2|, \dots, |L - S + 2|, |L - S + 1|, |L - S|$  as previously noted is called Russell-Saunders coupling, and this approximation can be applied to light atoms. In this case, the selection rule for spin quantum number is

$$\Delta S = 0. \quad (2.24)$$

Transitions with transition moments larger than a certain extent, are called the allowed transitions, and those with near-zero moments are called the forbidden transitions. For example, the transition between  $O(^3P) \leftrightarrow O(^1D)$  of O atoms is spin forbidden, and the light emission probability for  $O(^1D) \rightarrow O(^3P)$  is very small so that the radiative lifetime of  $O(^1D)$  is long and the reaction of  $O(^1D)$  with other molecule can be important in the atmosphere.

For diatomic molecules, the allowed transitions for the orbital angular momentum are for

$$\Delta \Lambda = 0, \pm 1. \quad (2.25)$$

In the case where g, u, +, and - are applicable for the  $\Sigma$  state,

$$g \leftrightarrow u, + \leftrightarrow +, - \leftrightarrow - \quad (2.26)$$

are allowed transitions. For example from the ground state of  $O_2$  molecule,  $O_2(X^3\Sigma_g^-) \leftrightarrow O_2(B^3\Pi_u)$  is an allowed transition, and  $O_2(X^3\Sigma_g^-) \leftrightarrow O_2(a^1\Delta_g), O_2(b^1\Sigma_g^+), O_2(A^3\Sigma_u^+)$  are forbidden transitions. For NO molecule,  $NO(X^2\Pi) \leftrightarrow NO(A^2\Sigma^+)$ ,

$\text{NO}(X^2\Pi) \leftrightarrow \text{NO}(B^2\Pi)$  are allowed transitions, and  $\text{NO}(X^2\Pi) \leftrightarrow \text{NO}(a^4\Pi)$  is a spin forbidden transition.

Even for the forbidden transitions, the transition moments are not absolutely zero but in general the absorption and emission of light can be seen with very small probability. This is because, for example, instead of electric dipole transition, magnetic dipole transition with  $\Delta\Lambda = \pm 2$  can occur for diatomic molecules, or the molecular symmetry collapses by a coupling between vibrational and electronic motion for polyatomic molecules. Further, the spin forbidden can be applied only when the Russell-Saunders coupling is applied. For heavy atoms, this rule is broken due to the spin-orbit coupling, and spin forbidden rule cannot be applied. For example, the  $\text{Hg}(^1S) \leftrightarrow \text{Hg}(^3P)$  transition of a mercury atom is spin forbidden, but has a strong absorption and emission of light at 253.7 nm. The ozone meter based on the absorption at this wavelength using the light from a mercury lamp are widely used for monitoring ambient ozone concentrations.

## 2.2 Bimolecular Reactions

### 2.2.1 Potential Surface and Transition State

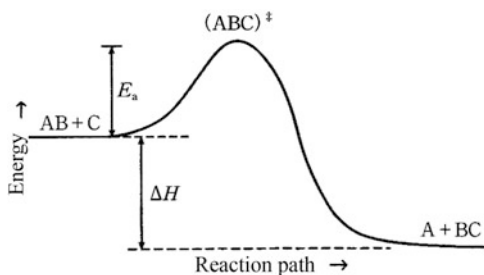
Many of atmospheric reactions are the following type, involving the rearrangement of atoms,



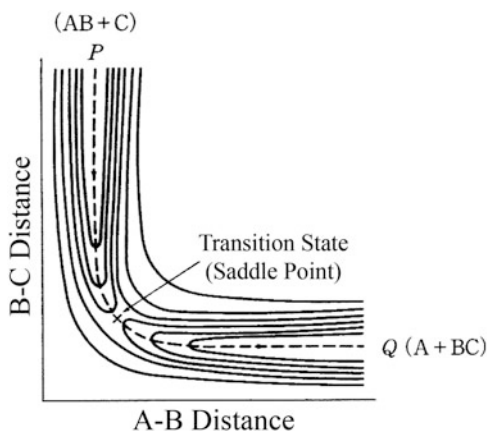
where AB is a molecule and C is a reactive species such as an atom or a free radical in most cases. Reactions in which rearrangement of atoms occurs between two chemical species are called bimolecular reactions. In view of molecular dynamics, a bimolecular reaction is a process in which AB and C collide to associate, passing through an energy barrier called transition state, and dissociate into A+BC. Figure 2.7 illustrates such a reaction pathway schematically. The abscissa is the reaction coordinate, and the ordinate is the potential energy. The left-hand side of the figure shows the state before the reaction AB+C, called reaction system, and the right-hand side corresponds to the state after the reaction A+BC, called the product system. The energy maximum in-between is called the transition state corresponding to the activated complex  $(\text{ABC})^\ddagger$ . Such a concept is based on the transition state theory, which will be discussed in the following Sect. 2.2.2.

Figure 2.7 schematizes the reaction pathway in one-dimension. However, a reaction pathway is actually represented by an energy surface with two axes,  $r(\text{A}-\text{B})$  and  $r(\text{B}-\text{C})$ , representing the inter-atomic distances, A-B, and B-C, respectively, as shown in Fig. 2.8. This surface is called the -potential energy surface. The solid lines in Fig. 2.8 are the energy contour connecting the equipotential points. The reaction system AB+C, and the product system A+BC

**Fig. 2.7** Change of potential energy along the reaction pathway of a bimolecular reaction



**Fig. 2.8** Potential energy surface for a bimolecular reaction



corresponds to the valley of potential energy open toward upper-left, and toward lower right, respectively. The broken line in the figure represents reaction pathway, which reaches from the reaction system to the product system along the lowest energy path passing through the energy maximum point shown by  $\times$ . The transition state  $(ABC)^\ddagger$  shown in Fig. 2.8 corresponds to the energy maximum point  $\times$  in Fig. 2.8. The point  $\times$  corresponds to a saddle point of the curved surface of the potential energy, which is the energy maximum along the reaction axis shown by the broken line, but the energy minimum toward the different direction along the surface. A molecule A-B-C in this transition state is called activated complex and represented by  $ABC^\ddagger$  habitually with a  $\ddagger$  mark. This maximum point acts as an energy barrier when the reaction proceeds from the reaction system to the product system. The difference of energy between the reaction system and the transition state is called the activation energy and is generally represented by  $E_a$ , as seen in Fig. 2.7.

Whether the Reaction (2.27) proceed to the right or, in reverse, to the left, is determined by the difference of the free energy  $\Delta G$  between the reaction system and the product system. According to the first law of thermodynamics, the free energy change  $\Delta G$  must be negative for the reaction to proceed. The  $\Delta G$  is defined by



$$\Delta G = \Delta H - T\Delta S, \quad (2.28)$$

where  $\Delta H$  is the enthalpy change,  $\Delta S$  is the entropy change, and  $T$  is temperature. For the bimolecular reactions to proceed, the entropy change is negligible so that  $\Delta H$  has to be negative. The reactions with negative  $\Delta H$  ( $\Delta H < 0$ ) are called exothermic reactions, and inversely those with positive  $\Delta H$  ( $\Delta H > 0$ ) are called endothermic reactions. The enthalpy change of the reaction  $\Delta H$  is obtained as the difference of enthalpy of formation  $\Delta H_f$  of atoms and molecules in the reaction and product system,

$$\Delta H = \{\Delta H_f(A) + \Delta H_f(BC)\} - \{\Delta H_f(AB) + \Delta H_f(C)\}. \quad (2.29)$$

Enthalpy of formation of typical atoms, molecules and free radicals relevant to atmospheric chemical reactions are cited in Table 2.5. The  $\Delta H$  shown in Fig. 2.7 is the enthalpy change of reaction given by Eq. (2.29), showing the reaction to proceed from left to right since  $\Delta H < 0$  in this figure.

The rate constant of bimolecular reactions represented by Reaction (2.26) is represented as

$$-\frac{d[AB]}{dt} = -\frac{d[C]}{dt} = \frac{d[A]}{dt} = \frac{d[BC]}{dt} = k_r[AB][C]. \quad (2.30)$$

Here, the quantities within the brackets [ ] represent concentration of each species, and the  $k_r$  defined above is called a reaction rate constant. The reaction rate constant of a bimolecular reaction has the dimension of (concentration)<sup>-1</sup>(time)<sup>-1</sup>. In atmospheric chemistry, the concentration of gaseous species is expressed in general by the number density of molecules, molecules cm<sup>-3</sup>, so that the unit of the rate constant of a bimolecular reaction is commonly expressed as cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

### 2.2.2 Activation Energy and Reaction Rate Constant

In this paragraph a reaction formula is expressed simply as



There are two types of molecular theories on reaction rates: collision theory and transition state theory. According to the collision theory, the upper limit of a bimolecular rate constant of a gaseous reaction is the molecular collision frequency obtained by gas kinetics. The molecular collision frequency  $Z_{AB}$  between molecules, A and B, is given by

**Table 2.5** Enthalpy of formation of molecules, atoms and radicals in the gas phase at 298 and 0 K ( $\Delta H_{f, 298}^\circ$ ,  $\Delta H_{f, 0}^\circ$ )

Chemical species	$\Delta H_{f, 298}^\circ$ kJ mol <sup>-1</sup>	$\Delta H_{f, 0}^\circ$ kJ mol <sup>-1</sup>	Chemical species	$\Delta H_{f, 298}^\circ$ kJ mol <sup>-1</sup>	$\Delta H_{f, 0}^\circ$ kJ mol <sup>-1</sup>	Chemical species	$\Delta H_{f, 298}^\circ$ kJ mol <sup>-1</sup>	$\Delta H_{f, 0}^\circ$ kJ mol <sup>-1</sup>
H	218.0	216.0	CH <sub>2</sub> OO (Cl) <sup>c</sup>	110	118	C <sub>2</sub> H <sub>5</sub> ONO	-99.4	
H <sub>2</sub>	0	0	CH <sub>2</sub> O <sub>2</sub> (dioxirane)	5.0	12.6	C <sub>2</sub> H <sub>5</sub> ONO <sub>2</sub>	-154.1 <sup>a</sup>	
O( <sup>3</sup> P)	249.2	246.8	CH <sub>3</sub> O	21.0	28.4	C <sub>2</sub> H <sub>5</sub> OONO <sub>2</sub>	-63.2 <sup>a</sup>	
O( <sup>1</sup> D)	438.9 <sup>a</sup>	436.6 <sup>a</sup>	CH <sub>3</sub> O <sub>2</sub>	9.0		CH <sub>3</sub> C(O) O <sub>2</sub> NO <sub>2</sub>	-240.1	
O <sub>2</sub>	0	0	CH <sub>2</sub> OH	-17.0	-10.7	C <sub>3</sub> H <sub>6</sub>	20.2	34.7 <sup>b</sup>
O <sub>2</sub> ( <sup>1</sup> Δ)	94.3 <sup>a</sup>	94.3 <sup>a</sup>	CH <sub>3</sub> OH	-201.0	-190.1	n-C <sub>3</sub> H <sub>7</sub>	101.3	119.1
O <sub>2</sub> ( <sup>1</sup> Σ)	156.9 <sup>a</sup>	156.9 <sup>a</sup>	CH <sub>2</sub> OOH	67.2		i-C <sub>3</sub> H <sub>7</sub>	86.6	107.1 <sup>b</sup>
O <sub>3</sub>	141.7	144.4	CH <sub>3</sub> OOH	-132.2		C <sub>3</sub> H <sub>8</sub>	-104.7	-82.4 <sup>b</sup>
HO	37.4	37.1	HC(O)OH	-378.8 <sup>a</sup>	-371.6 <sup>a</sup>	C <sub>2</sub> H <sub>5</sub> CHO	-185.6	-170.6 <sup>b</sup>
HO <sub>2</sub>	12.3	15.2	HOCH <sub>2</sub> O <sub>2</sub>	-162.1 <sup>a</sup>		CH <sub>3</sub> COCH <sub>2</sub>	-23.9 <sup>a</sup>	
H <sub>2</sub> O	-241.8	-238.9	CH <sub>3</sub> ONO	-64.0		CH <sub>3</sub> COCH <sub>3</sub>	-217.1	-200.5 <sup>b</sup>
H <sub>2</sub> O <sub>2</sub>	-135.9	-129.9	CH <sub>3</sub> ONO <sub>2</sub>	-122.2		C <sub>3</sub> H <sub>6</sub> OH	-74 <sup>a</sup>	
N	472.4	470.6	CH <sub>3</sub> O <sub>2</sub> NO <sub>2</sub>	-44 <sup>a</sup>		CH <sub>3</sub> C(O) CHO	-271 <sup>a</sup>	
N <sub>2</sub>	0	0	C <sub>2</sub> H <sub>2</sub>	227.4	228.0	S	277.2	274.9
NH <sub>2</sub>	186.2	189.1	C <sub>2</sub> H <sub>4</sub>	52.4	61.0	HS	142.9	142.5
NH <sub>3</sub>	-45.9	-39.0	C <sub>2</sub> H <sub>3</sub>	295.4		H <sub>2</sub> S	-20.6	-17.7
NO	91.0	90.5	C <sub>2</sub> H <sub>5</sub>	120.9	131.8	HSO	-6.1	-3.8
NO <sub>2</sub>	34.0	36.8	C <sub>2</sub> H <sub>6</sub>	-84.0	-68.4 <sup>b</sup>	SO	4.8	4.7
NO <sub>3</sub>	74.7	79.9	CH <sub>2</sub> CN	252.6	255.2	SO <sub>2</sub>	-296.8	-294.3
N <sub>2</sub> O	81.6	85.3	CH <sub>3</sub> CN	74.0	81.0	SO <sub>3</sub>	-395.9	-390.2
N <sub>2</sub> O <sub>4</sub>	11.1	20.4	CH <sub>2</sub> CO	-49.6	-46.4	HSO <sub>2</sub>	-178	
N <sub>2</sub> O <sub>5</sub>	13.3	22.9	CH <sub>3</sub> CO	-10.3	-3.6	HOSO <sub>2</sub>	-373	

HNO	109.2	112.1	CH <sub>2</sub> CHO	10.5		H <sub>2</sub> SO <sub>4</sub>	-732.7	-720.8
HONO	-78.5	-72.8	CH <sub>3</sub> CHO	-166.1	-160.2 <sup>b</sup>	CH <sub>3</sub> S	124.7	129.9 <sup>b</sup>
HNO <sub>3</sub>	-134.3	-124.6	C <sub>2</sub> H <sub>2</sub> OH	121	120 <sup>a</sup>	CH <sub>3</sub> SO	-70.3	
HO <sub>2</sub> NO <sub>2</sub>	-54.0		C <sub>2</sub> H <sub>5</sub> O	-13.6	-0.2	CH <sub>3</sub> SOO	75.7 <sup>a</sup>	87.9 <sup>a</sup>
CH <sub>3</sub>	146.7	150.0	C <sub>2</sub> H <sub>4</sub> OH	-31	-23 <sup>a</sup>	CH <sub>3</sub> SH	-22.9	-11.9 <sup>b</sup>
CH <sub>4</sub>	-74.6	-66.6	C <sub>2</sub> H <sub>5</sub> OH	-234.8	-217.1	CH <sub>3</sub> SCH <sub>2</sub>	136.3	
CO	-110.5	-113.8	(CHO) <sub>2</sub>	-212	206.4	CH <sub>3</sub> SCH <sub>3</sub>	-37.2 <sup>a</sup>	-21.0 <sup>a</sup>
CO <sub>2</sub>	-393.5	-393.1	CH <sub>3</sub> CO <sub>2</sub>	-207.5 <sup>a</sup>		CH <sub>3</sub> SSCH <sub>3</sub>	-24.7	
HCO	44.2	41.6 <sup>b</sup>	CH <sub>3</sub> C(O)OH	-432.8	-418.1 <sup>b</sup>	CS	279.8	276.5
trans-HOCO	-187.9	-183.7	C <sub>2</sub> H <sub>5</sub> O <sub>2</sub>	-27.4		CS <sub>2</sub>	116.7	115.9
cis-HOCO	-175.7	-171.5	CH <sub>3</sub> OOCH <sub>3</sub>	-125.5	-106.5	OCS	-141.7	-141.8
CH <sub>2</sub> O	-108.7	-104.9	CH <sub>3</sub> C(O)O <sub>2</sub>	-154.4		CS <sub>2</sub> OH	108.4	
F	79.4	77.3	ClOO	98.3	99.8	HOBr	-60.5	-50.0
HF	-273.3	-273.3	OCIO	99.4	99.0 <sup>b</sup>	BrO	123.4	131.0
FO	109	108	CINO	52.7	54.6	OB+O	163.9	171.1
FO <sub>2</sub>	25.4 <sup>a</sup>	27.2 <sup>a</sup>	CINO <sub>2</sub>	12.5	17.9	BrOO	119.8	128.2
FONO	67		cis-CIONO	64.4		BrNO	82.2	91.5
FONO <sub>2</sub>	15	22	CIONO <sub>2</sub>	22.9		BrONO <sub>2</sub>	42.7	
FNO	-65.7	-62.6 <sup>b</sup>	CH <sub>3</sub> Cl	-82.0 <sup>a</sup>	-74.0 <sup>a</sup>	CH <sub>2</sub> Br	172.8	
FNO <sub>2</sub>	-79		CHClF <sub>2</sub>	-482.6		CH <sub>3</sub> Br	-36.4	
FCO	-174.1	-174.5	COFCl	-427 <sup>a</sup>	-423 <sup>a</sup>	BrCl	14.8	22.2
F <sub>2</sub>	0	0	Cl <sub>2</sub>	0	0	Br <sub>2</sub> (g)	30.9	45.7
COF <sub>2</sub>	-634.7 <sup>a</sup>	-631.6 <sup>a</sup>	ClOCl	81.3	83.1	CHBr <sub>3</sub>	55.4	
CH <sub>3</sub> CF <sub>3</sub>	-745.6	-732.8	ClOOCl	129.0	132.4	CF <sub>2</sub> ClBr	-589.5	
CH <sub>2</sub> FCHF <sub>2</sub>	-665		Cl <sub>2</sub> O <sub>3</sub>	139	144	CF <sub>3</sub> Br	-641.1	-637.6
CH <sub>2</sub> FCF <sub>3</sub>	-896	-885	COCl <sub>2</sub>	-220.1 <sup>a</sup>	-218.4 <sup>a</sup>	I	106.8	107.2
CHF <sub>2</sub> CF <sub>3</sub>	-1105	-1095	CH <sub>3</sub> CCl <sub>3</sub>	-144.6	-131.9 <sup>b</sup>	HI	26.5	28.7 <sup>b</sup>

(continued)

Table 2.5 (continued)

Chemical species	$\Delta H_{f, 298}^{\circ}$ kJ mol <sup>-1</sup>	$\Delta H_{f, 0}^{\circ}$ kJ mol <sup>-1</sup>	Chemical species	$\Delta H_{f, 298}^{\circ}$ kJ mol <sup>-1</sup>	$\Delta H_{f, 0}^{\circ}$ kJ mol <sup>-1</sup>	Chemical species	$\Delta H_{f, 298}^{\circ}$ kJ mol <sup>-1</sup>	$\Delta H_{f, 0}^{\circ}$ kJ mol <sup>-1</sup>
CF <sub>3</sub>	-465.7	-462.8	CF <sub>3</sub> Cl	-709.2	-704.2	HOI	-69.6	-64.9
CF <sub>3</sub> O	-635		CF <sub>2</sub> Cl <sub>2</sub>	-493.3 <sup>a</sup>	-489.1 <sup>a</sup>	IO	125.1	127.2
CF <sub>3</sub> OH	-923.4 <sup>a</sup>		CFCl <sub>3</sub>	-284.9 <sup>a</sup>	-281.1 <sup>a</sup>	OIO	119.7	123.4
CF <sub>3</sub> O <sub>2</sub>	-614.0 <sup>a</sup>		CCl <sub>4</sub>	-95.8 <sup>a</sup>	-93.3 <sup>a</sup>	INO	121.3 <sup>a</sup>	124.3 <sup>a</sup>
Cl	121.3	119.6	CF <sub>2</sub> Cl	-279	-	INO <sub>2</sub>	60.2 <sup>a</sup>	66.5 <sup>a</sup>
HCl	-92.3	-92.1	CFCl <sub>2</sub>	-89.1		IONO <sub>2</sub>	37.5	46.1
HOCl	-74.8	-71.5 <sup>b</sup>	Br	111.9	117.9	CH <sub>3</sub> I	13.2	
ClO	101.7	101.1	HBr	-36.3	-28.4	I <sub>2</sub> (g)	62.4	65.5

Source: NASA/JPL Panel Evaluation No. 17 unless otherwise noted

<sup>a</sup>IUPAC Subcommittee Report Vol. 1

<sup>b</sup>CCCBDB List of Species with Enthalpy of Formation at 0 K in Database. <http://cccbdb.nist.gov/hf0k.asp>

<sup>c</sup>Criegee Intermediate (carbonyl oxide)

$$Z_{AB} = \pi(r_A + r_B)^2 u N_A N_B = \pi(r_A + r_B)^2 \left( \frac{8k_B T}{\pi \mu_{AB}} \right)^{1/2} N_A N_B, \quad (2.32)$$

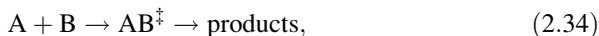
where  $r_A$ ,  $r_B$  are molecular radii of A and B, respectively,  $u$  is the molecular speed,  $k_B$  is the Boltzmann constant (Table 2.1),  $\mu_{AB}$  is the reduced mass of A and B, and  $N_A$  and  $N_B$  is the number density of each molecule. From the above equation, molecular collision frequency at normal temperature (298 K) is calculated to be  $2.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , for example, for molecules with a molecular radius of 0.2 nm, and molecular weight of  $50 \text{ g mol}^{-1}$ . This value is thought to be the upper limit of bimolecular rate constants, and the actual rate constants of many reactions are usually smaller than this.

The most important aspect of bimolecular reactions is that there is an energy barrier to overcome along the reaction path as shown in Figs. 2.7 and 2.8. Considering this factor, the collision theory posits that a molecule with kinetic energy larger than the energy barrier  $E_0$  can react and those with smaller energy than  $E_0$  cannot react. Thus, reflecting such collision probability,  $\exp(-E_0/kT)$ , the reaction rate constant  $k_r$  is given by,

$$k_r = P \sigma_{AB} \left( \frac{8k_B T}{\pi \mu_{AB}} \right)^{1/2} \exp(-E_0/k_B T), \quad (2.33)$$

where  $\sigma_{AB} = \pi(r_A + r_B)^2$  is the collision cross section between molecules A and B, and  $P$  is a steric factor discussed later.

On the other hand, for the transition state theory reaction formula is expressed as



considering the activated complex described in the previous section. A thermal equilibrium constant  $K^\ddagger$  between A, B and  $AB^\ddagger$  is defined by

$$K^\ddagger = \frac{[AB^\ddagger]}{[A][B]} = \exp(-\Delta G^{\circ\ddagger}/RT) = \exp(-\Delta H^{\circ\ddagger}/RT) \exp(\Delta S^{\circ\ddagger}/R), \quad (2.35)$$

using the free energy in Eq. (2.28). Here,  $R$  is the gas constant (Table 2.1). The superscript  $^\circ$  attached to  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$  in the above formula indicates that these values are those referred to the standard state at 1 atm. From this formulation, the reaction rate  $R_r$  and reaction rate constant  $k_r$  are expressed as,

$$R_r = k_B T / h [AB^\ddagger] = k_B T / h \exp(-\Delta G^\ddagger/RT) [A][B] \quad (2.36)$$

and

$$k_r = k_B T / h \exp(-\Delta G^\ddagger / RT) = k_B T / h \exp(\Delta S^\ddagger / R) \exp(-\Delta H^\ddagger / RT), \quad (2.37)$$

respectively. Replacing the enthalpy difference between the reaction system and transition state,  $\Delta H^\ddagger$  by the activation energy  $E_a$ ,  $k_r$  is given by

$$k_r = k_B T / h \exp(\Delta S^\ddagger / R) \exp(-E_a / RT). \quad (2.38)$$

Experimentally, in most of the cases bimolecular reaction rate constants are known to be expressed by

$$k_r(T) = A \exp(-E_a / RT). \quad (2.39)$$

This equation is called the Arrhenius expression and is the fundamental equation representing the temperature dependence of reaction rate constants. Comparing the Arrhenius expression Eq. (2.39), with rate constant Eq. (2.33) by the collision theory and (2.38) by the transition state theory, the temperature dependence of the exponential factor is exactly the same as derived by these theories, and  $E_a$  of the Arrhenius expression corresponds to the activation energy  $E_a$  of the transition state theory. A plot of the logarithm of a reaction rate constant,  $\ln k$  against  $1/RT$ , is called an Arrhenius plot, and the experimental value of activation energy can be obtained from the slope of the Arrhenius plot. This linear relationship is known to hold experimentally for numerous reactions, and the activation energy for each reaction has been obtained.

Meanwhile, the pre-exponential factor  $A$  in the Arrhenius Eq. (2.39) is the temperature independent factor related to reaction frequency. Comparing the Eq. (2.33) for the collision theory and Eq. (2.38) with the transition state theory, the pre-exponential factors in these theories contain temperature dependences of  $T^{1/2}$  and  $T^1$ , respectively. Experimentally, for most of reactions for which the activation energy is not close to zero, the temperature dependence of the reaction rate constants are known to be determined almost solely by exponential factor, and the Arrhenius expression holds as a good approximation. Only for the reaction with near-zero activation energy, the temperature dependence of the pre-exponential factor appears explicitly, and the deviation from the Arrhenius expression can be validated. In this case, an approximated equation modifying the Arrhenius expression can be used,

$$k_r(T) = B T^n \exp(-E_a / RT), \quad (2.40)$$

where  $B$  is the temperature independent constant, and the value of  $n$  is an experimentally-determined parameter.

The upper limit of the pre-exponential factor  $A$  is ca.  $2.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  from the collision theory as mentioned above, but an actual  $A$

value of the Arrhenius expression is often smaller than this value. According to the collision theory, it is thought that the molecules need to collide in a specific orientation for the reaction to occur. The  $P$  in Eq. (2.33) is called a steric factor reflecting the requirement for the specific orientation. As the steric constraint gets larger, the reaction probability decreases and the value of  $A$  gets smaller. In the transition theory, entropy term  $\exp(\Delta S^\ddagger/R)$  is included in the pre-exponential factor, and the steric hindrance for the activated complex is interpreted to be reflected in the decrease of entropy leading to smaller reaction rates.

## 2.3 Termolecular and Unimolecular Reactions

### 2.3.1 Association Reactions

Among atmospheric reactions, association reactions which are represented as termolecular reactions in the form of,



are included, where  $A$  and  $B$  are atoms, molecules or free radicals. As chain termination reactions, this type of association reaction is often important.  $M$  in the above formula is the third body of a reaction. When  $A$  and  $B$  associate, internal energy is gained ( $\Delta H < 0$ ) corresponding to the bond energy of  $A-B$ , and a vibrationally excited molecule  $AB^\ddagger$  is formed. Unless the vibrational energy is taken away,  $AB^\ddagger$  dissociates back into  $A+B$  again, and the reaction does not proceed practically. The third body  $M$  collides with the vibrationally excited molecule and removes energy to some extent, so that it is a necessary molecule to stabilize the molecule  $AB^\ddagger$  by preventing the dissociation into  $A+B$  and complete the reaction substantially. In the atmosphere,  $N_2$  and  $O_2$  molecules play a role of the third body.

Therefore, the termolecular reaction rate constant has pressure dependence, and it is explained by the following scheme, called the Lindemann mechanism. According to the mechanism,



The vibrationally excited molecule  $AB^\ddagger$  formed by the association of  $A$  and  $B$ , is assumed to be in equilibrium with the reaction and product system so that,

$$\frac{d[AB^\ddagger]}{dt} = k_a[A][B] - k_b[AB^\ddagger] - k_c[AB^\ddagger][M] = 0 \quad (2.45)$$

$$[AB^\ddagger] = \frac{k_a[A][B]}{k_b + k_c[M]} \quad (2.46)$$

$$\frac{d[AB]}{dt} = k_c[AB^\ddagger][M] = \frac{k_a k_c [A][B][M]}{k_b + k_c[M]} \quad (2.47)$$

From these equations, the termolecular reaction rate constant  $k_{ter}$  is derived as

$$k_{ter} = \frac{k_a k_c [M]}{k_b + k_c [M]} \quad (2.48)$$

where  $k_a$ ,  $k_b$  and  $k_c$  are a reaction rate constant of reaction (2.42) (2.43) and (2.44), respectively.

When the pressure is low enough, putting  $[M]=0$  in the denominator of Eq. (2.47), the rate equation is,

$$\frac{d[AB]}{dt} = \frac{k_a k_c}{k_b} [A][B][M]. \quad (2.49)$$

In this case, the termolecular reaction rate constant  $k_0$  is

$$k_0 = \frac{k_a k_c}{k_b} \quad (2.50)$$

and  $k_0$  is called the low-pressure limit rate constant. The dimension of the low-pressure limit rate constant is (concentration)<sup>-2</sup>(time)<sup>-1</sup> and the unit used in atmospheric chemistry is cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>.

On the other hand, when pressure is high enough, neglecting  $k_b$  in Eq. (2.47) the reaction rate equation is expressed as

$$\frac{d[A]}{dt} = k_a[A][B]. \quad (2.51)$$

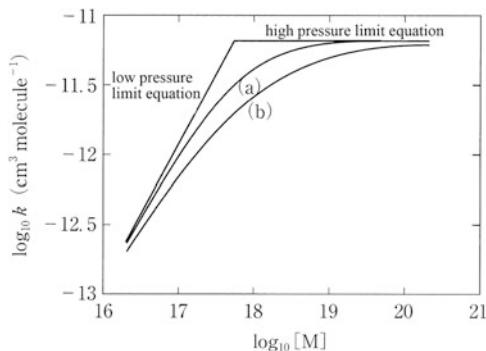
In this case, the reaction rate constant is

$$k_\infty = k_a \quad (2.52)$$

and  $k_\infty$  is called the high-pressure limit rate constant. Using these  $k_0$  and  $k_\infty$ , the rate constant Eq. (2.45) is expressed as



**Fig. 2.9** Pressure dependence of termolecular reaction rate constant for (a) Hinshelwood-Lindeman mechanism and (b) Troe's formula



$$k_{ter} = \frac{k_0 k_\infty [M]}{k_\infty + k_0 [M]} \quad (2.53)$$

The curve (a) in Fig. 2.9 is the schematic graph of the pressure dependence of a termolecular reaction rate constant according to the Lindemann mechanism. From the figure, it can be seen that the reaction rate constant is proportional to  $[M]$  (pressure) in the low-pressure limit, and gets nearly constant independent on the pressure in the high-pressure limit. The intermediate region between these two limits is called the fall-off region.

Although the Lindemann mechanism captures the basic feature of association reactions, and effectively represents the characteristics of pressure dependence of the termolecular reactions, it is not a good enough approximation in quantitative terms. The main reason is that the unimolecular decomposition reaction (see the next section) from  $AB^\ddagger$  to  $A + B$  cannot be represented by a simple first order rate constant. In order the vibrationally excited molecule  $AB^\ddagger$  to decompose, the vibrational energy in the molecule has to be localized into the dissociating bond, and the correct unimolecular reaction rate constant has to be determined considering such probability and the energy removed by a single collision. While the unimolecular decomposition theory is explained in the next paragraph, the following Troe's formula proposed by Troe (1979),

$$k_{ter}([M], T) = \left[ \frac{k_0(T)[M]}{1 + \frac{k_0(T)[M]}{k_\infty(T)}} \right] F_c \left\{ 1 + \left[ \log_{10} \left( \frac{k_0(T)[M]}{k_\infty(T)} \right)^2 \right] \right\}^{-1} \quad (2.54)$$

Is best used for representing the pressure dependence of the termolecular reaction rate constant. This equation is based on the curve fitting to the pressure dependence of the unimolecular decomposition rate by the Kassel theory. In Eq. (2.54),  $F_c$  is called a broadening factor, and it is a good experimental fitting for many termolecular reactions in atmospheric chemistry has been obtained by taking e.g.  $F_c = 0.6$ . The curve (b) in Fig. 2.9 shows the schematic pressure dependence

of a termolecular reaction by the Troe's formula. In this case, temperature dependence of  $k_0$  and  $k_\infty$  are represented by using parameters,  $n$  and  $m$  as

$$k_0(T) = k_0^{300} \left( \frac{T}{300} \right)^{-n} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \quad (2.55)$$

$$k_\infty(T) = k_\infty^{300} \left( \frac{T}{300} \right)^{-m} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \quad (2.56)$$

### 2.3.2 Unimolecular Decomposition Reactions

The molecule AB formed by the association reaction (2.41) may follow thermal decomposition reaction faster than photolysis or bimolecular reactions when the bond energy is small. In this case, the thermal decomposition reaction of AB is expressed by



This type of reaction is called unimolecular reactions.

Historically, the theory of the termolecular reaction mentioned in the previous paragraph has been developed through the unimolecular reaction theory. This paragraph describes unimolecular decomposition reactions in some detail. The chemical formula for the unimolecular decomposition reactions corresponding to the Lindemann mechanism can be shown as



Where M is the third body of a reaction previously described. In the above reaction scheme, assuming the stationary state of  $[\text{AB}^\ddagger]$ , the decomposition rate of AB,  $k_{\text{uni}}$  is given by

$$k_{\text{uni}} = \frac{k_1 k_2 [\text{M}]}{k_2 + k_{-1} [\text{M}]} = \frac{k_2 (k_1 / k_{-1})}{1 + (k_2 / k_{-1} [\text{M}])} \quad (2.60)$$

where  $k_1$ ,  $k_{-1}$  are the rate constants of the forward and reverse reaction of Eq. (2.58),  $k_2$  is the rate constant of reaction (2.59). From Eq. (2.60) the rate constant  $k_\infty$  in the high-pressure limit,  $k_2 \ll k_{-1} [\text{M}]$  is expressed by the first order rate constant ( $\text{s}^{-1}$ ) as

$$k_{\infty} = (k_1/k_{-1})k_2. \quad (2.61)$$

On the other hand, in the low pressure limit  $k_2 \gg k_{-1}[M]$ , the reaction rate is proportional to  $[M]$ , and the rate constant  $k_0$ ,

$$k_0 = k_1 \quad (2.62)$$

is expressed in a bimolecular reaction rate constant ( $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ ). According to the Lindemann mechanism, the formation rate of  $\text{AB}^\ddagger$  having energy higher than the dissociation energy  $E_0$  is obtained by a classical solid collision theory using the collision frequency  $Z$ , activation energy  $E_0$  and the Boltzmann constant  $k_B$ ,

$$k_1 = Z \exp(-E_0/k_B T) \quad (2.63)$$

Here, it is assumed that a single collision with  $M$  causes deactivation of  $\text{AB}^\ddagger$ . The rate constant  $k_{uni}$  calculated from Eq. (2.60) was found to qualitatively reproduce the experimental pressure dependence of the unimolecular decomposition, but to produce a large discrepancy for the high-pressure limit rate constants  $k_{\infty}$  with experimental values.

Hinshelwood proposed a formula for the rate of the  $k_1$  in which  $\text{AB}^\ddagger$  having the energy higher than the dissociation energy  $E_0$ , by considering not only the translational energy of a solid ball but also the distribution of vibrational energy. Thus,

$$k_0 = k_1 = \frac{Z}{(s-1)!} \left( \frac{E_0}{k_B T} \right)^{s-1} \exp\left( -\frac{E_0}{k_B T} \right) \quad (2.64)$$

where  $s$  is the freedom of normal vibrational modes of a molecule composed of  $n$  atoms,  $s = 2n - 1$ . The statistical fraction the  $\text{AB}^\ddagger$  having internal energy  $E \sim E + dE$  is

$$\frac{dk_1}{k_{-1}} = \frac{1}{(s-1)!} \left( \frac{E_0}{k_B T} \right)^{s-1} \exp\left( -\frac{E_0}{k_B T} \right) \left( \frac{dE}{k_B T} \right) \quad (2.65)$$

From this equation a formula corresponding to Eq. (2.57) is

$$k_{uni} = \int_{E_0}^{\infty} \frac{k_2(dk_1/k_{-1})}{1 + (k_2/k_{-1}[M])}. \quad (2.66)$$

Energy integration leads to the high-pressure limit equation,

$$k_{\infty} = \frac{k_2}{(s-1)!} \left( \frac{E_0}{k_B T} \right)^{s-1} \exp\left( -\frac{E_0}{k_B T} \right). \quad (2.67)$$

This treatment is called the Lindemann-Hinshelwood theory. Although the treatment of Hinshelwood was successful in reproducing the experimental values of high-pressure limit rate constants  $k_{\infty}$ , the theory still has one defect, that the values of  $s$  necessary to explain the experimental values differ largely from the actual number of vibrational freedom and there is a large discrepancy of  $k_{uni}$  with experimental values in the fall-off region.

Later development of the unimolecular decomposition theory is on the calculation of the statistical probability related to how the internal energy is distributed within the vibrationally excited molecule  $AB^{\ddagger}$  and is localized to a specific chemical bond to break it. The statistical probability of  $AB^{\ddagger}$  to have an internal energy  $E \sim E + dE$  is replaced by  $P(E)$ , and  $k_2$  is put  $k_2(E)$  considering the energy dependence in Eq. (2.66),  $k_{uni}$  can be written as,

$$k_{uni} = \int_{E_0}^{\infty} \frac{k_2(E)P(E)dE}{1 + k_2(E)/k_{-1}[M]}. \quad (2.68)$$

Presently established unimolecular decomposition theory is called the RRKM theory, taking the initials of Rice, Ramsperger, Kassel and Markus. In the RRK theory which preceded the RRKM theory, assuming the molecule is composed of  $s$  number of harmonic oscillators with frequency  $\nu$ , and the probability of total energy of the molecule concentrate into a single oscillator. The RRK theory advanced the idea of unimolecular decomposition, it still needed the  $s$  and  $\nu$  as adjusting parameters for reproducing experimental values, and their physical meaning was not clear.

Markus improved the idea and the RRKM theory and established the calculation method of the unimolecular decomposition rate constant based on the real vibration-rotation energy levels of reacting molecules. The RRKM theory is a transition state theory, and the equilibrium constant of the transition state is given by

$$K^{\ddagger} = \frac{W^{\ddagger}(E^{\ddagger})}{\rho(E_v)}. \quad (2.69)$$

Here,  $E^{\ddagger}$  is a transition state energy,  $W(E^{\ddagger})$  is state sum of vibrational-rotational freedom of the transition state molecule,  $\rho(E_v)$  is the state density of the reacting molecule with vibrational energy  $E_v$ . Thus,

$$k_2(E^{\ddagger}) = \frac{W^{\ddagger}(E^{\ddagger})}{h\rho(E_v)} \quad (2.70)$$

and the  $k_2(T)$  is obtained by

$$k_2(T) = \int_0^{\infty} k_2(E^\ddagger) P(E^\ddagger) dE^\ddagger. \quad (2.71)$$

Meanwhile,  $P(E^\ddagger)$  can be written using a partition function  $Q$  as

$$P(E^\ddagger) = \frac{\rho(E^\ddagger) \exp(-E^\ddagger/k_B T)}{Q} \quad (2.72)$$

Here, the partition function is a state sum defined in general by

$$Q = \int dE \exp(-E/k_B T) \quad (2.73)$$

From Eqs. (2.68) and (2.69),

$$k_2(T) = \frac{1}{hQ} \int_0^{\infty} \rho(E^\ddagger) \exp\left(-\frac{E^\ddagger}{k_B T}\right) dE^\ddagger \quad (2.74)$$

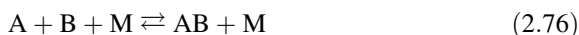
and the high-pressure limit equation is

$$k_\infty(T) = \frac{k_\infty T}{h} \frac{Q^\ddagger}{Q} \exp\left(-\frac{E_0}{k_B T}\right) \quad (2.75)$$

which agrees with the equation of the transition state theory. Practical calculation methods for rate constants using these equations should be referred to in the references at end of the chapter.

The RRKM theory reproduces experimental values well, and is now recognized as an established unimolecular reaction theory. The calculation by the RRKM theory has been applied to atmospheric reactions, for example, OH + CO (Sect. 5.2.3), OH + NO<sub>2</sub> + M (Sect. 5.2.4) for obtaining the theoretical rate constants based on quantum chemistry.

Because the termolecular association reaction (2.41) and the unimolecular decomposition are reverse reactions, a thermal equilibrium between A + B and AB,



is established, and each reaction rate constant is interlinked with the thermodynamic equilibrium constant,

$$k_{ter}[A][B] = k_{uni}[AB] \quad (2.77)$$

$$K(T) = \frac{[A][B]}{[AB]} = \exp\left(\frac{-\Delta G^\circ}{RT}\right) = \exp\left(-\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}\right) \quad (2.78)$$

$$k_{uni} = k_{ter}K(T). \quad (2.79)$$

From these relationships, unimolecular decomposition rate constants can be calculated from termolecular reaction rate constants and equilibrium constants (see Table 5.3).

## 2.4 Multiphase Reactions

A series of a processes including, for example, the uptake of atmospheric molecules into liquid particles such as fog or rain droplets followed by liquid phase reactions is called multiphase reactions, while a process in which molecules react on solid aerosol surface is often called heterogeneous reactions. However, since these terms are often used confusingly, and the processes contain common elements of chemical kinetics, they are treated together in this section.

### 2.4.1 Accommodation Coefficient and Uptake Coefficient

A fundamental parameter based on quantum chemistry to determine the rate of transfer of a molecule from the gas phase to the liquid or solid phase when a gas phase molecule collides with a particle surface is called a mass accommodation coefficient  $\alpha$  and is defined by

$$\alpha = \frac{\text{Number of molecules initially attached to the liquid or solid surface}}{\text{Number of molecule colliding to the liquid or solid surface}}. \quad (2.80)$$

According to the molecular scattering theory, a particle incident to the surface has a certain probability for a certain amount to stay on the surface, and the rest is scattered back into the gas phase.  $\alpha$  is an initial attaching probability and is a parameter to be determined through a molecular dynamics simulation based on quantum chemistry. Although in surface chemistry, a thermal accommodation coefficient is also used, in atmospheric chemistry a mass accommodation coefficient is solely used so that here it is simply called an accommodation coefficient. In general  $\alpha$  cannot be determined directly by experiments, and the experimentally determined parameter of intake of a gaseous molecule to the particle surface is an uptake coefficient  $\gamma$  defined by

$$\gamma = \frac{\text{Number of molecules lost from the gas phase into the liquid or solid phase}}{\text{Number of molecule colliding to the liquid or solid surface}}. \quad (2.81)$$

$\gamma$  is defined as a coefficient of a removal reaction rate constant of gaseous molecules as described below.

A flux of a number of molecules colliding on a liquid or solid surface per unit time and unit surface area,  $J_{col}$ , is given by

$$J_{col} = \frac{1}{4} u_{av} N_g \quad (2.82)$$

where  $u_{av}$  ( $\text{cm s}^{-1}$ ) is the average thermal kinetic velocity,  $N_g$  ( $\text{molecules cm}^{-3}$ ) is a molecular density in the gas phase.  $U_{av}$  in the above equation is given by gas kinetic theory,

$$u_{av} = \left( \frac{8k_B T}{\pi M} \right)^{1/2} \quad (2.83)$$

Where  $T$  is the temperature,  $M$  is the mass of a molecule,  $k_B$  is the Boltzmann constant. Thus, the net number of molecules taken into a particle surface per unit time and unit surface area,  $J_{het}$  ( $\text{molecules cm}^{-2} \text{s}^{-1}$ ), can be given by

$$J_{het} = \frac{1}{4} \gamma u_{av} N_g. \quad (2.84)$$

Multiplying with the surface area density  $A$  ( $\text{cm}^2 \text{cm}^{-3}$ ) of particles contained in the unit volume of gas, the removal rate of molecules in the gas phase by the surface heterogeneous process is given. When the removal rate of gas phase molecules is expressed by the pseudo first order rate equation,

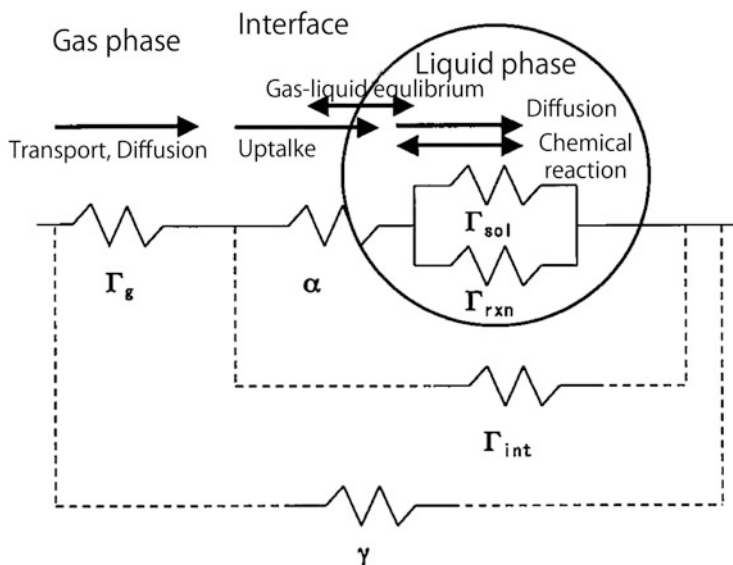
$$\frac{d[N_g]}{dt} = -k_{het} [N_g], \quad (2.85)$$

the heterogeneous reaction rate constant  $k_{het}$  ( $\text{s}^{-1}$ ) is given by

$$k_{het} = \frac{1}{4} \gamma u_{av} A. \quad (2.86)$$

From this equation,  $\gamma$  can be obtained experimentally from the experimental value of  $k_{het}$  and parameters  $u_{av}$  and  $A$ .

The surface area  $A$  is obtained for a spherical particle such as liquid particle by using size distribution  $n(r)$  for a radius in  $r \sim r + dr$ ,



**Fig. 2.10** Schematic diagram of resistant model for gas-liquid multiphase reactions

$$A = \int_0^{\infty} 4\pi r^2 n(r) dr. \quad (2.87)$$

However, solid particles in the atmosphere are mostly non-spherical. Furthermore, the surface is often porous with micropores. In such a case the actual surface area is much larger than the geometrical surface area, and the experimental values of  $\gamma$  differ much depending on which Fig. 2.10 surface area  $A$  is used (see Sects. 6.3 and 6.4).

Figure 2.10 illustrates a diagram of schematizing the processes of multiphase reactions on a liquid particle by the resistant model. As shown in the scheme, multiphase reactions include the processes, (1) transport and diffusion of a gaseous molecule to the gas-liquid surface, (2) accommodation at the interface, (3) - gas-liquid equilibrium at the interface, (4) physical dissolution and diffusion into the bulk liquid, and (5) chemical reaction in the bulk liquid.

The resistant model is a method which treats these series of the processes kinetically. In this model, the rate of each process is expressed by conductance  $\Gamma$ , which is the ratio the process to proceed per collision of a gaseous molecule to the interface. The uptake coefficient  $\gamma$  is expressed as the series and parallel coupling of the resistance, which is a reciprocal of  $\Gamma$ .

$$\frac{1}{\gamma} = \frac{1}{\Gamma_g} + \frac{1}{\alpha} + \frac{1}{\Gamma_{sol} + \Gamma_{rxn}} \quad (2.88)$$

where  $\alpha$  is the accommodation coefficient defined above,  $\Gamma_g$  is the conductance of diffusion of a gaseous molecule to the interface,  $\Gamma_{sol}$  and  $\Gamma_{rxn}$  are those of diffusion



of the taken-up molecule from the interface to the bulk liquid, and of the chemical reaction in the bulk liquid, respectively. In Fig. 2.10, the right side of the Eq. (2.88) lower than the second term is expressed by  $1/\Gamma_{\text{int}}$ . The  $\Gamma_{\text{sol}}$  depends not only on the solubility of molecules to the solution, but also on the surface concentration of the accumulated products formed in the surface reaction, so that is in general a time-dependent parameter. Therefore,  $\gamma$  itself is in general dependent on reaction time (see Chap. 6). In this treatment of  $\gamma$ , gas phase diffusion  $\Gamma_g$  can be neglected in the case of  $\alpha < 0.01$ , but the diffusion process to the interface represented by  $\Gamma_g$  becomes rate determining in the case of  $\alpha$  with larger than 0.01.

Since the diffusion rate of gaseous molecules to the spherical particle surface is given by  $4\pi r D_g N_g$  (molecules  $\text{s}^{-1}$ ) using the diffusion coefficient  $D_g$ , the flux of a number of gaseous molecules transported to the interface by diffusion per unit time and unit volume,  $J_g$  (molecules  $\text{cm}^{-2} \text{s}^{-1}$ ), is given by dividing with the surface area of the spherical particles  $4\pi r^2$ ,

$$J_g = \frac{4\pi r D_g N_g}{4\pi r^2} = \frac{D_g}{r} N_g. \quad (2.89)$$

Normalizing  $J_g$  with the collision flux to the surface  $J_{\text{col}}$  given by Eq. (2.82), diffusion conductance  $\Gamma_g$  near the interface is given by

$$\Gamma_g = \frac{J_g}{J_{\text{col}}} = \frac{4D_g}{r u_{\text{av}}} = \frac{4D_g}{r} \left( \frac{\pi M}{8k_B T} \right). \quad (2.90)$$

## 2.4.2 Gas-Liquid Equilibrium and Henry's Law Coefficients

The gas-liquid equilibrium constants determine the solubility of gaseous molecule into the liquid phase so that they are important parameters for the kinetic analysis of multiphase reactions. Liquid reactions are important in the atmosphere for fog and cloud water droplets with the particle diameter of 1–100  $\mu\text{m}$ . When those water droplets coexist in the atmosphere, water soluble molecules X in the gas phase is absorbed by the droplet, and the gas-liquid equilibrium,



is established. Here, X(g) and X(aq) are the chemical species X in the gas and aqueous phase, respectively. This gas-liquid equilibrium is expressed by using the equilibrium constant called the Henry's law coefficient,  $K_H$ ,

$$\frac{[\text{X(aq)}]}{p_x} = K_H. \quad (2.92)$$

**Table 2.6** Henry's law coefficients of atmospheric molecules for water<sup>a</sup> (298 K)

Chemical Species	$K_H$ (M atm <sup>-1</sup> )	Chemical species	$K_H$ (M atm <sup>-1</sup> )
O <sub>2</sub>	$1.3 \times 10^{-3}$	CO	$9.8 \times 10^{-4}$
O <sub>3</sub>	$1.0 \times 10^{-2}$	CO <sub>2</sub>	$3.4 \times 10^{-2}$
OH	39	CH <sub>3</sub> Cl	0.13
HO <sub>2</sub>	690	CH <sub>3</sub> Br	0.17
H <sub>2</sub> O <sub>2</sub>	$8.4 \times 10^4$	CH <sub>3</sub> I	0.20
NH <sub>3</sub>	60	HCHO	$3.2 \times 10^3$
NO	$1.9 \times 10^{-3}$	CH <sub>3</sub> CHO	13
NO <sub>2</sub>	$1.2 \times 10^{-2}$	CH <sub>3</sub> OH	200
NO <sub>3</sub>	$3.8 \times 10^{-2}$	CH <sub>3</sub> OOH	300
HNO <sub>2</sub> (HONO)	49 <sup>b</sup>	HOCH <sub>2</sub> OOH	$1.7 \times 10^6$
HNO <sub>3</sub> (HONO <sub>2</sub> )	$2.1 \times 10^{5b}$	CH <sub>3</sub> C(O)OOH	840
SO <sub>2</sub>	1.4	CH <sub>3</sub> COCH <sub>3</sub>	28
H <sub>2</sub> S	0.10	HCOOH	$8.9 \times 10^3$
CH <sub>3</sub> SCH <sub>3</sub>	0.54	CH <sub>3</sub> C(O)OH	$4.1 \times 10^3$
HCl	1.1 <sup>b</sup>	CH <sub>3</sub> ONO <sub>2</sub>	2.0 <sup>b</sup>
HOBr	$>1.3 \times 10^2$	CH <sub>3</sub> C(O)O <sub>2</sub> NO <sub>2</sub> (PAN)	2.9 <sup>c</sup>

<sup>a</sup>Unless otherwise specified, NASA/JPL Evaluation No.17 (Sander et al. 2011)

<sup>b</sup>Seinfeld and Pandis (2006)

<sup>c</sup>Pandis and Seinfeld (1989)

The  $[X(aq)]$  and  $p_X$  in the above equation are the concentration of X in the aqueous solution and the partial pressure of X in the gas phase, respectively. Usually, the Henry's law coefficient is expressed in the unit of [mole l<sup>-1</sup> atm<sup>-1</sup>]. If the molar concentration mole l<sup>-1</sup> is expressed by M, the unit is [M atm<sup>-1</sup>], and Table 2.6 tabulates the Henry's law coefficients in this unit for important molecules in the atmosphere. When the concentration of the molecules in the atmosphere is expressed not by partial pressure but by molar concentration  $[X(g)]$  in the same unit in the liquid phase, the dimensionless Henry's law coefficient,  $\hat{K}_H$  is defined by

$$\frac{[X(aq)]}{[X(g)]} = \frac{N_{aq}}{N_g} = K_H RT = \hat{K}_H. \quad (2.93)$$

The conversion from  $K_H$  to  $\hat{K}_H$  is obtained by multiplying  $RT$  to  $K_H$  as shown in the above equation where R is the gas constant (Table 2.1) and  $T(K)$  is the temperature.

The Henry's law coefficient is temperature dependent, and the dependence is given by van't Hoff equation, which is as follows,

$$\frac{d \ln K_H}{dT} = \frac{\Delta H_{A,298}}{RT^2} \quad (2.94)$$

where  $\Delta H_{A,298}$  (kJ mole<sup>-1</sup>) is the enthalpy change (the heat of dissolution) when the dissolution process (2.91) proceeds from left to right. Table 2.7 tabulates the values

**Table 2.7** Heat of dissolution of atmospheric molecules for water (298 K)

Chemical species	$\Delta H_A$ (kJ mol <sup>-1</sup> )	Chemical species	$\Delta H_A$ (kJ mol <sup>-1</sup> )
O <sub>3</sub>	-21.1	CO <sub>2</sub>	-20.3
H <sub>2</sub> O <sub>2</sub>	-60.7	HCHO	-53.6
NH <sub>3</sub>	-34.2	CH <sub>3</sub> OH	-40.6
NO	-12.1	CH <sub>3</sub> OOH	-46.4
NO <sub>2</sub>	-20.9	CH <sub>3</sub> C(O)OOH	-51.0
HNO <sub>2</sub> (HONO)	-39.7	HCOOH	-47.7
SO <sub>2</sub>	-26.2	CH <sub>3</sub> C(O)O <sub>2</sub> NO <sub>2</sub> (PAN)	-49.0
HCl	-16.7		

Source: Pandis and Seinfeld (1989)

of  $\Delta H_{A,298}$  for typical atmospheric molecules. As shown in the table, since enthalpy change associated with dissolution is negative in general, the Henry's law coefficients increases with the decrease of temperature. Namely, the solubility of gaseous molecule to aqueous solution increases with the decrease of temperature. Since the temperature dependence of  $\Delta H_A$  is negligible if the temperature change is not very large, the Henry's law coefficients at different temperatures can be obtained from Eq. 2.94 by

$$\ln \frac{K_H(T_2)}{K_H(T_1)} = \frac{\Delta H_{A,298}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (2.95)$$

using  $\Delta H_{A,298}$  values given in Table 2.7.

### 2.4.3 Diffusion and Reactions in the Liquid Phase

Here, the diffusion process is considered after a molecule X is taken into the liquid phase. Assuming the liquid phase is the aqueous solution, and the diffusion of dissolved molecules occurs in one-dimension, the process is expressed by the one-dimensional diffusion equation,

$$\frac{\partial N_{aq}}{\partial t} = D_{aq} \frac{\partial^2 N_{aq}}{\partial x^2}, \quad (2.96)$$

where  $x$  is the axis distance from the interface along the depth of solution,  $N_{aq}$  is the concentration of molecules X (molecules cm<sup>-3</sup>), and  $D_{aq}$  is the diffusion coefficient of the molecules in the aqueous solution. Since the diffusion equation is the partial differential equation of the first order with time and second order with space, one initial condition with regard to  $N_{aq}$  and two boundary conditions with regard to  $N_{aq}$  in a certain point of the space is necessary. Here, we take  $N_{aq} = N_{aq,bulk}$  as an initial condition at  $t = 0$  and  $x > 0$ , and  $N_{aq} = N_{aq,int}$  at  $x = 0$  (interface) regardless of time

$t$  as the first boundary condition (gas-liquid equilibrium is established very fast and the liquid interface concentration is always at the equilibrium concentration determined by the Henry's law coefficients), and  $N_{aq} = N_{aq,bulk}$  at  $x = \infty$  regardless of time  $t$  as the second boundary condition (deep inner part of the liquid droplet, the concentration of  $X$  does not change from the initial concentration). Solving the diffusion Eq. (2.96) under these conditions, the rate of molecules passing through the unit area of liquid phase after time  $t$  has elapsed,  $J_{sol}(t)$  (molecules  $\text{cm}^{-2} \text{s}^{-1}$ ), can be obtained as

$$J_{sol}(t) = (N_{aq,int} - N_{aq,bulk}) \sqrt{\frac{D_{aq}}{\pi t}}. \quad (2.97)$$

As expected, the diffusion rate is dependent on the difference of the concentrations near the gas-liquid interface and in the bulk liquid. Also, the diffusion rate decreases in inverse proportion to the square root of time. This is because the number of re-evaporating molecules from gas-liquid surface to the gas phase increases with time.

Here, putting  $N_{aq,bulk} = 0$  at  $t = 0$ , the above equation becomes

$$J_{sol}(t) = N_{aq,int} \sqrt{\frac{D_{aq}}{\pi t}}. \quad (2.98)$$

Assuming the gas-liquid equilibrium,

$$N_{aq,int} = N_g \hat{K}_H, \quad (2.99)$$

Eqs. (2.98) and (2.99) gives,

$$J_{sol}(t) = N_g \hat{K}_H \sqrt{\frac{D_{aq}}{\pi t}}. \quad (2.100)$$

By normalizing  $J_{sol}(t)$  with the flux  $J_{col}$ , the gaseous molecules collide at the interface in a unit surface area and unit time (Eq. 2.79), the diffusion conductance  $\Gamma_{sol}$  in the liquid phase in Eq. 2.84 is given by

$$\Gamma_{sol}(t) = \frac{J_{sol}(t)}{J_{col}} = \frac{4\hat{K}_H}{u_{av}} \sqrt{\frac{D_{aq}}{\pi t}}. \quad (2.101)$$

As shown in the above equation,  $\Gamma_{sol}$  decreases with time, reflecting the re-evaporation process from the liquid to gas phase. Therefore, after enough time has elapsed ( $t \rightarrow \infty$ ), uptake rate and re-evaporation rate gets equal to reach the gas-liquid equilibrium and  $\Gamma_{sol} \rightarrow 0$ . Meanwhile, when the liquid particles are very small, and the interface layer forms bulk layer, gas-liquid equilibrium is completed instantaneously, and Eq. (2.98) does not apply.

When the molecule  $X$  is consumed irreversibly by the chemical reactions in the liquid phase, putting the pseudo-first order reaction rate constant is  $k_{aq}$  ( $s^{-1}$ ), the diffusion equation, Eq. (2.93) becomes,

$$\frac{\partial N_{aq}}{\partial t} = D_{aq} \frac{\partial^2 N_{aq}}{\partial t^2} - k_{aq} N_{aq}. \quad (2.102)$$

Solving this equation under the same boundary conditions as mentioned above, assuming that the Henry's law equilibrium is established and that  $N_{aq,bulk} = 0$  and  $kt \gg 1$ , the flux of molecules dissipating by the reaction in a unit time and unit area (molecules  $cm^{-2} s^{-1}$ ), is given by

$$J_{rxn} = N_{aq,int} \sqrt{D_{aq} k_{aq}}. \quad (2.103)$$

Assuming the Henry equilibrium at the gas-liquid interface,

$$J_{rxn} = N_g \hat{K}_H \sqrt{D_{aq} k_{aq}}. \quad (2.104)$$

By normalizing with  $J_{col}$  given in Eq. (2.88), the conductance of the reactions in the liquid phase is

$$\Gamma_{rxn} = \frac{J_{rxn}}{J_{col}} = \frac{4\hat{K}_H}{u_{av}} \sqrt{D_{aq} k_{aq}}. \quad (2.105)$$

This equation is applicable for the irreversible reactions and when the solubility is large enough.

## 2.5 Literatures

Among the textbooks on atmospheric chemistry, relatively detailed descriptions on chemical reactions are given in the followings:

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## Chapter 3

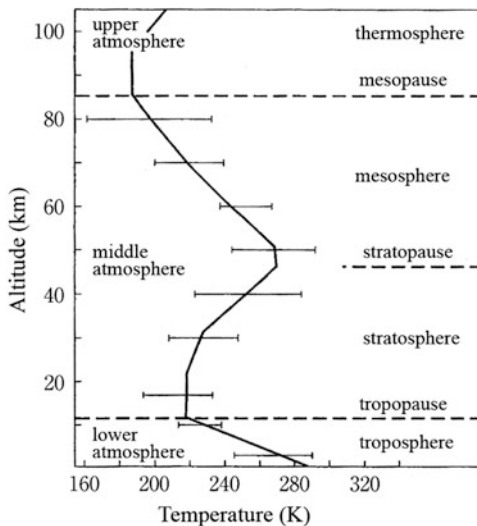
# Fundamentals of Atmospheric Photochemistry

The prime driver of the chemical system of the earth's atmosphere is photochemical reactions caused by solar radiation. The atmosphere of the earth is divided into levels called the troposphere, stratosphere, mesosphere and thermosphere from nearest the ground to farthest according to the characteristics of the temperature gradient as shown in Fig. 3.1. The cause of the temperature inversion in the stratosphere, which characterizes the earth's atmosphere, is the formation of an ozone layer by the photolysis of oxygen, one of the major components of the atmosphere. In this chapter, the spectrum of solar radiation, actinic flux, and so on, that is necessary to calculate the photolysis rate of atmospheric molecules are explained.

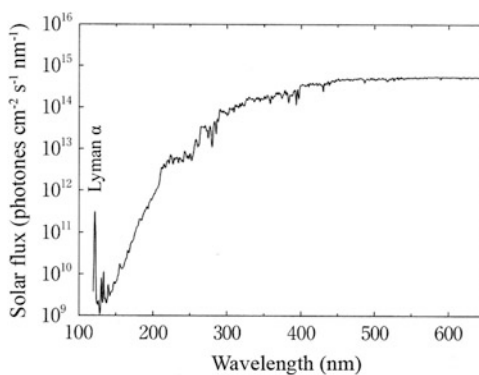
### 3.1 Extraterrestrial Solar Spectrum

In order to discuss the photochemical reactions in the earth's atmosphere, it is necessary to calculate quantitatively how the solar spectrum changes in reaching from outer space to the Earth's surface. For this purpose, let us first look at the extraterrestrial solar spectrum before it is affected by chemical species in the earth's atmosphere. The measurements of the solar radiant intensity outside of the earth's atmosphere are made by satellites for the shorter wavelength of the ultraviolet region, and by ground-based observations for longer wavelengths of the ultraviolet and visible region. Recent data is compiled by 2000 ASTM E490 database (Standard Extraterrestrial Spectrum Reference) by ASTM (American Society for Testing and Materials) (2006). This database covers from 120 nm in the far ultraviolet region to the infrared region with a wavelength longer than 10  $\mu\text{m}$ . It is based on the compilation of the observational data by several satellite sensors by Woods et al. (1996) for the wavelengths shorter than 330 nm, and those by ground-based observational data by Neckel and Labs (1984) for the longer wavelengths. Further, Wehrli Standard Extraterrestrial Solar Irradiance Spectrum by WMO/WRDC

**Fig. 3.1** Vertical temperature profile of the atmosphere based on US Standard Atmosphere (Adapted from Goody 1995 based on NOAA, 1976)



**Fig. 3.2** Extraterrestrial solar flux (irradiance) (base on ASTM International, 2006)



(World Radiation Data Center) (1985) has been widely used, which covers a wavelength region of 200 nm–10  $\mu\text{m}$ .

The spectral distribution of extraterrestrial standard solar irradiance (photons  $\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$ ) at the perpendicular surface to the sun is given in Fig. 3.2 with spectral resolution of 1 nm, and the numerical data in 5 nm intervals is given in Table 3.1. Here, the unit of the solar irradiance given in the figure and the table is photon per unit area, unit time and per given wavelength interval. Although the absorption lines called Fraunhofer lines originating from various atoms can be seen, solar irradiation can be basically treated as a continuous spectrum at wavelengths longer than 200 nm from the viewpoint of atmospheric photochemistry. At wavelengths shorter than 200 nm, line spectrum from the sun cannot be neglected, and the most important is the Lyman- $\alpha$  line at 121.6 nm corresponding to the  $2P \rightarrow 1S$  transition of a hydrogen atom, which has the intensity of ca.  $3 \times 10^{11}$



**Table 3.1** Extraterrestrial solar radiation flux <sup>a, b</sup> (average sun-earth distance) (per 5 nm, base e)

Wavelength (nm)	Radiation intensity (photons cm <sup>-2</sup> s <sup>-1</sup> 5 nm <sup>-1</sup> )	Wavelength (nm)	Radiation intensity (photons cm <sup>-2</sup> s <sup>-1</sup> 5 nm <sup>-1</sup> )	Wavelength (nm)	Radiation intensity (photons cm <sup>-2</sup> s <sup>-1</sup> 5 nm <sup>-1</sup> )
120–125 <sup>c</sup>	4.15 E+11	290–295	4.05 E+14	460–465	2.38 E+15
125–130	9.15 E+09	295–300	3.77 E+14	465–470	2.35 E+15
130–135	2.77 E+10	300–305	3.94 E+14	470–475	2.37 E+15
135–140	1.48 E+10	305–310	4.45 E+14	485–480	2.44 E+15
140–145	1.81 E+10	310–315	5.30 E+14	480–485	2.46 E+15
145–150	2.49 E+10	315–320	5.46 E+14	485–490	2.25 E+15
150–155	4.85 E+10	320–325	5.87 E+14	490–495	2.42 E+15
155–160	7.25 E+10	325–330	7.89 E+14	495–500	2.45 E+15
160–165	1.02 E+11	330–335	8.07 E+14	500–505	2.37 E+15
165–170	1.91 E+11	335–340	7.60 E+14	505–510	2.48 E+15
170–175	3.25 E+11	340–345	8.06 E+14	510–515	2.46 E+15
175–180	6.09 E+11	345–350	7.97 E+14	515–520	2.29 E+15
180–185	9.76 E+11	350–355	9.02 E+14	520–525	2.48 E+15
185–190	1.41 E+12	355–360	7.99 E+14	525–530	2.46 E+15
190–195	2.04 E+12	360–365	8.87 E+14	530–535	2.54 E+15
195–200	3.03 E+12	365–370	1.09 E+15	535–540	2.57 E+15
200–205	4.39 E+12	370–375	9.73 E+14	540–545	2.52 E+15
205–210	7.39 E+12	375–380	1.11 E+15	545–550	2.58 E+15
210–215	1.78 E+13	380–385	9.09 E+14	550–555	2.60 E+15
215–220	2.14 E+13	285–390	1.01 E+15	555–560	2.57 E+15
220–225	2.90 E+13	390–395	1.03 E+15	560–565	2.62 E+15
225–230	2.65 E+13	395–400	1.26 E+15	565–570	2.62 E+15
230–235	2.81 E+13	400–405	1.73 E+15	570–575	2.66 E+15
235–240	2.81 E+13	405–410	1.71 E+15	575–580	2.66 E+15
240–245	3.53 E+13	410–415	1.79 E+15	580–585	2.72 E+15
245–250	3.21 E+13	415–420	1.81 E+15	585–590	2.61 E+15
250–255	3.29 E+13	420–425	1.85 E+15	590–595	2.68 E+15
255–260	6.95 E+13	425–430	1.73 E+15	595–600	2.68 E+15
260–265	9.18 E+13	430–435	1.71 E+15	600–605	2.66 E+15
265–270	1.66 E+14	435–440	1.95 E+15	605–610	2.68 E+15
270–275	1.40 E+14	440–445	2.12 E+15	610–615	2.64 E+15
275–280	1.25 E+14	445–450	2.21 E+15	615–620	2.63 E+15
280–285	1.63 E+14	450–455	2.31 E+15	620–625	2.65 E+15
285–290	2.34 E+14	455–460	2.35 E+15	625–630	2.65 E+15

<sup>a</sup>Calculated based on ASTM International, Standard Solar Constant and Zero Air Mass Solar Spectral Irradiance Tables, E490-001, 2006

<sup>b</sup>Eleven-year cycle variation (<20 %) due to the solar activity is observed for the radiation intensity in the wavelength range of 120–300 nm (Brasseur and Simon 1981; Brasseur et al. 1999)

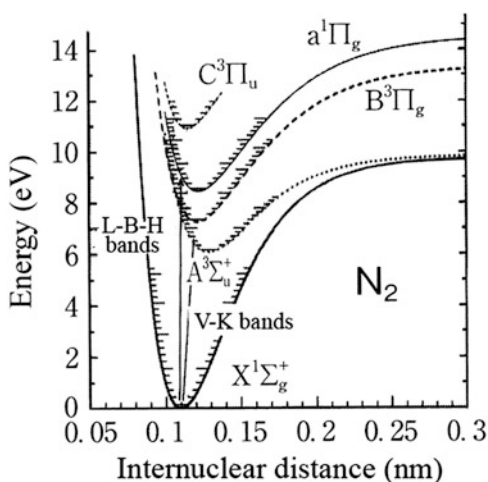
<sup>c</sup>Mainly contribution of 121.6 nm Lyman- $\alpha$  line ( $\pm 30$  % fluctuation). (Timothy and Timothy 1970)

(photons  $\text{cm}^{-2} \text{s}^{-1}$ ) as seen in Fig. 3.2. Solar radiation can be approximated by blackbody radiation at 5900 K at the wavelength longer than 400 nm, but the corresponding black body temperature gets lower at wavelengths shorter than 400 nm.

### 3.2 Attenuation of Solar Irradiance in the Atmosphere by $\text{N}_2$ , $\text{O}_2$ , and $\text{O}_3$

After entering into the earth's atmosphere, solar radiation is absorbed by  $\text{N}_2$  and  $\text{O}_2$ , the major component of the atmosphere. The bond energy of  $\text{N}_2$ ,  $D_0$  (N-N) is large, 9.76 eV corresponding to the photon energy at the wavelength of 127.9 nm. Figure 3.3 shows the potential energy diagram of molecular  $\text{N}_2$ . The  $\text{N}_2$  molecule has Lyman-Birge-Hopfield bands (L-B-H bands) corresponding to the  $a^1\Pi_g - X^1\Sigma_g^+$  transition in the wavelength region of 100–150 nm, which has a vibrational structure. The transition of L-B-H bands with peaks at 135.4 nm is electric dipole forbidden and the absorption cross section is smaller than  $4 \times 10^{-21} \text{ cm}^2$  (Lofthus and Krupenie 1977). Because a much stronger absorption spectrum of  $\text{O}_2$  exists in this wavelength region, the absorption of  $\text{N}_2$  does not actually affect the solar irradiance. The absorption to the lower energy level of  $\text{N}_2$   $A^3\Sigma_u^+ - X^1\Sigma_g^+$  is the spin forbidden transition, and the corresponding Vegard-Kaplan bands (V-K bands) is observed in aurora, but can be neglected when calculating solar irradiance. The strong absorption bands of  $\text{N}_2$  is in the wavelength region shorter than 100 nm, and a band spectrum and continuum exist in regions from 66 to 100 nm, and shorter than 66 nm, respectively. These are important for photochemistry in the thermosphere,

**Fig. 3.3** Potential energy curves of  $\text{N}_2$  (Adapted from Lofthus and Krupenie 1977)



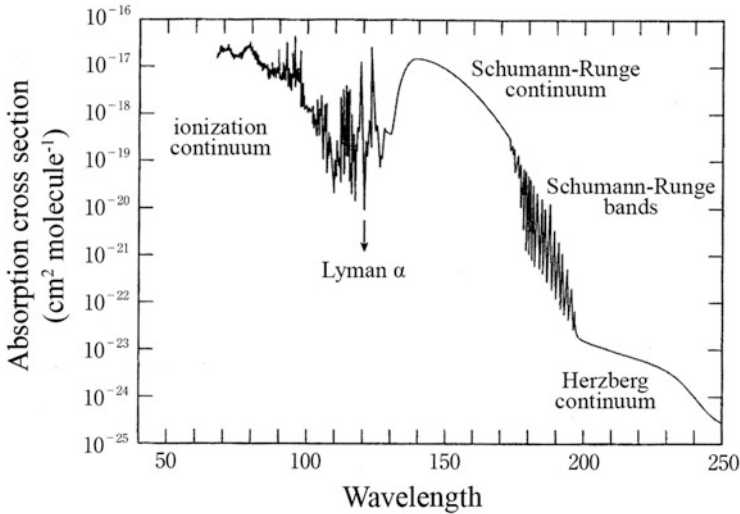


Fig. 3.4 Absorption spectrum of O<sub>2</sub> (Adapted from Goody 1995)

100–300 km above the ground, but the absorption and photolysis of N<sub>2</sub> will not be discussed in this book since it focuses on the troposphere and the stratosphere.

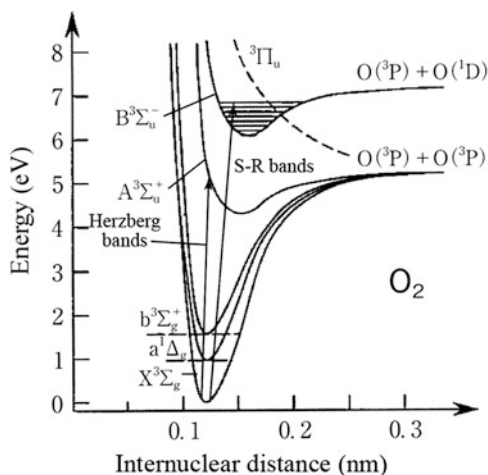
Absorption spectrum, cross sections and energy diagram of molecular O<sub>2</sub>, the second major component of the earth's atmosphere, are shown in Fig. 3.4, Table 3.2, and Fig. 3.5, respectively. As shown in Fig. 3.4, O<sub>2</sub> has a strong continuum called the Schumann-Runge Continuum (S-R Continuum) in the 130–175 nm region, which corresponds to the allowed  $B^3\Sigma_u^- - X^3\Sigma_g^-$  transition in Fig. 3.5. This continuum merges to the banded spectrum of the Schumann-Runge bands (S-R bands), in the wavelength range longer than 175 nm. This absorption band corresponds to the vibrational levels of the same  $B^3\Sigma_u^- - X^3\Sigma_g^-$  transition lower than the dissociation energy to  $O_2 \rightarrow O(^3P) + O(^1D)$ . In a strict sense, the Schumann-Runge bands overlaps with the continuum, which corresponds to the  $^3\Pi_u - X^3\Sigma_g^-$  transition to the repulsive potential curve in Fig. 3.5. As shown in Fig. 3.4, a very weak continuum called Herzberg bands are extended to the further longer wavelengths side of the Schumann-Runge bands in the 190–242 nm range, which corresponds to the forbidden transition  $A^3\Sigma_u^+ - X^3\Sigma_g^-$  (H-bands in Fig. 3.5). This continuum is thought to be the transition to the  $A^3\Sigma_u^+$  state at higher than the energy of dissociation to  $O_2 \rightarrow O(^3P) + O(^3P)$ . Absorption of solar radiation by these bands of O<sub>2</sub> is very important when considering the irradiance and chemical reaction system in the stratosphere. The solar radiation in the absorption spectrum range of O<sub>2</sub> is totally absorbed in the stratosphere and does not reach to the troposphere. Further transitions to the lower energy states of O<sub>2</sub>,  $a^1\Delta_g$  and  $b^1\Sigma_g^+$ , gives absorption in the near infrared and visible region at 1270, and 762 nm (0–0

**Table 3.2** Absorption cross sections of O<sub>2</sub> (205–245 nm) (base e)

Wavelength (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wavelength (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wavelength (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )
205	7.35	220	4.46	235	1.63
206	7.13	221	4.26	236	1.48
207	7.05	222	4.09	237	1.34
208	6.86	223	3.89	238	1.22
209	6.68	224	3.67	239	1.10
210	6.51	225	3.45	240	1.01
211	6.24	226	3.21	241	0.88
212	6.05	227	2.98	242	0.81
213	5.89	228	2.77	243	0.39
214	5.72	229	2.63	244	0.13
215	5.59	230	2.43	245	0.05
216	5.35	231	2.25		
217	5.13	232	2.10		
218	4.88	233	1.94		
219	4.64	234	1.78		

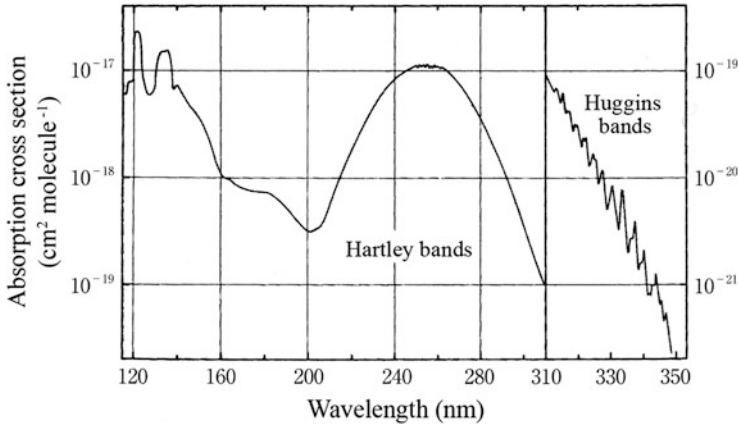
Source: NASA/JPL Panel Evaluation No. 17 (Sander et al. 2011)

**Fig. 3.5** Potential energy curves of O<sub>2</sub> (Adapted from Finlayson-Pitts and Pitts 2000 based on Gaydon 1968)



bands from  $v'' = 0$  to  $v' = 0$ ), respectively. They are both forbidden transitions and very weak.

The photolysis of O<sub>2</sub> at the Schumann-Runge system is an important chemical process to form the ozone layer in the stratosphere. The chemistry of the stratosphere will be discussed in Chap. 8. The absorption spectrum of O<sub>3</sub> formed there plays an important role to determine the vertical distribution of the solar spectrum at different altitude and also the shorter wavelength edge in the troposphere.



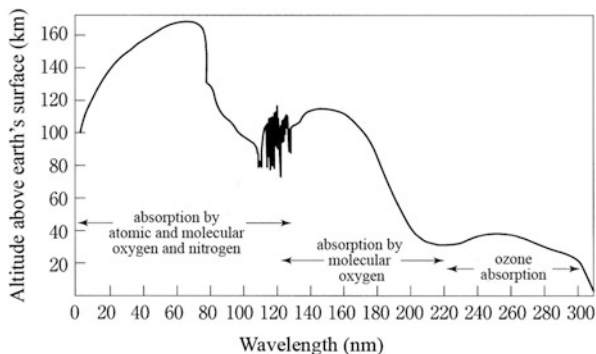
**Fig. 3.6** Absorption spectrum of  $O_2$  in the ultraviolet region (Adapted from Warneck 1988)

The absorption of  $O_3$  in the stratosphere is very important to calculate the solar irradiance in the troposphere. Figure 3.6 and Table 4.1 give the absorption spectrum and absorption cross sections of  $O_3$ . As shown in Fig. 3.6,  $O_3$  has strong absorption bands in 100–200 and 200–310 nm ranges. Since the stronger bands of  $O_2$  completely absorb the solar radiation in the 100–200 nm region, as an element for determining the solar irradiance spectrum, the absorption of  $O_3$  in this region is not important. In contrast, the absorption bands in the 200–310 nm range called the Hartley bands correspond to the spectral region where the absorption of  $O_2$  becomes weak so that the absorption by  $O_3$  plays a very important role in determining the solar spectrum in the lower stratosphere and the troposphere. This absorption corresponds to the  ${}^1B_2$ - $X{}^1A_2$  transition which is the transition to the higher energy level than the dissociation into  $O_3 \rightarrow O({}^1D) + O_2({}^1\Delta_g)$  to essentially give a continuum (see Fig. 4.8).

As seen in Fig. 3.6, the long wavelength edge of Hartley bands longer than 310 nm merges to a band spectrum called Huggins bands with a vibrational structure. The photolysis of  $O_3$  in the 310–350 nm range giving an excited oxygen atom  $O({}^1D)$  is extremely important in the troposphere as the source of OH radicals, and will be discussed in detail in Sect. 4.2.1. Furthermore,  $O_3$  has absorption bands called the Chappuis bands in visible region (440–850 nm) that is a weak continuum with an absorption cross section of  $5 \times 10^{-21} \text{ cm}^2 \text{ molecule}^{-1}$  (see Fig. 4.2), but the effect on the solar spectral irradiance is almost negligible.

The intensity of the solar radiation reached to the earth's atmosphere is attenuated according to altitude by the absorption of  $N_2$ ,  $O_2$  and  $O_3$  as mentioned above. Figure 3.7 depicts the plot of the altitude at which the intensity of the solar radiation by the overhead sun is attenuated 90 % by the absorption of these species against wavelength. As seen in the figure, the solar radiation shorter than 100 nm and 130–180 nm are absorbed by  $N_2$  and  $O_2$  at higher than 80 km above the ground in the thermosphere, and the Lyman  $\alpha$  line (121.6 nm) and the surroundings and the longer wavelength radiation reaches to the mesosphere, 45–80 km above the

**Fig. 3.7** Penetrating Depth of solar ultraviolet light into the earth's atmosphere. The height where the absorption of the solar light perpendicular to the earth surface by each atmospheric constituent is in the maximum (Adapted from Finlayson-Pitts and Pitts 2000 based on Friedman 1960)



ground. Solar radiation longer than 185 nm reached to the stratosphere (15–45 km). Especially, solar radiation at around 200 nm reaches deep into the stratosphere, and this fact plays an important role in ozone depletion by anthropogenic chlorofluorocarbons (CFC) as will be discussed in Chap. 8. Due to the absorption by  $O_3$  in the stratosphere, the solar radiation at wavelengths shorter than 310 nm are almost attenuated before reaching the troposphere. However, a small fraction of 295–310 nm radiation still reaches to the troposphere, and the formation of electronically excited  $O(^1D)$  atoms in the photolysis of  $O_3$  in this wavelength's region, and its subsequent reaction with water vapor give an important effect on the production of OH radicals in the troposphere.

### 3.3 Solar Zenith Angle and Air Mass

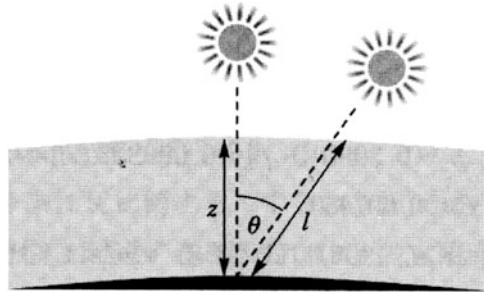
When the attenuation of solar radiation penetrating to the earth's atmosphere is caused by the absorption of  $O_2$  and  $O_3$ , the solar irradiance at the altitude  $z_0$  and wavelength  $\lambda$  on the surface perpendicular to the sun is expressed according to the Beer-Lambert law,

$$I(\lambda, z_0) = I_0(\lambda) \exp \left\{ - \int_{z_0}^{\infty} \left[ \sum_k \sigma_k(\lambda) n_k(z) \right] dz \right\} \quad (3.1)$$

$$\sum_k \sigma_k(\lambda) n_k(z) = \sigma_{o_2}(\lambda) n_{o_2}(z) + \sigma_{o_3}(\lambda) n_{o_3}(z). \quad (3.2)$$

Here,  $I_0$  is the extraterrestrial solar irradiance,  $\sigma_k$  and  $n_k$  are absorption cross section and molecular density of each molecular species, respectively.

**Fig. 3.8** The definition of solar zenith angle and air mass



**Table 3.3** Air mass for different solar zenith angle

Solar Zenith Angle $\theta$ ( $^\circ$ )	$m = \sec \theta$	Air mass
0	1.00	1.00
10	1.02	1.02
20	1.06	1.06
30	1.15	1.15
40	1.31	1.31
50	1.56	1.56
60	2.00	2.00
70	2.92	2.90
78	4.81	4.72
86	14.3	12.4

Source: Demerjian et al. (1980)

The distance  $l$  of a certain point on the earth surface from the sun gets longer with the solar zenith angle  $\theta$  than the vertical distance  $z$ , as shown in Fig. 3.8, and more photons are absorbed by the molecules. Considering the horizontal earth surface, the relationship between  $l$  and  $\theta$  is expressed as,

$$l = z / \cos \theta = z \sec \theta. \tag{3.3}$$

The ratio of the distance  $l$ , the direct radiation of the sun passes through the atmosphere, and the vertical distance  $z$  from the sun is called air mass  $m$ . The air mass can be closely approximated for  $\theta < 60^\circ$ , by

$$m = l/z = \sec \theta. \tag{3.4}$$

Table 3.3 shows the values of air mass comparing with those of  $\sec \theta$ . As seen in Table 3.3, the differences between them are not negligible only for the large solar zenith angle  $\theta > 60^\circ$ , due to the curvature and refraction of the atmosphere. The solar irradiance for air mass  $m$  at the altitude  $z_0$  from the earth's surface is given by

$$I(\lambda, z_0) = I_0(\lambda) \exp \left\{ -m \int_{z_0}^{\infty} \left[ \sum_k \sigma_k(\lambda) n_k(z) \right] dz \right\} \quad (3.5)$$

from Eq. (3.1).

The solar zenith angle  $\theta$  necessary to calculate air mass in Eq. (3.4) can be obtained from the latitude  $\varphi$  (degree), solar declination  $\delta$  (radian), and hour angle  $h$  (radian),

$$\cos \theta = \sin \delta \sin \varphi + \cos \delta \cos \varphi \cos h \quad (3.6)$$

where the solar declination  $\delta$  is given (Vermote et al. 1997) by

$$\delta(\text{radian}) = \beta_1 - \beta_2 \cos N + \beta_3 \sin N - \beta_4 \cos 2N + \beta_5 \sin 2N - \beta_6 \cos 3N + \beta_7 \sin 3N \quad (3.7)$$

$$N(\text{radian}) = \frac{2\pi d_h}{365} \quad (3.8)$$

$$\beta_1 = 0.006918, \beta_2 = 0.399912, \beta_3 = 0.070257, \beta_4 = 0.006758, \beta_5 = 0.000907, \\ \beta_6 = 0.002697, \beta_7 = 0.001480.$$

The  $d_n$  in Eq. (3.8) is the day number of a year with 0 on January 1st and 364 on December 31st. The hour angle  $h$  in Eq. (3.6) is obtained from Greenwich mean time GMT (hour), longitude  $\lambda$  (degree), and equation of time EQT (Vermote et al. 1997),

$$h(\text{radian}) = \pi[(\text{GMT}/12) - 1 + (\lambda/180)] + \text{EQT} \quad (3.9)$$

$$\text{EQT} = \alpha_1 + \alpha_2 \cos N - \alpha_3 \sin N - \alpha_4 \cos 2N - \alpha_5 \sin 2N \quad (3.10)$$

$$\alpha_1 = 0.000075, \alpha_2 = 0.001868, \alpha_3 = 0.032077, \alpha_4 = 0.014615, \alpha_5 = 0.040849$$

The equation of time is the difference of right ascension between the average and apparent sun, and caused by the fact that the movement of the sun in a day shifts east and west since the revolution angular velocity of the earth is different by season due to the elliptical orbit and the declination of the earth's axis from the celestial equator by  $23^\circ 27'$ .

### 3.4 Scatter by Atmospheric Molecules and Particles, and Surface Albedo

The solar radiation penetrating the atmosphere changes its intensity and spectral distribution as affected by the light scattering by atmospheric molecules and particulate matters (aerosols) besides the absorption by  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{O}_3$ . Particularly,



for the calculation of the actinic flux (see next section) in the troposphere, these effects have to be considered.

Taking in to consideration light scattering in addition to absorption, the Lambert-Beer law can be expressed by

$$\ln \frac{I}{I_0} = -sm \quad (3.11)$$

$$s = s_{sm} + s_{am} + s_{sp} + s_{ap}, \quad (3.12)$$

where,  $s_{sm}$ ,  $s_{am}$ ,  $s_{sp}$ , and  $s_{ap}$  are optical attenuation coefficients by the scattering and absorption by gaseous molecules, and the scatter and absorption by atmospheric particulates, respectively, and  $m$  is the air mass mentioned in the previous section.

The scattering by gaseous molecules is called Rayleigh scattering, and its scattering coefficient is given by

$$s_{sm} = \frac{24\pi^3}{\lambda^4 N^2} \left( \frac{n^2 - 1}{n^2 + 1} \right) \quad (3.13)$$

where  $n$  is refractive index and  $N$  (molecules  $\text{cm}^{-3}$ ) is the molecular density. Since the refractive index of air is close to unity (1.000278 at 530 nm), the equation can be approximated by

$$s_{sm} = \frac{32\pi^3}{3\lambda^4} \left( \frac{n - 1}{N} \right), \quad (3.14)$$

showing the Rayleigh scattering coefficient is inversely proportional to the fourth power of wavelength (Bohren and Huffman 1981; Ahrens 2007). In this way, the shorter wavelength's light is more easily scattered, and it is well known that the blue light of the solar radiation reaching to the troposphere is more strongly scattered, causing the blue sky. Using the atmospheric molecular density  $N_0 = 2.687 \times 10^{19} \text{ cm}^{-3}$  at the scale height  $H = 7.996 \times 10^5 \text{ cm}$ , approximately 8 km (the altitude where the atmospheric pressure is reduced to 1/e of the ocean surface;  $e$  is the base of natural logarithm), the Rayleigh scattering coefficient is

$$(s_{sm})_0 = \frac{1.044 \times 10^5 (m_{0,\lambda} - 1)^2}{\lambda^4} \quad (3.15)$$

where  $m_{0,\lambda}$  is the refractive index of air for the wavelength  $\lambda$  at this altitude (Leighton 1961; Finlayson-Pitts and Pitts 2000). From Eq. (3.15), light attenuation coefficient by the molecular scattering  $s_{sm}$  in the atmosphere for each altitude can be given by

$$s_{sm} = \frac{(s_{sm})_0 N}{N_0} = (s_{sm})_0 \frac{P}{P_0} \quad (3.16)$$

where  $P_0$  is the atmospheric pressure corresponding to the scale height, i.e. 1/e atm.

Detailed treatments of scattering and absorption by particles are given by Bohren and Huffman (1981). The scattering by particles is a function of particle diameter and light wavelength, and the light attenuation coefficient by particle scattering is in general expressed as

$$s_{sp} = \frac{b}{\lambda^a} \quad (3.17)$$

Here, if the parameter of particle diameter  $\alpha$  is defined by

$$\alpha = \frac{2\pi r}{\lambda}, \quad (3.18)$$

$a$  in Eq. (3.18) is  $a=4$  for small particle diameter ( $\alpha \ll 1$ ), the same as the molecular scattering, and  $a$  decreases with the increase of the diameter reaching to  $a=0$  for a large diameter compare to the wavelength ( $\alpha \gg 1$ ), i.e. the scatter is expressed by geometric optical approximation (Leighton 1961). The scattering by particles in the intermediate range is called Mie scattering.

In the case of scattering by molecules and particles, being different from the absorption, solar radiation is not lost but the scattered light is also utilized effectively for the photolysis of atmospheric molecules. Thus, although the direct radiation intensity is attenuated, multiple scattered lights contribute to actinic flux (Sect. 3.5).

Figure 3.9 shows plots of transmittance of light for each process against wavelengths in the troposphere considering molecular and particle scattering and absorption by ozone. The transmitting coefficients  $T$  in the figure are

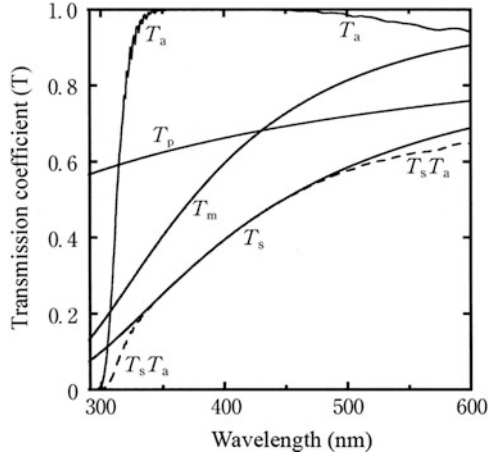
$$T = \frac{I}{I_0} \quad (3.19)$$

$$T_{\text{total}} = T_a T_m T_p \quad (3.20)$$

$$T_s = T_m T_p \quad (3.21)$$

where  $T_a$ ,  $T_m$ ,  $T_p$ ,  $T_s$ ,  $T_{\text{total}}$  are the transmittance for the molecular absorption, molecular scattering, particle scattering, total scattering and total transmittance, respectively. In the calculation of Fig. 3.9, solar zenith angle  $45^\circ$ , ozone column density 0.300 atm-cm (=300 D.U.; D.U. means Dobson unit), aerosol optical density 0.295 (at 500 nm) are used. The general characteristics of wavelength dependence of each process is well demonstrated; particle scattering is important for wavelengths longer than 450 nm, molecular scattering (Rayleigh scattering) is

**Fig. 3.9** Atmospheric transmittance at the solar zenith angle 45°.  $T_a$ : Absorption by ozone,  $T_m$ : Rayleigh scattering by molecules,  $T_p$ : Mie scattering by particles,  $T_s = T_m + T_p$ ,  $T_{total} = T_a T_s$  (Courtesy of H. Irie)



**Table 3.4** Typical albedos for various earth surfaces

Surface	Albedo
Snow (old snow ~ new snow)	0.40–0.95
Ocean ice	0.30–0.40
Water surface ( $\theta < 25^\circ$ )	0.03–0.10
Water surface ( $\theta > 25^\circ$ )	0.10–1.00
Tundra	0.18–0.25
Sands, Desert	0.15–0.45
Soil (dark wet soil ~ bright dry soil)	0.05–0.40
Grassland	0.16–0.26
Cultivated land (agricultural crops)	0.05–0.20
Forest (broadleaf trees)	0.15–0.20
Forest (coniferous trees)	0.05–0.15
Thick cloud	0.60–0.90
Thin cloud	0.30–0.50

Source: Budikova (2010)

important for the shorter wavelengths and absorption by ozone predominates in the shorter wavelength than 320 nm.

In addition, since a portion of the solar radiation which reaches the earth surface is reflected back into the atmosphere, it is necessary to take the surface reflected light into consideration when calculating the actinic flux, in addition to the direct and scattered radiation. The reflectance at the earth surface is called Albedo and differs depending on the nature of the surface. Table 3.4 summarizes the reported values of Albedo for various earth surfaces. The highest Albedo is for the fresh snow, 0.75–0.95 close to unity. Meanwhile, the Albedos for water surfaces, such as the ocean, is very small, 0.1 for the small solar zenith angle but increasing with the zenith angle. Further Albedos of surfaces covered by vegetation, such as forest,

grassland, and agricultural fields are in general middle ranged values of 0.1–0.3 and naturally changes by season. Although the values of Albedo depend on wavelength, details have not been studied much (McLinden et al. 1997).

### 3.5 Actinic Flux and Photolysis Rate Constants

Photolysis rate constants of atmospheric molecules can be calculated by the formula given in Chap. 2,

$$j_p = k_p = \int_{\lambda} \sigma(\lambda)\Phi(\lambda)F(\lambda)d\lambda \quad (2.18)$$

where  $\sigma(\lambda)$  ( $\text{cm}^2$ ) is the absorption cross section of a molecule to be photolyzed,  $\Phi(\lambda)$  is the quantum yield for giving a specific photolysis product, and  $F(\lambda)$  (photons  $\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$ ) is the actinic flux integrated spherically. Actinic flux  $F(\lambda)$  is the total number of photons incident to a small spherical surface in the atmosphere, which is obtained by integrating the solar radiance  $L(\lambda, \theta, \phi)$  (photons  $\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1} \text{sr}^{-1}$ ) for all angles (solar zenith angle  $\theta$ , and azimuth angle  $\phi$ ) (Madronich 1987),

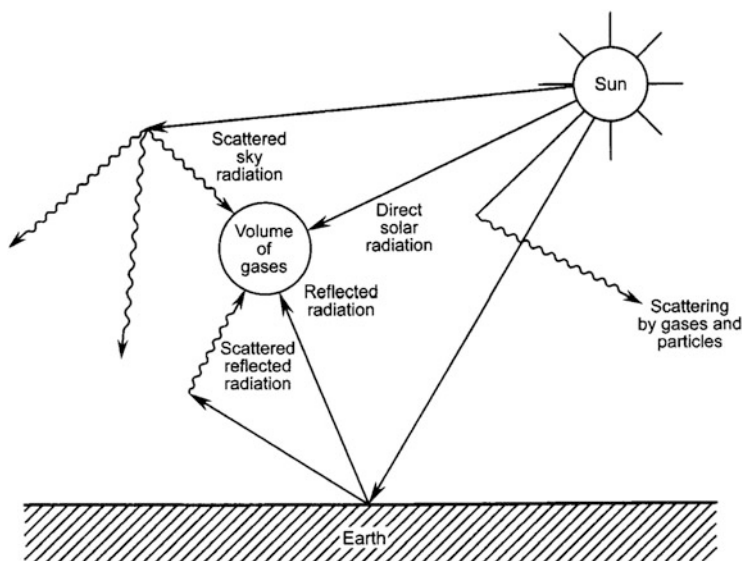
$$F(\lambda) = \int_0^{2\pi} \int_{-\pi/2}^{\pi/2} L(\lambda, \theta, \phi) \sin \theta d\theta d\phi, \quad (3.22)$$

where  $\sin \theta$  is a coefficient appearing in the conversion of the solid angle to the spherical coordinate. It should be noted that the intervals of integral is for  $-\pi/2 \sim \pi/2$ , which implies not only the radiation from the upper side but also the light from the lower side is also effective for photolysis.

Figure 3.10 illustrates the schematic diagram of various radiation types contributing to the actinic flux. Thus, for the calculation of  $F(\lambda)$ , all of the processes, such as absorption by stratospheric ozone, Rayleigh scattering by atmospheric molecules, scattering and absorption by aerosols and clouds, and reflection at the earth's surface have to be considered, and not only the direct radiation from the sun but also the light from all directions reflected and scattered by aerosols must also be accounted for.

Meanwhile, the solar irradiance  $E(\lambda)$  (photons  $\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$ ) mentioned in Sect. 3.1 is defined by

$$E(\lambda) = \int_0^{2\pi} \int_0^{\pi/2} L(\lambda, \theta, \phi) \cos \theta \sin \theta d\theta d\phi \quad (3.23)$$



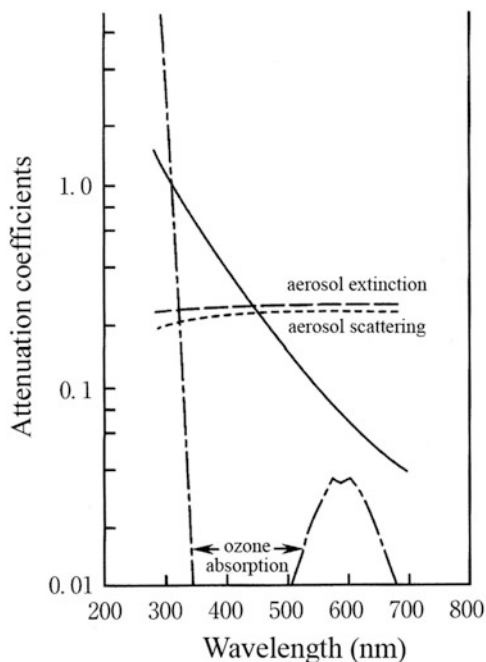
**Fig. 3.10** Various sources of radiation contributing to the actinic flux for a small volume in the atmosphere (Adapted from Finlayson-Pitts and Pitts 2000)

which is the radiation flux incident upon a plane in the atmosphere. That is,  $E(\lambda)$  is the hemispherically integrated direct and scattered solar radiation incident upon a plane in a fixed space orientation from the upper side, and differentiated from the actinic flux defined by Eq. (3.22) in the respect that it contains  $\cos \theta$  which depends on the direction of the irradiation.  $E(\lambda)$  is often given in the energy unit,  $\text{W cm}^{-2} \text{nm}^{-1}$ , and it can be converted to photon per unit time by using Eq. (2.2). Incidentally, in the discussion of the extraterrestrial solar spectrum, the irradiance  $E(\lambda)$  at the plane perpendicular to the sun ( $\cos \theta = 1$ ) is equal to the actinic flux  $F(\lambda)$ .

The actinic flux  $F(\lambda)$  is an important parameter necessary for calculations of photolysis rate constants in the atmosphere, and there are two methods to obtain the values; one is the method obtained by the theoretical calculation using the radiative transfer model, and the other is the method to measure the irradiance  $E(\lambda)$  by a radiometer and convert it to  $F(\lambda)$  by using a theoretical formula. Here, we shall see the method of obtaining actinic flux by using the radiative transfer model equation first. The pioneering work on this treatment was undertaken by Leighton (1961), and he calculated the actinic flux applicable to photochemical air pollution by using simplified radiative transfer model for different solar zenith angles in the wavelength region of 290–800 nm. Although the work of Leighton (1961) is already more than 50 years old, with all the factors mentioned in this chapter taken into consideration, it can be concluded that the basic view on photolysis in the atmosphere was established at this time.

Peterson (1976) developed the work of Leighton (1961) using new input parameters, and was further succeeded by Demerjian (1980) and Madronich (1987) giving the values of actinic flux with higher precision. Peterson (1976) calculated the

**Fig. 3.11** Attenuation coefficients of solar radiation due to absorption and scattering by atmospheric molecules and particles (Adapted from Peterson 1976)



actinic flux at the zenith angle  $0^\circ$  dividing the spectral region by 5 nm (290–420 nm), 10 nm (420–580 nm) and 20 nm (580–700 nm), and assuming the amount of stratospheric ozone of 0.285 atm-cm (285 D.U.) and the boundary layer ozone of 100 ppb in the 0–1 km layer from the ground. As for the calculation of radiation characteristics of aerosols, assuming the distribution of particle diameters given in Eq. (3.18), column density of  $4.99 \times 10^7$  particles  $\text{cm}^{-2}$  was used. The optical parameter of aerosols complex index of refraction,  $n = 1.5 - 0.01i$ , was used assuming partial absorption. Figure 3.11 shows the wavelength dependence of radiative extinction coefficient  $s$  defined by Eqs. (3.11) and (3.12) for absorption by ozone, scatter and absorption by particles, and Rayleigh scattering by atmospheric molecules using the above parameters. In Fig. 3.11, it is shown that the extinction by aerosol is mostly by scattering and the contribution of absorption is about 9 %, and the absorption by the Chappuis Bands at around 600 nm is less than 3 %.

It is known that in addition to these parameters, the surface albedo has a large effect on the actinic flux (Luther and Gelinas 1976). The contribution ratios of albedo are 5 % (290–400 nm), 6 % (400–450 nm), 8 % (450–500 nm), 10 % (500–550 nm), 11 % (550–600 nm), 12 % (600–640 nm), 13.5 % (640–660 nm), and 15 % (660–700 nm) according to Peterson (1976). Table 3.5 gives the values of actinic flux calculated by Peterson (1976). Figure 3.12 depicts the solar zenith angle dependence of the actinic flux for several wavelengths. As shown in Fig. 3.12, the decrease of the actinic flux is relatively small in the zenith angle range of 0– $50^\circ$ , but

**Table 3.5** Actinic flux at the earth surface for different solar zenith angles (photons  $\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$ )

Wavelength (nm)	Power	Actinic Flux: Solar Zenith Angle (°)													
		0	10	20	30	40	50	60	70	78	86				
290-295	14	0.001	0.001	—	—	—	—	—	—	—	—	—	—	—	—
295-300	14	0.041	0.038	0.030	0.019	0.009	0.003	—	—	—	—	—	—	—	—
300-305	14	0.398	0.381	0.331	0.255	0.167	0.084	0.027	0.004	0.001	—	—	—	—	—
305-310	14	1.41	1.37	1.25	1.05	0.800	0.513	0.244	0.064	0.011	0.002	—	—	—	—
310-315	14	3.14	3.10	2.91	2.58	2.13	1.56	0.922	0.357	0.090	0.009	—	—	—	—
315-320	14	4.35	4.31	4.10	3.74	3.21	2.52	1.67	0.793	0.264	0.030	—	—	—	—
320-325	14	5.48	5.41	5.19	4.80	4.23	3.43	2.43	1.29	0.502	0.073	—	—	—	—
325-330	14	7.89	7.79	7.51	7.01	6.27	5.21	3.83	2.17	0.928	0.167	—	—	—	—
330-335	14	8.35	8.25	7.98	7.50	6.76	5.72	4.30	2.54	1.15	0.241	—	—	—	—
335-340	14	8.24	8.16	7.91	7.46	6.78	5.79	4.43	2.69	1.25	0.282	—	—	—	—
340-345	14	8.89	8.80	8.54	8.09	7.38	6.36	4.93	3.04	1.44	0.333	—	—	—	—
345-350	14	8.87	8.79	8.54	8.11	7.43	6.44	5.04	3.15	1.51	0.352	—	—	—	—
350-355	14	10.05	9.96	9.70	9.22	8.48	7.39	5.83	3.69	1.77	0.414	—	—	—	—
355-360	14	9.26	9.18	8.94	8.52	7.86	6.88	5.47	3.50	1.69	0.391	—	—	—	—
360-365	14	10.25	10.16	9.91	9.46	8.76	7.71	6.17	3.99	1.94	0.444	—	—	—	—
365-370	15	1.26	1.25	1.22	1.17	1.08	0.958	0.772	0.505	0.247	0.055	—	—	—	—
370-375	15	1.14	1.13	1.10	1.06	0.983	0.873	0.708	0.467	0.230	0.051	—	—	—	—
375-380	15	1.27	1.26	1.23	1.18	1.10	0.983	0.802	0.535	0.265	0.058	—	—	—	—
380-385	15	1.05	1.04	1.02	0.980	0.917	0.820	0.673	0.453	0.226	0.049	—	—	—	—
385-390	15	1.15	1.15	1.12	1.08	1.01	0.909	0.750	0.510	0.257	0.054	—	—	—	—
390-395	15	1.19	1.18	1.16	1.11	1.05	0.943	0.783	0.537	0.273	0.057	—	—	—	—
395-400	15	1.44	1.43	1.40	1.35	1.28	1.15	0.962	0.666	0.341	0.070	—	—	—	—
400-405	15	1.73	1.72	1.69	1.63	1.53	1.39	1.16	0.809	0.418	0.085	—	—	—	—
405-410	15	1.94	1.93	1.90	1.83	1.71	1.57	1.32	0.926	0.482	0.097	—	—	—	—

(continued)

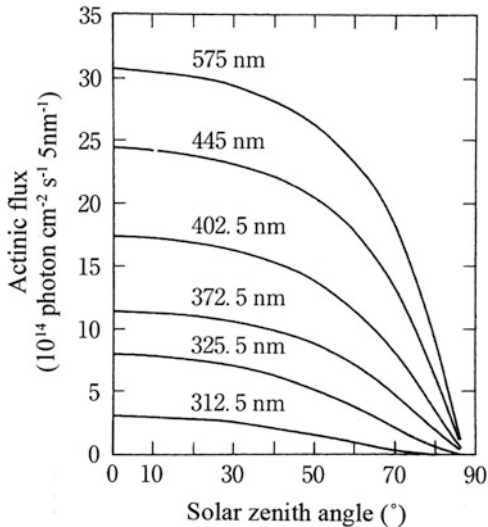
Table 3.5 (continued)

Wavelength (nm)	Power	Actinic Flux: Solar Zenith Angle (°)														
		0	10	20	30	40	50	60	70	78	86					
410-415	15	2.05	2.04	2.00	1.93	1.83	1.66	1.41	0.993	0.522	0.104					
415-420	15	2.08	2.07	2.03	1.96	1.86	1.70	1.44	1.03	0.543	0.107					
420-430	15	4.08	4.06	3.99	3.87	3.67	3.36	2.87	2.07	1.11	0.216					
430-440	15	4.20	4.18	4.11	3.99	3.80	3.49	3.01	2.19	1.20	0.229					
440-450	15	4.87	4.85	4.77	4.64	4.43	4.09	3.54	2.61	1.45	0.272					
450-460	15	5.55	5.51	5.43	5.27	5.03	4.64	4.02	2.99	1.67	0.312					
460-470	15	5.68	5.65	5.57	5.42	5.17	4.79	4.17	3.12	1.77	0.325					
470-480	15	5.82	5.79	5.70	5.55	5.31	4.91	4.32	3.26	1.87	0.341					
480-490	15	5.78	5.75	5.67	5.53	5.29	4.93	4.33	3.29	1.90	0.339					
490-500	15	5.79	5.76	5.68	5.54	5.31	4.96	4.37	3.34	1.95	0.344					
500-510	15	5.99	5.96	5.87	5.71	5.47	5.09	4.47	3.41	1.99	0.340					
510-520	15	5.88	5.86	5.77	5.62	5.38	5.02	4.43	3.40	2.00	0.340					
520-530	15	5.98	5.95	5.87	5.72	5.48	5.11	4.52	3.47	2.04	0.336					
530-540	15	5.98	5.95	5.87	5.72	5.48	5.12	4.52	3.48	2.05	0.326					
540-550	15	5.88	5.85	5.77	5.62	5.40	5.04	4.46	3.44	2.03	0.317					

Source: Peterson (1976)



**Fig. 3.12** Solar zenith angle dependence of the actinic flux at the earth surface (Adapted from Peterson 1976)



it decreases rapidly for 50–90°. This is because the air mass increases rapidly when the zenith angle increases over 50° as seen in Table 3.3. Further, the rapid increase of the actinic flux at the earth’s surface in the spectral range of 300–400 nm corresponds to the rapid decrease of absorption of ozone with the increase of wavelengths. The values of actinic flux for higher altitudes at 15, 25, 40 km are given by Finlayson-Pitts and Pitts (2000).

The direct physical measurement of the spectral actinic flux  $F(\lambda)$  is not easy, although attempts have been made (Shetter and Müller 1999; Hofzumahaus et al. 1999). Generally, irradiance  $E(\lambda)$  (radiation flux per unit area,  $\text{W m}^{-2} \text{nm}^{-1}$ ) is measured by radiometers, and experiments to compare solar spectral intensity in the field with radiative transfer models have been made in order to convert the spectral irradiance  $E(\lambda)$  to  $F(\lambda)$ . In these analyses, downward actinic flux  $F_d(\lambda)$  is obtained by upper-hemispherical integration of observed spectral radiance  $L(\lambda, \theta, \phi)$  (radiation flux per solid angle,  $\text{W sr}^{-1} \text{m}^{-2} \text{nm}^{-1}$ ), and  $F_d(\lambda)$  is expressed as the sum of the flux of direct radiation  $F_o(\lambda)$  and downward diffusive flux  $F_{\downarrow}(\lambda)$ ,

$$F_d(\lambda) = \int_0^{2\pi} \int_0^{\pi/2} L(\theta, \phi) \sin \theta d\theta d\phi = F_{\downarrow}(\lambda) + F_o(\lambda). \quad (3.24)$$

Similarly, the irradiance  $E(\lambda)$  is expressed as a sum of the direct component,  $E_o(\lambda)$  ( $= \cos \theta F_o(\lambda)$ ) and downward diffusive component,  $E_{\downarrow}(\lambda)$ ,

$$E(\lambda) = \int_0^{2\pi} \int_0^{\pi/2} L(\theta, \phi) \cos \theta \sin \theta d\theta d\phi = E_{\downarrow}(\lambda) + E_0(\lambda). \quad (3.25)$$

Using the approximation by van Weele et al. (1995), the ratio of  $F_d(\lambda)$  and  $E(\lambda)$  is given by

$$\frac{F_d(\lambda)}{E(\lambda)} = \frac{F_{\downarrow}(\lambda)}{E_{\downarrow}(\lambda)} + \left( \frac{1}{\cos \theta} - \frac{F_{\downarrow}(\lambda)}{E_{\downarrow}(\lambda)} \right) \frac{E_0(\lambda)}{E(\lambda)}. \quad (3.26)$$

The ratio of the downward actinic flux  $F_d$  and irradiance  $E$  have been obtained from several field observations, and comparisons have been made with model calculations (Kazandzis et al. 2000; Webb et al. 2002a, b; McKenzie et al. 2002; Bais et al. 2003; Kylling et al. 2005; Palancar et al. 2011). The ratio of  $F_{\downarrow}(\lambda)/E_{\downarrow}(\lambda)$  is expected to be 2 for the completely isotropic diffusive radiation, and the observed values are in general 1.4 to 2.6, depending on wavelength, solar zenith angle, and aerosol density (Kazandzis et al. 2000; Webb et al. 2002a). These values agree with the theoretical model in the case of no cloud, and the actinic flux can be obtained from the observed irradiance using the validated ratio.

On the contrary, if there are clouds, the discrepancy between the observation and the model is large in general, and the cause of uncertainty is thought to be the contribution of albedo of clouds. When the actinic flux  $F_{\text{tot}}$  is divided by direct radiation component  $F_0$ , and downward and upward diffusive radiation component  $F_{\downarrow}$ , and  $F_{\uparrow}$ , respectively, assuming a Lambertian surface i.e. a virtual completely diffusive surface for which radiance is constant being independent of the direction of observation (isotropic scattering),

$$F_{\uparrow} = A(2 \cos \theta_0 F_0 + F_{\downarrow}) \quad (3.27)$$

where  $A$  is the surface albedo, and

$$F_{\text{tot}} = F_0 + F_{\downarrow} + F_{\uparrow} = F_0(1 + 2A \cos \theta_0) + F_{\downarrow}(1 + A) \quad (3.28)$$

is derived (Madronich 1987). Here,  $\theta_0$  is the solar zenith angle. Equation (3.28), in the limiting case of  $A = 1$ ,  $\theta_0 = 0$ , and  $F_{\downarrow} = 0$ , gives  $F_{\text{tot}} = F_0 + F_{\downarrow} = 3F_0$ , showing that the actinic flux can be larger than the direct radiation component by a factor of 3. In general, direct radiation is reflected isotropically at the surface, and actinic flux increases by a factor of  $2A \cos \theta_0$ .

When the actinic flux is obtained, the photolysis rate constant  $j_p(\text{s}^{-1})$  can be calculated by Eq. (2.17). Practically, it is often calculated from the equation,

$$j_p(\text{s}^{-1}) = \sum_{\lambda} \sigma_{av}(\lambda) \phi_{av}(\lambda) F_{av}(\lambda) \quad (3.29)$$

by substituting the integral to the sectional mensuration. Here,  $\sigma_{av}(\lambda)$ ,  $\phi_{av}$ , and  $F_{av}$  are absorption cross section, photolysis quantum yield, and actinic flux, respectively, each averaged over wavelength interval  $\Delta\lambda$  around the central wavelength  $\lambda$ .

The photolysis rate constants calculated by Eq. (3.29) and actually measured values for example for NO<sub>2</sub> are sometimes agree well and sometimes have large discrepancy (Kraus and Hofzumahaus 1998). Particularly in the case of the photolysis rate above cloud, in cloud and above snow the discrepancy between the calculated and observed values are large. It is discussed that there are uncertainties in the treatments of albedo effects (Van Weele and Duynkerke 1993; Junkermann 1994; Wild et al. 2000; Lee-Taylor and Madronich 2002; Simpson et al. 2002; Brasseur et al. 2002; Thiel et al. 2008).

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## Chapter 4

# Spectra and Photolytic Reactions of Atmospheric Molecules

Photochemical reactions of atmospheric molecules are the primary driving force of chemical reaction systems in the troposphere and stratosphere. Therefore it is very important to understand the photolytic processes of each species for comprehending atmospheric chemistry. In this chapter, the absorption spectra and cross sections, photodissociation pathways, and their quantum yields (see Sect. 2.1.2) are described for atmospheric molecules that are photolyzed under the actinic flux in the troposphere and stratosphere. For atmospheric molecules at which altitudes they are photolyzed are determined by the overlap of the spectrum of the actinic flux and absorption spectrum, and by the photodissociation quantum yield at each wavelength. The photolysis of some molecules is important both in the troposphere and stratosphere. In particular, O<sub>3</sub> is mainly discussed in the section of the photolysis in the troposphere (Sect. 4.2.1), and supplemental description is given in the Sect. 4.3.2 for the processes which occur only in the stratosphere. Since the photolysis of organic halogen species including chlorofluorocarbons is particularly important in the stratosphere, they are compiled in the section for the photolysis in the stratosphere including several species that are photolyzed also in the troposphere. Further, since most of inorganic halogen species are relevant both in the troposphere and stratosphere, they are consolidated separately in Sect. 4.3 as the photolysis of inorganic halogens.

The absorption cross sections and photolytic processes of atmospheric molecules are evaluated and compiled by the NASA Panel for Data Evaluation and IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. The descriptions in this chapter refer to the NASA/JLP Panel Evaluation No. 17 (Sander et al. 2011) mainly for absorption cross sections, and to the IUPAC Subcommittee Reports Vol. I, II, III and IV (Atkinson et al. 2004, 2006, 2007, 2008, respectively) mainly for photolytic processes. Numerical values of absorption cross sections for each chemical species cited in this chapter are given at the end of this chapter as appended tables.

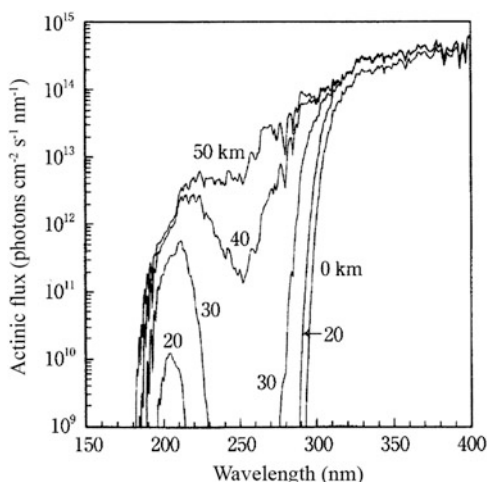
After each photolytic reaction formula, the reaction enthalpy  $\Delta H^\circ$  and threshold wavelength below which the photodissociation is energetically possible is given. It

should be noted that the values shown in this chapter is for the values of  $\Delta H_0^\circ$  calculated from heat of formation  $\Delta H_{f,0}^\circ$  at 0 K given in Table 2.5. For the heat of reaction, the values at 298 K  $\Delta H_{298}^\circ$  are generally used for gas phase reactions and they are given in Chap. 5. However, for the photolytic reactions the values at 0 K, the values of  $\Delta H_0^\circ$  are useful for the discussion of contribution of vibrational and rotational energies and they are employed in this chapter.

## 4.1 Solar Spectra in the Troposphere and Stratosphere

Figure 4.1 shows the solar actinic flux in the ultraviolet region for different altitudes at the solar zenith angle  $60^\circ$ , that are calculated considering the processes described in Chap. 3. As shown in the figure, the shortest wavelength of solar radiation reaching to the troposphere is ca. 295 nm, and the molecules that have absorption spectra in the ultraviolet and visible region longer than this wavelength are the subject of discussion. On the other hand, the solar radiation with wavelengths longer than ca. 185 nm reaches to the upper stratosphere, and the spectrum is very much dependent on the altitude due to the absorption of ozone present in the stratosphere. In particular, the ultraviolet radiation at 190–230 nm reaches to the middle and lower stratosphere, and this wavelength region is called “atmospheric window” of the stratosphere. This wavelength region happens to overlap with the absorption spectrum of chlorofluorocarbons, whose photolysis through the atmospheric window triggers ozone layer depletion.

**Fig. 4.1** Solar actinic flux for different altitudes. Solar zenith angle  $30^\circ$ , surface albedo 0.3 (Adapted from Demore et al. 1997)



## 4.2 Photolysis in the Troposphere

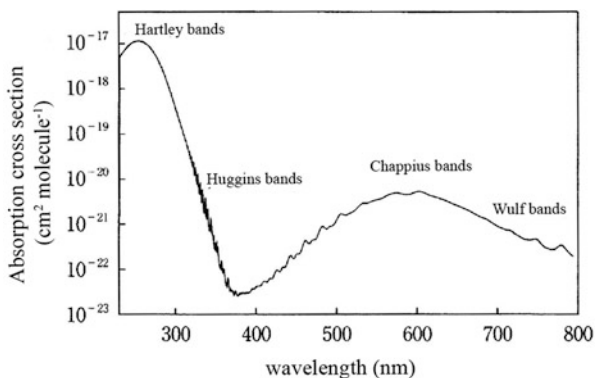
In this section, among the chemical species that are photodecomposed in the troposphere, important molecules in atmospheric chemistry are discussed, with the exception of inorganic halogens, which are described in Sect. 4.4.

### 4.2.1 Ozone ( $O_3$ )

The production of OH radicals by the reaction of  $H_2O$  with the electronically excited oxygen atoms  $O(^1D)$  formed in the photolysis of ozone ( $O_3$ ) is the most important reaction in the natural atmosphere to trigger tropospheric photochemistry. Here, the absorption spectrum and the  $O(^1D)$  production quantum yields in the photolysis in the troposphere are described in detail.

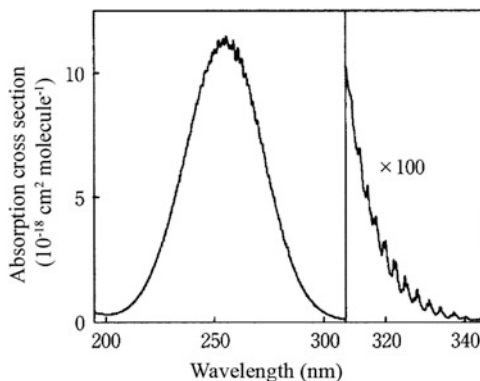
**Absorption Spectrum and Absorption Cross Sections** Although the absorption spectrum of  $O_3$  in the ultraviolet region has already been given in Fig. 3.6, Fig. 4.2 depicts the spectrum including the visible region, and Fig. 4.3 illustrates the UV absorption spectrum with the axis of ordinate in a linear scale. The strong absorption in the wavelength region of 200–310 nm is called the Hartley bands, and corresponds to the allowed transition from the ground  $X^1A_1$  state to the electronically excited  $^1B_2$  state (see Fig. 4.8 shown later). The absorption of Hartley bands is almost a continuum, and in most cases, a molecule excited to this electronic state is thought to dissociate. However, as seen in Fig. 4.3, a weak vibrational structure is discernible at the peak of the Hartley bands near 250 nm. This implies that the  $^1B_2$  state is a bound state crossed with a repulsive potential curve, which leads the most of the molecule to dissociate, but the transition to the higher energy than the crossing point still reveals vibrational structure due to the nuclear motion. The absorption cross

**Fig. 4.2** Absorption spectrum of  $O_3$  in the tropospheric actinic flux region (Adapted from Orphal 2003)





**Fig. 4.3** Ultraviolet absorption spectrum of  $O_3$  in a linear scale (Adapted from Matsumi and Kawasaki 2003)



sections (293–298 K) in the wavelength region of 186–390 nm based on the NASA/JPL Evaluation No. 17 (Sander et al. 2011) are tabulated in Table 4.1.

The absorption bands with vibrational structure in the region of wavelength longer than 310 nm are called the Huggins bands. Although the bands are thought to cause the overlapping of the transition to the energy state  $^1B_2$  lower than the crossing point with the dissociative potential curve, and to the bound electronically excited  $^1A_1$  state, the assignment of the excited states of the Huggins bands has not been established theoretically (Matsumi and Kawasaki 2003).

In addition,  $O_3$  has weak absorption bands called the Chappuis bands in the visible range and the Wulf bands in further longer wavelengths as shown in Fig. 4.2. These bands corresponds to the forbidden transitions to the lower electronically excited states that cross with repulsive potential curve dissociating into the ground states of an O atom and  $O_2$  molecule.

The important process in the troposphere is the photo-absorption in the Hartley and Huggins bands in the wavelength range from 295 nm to around 360 nm, the solar actinic flux region. It is known that the absorption cross sections in this region has strong temperature dependence and that they decrease with temperature. Figure 4.4 shows the absorption spectrum of  $O_3$  in this wavelength range at 293 and 202 K. As shown in the figure, the temperature dependence gets stronger with wavelength, and it can also be seen that the temperature dependence is very different for the peaks and valleys of spectrum in the Huggins bands. The absorption cross sections of  $O_3$  in the 186–390 nm has been given in Table 4.1, here those of Huggins bands (310–345 nm) at different temperatures at 298, 263, and 226 K (Molina and Molina 1986) are cited in Table 4.2. The temperature dependence of the  $O_3$  absorption cross sections are approximated by the empirical formula of a quadratic function (Orphal 2003),

**Table 4.1** Absorption cross sections of O<sub>3</sub> (186–390 nm, T = 293 ~ 298 K) (Base e)

Wavelength (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wavelength λ (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wavelength λ (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )
186	61.9	242	897	298	51.2
188	56.6	244	972	300	39.2
190	51.1	246	1033	302	30.3
192	46.1	248	1071	304	23.4
194	40.7	250	1124	306	17.9
196	36.7	252	1155	308	13.5
198	33.5	254	1159	310	10.2
200	31.5	256	1154	312	7.95
202	31.8	258	1124	314	6.25
204	33.7	260	1080	316	4.77
206	38.6	262	1057	318	3.72
208	46.4	264	1006	320	2.99
210	57.2	266	949	322	2.05
212	71.9	268	875	324	1.41
214	91.0	270	798	326	1.01
216	115	272	715	330	0.697
218	144	274	614	335	0.320
220	179	276	545	340	0.146
222	220	278	467	345	0.0779
224	268	280	400	350	0.0306
226	323	282	325	355	0.0136
228	383	284	271	360	0.0694
230	448	286	224	365	0.00305
232	518	288	175	370	0.00130
234	589	290	142	375	0.000850
236	672	292	111	380	0.000572
238	749	294	87.1	385	0.000542
240	831	296	67.3	390	0.000668

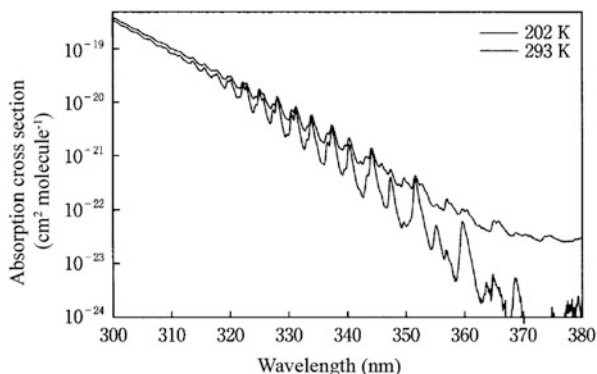
Source: 186–298 nm (298 K): Molina and Molina 1986. 300–390 nm (293–298 K): NASA/JPL Panel Evaluation No. 17

$$\sigma(\lambda, T) = a(\lambda) + b(\lambda)(T - 230) + c(\lambda)(T - 230)^2, \quad (4.1)$$

and the values of  $a(\lambda)$ ,  $b(\lambda)$  and  $c(\lambda)$  in the 280–320 nm range are given in the literatures (Molina and Molina 1986; Finlayson-Pitts and Pitts 2000).

**Photodissociation Quantum Yields** The wavelength thresholds below which photodissociation is energetically possible in the photolysis of O<sub>3</sub> are shown in Table 4.3 (Okabe 1978). From the table, energetically possible photodissociation processes by the solar flux reaching to the troposphere are the following five processes,

**Fig. 4.4** Absorption spectrum of O<sub>3</sub> Huggins bands at 201 and 293 K (Adapted from Orphal et al. 2003)



**Table 4.2** Absorption cross sections of O<sub>3</sub> in the 280–350 nm region<sup>a</sup> at 298, 263, and 226 K

Wavelength (nm)	Absorption Cross Sections ( $10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ )		
	298 K	263 K	226 K
310 <sup>b</sup>	10.5	9.66	9.14
315	5.55	4.92	4.56
320	2.80	2.46	2.21
325	1.38	1.18	1.01
330	0.706	0.599	0.506
335	0.329	0.263	0.214
340	0.149	0.112	0.0832
345	0.0781	0.0586	0.0442

<sup>a</sup>Average absorption cross sections for  $\lambda - 2.5 \text{ nm} \sim \lambda + 2.5 \text{ nm}$  unless otherwise noted

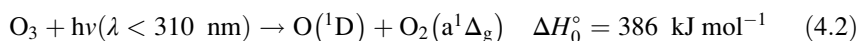
<sup>b</sup> $307.69 \text{ nm} < \lambda < 312.5 \text{ nm}$

Source: Molina and Molina (1986)

**Table 4.3** Wavelength thresholds (nm) below which the production of each pair of O and O<sub>2</sub> is energetically possible in the photolysis of O<sub>3</sub> (0 K)

O / O <sub>2</sub>	X <sup>3</sup> Σ <sup>-</sup> <sub>g</sub>	a <sup>1</sup> Δ <sub>g</sub>	b <sup>1</sup> Σ <sup>+</sup> <sub>g</sub>	A <sup>3</sup> Σ <sup>+</sup> <sub>u</sub>	B <sup>3</sup> Σ <sup>-</sup> <sub>u</sub>
<sup>3</sup> P	1180	611	463	230	173
<sup>1</sup> D	411	310	266	168	136
<sup>1</sup> S	237	200	180	129	109

Source: Okabe (1978)



The  $O(^1D)$  atoms formed in the photolysis of  $O_3$  reacts with water vapor,

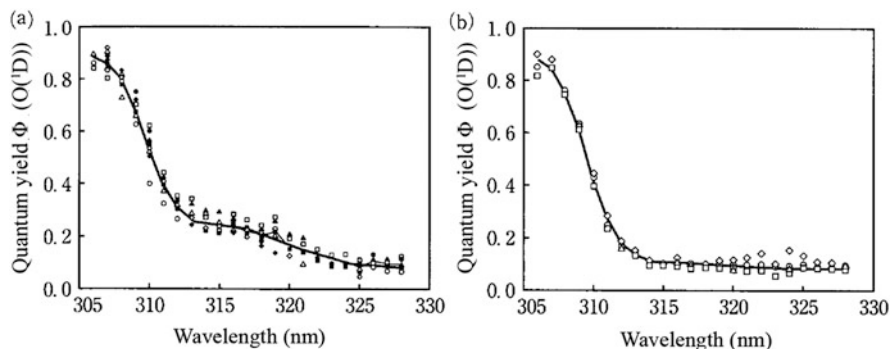


to produce OH radicals, that is very important in the tropospheric chemistry. Although it has been known that the allowed transition for the Hartley bands corresponds to the photolytic process, Eq. (4.2) to yield  $O(^1D)$  atoms, the quantum yield of  $O(^1D)$  production has not been measured accurately until recently. Particularly, the quantum yields of  $O(^1D)$  production in the Huggins bands gives large impact on tropospheric chemistry since the solar flux gets stronger at the wavelengths longer than 310 nm.

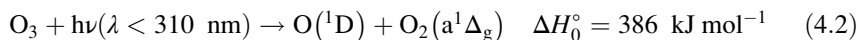
Matsumi's group (Matsumi and Kawasaki 2003) determined the  $O(^1D)$  production quantum yields in the region of 305–330 nm accurately by detecting  $O(^3P)$  and  $O(^1D)$  directly in the spectroscopic methods and their data superseded the past one (Ravishankara et al. 1998). Accordingly, the international evaluation panel was formed, and the results (Matsumi et al. 2002) were adopted in the NASA/JPL Evaluation 14 (Sander et al. 2003), which is succeeded in the later evaluation (Sander et al. 2011).

Absolute quantum yields at 308 nm measured by the spectroscopic method in the past (Greenblatt and Wiesenfeld 1983; Talukdar et al. 1997b, 1998) agrees well, and the value  $\Phi(^1D) = 0.79$  has been adopted at 298 K. Based on this value, re-normalized values of wavelength dependence (298 K) of  $O(^1D)$  production quantum yields are shown in Fig. 4.5(a) (Matsumi et al. 2002).

As shown in Fig. 4.5(a) the quantum yields of  $O(^1D)$  production decreases with wavelength from the value of 0.79 at 308 nm, and levels-off at 0.1 in wavelengths longer than 325 nm. As seen in Table 4.3, the energy threshold of 310 nm for the allowed transition corresponding to reaction (4.2)



**Fig. 4.5** Wavelength dependence of  $O(^1D)$  quantum yields in the photolysis of  $O_3$  at  $>305$  nm: (a) 298 K, (b) 227 K (Adapted from Matsumi et al. 2002). Symbols are experimental values (Refer to the source for each literature), Solid lines are the recommended curve fitting



is 310 nm, Fig. 4.5(a) shows the quantum yields of O(<sup>1</sup>D) production has substantial values even at wavelengths longer than this value. This means that a process other than reaction (4.2) is operating in the photolysis of O<sub>3</sub> in this wavelength range, which has a large implication for tropospheric photochemistry.

The hint of which processes are involved in the photolysis of O<sub>3</sub> at the Huggins bands is given by the temperature dependence of the quantum yields of O(<sup>1</sup>D) production. The temperature dependence has been obtained in the 200–320 K, and the quantum yields  $\Phi(308 \text{ nm}, T)$  at 308 nm at temperature T when normalized at 0.79 at 298 K is expressed (Matsumi et al. 2002) as

$$\Phi(308 \text{ nm}, T) = (6.10 \times 10^{-4})T + 0.608. \quad (4.8)$$

The wavelength dependence of the quantum yields of O(<sup>1</sup>D) production at 277 K obtained by several studies are shown Fig. 4.5(b). As shown in Fig. 4.5(b), the O(<sup>1</sup>D) production quantum yields at 277 K decreases more rapidly from the value at 0.75 at 308 nm than at 298 K and levels-off at ca. 0.1 for wavelengths longer than 315 nm. The wavelength dependence of the quantum yields of O(<sup>1</sup>D) production obtained from these results are given in Table 4.4 for 306–328 nm at 321, 298, 273, 253, 223, and 203 K (Matsumi et al. 2002).

The production quantum yields of O(<sup>1</sup>D) at 290–305 nm for wavelengths shorter than 308 nm, is recommended as  $0.90 \pm 0.09$  by NASA/JPL Evaluation (Matsumi et al. 2002; Sander et al. 2011) based on the results of recent measurements (Talukdar et al. 1998; Taniguchi et al. 2000). The quantum yields of O(<sup>1</sup>D) production for further shorter wavelength have been reported as 0.85–0.95. Including these values the data for the O(<sup>1</sup>D) production quantum yields in the Hartley bands in 220–290 nm are shown in Fig. 4.6. In this wavelength range, temperature dependence is not observed, and NASA/JPL Evaluation No. 17 recommends the value of 0.90 at the wavelength shorter than 306 nm (Sander et al. 2011).

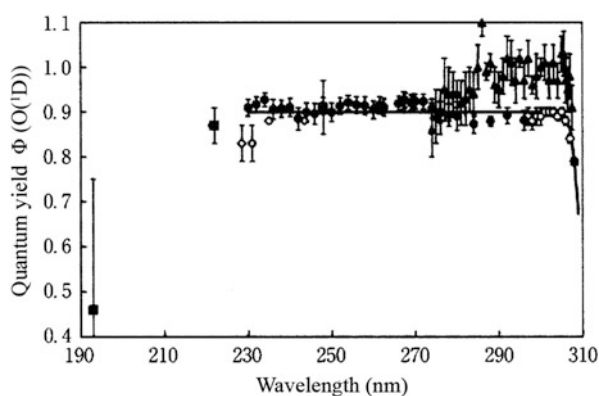
Meanwhile, the production quantum yields of O(<sup>1</sup>D) is not 0 even for wavelengths longer than 328 nm, and the corresponding photolytic process is thought to be O(<sup>1</sup>D) + O<sub>2</sub> (X<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) as will be discussed later. Since the threshold wavelength for this process is 411 nm, the production of O(<sup>1</sup>D) is thought to continue to this wavelength. NASA/JPL Evaluation No. 17 (Sander et al. 2011) recommends the O(<sup>1</sup>D) production quantum yield of  $0.08 \pm 0.04$  for wavelengths longer than 340 nm being independent of temperature, although the photolysis in this region is not so important for the tropospheric photochemistry since the absorption cross section of O<sub>3</sub> is very small at wavelengths longer than 340 nm.

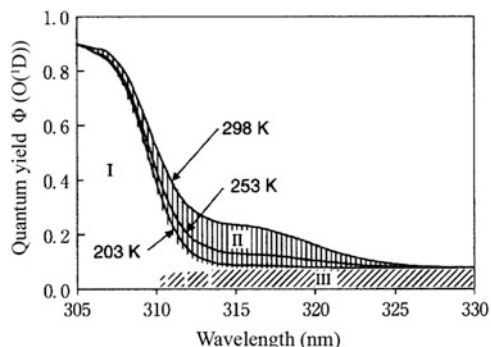
Here again, let us see what photochemical processes are participated in the photolysis of O<sub>3</sub> based on the wavelength and temperature dependence of the O(<sup>1</sup>D) production quantum yields shown in Figs. 4.5 and 4.6. Figure 4.7 depicts wavelength and temperature dependence of the O(<sup>1</sup>D) production quantum yields in 305–330 nm region calculated by Matsumi et al. (2002). Also, a schematic

**Table 4.4** Quantum yields of  $O(^1D)$  production in the photolysis of  $O_3$  at each temperature (321, 298, 273, 253, 223, 203 K)

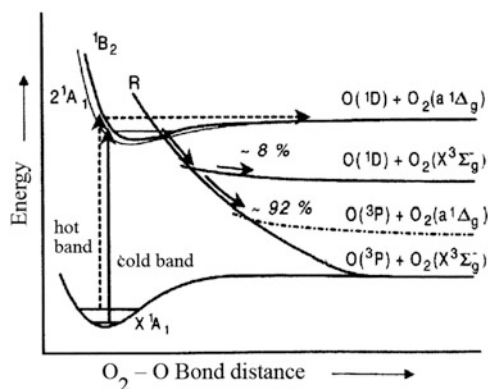
Wavelength (nm)	$O(^1D)$ Production Quantum Yields					
	321 K	298 K	273 K	253 K	223 K	203 K
306	0.893	0.884	0.878	0.875	0.872	0.872
307	0.879	0.862	0.850	0.844	0.838	0.835
308	0.821	0.793	0.772	0.760	0.748	0.744
309	0.714	0.671	0.636	0.616	0.595	0.585
310	0.582	0.523	0.473	0.443	0.411	0.396
311	0.467	0.394	0.334	0.298	0.259	0.241
312	0.390	0.310	0.246	0.208	0.169	0.152
313	0.349	0.265	0.200	0.162	0.126	0.112
314	0.332	0.246	0.180	0.143	0.108	0.095
315	0.325	0.239	0.173	0.136	0.102	0.090
316	0.317	0.233	0.168	0.133	0.100	0.088
317	0.300	0.222	0.162	0.129	0.098	0.087
318	0.275	0.206	0.152	0.123	0.096	0.086
319	0.246	0.187	0.141	0.116	0.093	0.085
320	0.214	0.166	0.129	0.109	0.090	0.083
321	0.183	0.146	0.117	0.101	0.087	0.082
322	0.155	0.128	0.107	0.095	0.084	0.080
323	0.132	0.113	0.098	0.089	0.082	0.079
324	0.114	0.101	0.091	0.085	0.080	0.078
325	0.101	0.092	0.086	0.082	0.079	0.078
326	0.091	0.086	0.082	0.080	0.078	0.077
327	0.085	0.082	0.080	0.079	0.077	0.077
328	0.081	0.080	0.078	0.078	0.077	0.077

Source: Matsumi et al. (2002)

**Fig. 4.6** Wavelength dependence of  $O(^1D)$  quantum yields in the photolysis of  $O_3$  at  $<310$  nm (Adapted from Matsumi et al. 2002)



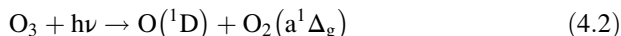
**Fig. 4.7** Calculated recommended values of  $O(^1D)$  quantum yields in the photolysis of  $O_3$  at  $>305$  nm for 203, 253 and 298 K (Adapted from Matsumi et al. 2002). Region I:  $O(^1D) + O_2(a^1\Delta_g)$  via reaction (4.2a), Region II:  $O(^1D) + O_2(a^1\Delta_g)$  by the hot band excitation via reaction (4.2a), Region III:  $O(^1D) + O_2(X^3\Sigma_g^-)$  via reaction (4.2b)



**Fig. 4.8** Schematic potential energy curves of  $O_3$  (Adapted from Matsumi and Kawasaki 2003)

potential diagram of  $O_3$  (Matsumi and Kawasaki 2003) taking a dissociating bond length as an axis of abscissa is shown in Fig. 4.8.

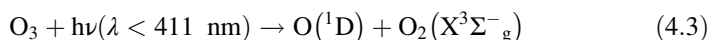
In the Hartley bands corresponding the  $^1B_2 - X^1A_1$  transition shown in Fig. 4.8,



are the main pathways, and the production of  $O(^1D)$  and  $O(^3P)$  occurs in the ratios of 0.9 and 0.1, respectively (Adler-Golden et al. 1982). According to the measurement of accurate O-O bond energy by Taniguchi et al. (1999),  $\Delta H_f^\circ(O_3)$  is  $-144.31 \pm 0.14$  kJ mol $^{-1}$  and the wavelength threshold for reaction (4.2) is  $309.44 \pm 0.02$  nm. However, the production of  $O(^1D)$  is discernible at the

wavelength longer than this value. From the fact that the temperature dependence is observed for the O(<sup>1</sup>D) production quantum yields in this wavelength region, the formation of O(<sup>1</sup>D) here is thought to be due to the photoabsorption from the vibrationally excited ground state molecule of O<sub>3</sub> to the Hartley bands (hot bands). Although the ratio of vibrationally excited molecules is not large at the temperature range of 200–320 K, the transition probability from the ground state with the excited anti-symmetric stretching vibration ( $\nu_3$ ) to the <sup>1</sup>B<sub>2</sub> state is large, and the absorption cross sections of the hot bands are sizable, since the O<sub>3</sub> in the <sup>1</sup>B<sub>2</sub> state is an asymmetric molecule with unequal O-O bond lengths in contrast to in the ground state which is symmetric molecule with equal O-O bond distances. Theoretical calculation also shows that the absorption cross sections for the long-wavelength edge of Hartley bands get larger with the excitation of anti-symmetric stretching vibration  $\nu_3$  (Adler-Golden 1983). In Fig. 4.7, the O(<sup>1</sup>D) production quantum yields for the transition from the vibrational ground state in the Hartley bands correspond to region I, and those for the transition from the  $\nu_3$  vibrationally excited states correspond to region II at 298, 253, and 203 K.

For the O(<sup>1</sup>D) formation pathways in the Huggins bands, it is known that the reaction pathway,



is involved in addition to reaction (4.2), which is proved from the measurement of translational energy of formed O(<sup>1</sup>D) (Takahashi et al. 1996; Denzer et al. 1998). The temperature independent production of O(<sup>1</sup>D) seen in Figs. 4.5 and 4.7 assigned to the spin forbidden process (4.3) and corresponds to region III in Fig. 4.7. The O(<sup>1</sup>D) production quantum yields by this spin forbidden process are nearly constant at about 0.08 in the wavelength longer than 310 nm for the absorption by the Huggins bands, and the wavelength dependence corresponding to the vibrational structure of the absorption spectrum in 313–320 nm is not observed (Takahashi et al. 1996, 1998). Although the assignment of the upper state of the spin forbidden transition for the Huggins bands has not been established distinctively, Takahashi et al. (1997) proposed the 2<sup>1</sup>A<sub>1</sub> state as shown in Fig. 4.8 from the recent measurement of rotational constants.

Using these new data of the quantum yields, the contributions to the O(<sup>1</sup>D) formation in the tropospheric chemistry by the above mentioned vibrationally excited O<sub>3</sub> molecule in the Hartley bands, and the spin forbidden transition process are estimated as 25–40 %, and 30 % at the solar zenith angle of 40–80°, and 80°, respectively (Matsumi et al. 2002).

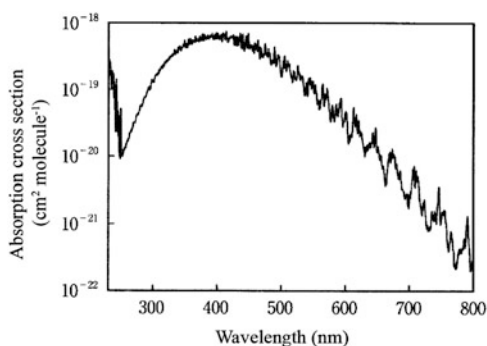


### 4.2.2 Nitrogen Dioxide ( $\text{NO}_2$ )

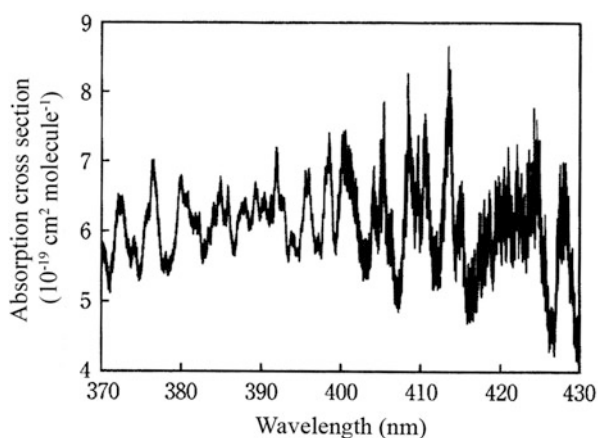
The formation of oxygen atom  $\text{O}(^3\text{P})$  in the photolysis of nitrogen dioxide ( $\text{NO}_2$ ) is the fundamental reaction that causes direct production of  $\text{O}_3$  in the troposphere. In this section, absorption spectrum and  $\text{O}(^3\text{P})$  production quantum yields relevant to the tropospheric photochemistry are described.

**Absorption Spectrum and Cross Section** The absorption spectrum of  $\text{NO}_2$  in 240–800 nm region is shown in Fig. 4.9 (Orphal 2003). As shown in the figure,  $\text{NO}_2$  has a continuous absorption spectrum from ultraviolet to a whole range of visible and near infrared with a maximum at around 400 nm. This spectrum has been assigned to the  $\text{D}^2\text{B}_2\text{-X}^2\text{A}_1$  transition for the wavelength shorter than 240 nm, and to the  $\text{B}^2\text{B}_1\text{-X}^2\text{A}_1$ , and  $\text{A}^2\text{B}_2\text{-X}^2\text{A}_1$  mixed with the  $\text{C}^2\text{A}_2\text{-X}^2\text{A}_1$  (forbidden transition) transitions for the 300–790 nm region (Douglas 1966; Stevens et al. 1973). Therefore, the absorption spectrum of  $\text{NO}_2$  in the near ultraviolet and visible region is very complex. Figure 4.10 shows the high resolution absorption spectrum in the

**Fig. 4.9** Absorption spectrum of  $\text{NO}_2$  in the ultraviolet and visible region (Adapted from Orphal 2003)



**Fig. 4.10** High-resolution absorption spectrum of  $\text{NO}_2$  near the dissociation wavelength threshold (398 nm) for  $\text{NO}_2 \rightarrow \text{NO} + \text{O}(^3\text{P})$ . Resolution 0.03 nm at 445 nm (Adapted from Orphal et al. 2003)



region of 370–430 nm (Orphal 2003). The rotational lines are very sharp and dense particularly near the dissociation limit of 398 nm, and the line widths are determined by the pressure broadening. Since the lifetime of the excited state is shorter at wavelengths shorter than the dissociation limit, the line widths are broader according to the uncertainty principle as seen in the figure. It is known that the absorption spectrum of NO<sub>2</sub> has temperature dependence, and the differences between peaks and valleys of absorption lines are larger at lower temperature which makes the absorption lines more distinct (Harder et al. 1997; Vandaele et al. 2002). The temperature and pressure dependence of the high resolution spectrum of NO<sub>2</sub> are important for the spectral analysis of remote sensing data of satellites.

Table 4.5 tabulates the absorption cross sections of NO<sub>2</sub> at 298 K recommended by IUPAC Subcommittee Report Vol. I (Atkinson et al. 2004) based on Vandaele et al. (1998) and others.

**Photolysis Quantum Yields.** Table 4.6 shows the wavelength threshold below which the production of the pairs of either the ground or excited states of NO(X<sup>2</sup>Π, A<sup>2</sup>Σ<sup>+</sup>) and O(<sup>3</sup>P, <sup>1</sup>D, <sup>1</sup>S) in the photolysis of NO<sub>2</sub> (Okabe 1978). From Table 4.6 it

**Table 4.5** Absorption cross sections of NO<sub>2</sub>(298 K)

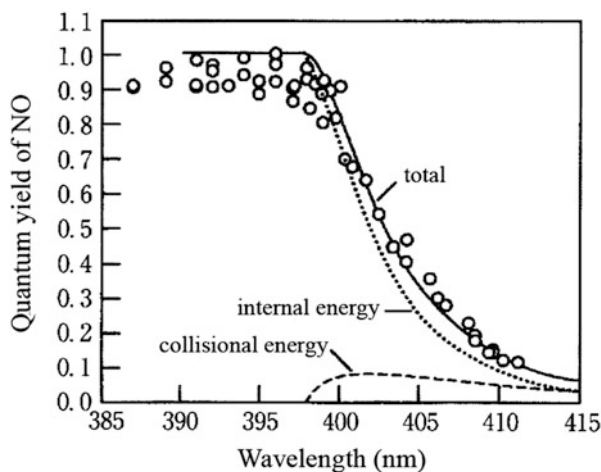
Wavelength (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wavelength λ (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wavelength λ (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )
205	33.8	305	16.0	405	57.7
210	44.5	310	18.8	410	61.5
215	48.9	315	21.6	415	58.9
220	46.7	320	25.4	420	59.2
225	39.0	325	28.8	425	56.7
230	27.7	330	31.9	430	54.0
235	16.5	335	35.9	435	55.5
240	8.30	340	40.2	440	48.4
245	3.75	345	41.8	445	48.8
250	1.46	350	46.1	450	48.1
255	1.09	355	49.8	455	41.2
260	1.54	360	50.8	460	43.0
265	2.18	365	55.0	465	40.9
270	2.92	370	56.1	470	33.6
275	4.06	375	58.9	475	38.5
280	5.27	380	59.2	480	33.4
285	6.82	385	59.4	485	25.2
290	8.64	390	62.0	490	30.7
295	10.6	395	59.2	495	29.3
300	13.0	400	63.9		

Source: IUPAC Subcommittee Report Vol. I (Atkinson et al. 2004)

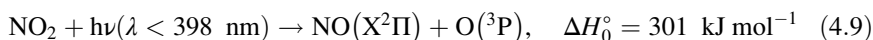
**Table 4.6** Wavelength thresholds (nm) below which the production of each pair of NO and O is energetically possible in the photolysis of NO<sub>2</sub> (0 K)

NO / O	<sup>3</sup> P	<sup>1</sup> D	<sup>1</sup> S
X <sup>2</sup> Π,	397.8	243.9	169.7
A <sup>2</sup> Σ <sup>+</sup>	144.2	117.4	97.0

Source: Okabe (1978)

**Fig. 4.11** Quantum yields of NO formation in the photolysis of NO<sub>2</sub>. The dotted and broken lines show the contribution of the internal energy of vibration and rotation, and the collisional energy to the photolysis beyond the dissociation limit, respectively (Adapted from Roehl et al. 1994)

can be seen that only the photolytic process which is possible by the actinic flux in the troposphere, is



and the threshold wavelength to give the ground states of NO and O is 397.8 nm at 0 K. The NO production quantum yields in the photolytic process (4.9) near the threshold wavelength at 298 K is shown in Fig. 4.11 (Roehl et al. 1994; Troe 2000). Also, the quantum yields of the photodissociation of NO<sub>2</sub> in the 300–420 nm range recommended by NASA/JPL Evaluation No. 17 based on Roehl et al. (1994) and Troe (2000) are shown in Table 4.7. As clearly shown in Fig. 4.11, Although the quantum yields of NO production falls rapidly at wavelengths longer than the dissociation limit of 398 nm, it is not zero even beyond the threshold wavelength and the production of NO extends to around 420 nm. The production of NO beyond the wavelength range of dissociation limit is interpreted as it is mainly due to the addition of internal energy from the vibronic excited states of ground state molecules and also to the further supplement of the translational energy by a collision of another molecule to the excited NO<sub>2</sub> molecule after photoabsorption. Figure 4.11 depicts the calculated contributions of these processes by dotted and broken lines, respectively.

**Table 4.7** Quantum yields for the NO<sub>2</sub> photolysis in the 300–420 nm region (298, 248 K)

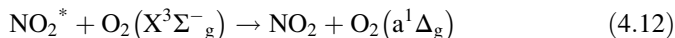
Wavelength (nm)	Quantum Yields $\phi$		Wavelength (nm)	Quantum Yields $\phi$		Wavelength (nm)	Quantum Yields $\phi$	
	298 K	248 K		298 K	248 K		298 K	248 K
300–398	1.00	1.00	406	0.30	0.22	414	0.08	0.04
399	0.95	0.94	407	0.26	0.18	415	0.06	0.03
400	0.88	0.86	408	0.22	0.14	416	0.05	0.02
401	0.75	0.69	409	0.18	0.12	417	0.04	0.02
402	0.62	0.56	410	0.15	0.10	418	0.03	0.02
403	0.53	0.44	411	0.13	0.08	419	0.02	0.01
404	0.44	0.34	412	0.11	0.07	420	0.02	0.01
405	0.37	0.28	413	0.09	0.06			

As seen in Fig. 4.9, the absorption spectrum of  $\text{NO}_2$  extends over the whole range of the visible region, and the formation rate of excited  $\text{NO}_2$  molecules by the absorption of solar radiation beyond the wavelength longer than the dissociation threshold is large. Most of the non-dissociative electronic excited  $\text{NO}_2$  molecules undergo the processes,



and return to the ground state either by emitting fluorescence or being deactivated (quenched) by other atmospheric molecules. The radiative rate of electronically excited  $\text{NO}_2$  is  $\sim 1.5 \times 10^4 \text{ s}^{-1}$  and the fluorescence lifetime is  $\sim 70 \mu\text{s}$  (Donnelly and Kaufman 1978). Meanwhile, the rate constants of quenching by  $\text{N}_2$  and  $\text{O}_2$  molecules are  $\sim 5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Donnelly et al. 1979), and the fluorescence quantum yield is about  $10^{-5}$  under the pressure of the lower troposphere, so that most of the excited  $\text{NO}_2$  formed by the absorption of the solar radiation are quenched by  $\text{N}_2$  and  $\text{O}_2$ .

However, if the rate constants of the reaction or energy transfer between the electronically excited  $\text{NO}_2$  and other atmospheric molecules are large enough, the possibility of such processes cannot be denied. An energy transfer process,



to form  $\text{O}_2(\text{a}^1\Delta_g)$  has been studied by Jones and Bayes (1973), but the role of the electronically excited  $\text{O}_2$  molecules formed in reaction (4.12) are thought to be unimportant in the lower atmosphere. On the other hand, it has recently been reported that OH radicals are formed when  $\text{NO}_2$  molecules are excited by visible light at 565, 590, 613 nm in the presence of water vapor, and the reaction,

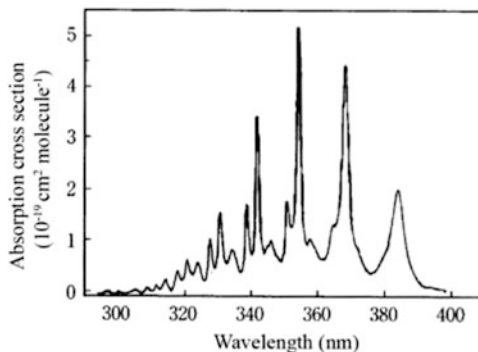


has been proposed (Li et al. 2008). If the reaction has the rate constant  $k_{4.13} = 1.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  as reported by Li et al. (2008), this reaction could have the importance in the lower troposphere comparable to the reaction of  $\text{O}(\text{D}) + \text{H}_2\text{O}$  succeeding to the photolysis of  $\text{O}_3$ . Replication experiments (Carr et al. 2009) and theoretical studies are attempted (Fang et al. 2010).

### 4.2.3 Nitrous Acid (HONO)

Nitrous acid (HONO) is formed not only by the homogeneous reaction of  $\text{OH} + \text{NO}$ , but by the heterogeneous reactions of  $\text{NO}_2$  with ground surface, which is further enhanced by photo-irradiation (see Sect. 6.4.2), it exists in the polluted air

**Fig. 4.12** Absorption spectrum of HONO (Adapted from Stutz et al. 2000)



at relatively high concentration even in the daytime when the photolysis rate is fast. Therefore, the photolytic reaction of HONO is very important as a source of the OH radicals in the polluted atmosphere.

**Absorption Spectrum and Cross Sections** The absorption spectrum of HONO is shown in Fig. 4.12. Since pure HONO cannot be obtained in the laboratory, and a trace amount of NO<sub>2</sub> is always present in the sample, it has been a big problem about how to remove the effect of NO<sub>2</sub> in the measurements of absorption spectrum and cross sections of HONO (Stockwell and Calvert 1978). The absorption spectrum shown in Fig. 4.12 is based on Stutz et al. (2000) with the resolution 0.08 nm, which agrees well with the previous data (Vasudev 1990; Bongartz et al. 1991). The absorption bands of HONO in the wavelength region of 300–400 nm is assigned to the A A'' ← X A' transition, and the spectrum reveals a clear vibrational structure. This vibrational structure corresponds to the -N=O stretching frequency of the excited states, and the bands at 369, 355 and 342 nm are assigned to 1–0, 2–0 and 3–0, respectively (Vasudev et al. 1984). As for the absolute values of absorption cross sections, the uncertainty was large due to the effect of the impurity NO<sub>2</sub>. The absolute values of absorption cross sections are usually compared at the maximum peak of the absorption bands at 354 nm, and relative values normalized to this are given. It should be noted, however, that the recent values are for the measurements with 0.1 nm or higher resolution, but the previous values are for the measurements with lower resolution, care should be taken for the comparison. The absorption cross section at 354 nm by Stutz et al. (2000) is  $51.9 \pm 0.03 \times 10^{-20} \text{ cm}^2$  (resolution 0.08 nm), that agrees well with the values by Stockwell and Calvert (1978), Bongartz et al. (1994), and Pagsberg et al. (1997) within 5 %. Table 4.8 gives absorption cross sections recommended by NASA/JPL Evaluation No. 17 (Sander et al. 2011). These values are based on Stutz et al. (2000) and averaged over 1 nm intervals.

**Photolysis Quantum Yields** The broad bands without rotational structure in the spectrum shown in Fig. 4.12 implies that the dissociation lifetime of the excited states is short. Indeed, the HONO molecules absorbing the radiation in this wavelength region is known to dissociate in the pathway,

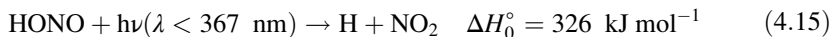
**Table 4.8** Absorption cross section of HONO (298 K)

Wave-length (nm)	$10^{20} \sigma$ ( $\text{cm}^2 \text{ molecule}^{-1}$ )	Wave-length (nm)	$10^{20} \sigma$ ( $\text{cm}^2 \text{ molecule}^{-1}$ )	Wave-length (nm)	$10^{20} \sigma$ ( $\text{cm}^2 \text{ molecule}^{-1}$ )	Wave-length (nm)	$10^{20} \sigma$ ( $\text{cm}^2 \text{ molecule}^{-1}$ )	Wave-length (nm)	$10^{20} \sigma$ ( $\text{cm}^2 \text{ molecule}^{-1}$ )
300	0.617	320	4.66	340	7.79	360	6.87	380	7.21
301	0.690	321	5.96	341	16.1	361	6.05	381	9.13
302	0.579	322	4.05	342	29.4	362	5.98	382	12.4
303	0.925	323	4.56	343	11.4	363	7.39	383	17.0
304	1.04	324	5.89	344	7.79	364	11.5	384	19.5
305	1.57	325	4.05	345	8.77	365	12.8	385	16.1
306	1.29	326	2.65	346	9.64	366	14.8	386	10.5
307	0.916	327	6.44	347	7.80	367	25.1	387	6.59
308	1.45	328	9.22	348	6.63	368	43.6	388	4.30
309	2.01	329	5.20	349	6.00	369	31.5	389	2.81
310	1.51	330	9.92	350	9.06	370	15.1	390	1.71
311	2.07	331	14.3	351	16.9	371	9.49	391	0.992
312	2.42	332	6.94	352	12.4	372	7.96	392	0.731
313	2.25	333	6.31	353	16.3	373	6.30	393	0.597
314	3.35	334	8.35	354	48.7	374	4.59	394	0.528
315	2.54	335	7.71	355	27.6	375	3.55	395	0.403
316	1.61	336	5.33	356	11.1	376	3.36	396	0.237
317	3.21	337	4.23	357	9.45	377	3.66		
318	4.49	338	9.38	358	9.84	378	4.33		
319	3.19	339	14.3	359	8.37	379	5.66		

Source: NASA/JPL Panel Evaluation No. 17 (Sander et al. 2011)



with quantum yields of unity (Cox and Derwent 1976). The ratio of another conceived photolytic pathway,



to produce H atoms has been reported to be less than 0.01 (Wollenhaupt et al. 2000).

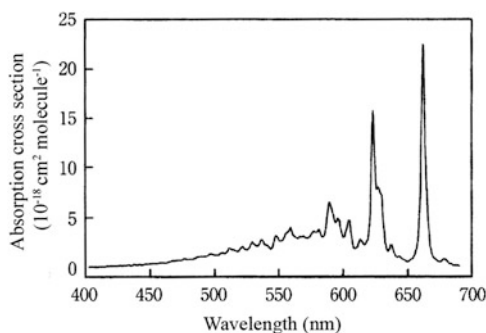
#### 4.2.4 Nitrogen Trioxide ( $\text{NO}_3$ ), Dinitrogen Pentoxide ( $\text{N}_2\text{O}_5$ )

Nitrogen trioxide ( $\text{NO}_3$ ) is also called nitrate radical, and is formed by the reaction of  $\text{O}_3 + \text{NO}_2$ . Dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ) is then formed from the  $\text{NO}_3$  and  $\text{NO}_2$  in the equilibrium reaction of  $\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5$ . The  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  are important intermediates in nighttime chemistry, and their daytime concentrations are very low since  $\text{NO}_3$  absorbs solar radiation strongly and is easily photolyzed.

**Absorption Spectrum and Cross Sections of  $\text{NO}_3$**   $\text{NO}_3$  is a free radical with unpaired electron, and many studies have been performed from spectroscopic interest (Wayne et al. 1991). Figure 4.13 shows the absorption spectrum of  $\text{NO}_3$  in the visible region (Sander et al. 2011). As seen in the figure,  $\text{NO}_3$  has very strong absorption bands with vibrational structures in the broad range of the visible region 400–700 nm, particularly in the red region of 600–700 nm. These absorption bands correspond to the B-X transition, and the strongest peaks at 662 and 623 nm are assigned to 0–0 and 1–0 bands. The spectrum shown in Fig. 4.13 is those averaged over 1 nm interval. These bands consist of many rotational lines and the high-resolution spectrum separating them are also obtained (Orphal et al. 2003; Osthoff et al. 2007).

The absorption cross section at 662 nm has been used for obtaining the concentration of  $\text{NO}_3$  in its detection in the laboratory and ambient air, and many laboratory studies have been conducted to obtain the value. The recommended

**Fig. 4.13** Absorption spectrum of  $\text{NO}_3$  (Adapted from Sander et al. 2011)





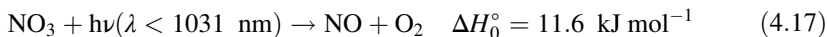
value by Wayne et al. (1991) is  $(2.10 \pm 0.20) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$  and agrees well with the recommended value of  $(2.25 \pm 0.15) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$  by the NASA/JPL Evaluation No. 17 (Sander et al. 2011). The absorption cross section of  $\text{NO}_3$  at 662 nm peak is known to have temperature dependence, and Osthoff et al. (2007) presented the formula

$$\begin{aligned} \sigma(662 \text{ nm}, T) &= (4.582 \pm 0.096) \\ &= [(0.00796 \pm 0.0031) \times T] \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1} \end{aligned} \quad (4.16)$$

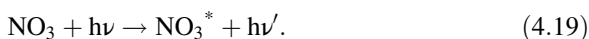
modifying the parameters of the experimental formula by Yokelson et al. (1994). The cause of the temperature dependence has been ascribed to the temperature change in the Boltzmann distribution of the vibration-rotation levels (Orphal et al. 2003).

The absorption cross sections of  $\text{NO}_3$  averaged over 1 nm intervals recommended by NASA/JPL Evaluation No. 17 (Sander et al. 2011) are given in Table 4.9. These values are based on the data by Sander (1986) that were normalized by the value at 662 nm mentioned above.

**Photolysis Quantum Yields of  $\text{NO}_3$**  The two reaction pathways of the photolysis of  $\text{NO}_3$  in the visible region can be,



Furthermore, as judged from the high resolution spectrum, the dissociation lifetime of the excited state of  $\text{NO}_3$  for the bands at wavelengths longer than 600 nm where sharp vibration-rotation structure is observed, is long and the observation of fluorescence has been known from the laboratory studies,



Reaction (4.17) is nearly thermo-neutral and there is no energy restriction, but it has large energy barrier since it passes the three-centered O-N-O transition state. The barrier height has been obtained as  $198 \text{ kJ mol}^{-1}$  from the photofragment experiment (Davis et al. 1993). On the other hand, the wavelength threshold for reaction (4.18) has been determined as  $587 \pm 3 \text{ nm}$ , from which the new values of heat of formation of  $\text{NO}_3$  at 0 K and 298 K are obtained as  $79.0 \pm 1.4$ ,  $73.7 \pm 1.4 \text{ kJ mole}^{-1}$ , respectively.

Figure 4.14 depicts the plot of quantum yields of  $\Phi(\text{NO} + \text{O}_2)$  and  $\Phi(\text{NO}_2 + \text{O})$  for the reaction (4.17) and (4.18) as a function of wavelength together with the fluorescence quantum yields. As shown in Fig. 4.14,  $\Phi(\text{NO}_2 + \text{O})$  is nearly unity at the threshold wavelength of 587 nm.  $\Phi(\text{NO}_2 + \text{O})$  decreases with the wavelength in the longer wavelength region, but still has the value of ca. 0.1 at around 635 nm. In the photolysis of reaction (4.18) in the longer wavelength range than 587 nm, the

**Table 4.9** Absorption cross sections of NO<sub>3</sub> (298 K)

Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )
420	9	470	63	520	180	570	299	620	350
422	10	472	69	522	206	572	294	622	1090
424	10	474	66	524	176	574	306	624	1290
426	15	476	84	526	175	576	350	626	783
428	13	478	78	528	225	578	354	628	789
430	18	480	75	530	239	580	358	630	724
432	16	482	76	532	216	582	351	632	350
434	20	484	83	534	218	584	302	634	176
436	16	486	98	536	275	586	355	636	181
438	23	488	102	538	251	588	540	638	217
440	21	490	111	540	225	590	638	640	132
442	23	492	107	542	201	592	548	642	99
444	21	494	109	544	183	594	449	644	102
446	26	496	129	546	260	596	495	646	80
448	26	498	128	548	320	598	393	648	66
450	31	500	121	550	265	600	296	650	53
452	36	502	118	552	264	602	355	652	65
454	38	504	135	554	298	604	468	654	88
456	38	506	143	556	349	606	355	656	142
458	39	508	136	558	376	608	198	658	260
460	42	510	162	560	355	610	189	660	798
462	42	512	189	562	311	612	239	662	2250

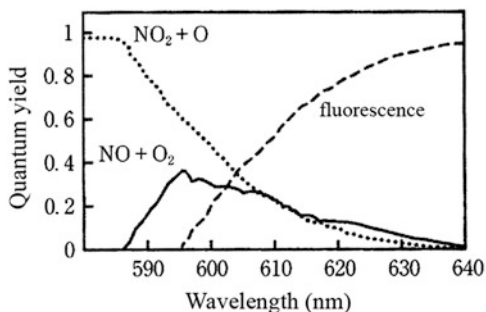
(continued)

**Table 4.9** (continued)

Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )
464	51	514	169	564	291	614	273	664	1210
466	58	516	167	566	305	616	224	666	532
468	60	518	154	568	305	618	256	668	203

Source: NASA/JPL Panel Evaluation No.17 (Sander et al. 2011)

**Fig. 4.14** Photolysis and fluorescence quantum yields of  $\text{NO}_3$  (Adapted from Johnston et al. 1996)



energy is supplemented by the vibronic energy in the ground state molecule as in the case of  $\text{NO}_2$  mentioned before. The values of  $\Phi(\text{NO} + \text{O}_2)$  and  $\Phi(\text{NO}_2 + \text{O})$  obtained by Johnston et al. (1996) agrees well with those obtained by different experimental method by Orlando et al. (1993) except a part of wavelength region (605–620 nm). As seen in Fig. 4.14, the values of  $\Phi(\text{NO} + \text{O}_2)$  is 0 at the shorter wavelength where  $\Phi_2(\text{NO}_2 + \text{O})$  is unity, it increases with wavelength and take a maximum value of 0.35 at 595 nm. The  $\Phi(\text{NO} + \text{O}_2)$  decreases gradually at the longer wavelength, and is ca. 0.1 at around 630 nm. In the longer wavelength than 587 nm, the photodissociation quantum yields of  $\text{NO}_3$ , the sum of  $\Phi(\text{NO} + \text{O}_2)$  and  $\Phi(\text{NO}_2 + \text{O})$  is smaller than unity, and the fluorescence quantum yields of the pathway (4.13) increases. Photolysis quantum yields of  $\text{NO}_3$  in the wavelength region longer than 587 nm shows large temperature dependence and decreases with temperature (Johnston et al. 1996). Particularly, since the reaction (4.18) in this region is due to the hot bands the temperature dependence of  $\Phi(\text{NO}_2 + \text{O})$  is much larger than  $\Phi(\text{NO} + \text{O}_2)$ . Table 4.10 gives photolytic quantum yields of  $\text{NO}_3$  at 298, 230 and 190 K recommended by NASA/JPL Evaluation No. 17 (Sander et al. 2011).

**Absorption Spectrum and Cross Sections of  $\text{N}_2\text{O}_5$**  Figure 4.15 shows absorption spectrum of  $\text{N}_2\text{O}_5$  (Harwood et al. 1998). The absorption spectrum of  $\text{N}_2\text{O}_5$  has a maximum at 160 nm, decreases monotonically toward longer wavelength, and extends to near ultraviolet region of tropospheric solar actinic flux. Table 4.11 tabulates absorption cross sections of  $\text{N}_2\text{O}_5$  recommended by IUPAC Subcommittee Report Vol. I (Atkinson et al. 2004). The recommendation is based on the values of Harwood et al. (1993, 1998) in the wavelength region longer than 240 nm, and of Yao et al. (1982), Osborne et al. (2000), etc. in regions shorter than this.

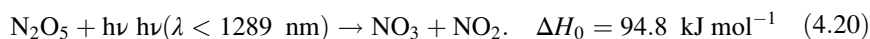
The temperature dependence is also found in the absorption cross sections of  $\text{N}_2\text{O}_5$ . The dependence is particularly large in wavelength regions longer than 280 nm where the photolysis occurs in the troposphere, and the cross sections decreases with the decrease of temperature.

**Photolysis Quantum Yields of  $\text{N}_2\text{O}_5$**  The photolytic process of  $\text{N}_2\text{O}_5$  of the interest in tropospheric chemistry is

**Table 4.10** Quantum yields of the photolysis of NO<sub>3</sub> (298, 230, 190 K)

$\lambda$ (nm)	$\Phi$ (NO + O <sub>2</sub> )			$\Phi$ (NO <sub>2</sub> + O)		
	298 K	230 K	190 K	298 K	230 K	190 K
586	0.015	0.026	0.038	0.97	0.97	0.96
588	0.097	0.16	0.22	0.89	0.84	0.78
590	0.19	0.30	0.40	0.79	0.70	0.60
592	0.25	0.38	0.50	0.73	0.61	0.51
594	0.33	0.49	0.61	0.65	0.51	0.39
596	0.36	0.50	0.60	0.59	0.43	0.31
598	0.32	0.42	0.47	0.53	0.37	0.25
600	0.29	0.35	0.36	0.47	0.31	0.20
602	0.29	0.32	0.31	0.42	0.25	0.15
604	0.28	0.28	0.50	0.35	0.20	0.11
606	0.27	0.25	0.21	0.30	0.16	0.080
608	0.25	0.22	0.17	0.26	0.13	0.062
610	0.24	0.19	0.14	0.23	0.11	0.048
612	0.20	0.15	0.10	0.21	0.10	0.042
614	0.17	0.11	0.071	0.17	0.068	0.028
616	0.16	0.10	0.060	0.14	0.053	0.020
618	0.14	0.084	0.045	0.11	0.039	0.014
620	0.13	0.072	0.036	0.090	0.030	0.010
622	0.12	0.062	0.029	0.070	0.022	0.0070
624	0.11	0.050	0.022	0.055	0.016	0.0048
626	0.092	0.041	0.017	0.044	0.012	0.0034
628	0.074	0.030	0.012	0.034	0.0087	0.0023
630	0.065	0.025	0.0090	0.026	0.0063	0.0015
632	0.051	0.018	0.0060	0.020	0.0043	0.0010
634	0.043	0.014	0.0045	0.016	0.0034	0.0007
636	0.032	0.0099	0.0029	0.012	0.0023	0.0005
638	0.027	0.0077	0.0022	0.0096	0.0018	0.0003
640	0.020	0.0054	0.0014	0.0072	0.0012	0.0002

Source: Extracted from NASA/JPL Evaluation No.17 (Sander et al. 2011)

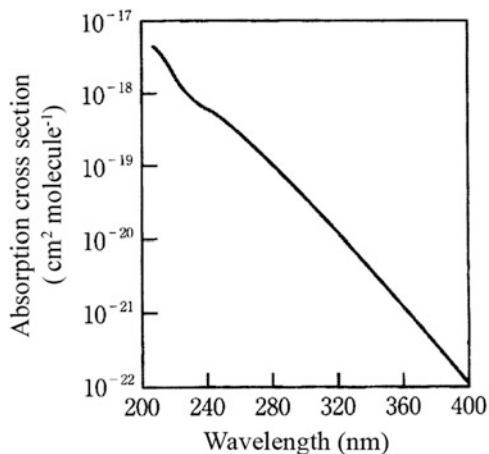


The photolytic quantum yields of N<sub>2</sub>O<sub>5</sub> is reported to be close to unity (Harwood et al. 1993, 1998).

#### 4.2.5 Formaldehyde (HCHO), Acetaldehyde (CH<sub>3</sub>CHO)

Formaldehyde (HCHO) exists globally in the natural atmosphere as an oxidation product of CH<sub>4</sub>. It is also an oxidation product of biogenic hydrocarbons of plant

**Fig. 4.15** Absorption spectrum of  $\text{N}_2\text{O}_5$  (Adapted from Harwood et al. 1998)



**Table 4.11** Absorption cross sections of  $\text{N}_2\text{O}_5$  (298 K)

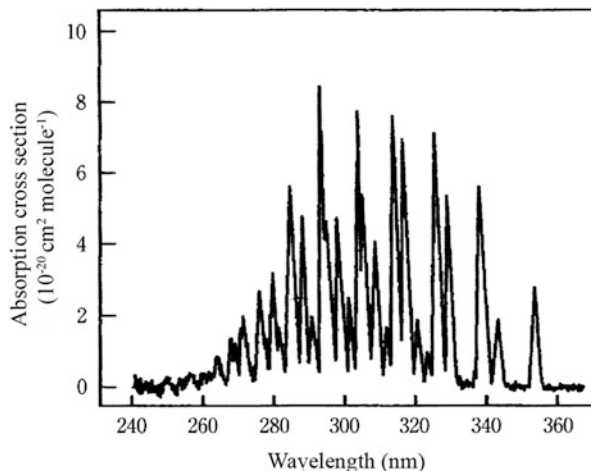
Wavelength (nm)	$10^{20} \sigma$ ( $\text{cm}^2 \text{ molecule}^{-1}$ )	Wavelength (nm)	$10^{20} \sigma$ ( $\text{cm}^2 \text{ molecule}^{-1}$ )	Wavelength $\lambda$ (nm)	$10^{20} \sigma$ ( $\text{cm}^2 \text{ molecule}^{-1}$ )
210	470	280	11	350	0.22
215	316	285	8.6	355	0.16
220	193	290	6.7	360	0.12
225	128	295	5.1	365	0.091
230	91	300	3.9	370	0.072
235	73	305	2.9	375	0.053
240	60	310	2.2	380	0.041
245	51	315	1.6	385	0.032
250	40	320	1.2	390	0.023
255	32	325	0.89	395	0.017
260	26	330	0.67	400	0.014
265	20	335	0.50	405	0.010
270	16	340	0.38	410	0.008
275	13	345	0.28		

Source: IUPAC Subcommittee Report Vol. I (Atkinson et al. 2004)

origin over lands. On the other hand, HCHO is a secondary pollutant formed by the oxidation of anthropogenic hydrocarbons in the polluted atmosphere, and also a primary pollutant emitted from auto-exhaust and biomass burning. HCHO is the aldehyde that exists usually in the highest concentration in polluted atmospheres. Photolysis of HCHO gives H atoms HCO radicals which transform to  $\text{HO}_2$  radicals in the atmosphere, and has a large impact on the photochemical ozone production in the polluted atmosphere.

Acetaldehyde ( $\text{CH}_3\text{CHO}$ ) is an important aldehyde next to HCHO in polluted atmospheres. As with HCHO,  $\text{CH}_3\text{CHO}$  is formed as a secondary pollutant from

**Fig. 4.16** Absorption spectrum of HCHO. Resolution 0.1 nm (Adapted from Rogers 1990)



anthropogenic hydrocarbons and also emitted as a primary pollutant from auto-exhaust and biomass burning. The photolysis of  $\text{CH}_3\text{CHO}$  is also important for the photochemical ozone production as a source of radicals.

**Absorption Spectrum and Cross Sections of HCHO** For carbonyl compounds such as aldehydes and ketones, absorption bands due to the electronic transition called  $n - \pi^*$  transition, in which the isolated pair of lone-pair electrons on the O atom of carbonyl group ( $-\text{C}=\text{O}$ ) is excited to the excited  $\pi$  orbital of the double bond, appears around 300 nm. Since this transition is a forbidden transition, the absorption cross sections are not very large ( $\sim 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ ) in general. However, since the absorption bands extend to near 350 nm where solar actinic flux grows, their photolyses are very important in the troposphere.

Figure 4.16 shows absorption spectrum of HCHO (Rogers 1990). As shown in Fig. 4.16, the absorption spectrum of HCHO spreads over 260–360 nm and it characterized by many vibrational structures. Since the absorption has the banded structure, its spectral shape is very much dependent on the spectral resolution. The spectrum with the resolution less than 0.1 nm has been obtained by Rogers(1990), Cantrell et al. (1990), Meller and Moortgat (2000), etc. with good agreement to each other. Higher resolution spectrum ( $0.001 \text{ nm}$ ,  $0.1 \text{ cm}^{-1}$ ) separates the rotational lines (Pope et al. 2005a; Co et al. 2005; Smith et al. 2006).

Temperature dependence is known for the absorption cross sections of HCHO (Cantrell et al. 1990; Meller and Moortgat 2000; Smith et al. 2006), and a linear approximation formula,

$$\sigma(\lambda, T) = \sigma(\lambda, 298 \text{ K}) + \Gamma(\lambda) \times (T - 298), \quad (4.21)$$

has been proposed by Meller and Moortgat (2000) in the 223–323 nm region.

Table 4.12 gives absorption cross sections of HCHO taken form the NASA/JPL Evaluation No. 17 (Sander et al. 2011) and IUPAC Subcommittee Report Vol. II (Atkinson et al. 2006). These values are based on the high-resolution absorption

**Table 4.12** Absorption cross sections of HCHO (298 K) (Averaged over 1 nm interval)

Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )
240	0.078	270	0.963	300	0.964	330	3.87
241	0.078	271	1.94	301	1.62	331	1.41
242	0.123	272	1.43	302	0.854	332	0.347
243	0.159	273	0.811	303	3.02	333	0.214
244	0.110	274	0.658	304	7.22	334	0.159
245	0.131	275	2.14	305	4.75	335	0.097
246	0.163	276	2.58	306	4.29	336	0.126
247	0.151	277	1.57	307	1.78	337	0.383
248	0.234	278	1.03	308	1.38	338	1.92
249	0.318	279	2.45	309	3.25	339	5.38
250	0.257	280	2.34	310	1.74	340	3.15
251	0.204	281	1.56	311	0.462	341	0.978
252	0.337	282	0.973	312	1.19	342	0.509
253	0.289	283	0.722	313	0.906	343	1.92
254	0.342	284	4.26	314	5.64	344	1.27
255	0.450	285	4.05	315	5.57	345	0.437
256	0.628	286	2.10	316	2.56	346	0.119
257	0.443	287	1.15	317	5.78	347	0.044
258	0.307	288	3.17	318	3.15	348	0.075
259	0.617	289	3.22	319	0.978	349	0.038
260	0.605	290	1.17	320	1.19	350	0.036
261	0.659	291	1.84	321	1.60	351	0.089
262	0.603	292	0.797	322	0.722	352	0.729
263	1.08	293	3.12	323	0.328	353	2.27

(continued)



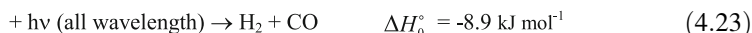
Table 4.12 (continued)

Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )
264	0.947	294	7.15	324	0.858	354	1.64
265	0.531	295	4.05	325	1.58	355	0.696
266	0.539	296	2.47	326	6.88	356	0.148
267	1.36	297	1.37	327	4.37	357	0.035
268	1.24	298	4.22	328	1.22	358	0.019
269	0.991	299	3.17	329	3.12	359	0.011

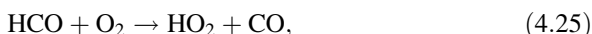
Source: IUPAC Subcommittee Report Vol. II (Atkinson et al. 2006)

coefficients by Meller and Moortgat (2000), and are averaged over the wavelength intervals for the use of atmospheric model calculations.

**Photolysis Quantum Yields of HCHO** Two reaction pathways,

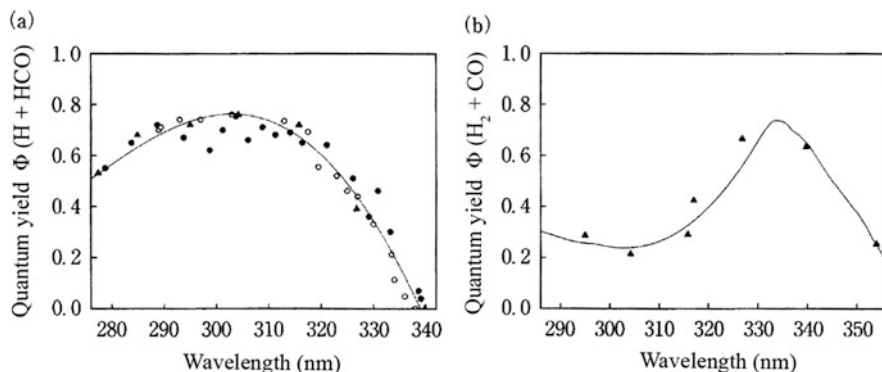


are energetically possible in the photolysis of HCHO in the near ultraviolet region. The energy threshold of reaction (4.22) is 363 kJ mole<sup>-1</sup>, and the corresponding wavelength threshold is 330 nm. On the other hand, the reaction enthalpy of the process (4.23) is negative and there is no thermochemical threshold restriction. Among these processes, reaction (4.23) produces only stable molecules whereas HO<sub>2</sub> radicals are produced from H atoms and HCO radicals formed in the reaction (4.22) by,



and affects largely photochemical processes in the troposphere. Therefore, obtaining the accurate value of quantum yield of reaction (4.22) is very important from the atmospheric chemistry point of view.

Photolytic quantum yields  $\Phi$  (H + HCO) for reaction (4.22) have been measured with the middle-resolution (0.62 nm) (Smith et al. 2002), and the high-resolution (0.0035 nm) (Carbajo et al. 2008). Troe (2007) reviewed the literature values of  $\Phi$  (H + HCO) and  $\Phi$  (H<sub>2</sub> + CO), and summarized their wavelength dependence at 300 K and 1 atm as illustrated in Fig. 4.17. The recent values of photolytic quantum



**Fig. 4.17** Photolytic quantum yields of HCHO: (a)  $\Phi(\text{H} + \text{HCO})$ , (b)  $\Phi(\text{H}_2 + \text{CO})$  (Adapted from Troe 2007)

**Table 4.13** Quantum yields for the photolysis of HCHO (300 K, 1 atm)

$\lambda$ (nm)	$\Phi$ (H + HCO)	$\Phi$ (H <sub>2</sub> + CO)	$\lambda$ (nm)	$\Phi$ (H + HCO)	$\Phi$ (H <sub>2</sub> + CO)
250	0.310	0.490	310	0.737	0.263
255	0.304	0.496	315	0.685	0.315
260	0.307	0.493	320	0.603	0.397
265	0.343	0.477	325	0.489	0.511
270	0.404	0.441	330	0.343	0.657
275	0.479	0.391	335	0.165	0.735
280	0.560	0.347	340	0.0	0.645
285	0.633	0.307	345	0.0	0.505
290	0.690	0.278	350	0.0	0.375
295	0.734	0.256	355	0.0	0.220
300	0.758	0.242	360	0.0	0.04
305	0.760	0.240			

Source: NASA/JPL Evaluation No.17 (Sander et al. 2011)

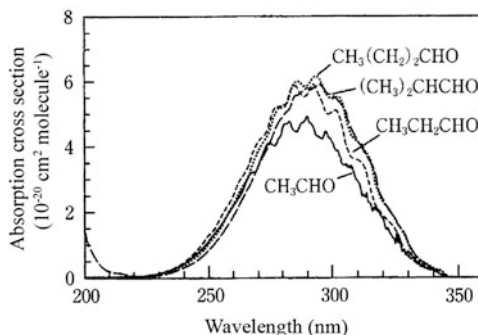
yields  $\Phi$  (H + HCO) agree well with the previous one when normalized by the value of 0.753 at 303.75 nm. However, the values of  $\Phi$  (H + HCO) obtained in the high-resolution showed banded structure and gave considerably smaller values particularly around 305 nm (Carbajo, et al. 2008).

Table 4.13 gives the values of  $\Phi$  (H + HCO) and  $\Phi$  (H<sub>2</sub> + CO) recommended by NASA/JPL Evaluation No. 17. These values are obtained by integrating the previous data by Horowitz and Calvert (1978), Moortgat and Warneck (1979), Moortgat et al. (1983) and others, and the recent one by Smith et al. (2002), Pope et al. (2005b) and Carbajo et al. (2008). The quantum yields of the formation of CO combining reaction (4.22) and (4.23) is unity for the range of 290–350 nm being independent on temperature and pressure (Moortgat and Warneck 1979; Moortgat et al. 1983). In the wavelength region longer than 350 nm,  $\Phi$  (H + HCO) does not show any temperature and pressure dependence, but large temperature and pressure dependences are seen for  $\Phi$  (H<sub>2</sub> + CO) (Moortgat et al. 1983).

**Absorption Spectrum and Cross Sections of CH<sub>3</sub>CHO** Figure 4.18 shows the absorption spectrum of CH<sub>3</sub>CHO together with those for other open-chain aldehydes such as propanal CH<sub>3</sub>CH<sub>2</sub>CHO, butanal CH<sub>3</sub> (CH<sub>2</sub>)<sub>2</sub>CHO, and iso-butanal (CH<sub>3</sub>)<sub>2</sub>CHCHO (Martinez et al. 1992). For these aldehydes, absorption peaks corresponding to the n –  $\pi^*$  transition appear near 290 nm similar to formaldehyde. The absorption spectra of these aldehydes are characterized by diffuse vibrational structures near the peak of absorption, that are different from the sharp bands of formaldehyde, and also shifted to a shorter wavelength than formaldehyde. The wavelength range of the absorption spectra does not change, but the absorption cross section in the longer wavelength side increases as the carbon number increase for these open-chain aldehydes.

Table 4.14 gives the absorption cross sections of CH<sub>3</sub>CHO recommended by NASA/JPL Evaluation No. 17 (Sander et al. 2011), which is based on Martinez et al. (1992) and Libuda and Zabel (1995).

**Fig. 4.18** Absorption spectra of  $\text{CH}_3\text{CHO}$  and other aliphatic aldehydes (Adapted from Martinez et al. 1992)

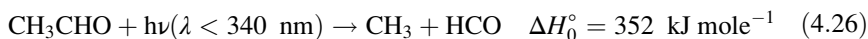


**Table 4.14** Absorption cross sections of  $\text{CH}_3\text{CHO}$  (298 K)

Wavelength (nm)	$10^{20} \sigma$ ( $\text{cm}^2 \text{ molecule}^{-1}$ )	Wavelength (nm)	$10^{20} \sigma$ ( $\text{cm}^2 \text{ molecule}^{-1}$ )	Wavelength (nm)	$10^{20} \sigma$ ( $\text{cm}^2 \text{ molecule}^{-1}$ )
230	0.151	290	4.86	326	1.09
234	0.241	292	4.66	328	0.715
238	0.375	294	4.31	330	0.699
242	0.639	296	4.24	332	0.496
246	0.887	298	4.41	334	0.333
250	1.18	300	4.15	336	0.227
254	1.57	302	3.87	338	0.212
258	2.03	304	3.46	340	0.135
262	2.45	306	3.41	342	0.042
266	3.06	308	3.31	344	0.027
270	3.38	310	2.92	346	0.020
274	4.03	312	2.52	348	0.016
278	4.15	314	2.38	350	0.008
280	4.48	316	2.07	352	0.005
282	4.66	318	1.98	354	0.004
284	4.58	320	1.70	356	0.005
286	4.41	322	1.38	358	0.004
288	4.69	324	1.06	360	0.003

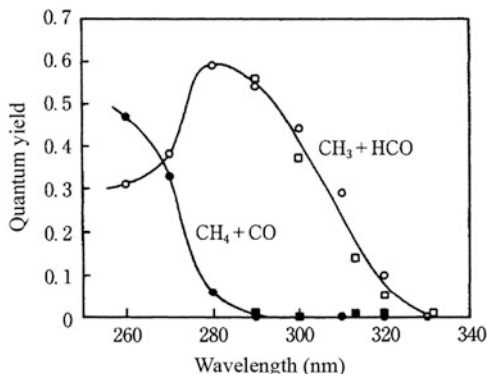
Source: NASA/JPL Panel Evaluation No. 17 (Sander et al. 2011)

Photolysis Quantum Yields of  $\text{CH}_3\text{CHO}$ : Three reaction pathways,



are known for the photolytic processes of  $\text{CH}_3\text{CHO}$  in the wavelength range of solar actinic flux in the troposphere. Among these processes, the energy thresholds (0 K)

**Fig. 4.19** Photolytic quantum yields of  $\text{CH}_3\text{CHO}$ .  $\circ$ ,  $\square$ :  $\Phi(\text{CH}_3 + \text{HCO})$ ,  $\bullet$ ,  $\blacksquare$ :  $\Phi(\text{CH}_4 + \text{CO})$  (Adapted from Atkinson and Lloyd 1984)



of reaction (4.26) and (4.28) are 352, 373  $\text{kJ mole}^{-1}$  corresponding to the wavelengths thresholds of 340, 321 nm, respectively. Meanwhile, reaction (4.27) is an exothermic process, so there exists no thermochemical threshold.

The measurements of photolytic quantum yields of  $\text{CH}_3\text{CHO}$  is reported in the 250–330 nm region at 1 atm. as a function of wavelength by Meyrahn et al. (1981), Horowitz and Calvert (1982) based on the product yield analysis. Figure 4.19 depicts the wavelength dependence of  $\Phi(\text{CH}_3 + \text{HCO})$  and  $\Phi(\text{CH}_4 + \text{CO})$  of the photolysis of  $\text{CH}_3\text{CHO}$  at 1 atm. given by Atkinson and Lloyd (1984). Also, the recommended numerical values by the NASA/JPL Evaluation No. 17 (Sander et al. 2011) for  $\Phi(\text{CH}_3 + \text{HCO})$  and  $\Phi(\text{CH}_4 + \text{CO})$  for 256–332 nm at 1 atm. are shown in Table 4.15. These values are based on the Meyrahn et al. (1981), Horowitz and Calvert (1982), and the review by Atkinson and Lloyd (1984). According to these results,  $\Phi(\text{CH}_4 + \text{CO})$  is 0.48 at 256 nm, and decreases with the increase of wavelengths to 0 at 294 nm. On the contrary, the peak value of  $\Phi(\text{CH}_3 + \text{HCO})$  is 0.59 at around 283 nm, decreases with the increase of wavelength, but maintains a value larger than 0.01 until 330 nm. The values of  $\Phi(\text{CH}_3\text{CO} + \text{H})$ , which are not shown in the figure and table is 0.025 at 300 nm and decreases with wavelength reaching to 0 at 320 nm. Therefore, reaction (4.27) does not occur in the photolysis in the troposphere, and the quantum yields of reaction (4.28) are very small so that only reaction (4.26) should be considered in the tropospheric chemistry. Temperature and pressure dependences are known for the photolysis quantum yields of  $\text{CH}_3\text{CHO}$ , and they decrease with pressure. This suggests that the dissociative lifetime of the excited state of  $\text{CH}_3\text{CHO}$  is long enough to be subjected to molecular collisions and the quenching of the excited state occurs as the pressure increases.

#### 4.2.6 Acetone ( $\text{CH}_3\text{COCH}_3$ )

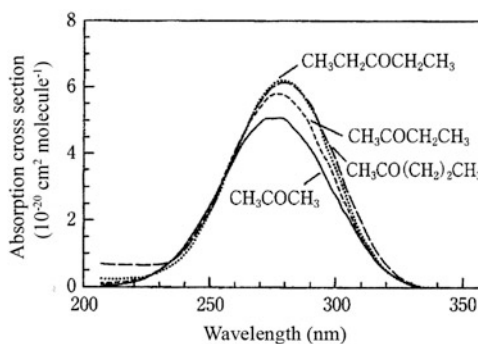
Acetone  $\text{CH}_3\text{COCH}_3$  is formed secondarily in the atmosphere by the oxidation reactions of non-methane hydrocarbons in addition to direct emissions from

**Table 4.15** Quantum yields for the photolysis of CH<sub>3</sub>CHO (298 K, 1 atm)

$\lambda$ (nm)	$\Phi$ (CH <sub>3</sub> + HCO)	$\Phi$ (CH <sub>4</sub> + CO)	$\lambda$ (nm)	$\Phi$ (CH <sub>3</sub> + HCO)
256	0.29	0.48	296	0.47
258	0.30	0.47	298	0.45
260	0.31	0.45	300	0.43
262	0.32	0.43	302	0.40
264	0.34	0.40	304	0.38
266	0.36	0.37	306	0.35
268	0.38	0.33	308	0.31
270	0.41	0.29	310	0.28
272	0.44	0.25	312	0.24
274	0.48	0.20	314	0.19
276	0.53	0.16	316	0.15
278	0.56	0.09	318	0.12
280	0.58	0.06	320	0.10
282	0.59	0.04	322	0.07
284	0.59	0.03	324	0.05
286	0.58	0.02	326	0.03
288	0.56	0.01	328	0.02
290	0.54	0.01	330	0.01
292	0.52	0.005	332	0.00
294	0.50	0.00		

Source: NASA/JPL Evaluation No.17 (Sander et al. 2011)

**Fig. 4.20** Absorption spectra of CH<sub>3</sub>COCH<sub>3</sub> and other aliphatic ketones (Adapted from Martinez et al. 1992)



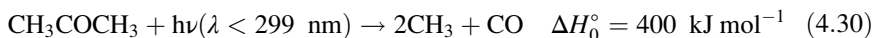
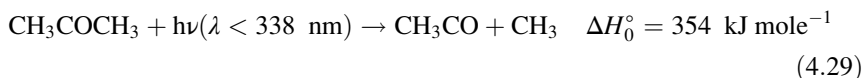
biogenic and anthropogenic sources. Since the atmospheric lifetime of acetone is relatively long, it exists over the whole range of the troposphere at the concentration of ca. 1 ppbv. The photolysis of acetone in the troposphere is important as a source of HO<sub>x</sub> radicals in the free troposphere as well as the major loss process of acetone itself.

**Absorption Spectrum and Cross Sections** Figure 4.20 shows the absorption spectrum of CH<sub>3</sub>COCH<sub>3</sub> together with other homologue ketones (Martinez

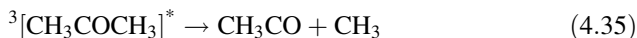
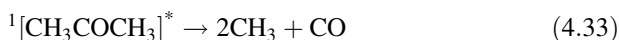
et al. 1992). The ketones show absorption in 200–350 nm due to the  $n\text{-}\pi^*$  transitions similar to the aldehydes, but the absorption shifts to a little shorter wavelength and vibrational structures are inconspicuous compared to aldehydes.

The absorption spectrum of  $\text{CH}_3\text{COCH}_3$  has temperature dependence and the absorption cross sections decrease as the temperature decreases (Hynes et al. 1992; Gierczak et al. 1998). Table 4.16 shows the extracts of absorption cross sections (1 nm resolution) recommended by NASA/JPL Evaluation No. 17 (Sander et al. 2011) based on Gierczak et al. (1998).

Photolytic Quantum Yields: Two reaction pathways,



are known for the photolytic processes of  $\text{CH}_3\text{COCH}_3$ , and the wavelength thresholds for reactions (4.29) and (4.30) are 338, 299 nm, respectively (Atkinson et al. 2002). From these wavelength thresholds, it can be conceived that the reaction (4.29) is the more important photolytic process in the troposphere. It is also known that the photolytic quantum yields of  $\text{CH}_3\text{COCH}_3$  has strong pressure dependence as well as temperature dependence (Meyrahn et al. 1986; Gierczak et al. 1998; Emrich and Warneck 2000; Blitz et al. 2004). From these results, the photolysis of  $\text{CH}_3\text{COCH}_3$  is thought to actually proceed in the following processes,



Here,  ${}^1[\text{CH}_3\text{COCH}_3]^*$  is the excited singlet state molecule reached directly by the photo-absorption,  ${}^3[\text{CH}_3\text{COCH}_3]^*$  is the excited triplet state molecule formed by intersystem crossing (non-radiative transition between the different spin multiplicity such as between the singlet and triplet states). It has been shown that the reaction processes (4.29) and (4.30) occur through the  ${}^3[\text{CH}_3\text{COCH}_3]^*$  and  ${}^1[\text{CH}_3\text{COCH}_3]^*$  molecule, respectively (Emrich and Warneck 2000). Both  ${}^1[\text{CH}_3\text{COCH}_3]^*$  and  ${}^3[\text{CH}_3\text{COCH}_3]^*$  have relatively long lifetimes and are subject to collisional deactivation such as (4.34) and (4.36). This is the cause of the strong pressure dependence of  $\Phi(\text{CH}_3\text{CO} + \text{CH}_3)$  and  $\Phi(2\text{CH}_3 + \text{CO})$  (Meyrahn et al. 1986; Emrich and Warneck 2000; Blitz et al. 2004).

**Table 4.16** Absorption cross sections of CH<sub>3</sub>COCH<sub>3</sub> (298 K)

Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )
220	0.246	250	2.47	280	4.91	310	1.36
222	0.294	252	2.74	282	4.79	312	1.14
224	0.346	254	3.01	284	4.62	314	0.944
226	0.419	256	3.30	286	4.44	316	0.760
228	0.492	258	3.57	288	4.28	318	0.598
230	0.584	260	3.81	290	4.06	320	0.455
232	0.693	262	4.07	292	3.82	322	0.348
234	0.815	264	4.32	294	3.57	324	0.248
236	0.956	266	4.49	296	3.26	326	0.174
238	1.11	268	4.64	298	2.98	328	0.113
240	1.30	270	4.79	300	2.67	330	0.0740
242	1.50	272	4.91	302	2.45	332	0.0465
244	1.72	274	4.94	304	2.18	334	0.0311
246	1.95	276	4.93	306	1.89	336	0.0199
248	2.20	278	4.94	308	1.61	338	0.0135

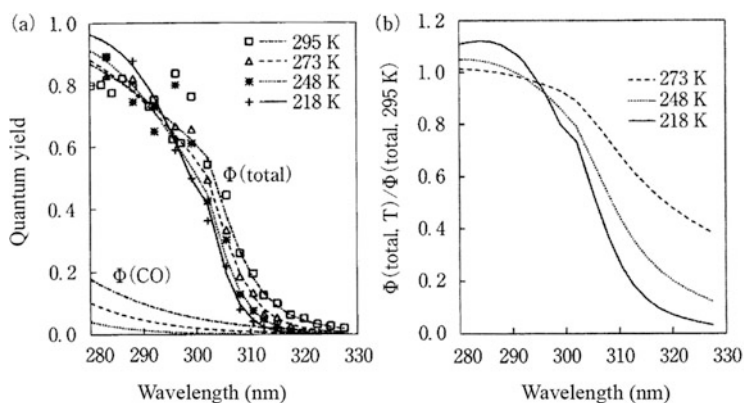
Source: NASA/JPL Panel Evaluation No. 17 (Sander et al. 2011)



**Table 4.17** Quantum yields for the photolysis of  $\text{CH}_3\text{COCH}_3$  (295, 273, 218 K)

$\lambda$ (nm)	$\Phi$			$\lambda$ (nm)	$\Phi$		
	295 K	273 K	218 K		295 K	273 K	218 K
280	0.60	0.55	0.66	304	0.18	0.087	0.056
282	0.56	0.51	0.62	306	0.14	0.061	0.032
284	0.52	0.47	0.57	308	0.10	0.043	0.018
286	0.48	0.43	0.50	310	0.077	0.030	0.010
288	0.45	0.39	0.43	312	0.058	0.022	0.0057
290	0.41	0.35	0.36	314	0.045	0.016	0.0033
292	0.38	0.31	0.29	316	0.035	0.012	0.0019
294	0.35	0.28	0.23	318	0.028	0.0088	0.0011
296	0.32	0.25	0.18	320	0.022	0.0068	0.0007
298	0.27	0.20	0.16	322	0.018	0.0053	0.0004
300	0.26	0.20	0.11	324	0.015	0.0041	0.0002
302	0.24	0.13	0.079	326	0.012	0.0033	0.0001

Source: NASA/JPL Evaluation No. 17 (Sander et al. 2011)



**Fig. 4.21** Quantum yields of the photolysis of  $\text{CH}_3\text{CCH}_3$ : (a)  $\Phi(\text{total})$  and  $\Phi(\text{CO})$ , symbols are experimental values and lines are calculation by parameterized formula  $[\text{M}] = 5 \times 10^{18}$  molecules  $\text{cm}^{-3}$ , (b)  $\Phi(\text{total, T})/\Phi(\text{total, 295 K})$  (Adapted from Blitz et al. 2004)

As for the temperature dependence of the photolytic quantum yields of  $\text{CH}_3\text{COCH}_3$ , the total quantum yields increase with temperature in the wavelength region shorter than 295 nm, while they decrease with temperature in the wavelength region longer than 295 nm. NASA/JPL Evaluation No. 17 (Sander et al. 2011) gives the approximation formula of the quantum yields for the pressure and the temperature dependence based on Blitz et al. (2004). Table 4.17 shows the temperature dependent photolysis quantum yields and Fig. 4.21 depicts the photolytic quantum yields calculated by the approximation compared with experimental values (Blitz et al. 2004).

### 4.2.7 Hydrogen Peroxide ( $H_2O_2$ ), Methyl Hydroperoxide ( $CH_3OOH$ )

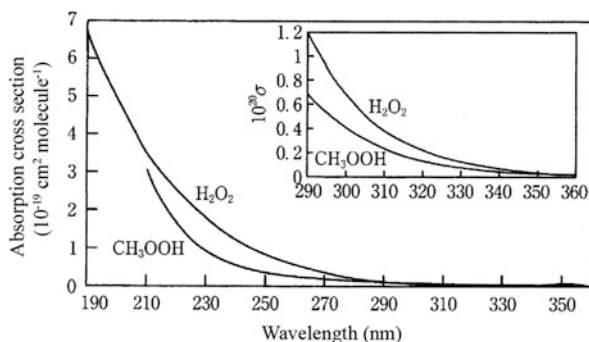
Hydrogen peroxide  $H_2O_2$  is formed by the radical termination reaction  $HO_2 + HO_2$ , and exists in the troposphere generally at the mixing ratio in order of ppbv. Since  $H_2O_2$  is water soluble, it is removed by the dissolution into cloud and fog water, while photolytic reaction is another important removal process. Methyl hydroperoxide  $CH_3OOH$  also exists in the whole region of the troposphere in natural atmosphere as an oxidation product of methane. Its photolytic reaction is important as its removal process, and also as a radical source in the upper troposphere.

The absorption spectrum of  $H_2O_2$  is a continuum decreasing monotonically from vacuum ultraviolet region (wavelength shorter than 200 nm) of 190 nm toward the longer wavelength as shown in Fig. 4.22 (Vaghjiani and Ravishankara 1989). Although the absorption cross sections are relatively small  $\sigma < 1 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ , the spectrum extends to 350 nm and the photolysis in the troposphere is important. The absorption cross sections obtained after the latter half of 1970s agree well each other (Lin et al. 1978; Molina and Molina 1981; Nicovich and Wine 1988; Vaghjiani and Ravishankara 1989). Table 4.18 cites the extracted values from the NASA/JPL Evaluation No. 17 (Sander et al. 2011), based on the average of these studies.

The absorption cross sections of  $H_2O_2$  are known to have temperature dependence due to the effect of transition from vibronic excited states in the electronic ground state (Nicovich and Wine 1988; Knight et al. 2002), and their temperature dependence at 260 nm is given by Nicovich and Wine (1988) as a function of wavelength.

The absorption spectrum of  $CH_3OOH$  bears a resemblance to  $H_2O_2$ , and a continuum in which the absorption cross sections decreases monotonically from ultraviolet to near ultraviolet region as shown in Fig. 4.22. There has been considerable uncertainty in the absorption cross sections of  $CH_3OOH$  due to the effect of impurities, and the recommended values of NASA/JPL Evaluation No. 17 based on Vaghjiani and Ravishankara (1989) are cited in Table 4.18.

**Fig. 4.22** Absorption spectra of  $H_2O_2$  and  $CH_3OOH$  (Adapted from Finlayson-Pitts and Pitts, 2000 based on Vaghjiani and Ravishankara, 1989)

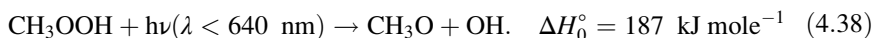


**Table 4.18** Absorption cross sections of H<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>OOH (298 K)

wavelength (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )		wavelength (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )	
	H <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> OOH		H <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> OOH
200	47.5	–	280	2.0	1.09
205	40.8	–	285	1.5	0.863
210	35.7	31.2	290	1.2	0.691
215	30.7	20.9	295	0.90	0.551
220	25.8	15.4	300	0.68	0.413
225	21.7	12.2	305	0.51	0.313
230	18.2	9.62	310	0.39	0.239
235	15.0	7.61	315	0.29	0.182
240	12.4	6.05	320	0.22	0.137
245	10.2	4.88	325	0.16	0.105
250	8.3	3.98	330	0.13	0.079
255	6.7	3.23	335	0.10	0.061
260	5.3	2.56	340	0.07	0.047
265	4.2	2.11	345	0.05	0.035
270	3.3	1.70	350	0.04	0.027
275	2.6	1.39	355	–	0.021

Source: NASA/JPL Panel Evaluation No. 17 (Sander et al. 2011)

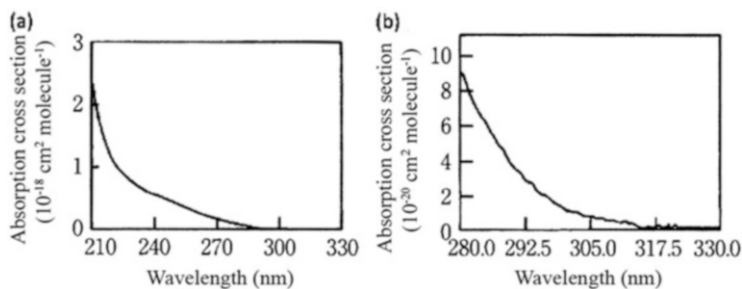
The photolytic processes of H<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>OOH in near ultraviolet region are



The photolytic quantum yield for each process is unity, as expected from the complete continuum of the absorption spectrum (Vaghjiani and Ravishankara 1989).

#### 4.2.8 Peroxynitric Acid (HO<sub>2</sub>NO<sub>2</sub>)

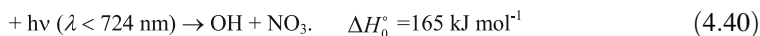
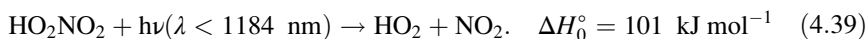
Peroxynitric acid HO<sub>2</sub>NO<sub>2</sub> is a molecule formed in the recombination reaction between HO<sub>2</sub> radicals and NO<sub>2</sub>. Although it is not detected in the atmosphere, it is thought to be an important atmospheric species to be included in the tropospheric chemistry models. In the lower troposphere thermal decomposition reaction is as a major loss process of HO<sub>2</sub>NO<sub>2</sub>, but in the middle and upper troposphere where the temperature is lower, the regeneration of HO<sub>2</sub> radicals by the photolysis becomes important.



**Fig. 4.23** Absorption spectrum of  $\text{HO}_2\text{NO}_2$ : (a) 210–330 nm, (b) enlarged for 280–330 nm (Adapted from Singer et al. 1989)

**Absorption Spectrum and Cross Sections** Figure 4.23 depicts absorption spectrum of  $\text{HO}_2\text{NO}_2$ . Similar to  $\text{H}_2\text{O}_2$ , the absorption spectrum of  $\text{HO}_2\text{NO}_2$  has a maximum at wavelengths shorter than 200 nm and decreases toward longer wavelengths monotonically and extends to around 320 nm (Molina and Molina 1981; Singer et al. 1989; Knight et al. 2002). The absorption cross sections at 298 K recommended by the NASA/JPL Evaluation No. 17 (Sander et al. 2011) are given in Table 4.19. The absorption cross sections of  $\text{HO}_2\text{NO}_2$  are known to be temperature dependent (Knight et al. 2002).

**Photolytic Quantum Yields** The major photolytic processes for  $\text{HO}_2\text{NO}_2$  are thought to be,



Other reaction pathway which split into three product species, e.g., are also energetically possible within the wavelength range of tropospheric solar actinic flux. The photolytic quantum yields of  $\text{HO}_2\text{NO}_2$  are unity at the wavelength longer than 200 nm measured by MacLeod et al. (1988), Roehl et al. (2001), and Jimenez et al. (2005). Since the quantum yields of  $\text{HO}_2$  and  $\text{NO}_2$  are 0.8 and those of  $\text{OH}$  and  $\text{NO}_3$  are 0.2 (Sander et al. 2011),  $\Phi(\text{HO}_2 + \text{NO}_2) = 0.8$ , and  $\Phi(\text{OH} + \text{NO}_3) = 0.2$ , if they are ascribed to reactions (4.39) and (4.40), respectively.

### 4.2.9 Nitric Acid ( $\text{HNO}_3$ ) and Methyl Nitrate ( $\text{CH}_3\text{ONO}_2$ )

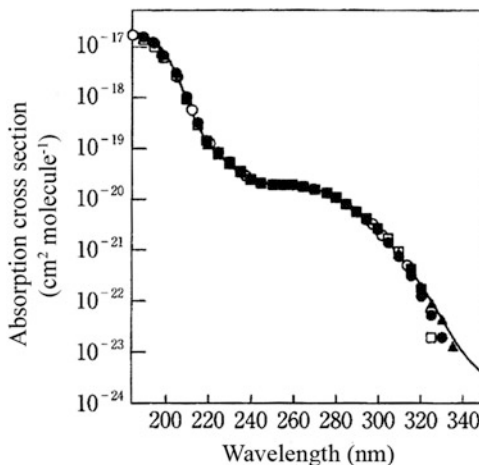
Nitric acid  $\text{HNO}_3$  ( $\text{HONO}_2$ ) is mainly formed by the chain termination reaction  $\text{OH} + \text{NO}_2$ , and ubiquitously exists in the troposphere. The photolysis rate of  $\text{HNO}_3$  in the troposphere is not very large, and the formation of ammonium nitrate aerosols

**Table 4.19** Absorption cross sections of HO<sub>2</sub>NO<sub>2</sub> (298 K)

Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )
200	563	240	58.1	280	9.29	312	0.465
205	367	245	49.0	284	6.93	316	0.313
210	239	250	41.3	288	4.91	320	0.216
215	161	255	35.0	292	3.37	324	0.152
220	118	260	28.5	296	2.30	328	0.110
225	93.5	265	23.0	300	1.52	332	0.079
230	79.2	270	18.1	304	1.05	336	0.054
235	68.3	275	13.4	308	0.702	340	0.037

Source: NASA/JPL Panel Evaluation No. 17 (Sander et al. 2011)

**Fig. 4.24** Absorption spectrum of  $\text{HNO}_3$  (Adapted from Burkholder et al. 1993)



and wet and dry deposition occurs preferentially to remove the species in the lower troposphere. However, the photolysis is important both as the loss process of  $\text{HNO}_3$  and the OH radical source in the upper troposphere. Similarly, methyl nitrate  $\text{CH}_3\text{ONO}_2$  is formed by the reaction of  $\text{NO}_2$  with  $\text{CH}_3\text{O}$  radicals. The  $\text{CH}_3\text{O}$  is formed in the oxidation processes of  $\text{CH}_4$  and other hydrocarbons. As well as the reaction with OH radicals, photolysis is an important removal process of  $\text{CH}_3\text{ONO}_2$ .

**Absorption Spectrum and Cross Sections** As shown in Fig. 4.24, the absorption spectrum of  $\text{HNO}_3$  consists of a very strong band with a maximum at around 180 nm, and a second continuum with a shoulder peak near 270 nm overlapping to the skirt of the former band (Rattigan et al. 1992; Burkholder et al. 1993). The absorption cross sections are known to have strong temperature dependence, and Burkholder et al. (1993) presented an approximate expression,

$$\sigma(\lambda, T) = \sigma(\lambda, 298 \text{ K}) \exp[B(\lambda)(T - 298)]. \quad (4.41)$$

Table 4.20 carries absorption cross sections at 298 K for 200–345 nm recommended by IUPAC Subcommittee Report Vol. I (Atkinson et al. 2004) based on the data of Burkholder et al. (1993).

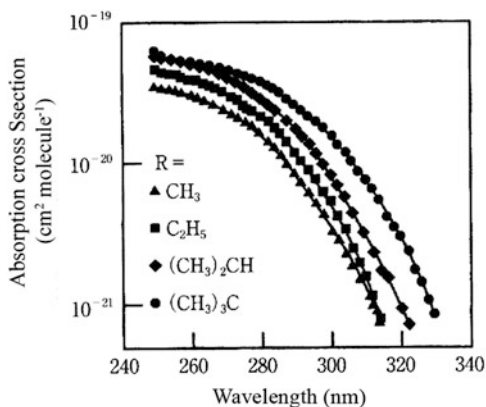
The absorption spectrum of  $\text{CH}_3\text{ONO}_2$  and other alkyl nitrates are similar to  $\text{HNO}_3$ , and consist of a strong continuum in 190–250 nm which is followed by monotonically decreasing continuum in the 250–340 nm region as shown in Fig. 4.25 (Roberts and Fajer 1989). The absorption cross sections of  $\text{CH}_3\text{ONO}_2$  are also known to have temperature dependence (Talukdar et al. 1997a), and the absorption cross sections at 298 K are given in Table 4.20 together with  $\text{HNO}_3$  (Sander et al. 2011; Atkinson et al. 2006) based on the data of Talukdar et al. (1997a) and Taylor et al. (1980).

**Table 4.20** Absorption cross sections of  $\text{HNO}_3^a$ , and  $\text{CH}_3\text{ONO}_2^b$  (298 K)

Wave-Length (nm)	$10^{20} \sigma$ ( $\text{cm}^2 \text{ molecule}^{-1}$ )		Wave-length (nm)	$10^{20} \sigma$ ( $\text{cm}^2 \text{ molecule}^{-1}$ )		Wave-length (nm)	$10^{20} \sigma$ ( $\text{cm}^2 \text{ molecule}^{-1}$ )	
	$\text{HNO}_3$	$\text{CH}_3\text{ONO}_2$		$\text{HNO}_3$	$\text{CH}_3\text{ONO}_2$		$\text{HNO}_3$	$\text{CH}_3\text{ONO}_2$
200	588	1180	250	1.97	3.59	300	0.263	0.360
205	280	700	255	1.95	3.30	305	0.150	0.214
210	104	360	260	1.91	3.06	310	0.081	0.134
215	36.5	145	265	1.80	2.77	315	0.041	0.063
220	14.9	70	270	1.62	2.39	320	0.020	0.032
225	8.81	33	275	1.38	2.00	325	0.0095	0.014
230	5.78	18	280	1.12	1.58	330	0.0043	0.0066
235	3.75	10	285	0.858	1.19	335	0.0022	0.0027
240	2.58	5.88	290	0.615	0.850	340	0.0010	0.0012
245	2.11	4.19	295	0.412	0.568	345	0.0006	

Source: <sup>a</sup>IUPAC Subcommittee Report Vol. I (Atkinson et al. 2004), <sup>b</sup>200–235 nm: NASA/JPL Panel Evaluation No.17 (Sander et al. 2011); 240–345 nm: IUPAC Subcommittee Report Vol. II (Atkinson et al. 2006)

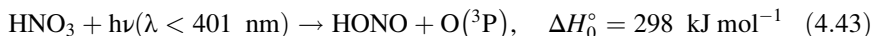
**Fig. 4.25** Absorption spectra of  $\text{CH}_3\text{ONO}_2$  and other alkyl nitrates (Adapted from Roberts and Fajer 1989)



**Photolysis Quantum Yield** The photolytic process of  $\text{HNO}_3$  is known to occur via

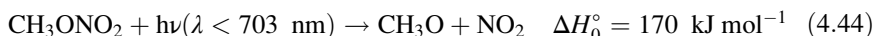


with a quantum yield of unity for the wavelength range of 200–350 nm (Johnston et al. 1974). Only for the wavelength shorter than 200 nm, the reaction

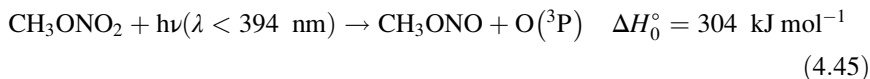


is reported to be important (Sander et al. 2011).

The photolytic process of  $\text{CH}_3\text{ONO}_2$  analogous to reaction (4.42) for  $\text{HNO}_3$  is thought to occur at wavelengths longer than 200 nm,



with a quantum yield of unity. At 193 nm the production of  $\text{O}({}^3\text{P})$  atoms by the process analogous to the reaction (4.43),



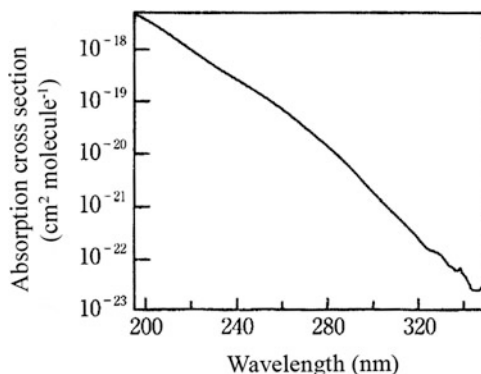
is important (Sander et al. 2011).

#### 4.2.10 Peroxyacetyl Nitrate ( $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ )

Peroxyacetyl nitrate  $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$  usually called PAN is a unique compound produced in the polluted atmosphere, and is important as a reservoir to carry  $\text{NO}_x$  to clean free troposphere. The atmospheric concentration of  $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$  is



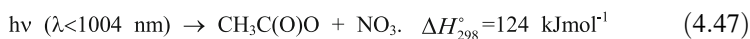
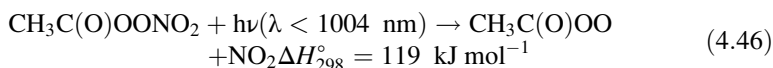
**Fig. 4.26** Absorption spectrum of  $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$  (Adapted from Talukdar et al. 1995)



maintained in equilibrium with the thermal decomposition reaction. The thermal decomposition is preferential in the lower troposphere where temperature is relatively high, but the photolysis becomes important as a removal process in the upper troposphere together with the OH radical reaction (Talukdar et al. 1995).

**Absorption Spectrum and Cross Sections** As shown in Fig. 4.26, the absorption spectrum of  $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$  is similar to  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$ , and consists of continuum with a peak at wavelengths shorter than 200 nm and decreases monotonically toward longer wavelengths in the 200–340 nm range (Talukdar et al. 1995). Absorption cross sections reported by Harwood et al. (2003) are given in Table 4.21 (Sander et al. 2011).

**Photolysis Quantum Yields** The photolytic processes of  $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$  can be conceived as,



Harwood et al. (2003) reported the quantum yields of  $\text{NO}_3$  formation to be  $0.22 \pm 0.04$ ,  $0.39 \pm 0.04$  at 248 and 308 nm, respectively. These values are thought to correspond to  $\Phi(\text{CH}_3\text{C}(\text{O})\text{O} + \text{NO}_3)$ , so that  $\Phi(\text{CH}_3\text{C}(\text{O})\text{OO} + \text{NO}_2) = 1 - \Phi(\text{CH}_3\text{C}(\text{O})\text{O} + \text{NO}_3)$  since the total photolytic quantum yield is thought to be unity.

### 4.3 Photolysis in the Stratosphere

In this section, absorption spectra and cross sections, and photolytic processes of atmospheric molecules that are not photolyzed by the solar actinic flux in the troposphere and photolyzed only in the stratosphere are described. Photolyses of many inorganic halogen molecules, which are important in the stratosphere, are

**Table 4.21** Absorption cross section of CH<sub>3</sub>C(O)OONO<sub>2</sub> (PAN) (298 K)

Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )
200	361	240	24.4	280	1.46	320	0.0252
204	292	244	18.8	284	1.01	324	0.0166
208	226	248	14.6	288	0.648	328	0.0117
212	168	252	11.4	292	0.447	332	0.0086
216	122	256	8.86	296	0.297	336	0.0061
220	89.7	260	6.85	300	0.189	340	0.0042
224	67.6	264	5.23	304	0.125	344	0.0029
228	52.0	268	3.94	308	0.0816	348	0.0020
232	40.4	272	2.87	312	0.0538		
236	31.4	276	2.07	316	0.0363		

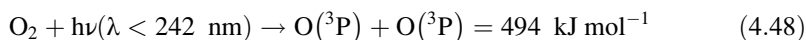
Source: NASA/JPL Panel Evaluation No. 17 (Sander et al. 2011) (Data for 336–348 nm are smoothed)

summarized separately in the next Sect. 4.4 since most of them play a role also in the troposphere.

### 4.3.1 Oxygen ( $O_2$ )

Photolytic reaction of oxygen  $O_2$  is the most fundamental reaction of stratosphere chemistry. In the first place, the formation of stratosphere in the earth's atmosphere has been brought on by the temperature inversion of the atmosphere due to the absorption of solar radiation by  $O_3$  molecules that were produced by the reaction of  $O(^3P)$  atoms from the photolysis of  $O_2$  with another  $O_2$  molecule. In this sense the photolytic reaction of  $O_2$  is the basic of basics of stratospheric chemistry.

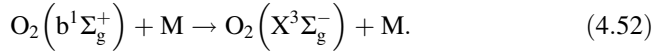
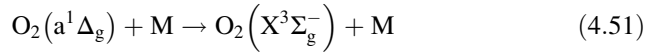
As the absorption spectrum, absorption cross sections, and potential curves has already been described in Chap. 3 (Sect. 3.2, Fig. 3.4, 3.5, Table 3.2), only photolytic processes will be discussed here. In the photolysis of  $O_2$ , three different electronic states of oxygen atoms can be formed as follows,



Since the wavelengths of the solar radiation to reach to the stratosphere is  $\lambda \geq \sim 190 \text{ nm}$  as seen in Fig. 4.1, only reaction (4.48) to form  $O(^3P)$  is energetically possible as a photolytic process of  $O_2$  in the stratosphere. The absorption bands of  $O_2$  in this wavelength region are the Herzberg bands in  $200 < \lambda < 250 \text{ nm}$  and the Schuman-Runge (S-R) bands in  $175 < \lambda < 200 \text{ nm}$  with a vibrational structure as shown in Fig. 3.4. As seen in the potential energy curves of Fig. 3.5,  $O_2$  molecules which are excited to the Herzberg bands with shorter wavelength radiation than the dissociation threshold of 242 nm are dissociated to  $O(^3P) + O(^3P)$  along with the  $A^3\Sigma_u^+$  potential curve with a quantum yield of unity. On the other hand,  $O_2$  molecules excited to the Schuman-Runge bands reaches to the bound state of  $B^3\Sigma_u^-$  then crosses to the repulsive  $^3\Pi_u$  state and predissociate also into  $O(^3P) + O(^3P)$  with a quantum yield of unity. Incidentally,  $O_2$  excited to the Schuman-Runge continuum at wavelength shorter than 175 nm dissociates into  $O(^3P) + O(^1D)$  with a quantum yield of unity, which occurs only in the higher altitude than the mesosphere.

Furthermore,  $O_2$  has forbidden transitions to two low lying energy levels  $a^1\Delta_g$  (94 kJ mol<sup>-1</sup> higher than the ground state) and  $b^1\Sigma_g^+$  (157 kJ mol<sup>-1</sup> higher than the ground state), and their 0–0 bands are observed at 1270 nm and 762 nm, respectively. The radiative lifetimes of the  $O_2(a^1\Delta_g)$  and  $O_2(b^1\Sigma_g^+)$  are long, 67 min and 12 s, respectively (Wallace and Hunten 1968; Slinger and Cosby 1988). Thus, the

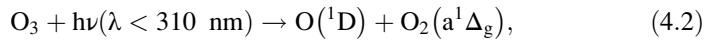
O<sub>2</sub> molecules excited into these states are mostly deactivated by collisions with atmospheric molecules and returns to the ground state O<sub>2</sub> as,



### 4.3.2 Ozone (O<sub>3</sub>)

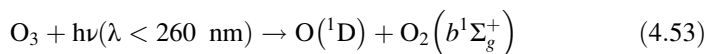
The photolysis of O<sub>3</sub> has an unambiguous importance in the stratospheric chemistry together with the photolysis of O<sub>2</sub> mentioned above. In the stratosphere, ozone layer has been formed by the equilibrium between the formation of O<sub>3</sub> by the reaction of O(<sup>3</sup>P) atoms generated by the photolysis of O<sub>2</sub> with O<sub>2</sub> molecules and the loss of O<sub>3</sub> by the photolysis of O<sub>3</sub> itself and the reaction with O(<sup>3</sup>P) atoms (refer to Sect. 8.1).

Since the absorption spectrum, absorption cross sections, and photolytic processes in the tropospheric solar actinic flux region, and photolytic quantum yields have already been described in detail in the Sects. 3.2 (Fig. 3.6) and 4.2.1 (Fig. 4.2, 4.3, 4.4, 4.5, 4.6, 4.7, and 4.8, Table 4.1, 4.2, 4.3, and 4.4), only photolytic processes in the stratosphere will be described here. As seen in Fig. 3.6, the absorption spectrum of the Hartley bands of O<sub>3</sub> extend over broad range of 200–300 nm that is the most important in the stratospheric solar actinic flux. The photolytic process of O<sub>3</sub> molecules reached by the absorption of photons in the Hartley bands is thought to be



as mentioned in the Sect. 4.2.1, and the quantum yields of O(<sup>1</sup>D) formation have been obtained in laboratory studies (see Fig. 4.6) (Cooper et al. 1993; Takahashi et al. 2002; Matsumi and Kawasaki 2003). Based on these data, NASA/JPL Evaluation No. 17 recommended 0.90 as the quantum yield of O(<sup>1</sup>D) formation in this wavelength region (Sander et al. 2011). Since the total quantum yield of the O<sub>3</sub> photolysis in the Hartley bands is thought to be unity, the quantum yield of O(<sup>1</sup>D) formation less than unity implies the formation of O(<sup>3</sup>P) by some other processes.

Furthermore, the quantum yields of O(<sup>3</sup>P) and O(<sup>1</sup>D) formation at 193 nm have been reported to be  $0.57 \pm 0.14$  and  $0.46 \pm 0.2$ , respectively, thus showing the quantum yields of O(<sup>1</sup>D) formation in this region is much smaller than in the Hartley bands as shown in Fig. 4.6 (Turnipseed et al. 1991). Also, at this wavelength the formation of O<sub>2</sub> ( ) has been measured with the quantum yield  $0.50 \pm 0.38$ , and the occurrence of the process,



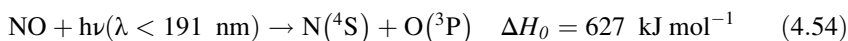
has been suggested (Turnipseed et al. 1991).

### 4.3.3 Nitric Oxide (NO)

Nitric oxide NO is a major oxides of nitrogen formed by the photolysis of  $N_2O$  in the stratosphere, but it was not paid much attention in the past since the photolysis rate is not very large. However, the photolysis of NO forms N atoms that leads to the loss of odd nitrogen by the reaction  $N + NO \rightarrow N_2 + O$ , so that it is now recognized to be important in the stratospheric chemistry.

The absorption spectrum of NO has long been measured and shows band structure at wavelengths shorter than 250 nm, as shown in Fig. 4.27. The assignment of electronic transitions and vibrational levels are also shown in the figure, and Fig. 4.28 shows the potential energy curves of NO (Okabe 1978). The  $\gamma$ -,  $\beta$ -,  $\delta$ - and  $\epsilon$ -bands in the 196–227 nm range shown in Fig. 4.27 correspond to the  $A^2\Sigma-X^2\Pi$ ,  $B^2\Pi-X^2\Pi$ ,  $C^2\Pi-X^2\Pi$ , and  $D^2\Sigma-X^2\Pi$  transition in Fig. 4.28, respectively (Callear and Pilling 1970).

As the photolytic process of NO,



is energetically possible at wavelengths shorter than 191 nm. It is known from laboratory studies that the excitation to the  $\beta$ - and  $\gamma$ -band (Fig. 4.28) in the stratospheric solar actinic flux region, yields the fluorescence of NO as follows,



In contrast, the fluorescence of NO is not observed for the excitation by the  $\delta(0-0)$  and  $\delta(1-0)$  bands, and the photolytic process (4.54) occurs with the quantum yield

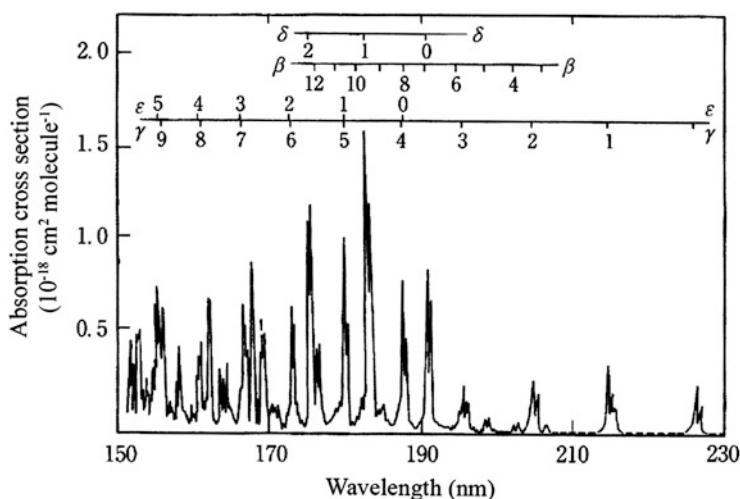


Fig. 4.27 Absorption spectrum of NO (Adapted from Okabe 1978)

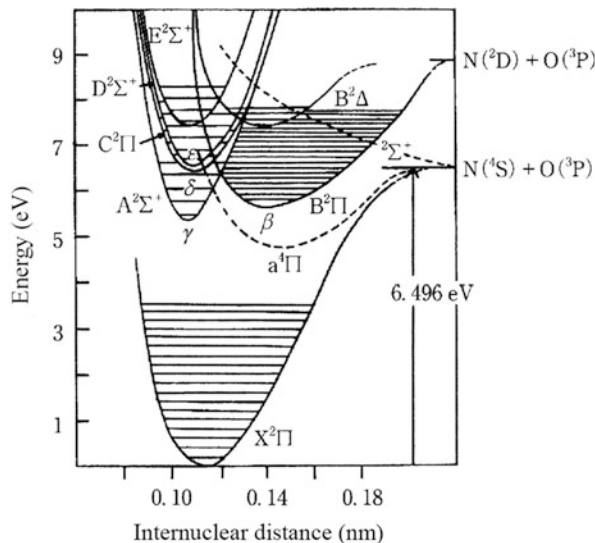


Fig. 4.28 Potential energy curves of NO (Adapted from Okabe 1978)

of unity. Therefore, it is enough to consider only the absorption by these  $\delta(0-0)$  and  $\delta(1-0)$  bands for the photolysis rate of NO in the stratosphere.

Since the wavelength region of the absorption bands of the  $\delta(0-0)$  (189.4–191.6 nm) and  $\delta(1-0)$  (181.3–183.5 nm) overlaps with those of the Schuman-Runge bands of  $O_2$ , the accurate wavelengths of rotational lines of both NO and  $O_2$  and oscillator strengths data which are the bases of absorption cross sections for individual rotational lines of NO is necessary. The oscillator strengths is a non-dimensional number to express the ratio of contribution of a single electron to the absorption. Although the oscillator strength of electronic transition is in general smaller than unity, it is close to unity for the very strong allowed transition. For the oscillator strength of NO, the values of  $5.78 \times 10^{-3}$  ( $\delta(1-0) + \beta(10-0)$ ) and  $2.49 \times 10^{-3}$  ( $\delta(0-0) + \beta(7-0)$ ) by Bethke (1959) have long been used, but about 50 % smaller values than these were reported and the  $J_{NO}$  by using these values were reported later (Fredlick and Hudson 1979; Nicolet and Cieslik 1980). However, Minschwaner and Siskind (1993) made a line-by-line calculation of the NO photolysis rate  $J_{NO}$  using the high-resolution spectrum of  $O_2$  in which rotational lines are separated (Yoshino et al. 1983; Lewis et al. 1986) and newly observed high resolution spectrum and cross sections of NO  $\delta(0-0)$  and  $\delta(1-0)$  bands. The absorption cross sections used here coincide with those of Bethke (1959), and recent values by Imajo et al. (2000) (oscillator strength of  $5.4 \times 10^{-3}$  and absorption cross section of  $4.80 \times 10^{-15} \text{ cm}^2 \text{ cm}^{-1}$  for  $\delta(1-0)$ ). The calculated photolysis rate of NO  $J_{NO} \approx 10^{-7} \text{ s}^{-1}$  (the sum of  $\delta(0-0)$  and  $\delta(1-0)$ ) is not negligible as the loss process of odd nitrogen in the upper stratosphere (Minschwaner and Siskind 1993; Mayor et al. 2007).

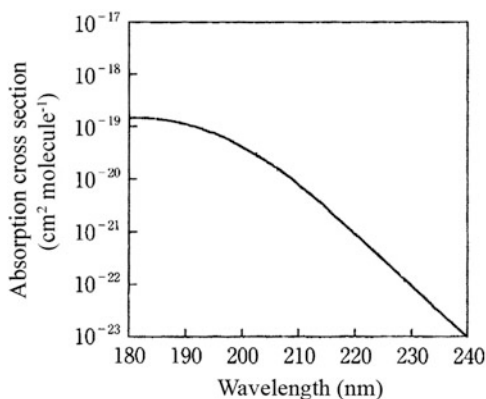
### 4.3.4 Dinitrogen Monoxide ( $N_2O$ )

Dinitrogen monoxide  $N_2O$  is also called nitrous oxide, and emitted from natural and anthropogenic sources from the ground. Since  $N_2O$  does not dissipate in the troposphere, it reaches to the stratosphere and subjects photolysis to provide reactive oxides of nitrogen (odd nitrogen). For this reason, the photolysis of  $N_2O$  in the stratosphere is very important.

As shown in Fig. 4.29, absorption spectrum of  $N_2O$  is a broad continuum with a peak at around 180 nm, decreases monotonically toward longer wavelengths and extends to near 240 nm (Johnston and Selwyn 1975). Table 4.22 cites the absorption cross sections of  $N_2O$  in the 160–240 nm region as recommended by NASA/JPL Evaluation No. 17 (Sander et al. 2011). These values are based on the data by Hubrich and Stuhl (1980) (160, 165, 170 nm), and Selwyn et al. (1977) (173–240 nm). The absorption cross sections are temperature dependent and decrease with the increase of temperature for which the formula for approximation is given by Selwyn et al. (1977) (Sander et al. 2011).

The following photolytic process has been known to occur with a quantum yield of unity for 140–230 nm covering the stratospheric photolysis region,

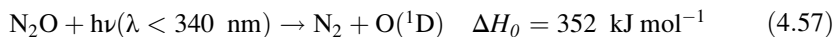
**Fig. 4.29** Absorption spectrum of  $N_2O$  (Adapted from Carlon et al. 2010)



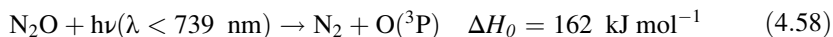
**Table 4.22** Absorption cross sections of  $N_2O$  (298 K)

Wavelength (nm)	$10^{20} \sigma$ ( $\text{cm}^2 \text{ molecule}^{-1}$ )	Wavelength (nm)	$10^{20} \sigma$ ( $\text{cm}^2 \text{ molecule}^{-1}$ )	Wavelength (nm)	$10^{20} \sigma$ ( $\text{cm}^2 \text{ molecule}^{-1}$ )
160	4.30	190	11.1	220	0.922
165	5.61	195	7.57	225	0.030
170	8.30	200	4.09	230	0.0096
175	12.6	205	1.95	235	0.0030
180	14.6	210	0.755	240	0.0010
185	14.3	215	0.276		

Source: NASA/JPL Panel Evaluation No. 17 (Sander et al. 2011)



by the studies before 1970s (Paraskevopoulos and Cvetanovic 1969; Preston and Barr 1971). The result is confirmed by recent studies, and the formations of  $\text{O}({}^3\text{P})$  and  $\text{N}({}^4\text{S})$  by the spin forbidden processes,



are less than 1 %, respectively (Nishida et al. 2004; Greenblatt and Ravishankara 1990).

#### 4.3.5 *Other Oxides of Nitrogen ( $\text{NO}_2$ , $\text{NO}_3$ , $\text{N}_2\text{O}_5$ , $\text{HNO}_3$ , $\text{HO}_2\text{NO}_2$ ), Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), Formaldehyde ( $\text{HCHO}$ )*

Other than  $\text{NO}$  and  $\text{N}_2\text{O}$ ,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_3$ ,  $\text{HO}_2\text{NO}_2$  are also important oxides of nitrogen in the stratosphere. Since their photolyses are also all important in the troposphere, their absorption spectra, cross sections, and photolytic processes have been described in the previous section including the stratospheric actinic flux region.  $\text{H}_2\text{O}_2$  and  $\text{CH}_4$  also exist in the stratosphere in considerable concentration as they are formed by the mutual chain termination reaction of  $\text{HO}_2$ , and in the oxidation process of  $\text{CH}_4$ , respectively, as in the troposphere. Their absorption spectra, cross sections, and photolytic processes have already been described in the previous section to be referred.

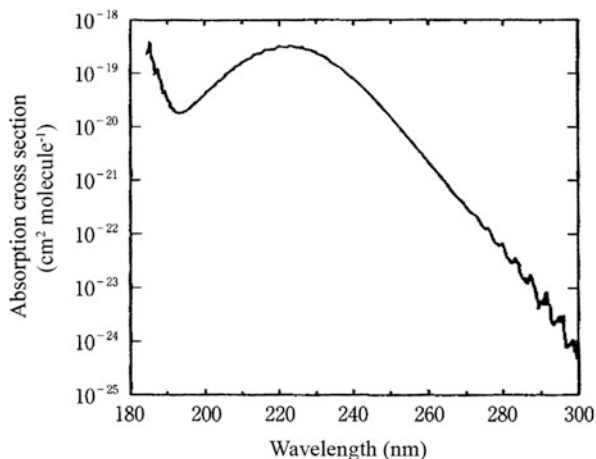
#### 4.3.6 *Carbonyl Sulfide (COS)*

Carbonyl sulfide  $\text{COS}$  is emitted from terrestrial soil, ocean and biomass burning into the atmosphere, but since their loss rate in the troposphere is very small, most of them reach to the stratosphere. The photolysis of  $\text{COS}$  in the stratosphere is a very crucial reaction as it provides sulfur into the atmosphere forming sulfuric aerosol layer (the Junge Layer) in the stratosphere. Incidentally, although  $\text{COS}$  is often described as  $\text{OCS}$  in the textbooks and literature of atmospheric chemistry, the notation of  $\text{COS}$  is used in this book according to the recommendation of IUPAC (International Union of Pure and Applied Chemistry).

As shown in Fig. 4.30, the absorption spectrum of  $\text{COS}$  is a broad continuum with a peak at ca. 222 nm extending to around 300 nm, and a weak vibrational structure can be seen near the maximum (Okabe 1978; Molina et al. 1981; Rudolph and Inn 1981). The absorption cross sections of  $\text{COS}$  are known to have



**Fig. 4.30** Absorption spectrum of COS (Adapted from Molina et al. 1981)



**Table 4.23** Absorption cross sections of COS (295 K)

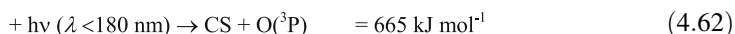
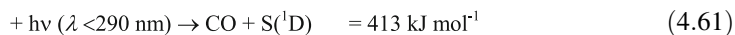
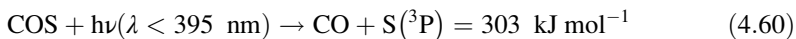
Wavelength (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wavelength (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wavelength (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )
185	19.0	225	31.0	265	0.096
190	3.97	230	24.3	270	0.038
195	2.02	235	15.4	275	0.015
200	3.93	240	8.13	280	0.0054
205	8.20	245	3.82	285	0.0022
210	15.1	250	1.65	290	0.0008
215	24.2	255	0.664	295	0.0002
220	30.5	260	0.252	300	0.0001

Source: IUPAC Subcommittee Report Vol. I (Atkinson et al. 2004)

temperature dependence, and Wu et al. (1999) reported from the high resolution measurement (0.06 nm) that hot bands can be seen in the 215–260 nm region, and the temperature dependence is particularly large at wavelengths longer than 224 nm.

Table 4.23 gives absorption cross sections of COS recommended by NASA/JPL Evaluation No. 17 (Sander et al. 2011) based on Molina et al. (1981).

The photolytic processes of COS,



have threshold wavelengths of 395, 290 and 180 nm, respectively. Therefore, the formation of CO and S atoms by reactions (4.60) and (4.61) are possible in the

stratosphere referring to the absorption spectrum depicted in Fig. 4.30. Experimentally, the formation of CO has been confirmed to be a main product in the photolysis of 214–254 nm region, and the CO formation quantum yield of  $>0.95$  at 248 nm has been reported (Zhao et al. 1995). Based on these results, NASA/JPL Evaluation No. 17 recommends the quantum yield of unity for the photolysis of COS in the wavelength range of 220–254 nm. There are two possibilities for the formation of S atoms in the photolysis of COS; the formation of  $S(^1D)$  by the direct dissociation from the excited singlet state reached by the photoexcitation, and the formation of  $S(^3P)$  by the dissociation from to the excited triplet state reached by intersystem crossing. From the recent research of molecular dynamics, S atoms formed by the photoabsorption at 228 nm are found to be mostly  $S(^3P)$ , so that at least at this wavelength the reaction (4.60) via the excited triplet state is the major photolytic process of COS (Zhao et al. 1995; Katayanagi et al. 1995).

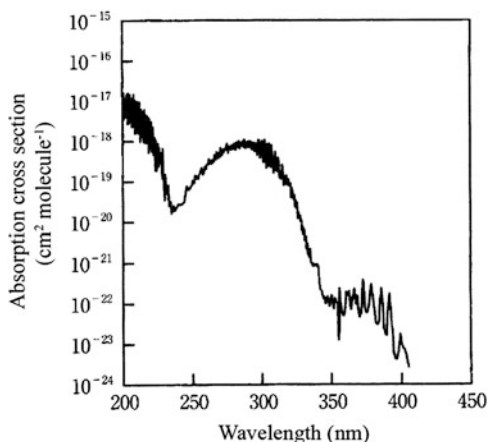
### 4.3.7 Sulfur Dioxide ( $SO_2$ )

Sulfur dioxide  $SO_2$  is one of the most typical air pollutants, as is  $NO_x$ . Although  $SO_2$  has an absorption spectrum in the tropospheric actinic flux region, the  $SO_2$  molecules absorbing the radiation in this region reach an excited state which does not dissociate. Meanwhile, the molecule that absorbs radiation shorter than 219 nm in the stratospheric actinic flux region can be photolyzed, but since the  $SO_2$  molecules emitted in the troposphere are mostly removed by the reaction with OH radicals or uptake into cloud and fog water, they do not reach to the stratosphere. Therefore, it is necessary to consider the photolysis of  $SO_2$  only for those formed by the photochemical reactions of COS in the stratosphere, and for those introduced directly into the stratosphere by large eruptions of volcanoes or by the emissions of aircrafts. Therefore, although the photolysis of  $SO_2$  is not in general very important in atmospheric chemistry, it is described here in the interest of fundamental photochemistry of the atmospheric molecule.

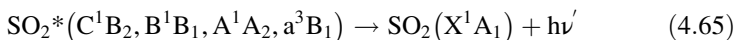
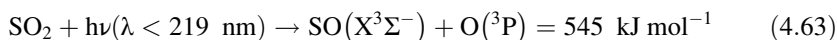
As shown in Fig. 4.31 (Manatt and Lane 1993), the absorption spectrum of  $SO_2$  consists of a very strong band which extends to 230 nm with a peak at around 200 nm, medium strength bands in the region of 230–340 nm with a peak at 290 nm, and a very weak band in the 340–400 nm region. These absorption bands are assigned to the transitions from the ground state to the  $C^1B_2$ , the mixed state of  $B^1B_1$  and  $A^1A_2$ , and a  $^3B_1$  state, respectively (Okabe 1978). Among these bands, the  $C^1B_2-X^1A_1$  and  $B^1B_1-X^1A_1$  are allowed transitions, and  $A^1A_2-X^1A_1$  and  $^3B_1-X^1A_1$  are forbidden transitions. Theoretical calculations on photochemical processes and potential energy surfaces have been studied by Katagiri et al. (1997) and Li et al. (2006).

The data of absorption cross sections of  $SO_2$  prior to 1993 have been compiled by Manatt and Lane (1993) for the 106–403 nm, and later the measurements in high-resolution (Vandaele et al. 1994; Rufus et al. 2003) and the temperature dependence have been reported (Prahlaad and Kumar 1997; Bogumil et al. 2003).

**Fig. 4.31** Absorption spectrum of SO<sub>2</sub> (Adapted from Manatt and Lane 1993)



The photochemical processes of SO<sub>2</sub> are known (Okabe 1978) to be,



The energy threshold for the photolytic reaction (4.63) to form ground states, SO (X<sup>3</sup>Σ<sup>-</sup>) and O (<sup>3</sup>P) is 545 kJ mole<sup>-1</sup> corresponding to the wavelength threshold of 219 nm. Therefore, even though there are lower lying excited states reached by the absorption of the tropospheric and stratospheric actinic flux, the high dissociation energy is the reason that the photolysis of SO<sub>2</sub> is not very important in the atmosphere. Thus, the photolysis of SO<sub>2</sub> is possible only at the wavelengths shorter than 219 nm in the stratosphere. Indeed, Okabe (1971) found that the fluorescence of SO<sub>2</sub> from the C<sup>1</sup>B<sub>2</sub> state is not observed with the divide of 219 nm suggesting that the photolysis occurs at shorter wavelengths than this. The absolute quantum yield of photolytic reaction (4.63) has not been known until fairly recently, and Abu-Bajeh et al. (2002) reported the formation quantum yield of O (<sup>3</sup>P) as Φ(O(<sup>3</sup>P)) = 0.13 ± 0.05 at 222.4 nm where photo-dissociation can occur by the absorption from the rotationally excited levels in the electronic ground state. As expected from the vibrational structure in the absorption spectrum near 200 nm, the SO<sub>2</sub> molecule in the C<sup>1</sup>B<sub>2</sub> state is in the bound state and predissociation is suggested to occur by the transfer to another dissociating state.

The absorption of the solar radiation at wavelengths longer than 219 nm forms the excited SO<sub>2</sub> molecules following the reaction (4.64), and photo-emission is observed in laboratory studies. The radiative lifetime of the excited state reached by the absorption of photons at 340–400 nm is rather long, 8.1 ± 2.5 ms (Su et al. 1977), which is thought to correspond to phosphorescence (light-emission between the

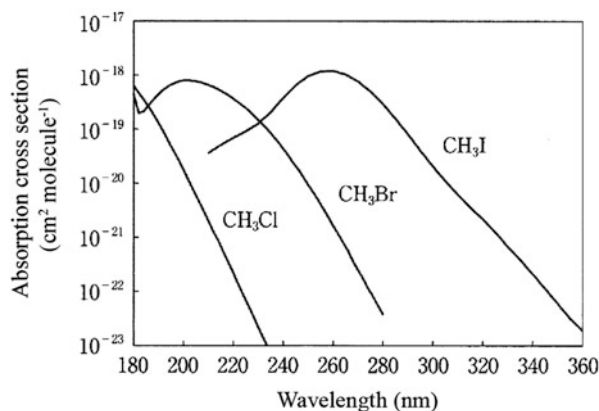
electronic state with different spin multiplicity) from the  $a^3B_1$  state. On the other hand, fluorescence (light-emission between the electronic state with same spin multiplicity) lifetime in the 230–340 nm region consists of a shorter component of  $\sim 50$   $\mu\text{s}$  which is independent of the wavelength, and the longer one, 80–600  $\mu\text{s}$ , which is longer at the longer wavelengths. Each of them are assigned to the emissions from  $B^1B_1$  and  $A^1A_2$  state, respectively (Brus and McDonald 1974). Furthermore, the fluorescence lifetime from the  $C^1B_2$  state in the longer wavelengths than 219 nm is very short  $\sim 50$  ns (Hui and Rice 1972). In any case, the  $\text{SO}_2$  molecules excited to the non-dissociative state are returned to the electronic ground state mostly through quenching by the atmospheric species and partially through light-emission, and the photolysis of  $\text{SO}_2$  does not generally play an important role in atmospheric chemistry.

#### 4.3.8 Methyl Chloride ( $\text{CH}_3\text{Cl}$ ), Methyl Bromide ( $\text{CH}_3\text{Br}$ ), Methyl Iodide ( $\text{CH}_3\text{I}$ )

Methyl halides such as methyl chloride  $\text{CH}_3\text{Cl}$ , methyl bromide  $\text{CH}_3\text{Br}$ , and methyl iodide  $\text{CH}_3\text{I}$  are natural origin species emitted from terrestrial and oceanic sources, but anthropogenic emissions are also important for  $\text{CH}_3\text{Br}$ . Among these,  $\text{CH}_3\text{I}$  are photolyzed mostly by the actinic flux in the troposphere.

Figure 4.32 depicts absorption spectra of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$  in the 180–360 nm region drawn according to the absorption cross sections recommended by the NASA/JPL Evaluation No. 17 (Sander et al. 2011). As seen in the figure, the absorption spectra of methyl halides are all continuum without vibrational structure.  $\text{CH}_3\text{Cl}$  has a broad absorption band with a strong peak at around 170 nm and an extended tail to 230 nm (Hubrich and Stuhl 1980). The shape of the spectrum of  $\text{CH}_3\text{Br}$  is similar to  $\text{CH}_3\text{Cl}$  but shifted to longer wavelength with a peak at around 180 nm and a tail is extended to 280 nm (Robbins 1976; Molina et al. 1982). The peak and the

**Fig. 4.32** Absorption spectra of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{I}$  (Constructed based on NASA/JPL Evaluation No. 17, Sander et al. 2011)



**Table 4.24** Absorption cross sections of CH<sub>3</sub>Cl and CH<sub>3</sub>Br (298 K)

Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )		Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )		Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )	
	CH <sub>3</sub> Cl	CH <sub>3</sub> Br		CH <sub>3</sub> Cl	CH <sub>3</sub> Br		CH <sub>3</sub> Cl	CH <sub>3</sub> Br
180	63.6	44.6	214	0.0860	54.2	248	–	1.31
182	46.5	19.8	216	0.0534	47.9	250	–	0.921
184	35.0	21.0	218	0.0345	42.3	252	–	0.683
186	25.8	27.8	220	0.0220	36.6	254	–	0.484
188	18.4	35.2	222	0.0135	31.1	256	–	0.340
190	12.8	44.2	224	0.0086	26.6	258	–	0.240
192	8.84	53.8	226	0.0055	22.2	260	–	0.162
194	5.83	62.6	228	0.0035	18.1	262	–	0.115
196	3.96	69.7	230	0.0022	14.7	264	–	0.0795
198	2.68	76.1	232	0.0014	11.9	266	–	0.0551
200	1.77	79.0	234	0.0009	9.41	268	–	0.0356
202	1.13	79.2	236	0.0006	7.38	270	–	0.0246
204	0.731	78.0	238	–	5.73	272	–	0.0172
206	0.482	75.2	240	–	4.32	274	–	0.0114
208	0.313	70.4	242	–	3.27	276	–	0.0081
210	0.200	65.5	244	–	2.37	278	–	0.0055
212	0.127	59.9	246	–	1.81	280	–	0.0038

Source: NASA/JPL Panel Evaluation No. 17 (Sander et al. 2011)

**Table 4.25** Absorption cross sections of CH<sub>3</sub>I (298 K)

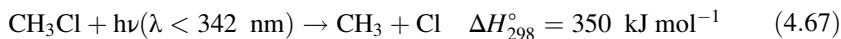
λ (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> )	λ (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> )	λ (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> )	λ (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> )
210	3.62	250	96.3	290	8.04	330	0.0684
215	5.08	255	117.7	295	4.00	335	0.0388
220	6.90	260	119.7	300	2.06	340	0.0212
225	9.11	265	102.9	305	1.10	345	0.0114
230	12.6	270	75.9	310	0.621	350	0.0061
235	20.5	275	49.6	315	0.359	355	0.0032
240	38.1	280	29.2	320	0.221	360	0.0019
245	65.6	285	15.6	325	0.126	365	0.0009

Source: NASA/JPL Panel Evaluation No. 17 (Sander et al. 2011)

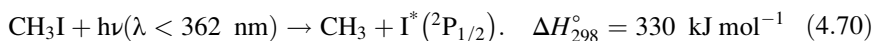
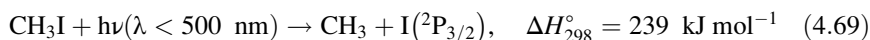
extended tail edge of the absorption bands of CH<sub>3</sub>I are further shifted to the longer wavelengths to 260, and 360 nm, respectively (Fahr et al. 1995; Roehl et al. 1997).

Absorption cross sections recommended by the NASA/JPL Evaluation No. 17 (Sander et al. 2011) are the averaged values based on above and other studies. Tables 4.24, and 4.25 give the absorption cross sections of CH<sub>3</sub>Cl and CH<sub>3</sub>Br, and CH<sub>3</sub>I extracted from the evaluation, respectively. The approximation formula of the temperature dependences of absorption cross sections are also given by Sander et al. (2011).

Photolytic processes of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  in the above spectral regions are thought to be



whose quantum yields are unity (Takacs and Willard 1977; Talukdar et al. 1992). In the case of  $\text{CH}_3\text{I}$  processes forming two different electronic states of I atom  $\text{I}(^2\text{P}_{3/2})$  (ground state) and  $\text{I}^*(^2\text{P}_{1/2})$  are known to occur,



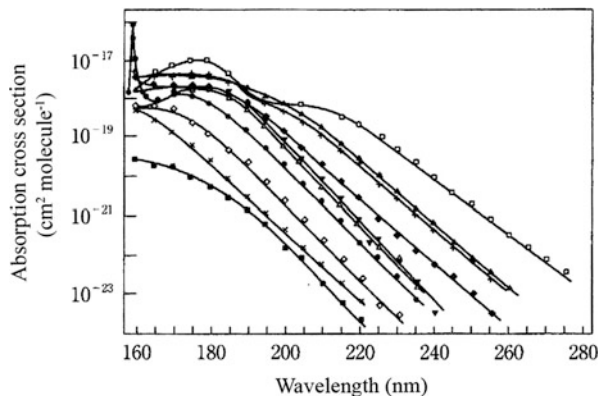
The quantum yields of each process are reported at several wavelengths, but the total photolytic quantum yield summing the reactions (4.69) and (4.70) is thought to be unity (Kang et al. 1996).

### 4.3.9 Chlorofluorocarbons (CFCs), Hydrochlorofluorocarbons (HCFCs)

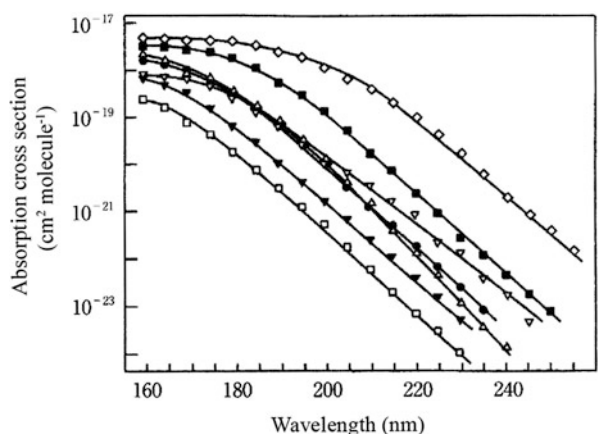
Chlorofluorocarbons CFCs and hydrochlorofluorocarbons HCFCs are all anthropogenic species and are the causative agents of ozone layer destruction as well as greenhouse gasses. CFCs are the molecules in which all the hydrogen atoms of hydrocarbons are substituted by chlorine and fluorine atoms. They do not have absorption bands in the tropospheric actinic flux region and also do not react with OH radicals. Therefore, they do not have any dissipation process in the troposphere, and can be photolyzed only after they reached to the stratosphere. On the other hand, HCFCs is molecules in which at least one of chlorine or fluorine atom of CFCs is substituted by hydrogen atom. Since HCFCs react with OH radicals, they are removed in the troposphere, but a portion of them reach the stratosphere and photolyzed, similar to CFCs.

Among organic chlorinated compounds which do not contain H atoms in molecules, five CFCs; CFC-11 ( $\text{CFCl}_3$ ), CFC-12 ( $\text{CF}_2\text{Cl}_2$ ), CFC-113 ( $\text{CF}_2\text{ClCFCl}_2$ ), CFC-114 ( $\text{CF}_2\text{ClCF}_2\text{Cl}$ ) and CFC-115 ( $\text{CF}_3\text{CF}_2\text{Cl}$ ) and carbon tetrachloride ( $\text{CCl}_4$ ), have relatively high concentrations in the stratosphere. Figure 4.33 depicts absorption spectra of these compound (Hubrich and Stuhl 1980). As can be seen in the figure, all the spectra have peaks around 180–200 nm in common, and have extended tails toward longer wavelength side, whose shape is similar to  $\text{CH}_3\text{Cl}$  shown in Fig. 4.32. In the figure, it can be seen that the absorption cross sections are larger and the absorption shift to longer wavelengths as the number of chlorine atoms in a molecule increases.

**Fig. 4.33** Absorption spectra of CFCs. 298 K: +  $\text{CHCl}_3$ ;  $\Delta$   $\text{CHFCl}_2$ ;  $\times$   $\text{CHF}_2\text{Cl}$ ;  $\blacklozenge$   $\text{CH}_2\text{Cl}_2$ ;  $\diamond$   $\text{CH}_2\text{FCl}$ ;  $\bullet$   $\text{CH}_3\text{Cl}$ ;  $\square$   $\text{CCl}_4$ ;  $\blacktriangle$   $\text{CFCl}_3$  (CFC-11);  $\blacktriangledown$   $\text{CF}_2\text{Cl}_2$  (CFC-12);  $\blacksquare$   $\text{CF}_3\text{Cl}$  (Adapted from Hubrich and Stuhl 1980)



**Fig. 4.34** Absorption spectra of HCFCs. 298 K:  $\Delta$   $\text{CH}_3\text{CCl}_3$ ;  $\nabla$   $\text{CF}_3\text{CH}_2\text{Cl}$ ;  $\triangle$   $\text{CH}_3\text{CH}_2\text{Cl}$ ;  $\square$   $\text{CF}_3\text{CF}_2\text{Cl}$ ;  $\blacktriangledown$   $\text{CH}_3\text{CF}_2\text{Cl}$ ;  $\bullet$   $\text{CF}_2\text{ClCF}_2\text{Cl}$ ;  $\blacksquare$   $\text{CFCl}_2\text{CF}_2\text{Cl}$  (Adapted from Hubrich and Stuhl 1980)



Meanwhile, among the HCFCs, HCFC-22 ( $\text{CHF}_2\text{Cl}$ ), HCFC-141b ( $\text{CH}_3\text{CFCl}_2$ ), and HCFC-142b ( $\text{CH}_3\text{CF}_2\text{Cl}$ ) have relatively high concentrations in the stratosphere. Figure 4.34 shows the absorption spectra of these molecules (Hubrich and Stuhl 1980). The absorption spectra of HCFCs also have peaks near 180–200 nm with tails extending toward longer wavelengths, similar to those of CFCs.

As seen in Fig. 4.1, the 190–220 nm region is the valley between the strong absorption of  $\text{O}_2$  in the shorter wavelength side and that of  $\text{O}_3$  in the longer wavelength side. The actinic flux in this range reaches the middle stratosphere. The absorption peaks of CFCs and HCFCs shown in Figs. 4.33 and 4.34 incidentally coincide with this range, they are efficiently photolyzed in the stratosphere, which is the direct cause of ozone layer destruction by the anthropogenic species.

NASA/JPL Evaluation No. 17 (Sander et al. 2011) gives recommended absorption cross sections and their temperature dependence for these compounds based on

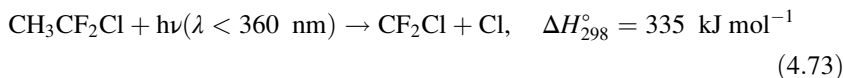
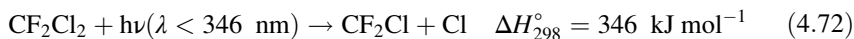
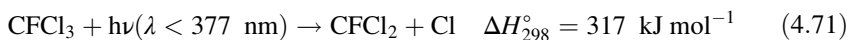
**Table 4.26** Absorption cross sections of CCl<sub>4</sub> and CFCs (295–298 K)

Wavelength (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )					
	CCl <sub>4</sub>	CFCl <sub>3</sub> (CFC-11)	CF <sub>2</sub> Cl <sub>2</sub> (CFC-12)	CF <sub>2</sub> ClCFCl <sub>2</sub> (CFC-113)	CF <sub>2</sub> ClCF <sub>2</sub> Cl (CFC-114)	CF <sub>3</sub> CF <sub>2</sub> Cl (CFC-115)
176	1010	324	186	(192) <sup>a</sup>	43.0	3.08
180	806	314	179	155	26.2	1.58
184	479	272	134	123	15.0	0.790
188	227	213	82.8	83.5	7.80	0.403
192	99.6	154	45.5	48.8	3.70	0.203
196	69.5	99.1	21.1	26.0	1.75	0.0985
200	66.0	63.2	8.71	12.5	0.800	0.0474
204	61.0	37.3	3.37	5.80	0.370	0.0218
208	52.5	20.4	1.26	2.65	0.160	(0.0187) <sup>b</sup>
212	41.0	10.7	0.458	1.15	0.0680	(0.0070) <sup>c</sup>
216	27.8	5.25	0.163	0.505	0.0290	(0.0027) <sup>d</sup>
220	17.5	2.51	0.062	0.220	0.0122	0.0011
224	10.2	1.17	0.023	0.0950	0.0053	–
228	5.65	0.532	0.0090	0.0410	0.0023	–
232	3.04	–	0.0034	0.0188	0.0010	–
236	1.60	(0.132) <sup>e</sup>	0.0013	0.008	–	–
240	0.830	0.047	–	0.0036	–	–
244	0.413	(0.017) <sup>f</sup>	–	0.0016	–	–
248	0.210	–	–	0.0007	–	–
250	0.148	0.0066	–	0.0005	–	–
260	0.025	0.0015	–	–	–	–

Source: NASA/JPL Panel Evaluation No. 17 (Sander et al. 2011), <sup>a</sup>175 nm, <sup>b</sup>205 nm, <sup>c</sup>210 nm, <sup>d</sup>215 nm, <sup>e</sup>235 nm, <sup>f</sup>245 nm

measurements by Hubrich and Stuhl (1980), Simon et al. (1988), Mérienne et al. (1990), Gillotay and Simon (1991), and Fahr et al. (1993) and others. Table 4.26 gives absorption cross sections of CCl<sub>4</sub>, CFCl<sub>3</sub>, CF<sub>2</sub>Cl<sub>2</sub>, CF<sub>2</sub>ClCFCl<sub>2</sub>, CF<sub>2</sub>ClCF<sub>2</sub>Cl, and CF<sub>3</sub>CF<sub>2</sub>Cl, and Table 4.27 cites those of CHF<sub>2</sub>Cl, CH<sub>3</sub>CFCl<sub>2</sub>, and CH<sub>3</sub>CF<sub>2</sub>Cl extracted from the evaluation.

The photolytic processes of CFCs and HCFCs in the region of stratospheric actinic flux are in general known as,



and Cl atoms are released (Clark and Husain 1984; Brownsword et al. 1999; Hanf et al. 2003). Recently, Taketani et al. (2005) detected Cl(<sup>2</sup>P<sub>3/2</sub>) and Cl(<sup>2</sup>P<sub>1/2</sub>)



**Table 4.27** Absorption cross sections of HCFCs (298 K)

Wave-length (nm)	$10^{30} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )			Wave-length (nm)	$10^{30} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )		
	CHF <sub>2</sub> Cl (HCFC-22)	CH <sub>3</sub> CFCl <sub>2</sub> (HCFC-141b)	CH <sub>3</sub> CF <sub>2</sub> Cl (HCFC-142b)		CHF <sub>2</sub> Cl (HCFC-22)	CH <sub>3</sub> CFCl <sub>2</sub> (HCFC-141b)	CH <sub>3</sub> CF <sub>2</sub> Cl (HCFC-142b)
176	4.04	163	(14.0) <sup>a</sup>	212	0.0029	1.40	0.0105
180	1.91	172	6.38	216	0.0013	0.589	0.0040
184	0.842	146	(2.73) <sup>b</sup>	220	0.0006	0.248	0.0015
188	0.372	104	—	224	—	0.105	0.0005
192	0.156	63.6	0.706	228	—	0.0444	0.0001
196	0.072	34.1	0.324	232	—	0.0189	—
200	0.032	16.6	0.145	236	—	0.0080	—
204	0.0142	7.56	0.0622	240	—	0.0033	—
208	0.00636	3.30	0.0256	—	—	—	—

Source: NASA/JPL Panel Evaluation No. 17 (Sander et al. 2011), <sup>a</sup>175 nm, <sup>b</sup>185 nm

spectroscopically in the photolysis of CFCs,  $\text{CCl}_4$  and HCFCs, and determined the formation quantum yields of Cl atoms. The obtained quantum yields are  $1.03 \pm 0.09$ ,  $1.01 \pm 0.08$ ,  $1.41 \pm 0.14$ ,  $1.02 \pm 0.08$  for  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCl}_3$ ,  $\text{CCl}_4$  and  $\text{CHFCl}_2$ , respectively, which implies that single C-Cl bond rupture occurs with the quantum yields of unity for CFCs and HCFCs except  $\text{CCl}_4$ . It has been revealed that the process releasing two Cl atoms such as,



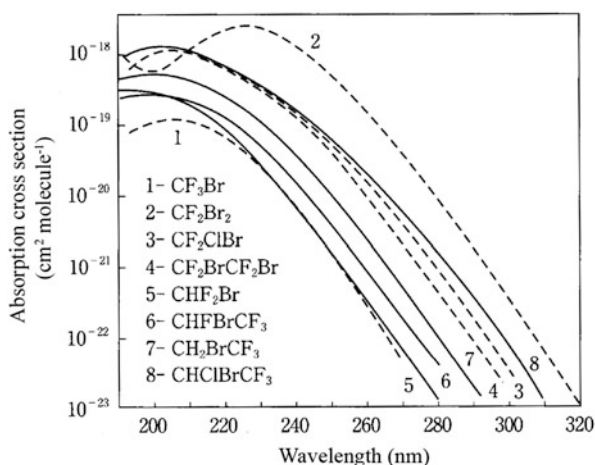
occurs partially in the photolysis of  $\text{CCl}_4$  at 193 nm.

### 4.3.10 Bromochlorofluorocarbons (Halon)

Among halocarbons (halogenated hydrocarbons), bromochlorofluorocarbons in which at least one chlorine or fluorine atom of chlorofluorocarbons is substituted by bromine is called halons. Halons, as with CFCs, do not have any dissipating process in the troposphere, and reach to the stratosphere and are photolyzed, which affects the ozone layer destruction. Among halons,  $\text{CF}_2\text{ClBr}$  (halon-1211) and  $\text{CF}_3\text{Br}$  (halon-1301) have the highest atmospheric concentrations, and these two compounds are taken up here.

Figure 4.35 depicts absorption spectra of halons and bromohydrofluorocarbons (Orkin and Kasimovskaya 1995). As seen in the figure the absorption bands of halons have peaks at around 200–210 nm, and extend abroad tails to 300, and 280 nm for  $\text{CF}_2\text{ClBr}$  and  $\text{CF}_3\text{Br}$ , respectively. Although its absorption band overlaps with the tropospheric actinic flux region particularly for  $\text{CF}_2\text{ClBr}$ , the absorption cross sections are very small so that the photolysis in the troposphere is almost negligible. Since halons has large absorption cross sections near 200 nm, they are easily photolyzed in the stratosphere.

**Fig. 4.35** Absorption spectra of halons (Adapted from Orkin and Kasimovskaya 1995)



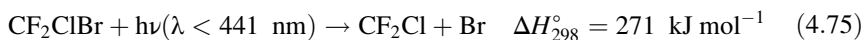
**Table 4.28** Absorption cross sections of CF<sub>2</sub>ClBr and CF<sub>3</sub>Br (298 K)

Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )		Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )		Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )	
	CF <sub>2</sub> ClBr	CF <sub>3</sub> Br		CF <sub>2</sub> ClBr	CF <sub>3</sub> Br		CF <sub>2</sub> ClBr	CF <sub>3</sub> Br
	Halon-1211	Halon-1301		Halon-1211	Halon-1301		Halon-1211	Halon-1301
176	121	1.60	228	45.7	3.69	280	0.0991	0.0006
180	58.1	2.61	232	33.8	2.32	284	0.0527	(0.0002) <sup>a</sup>
184	35.0	4.02	236	24.4	1.39	288	0.0282	–
188	38.9	5.82	240	16.9	0.766	292	0.0148	–
192	57.0	7.58	244	11.4	0.414	296	0.0076	–
196	81.4	9.61	248	7.50	0.212	300	0.0039	–
200	106	11.3	252	4.76	0.107	304	0.0021	–
204	117	12.4	256	2.94	0.0516	308	0.0011	–
208	118	12.4	260	1.76	0.0248	312	0.0006	–
212	109	11.4	264	1.03	0.0118	316	0.0003	–
216	93.6	9.71	268	0.593	0.0058	320	0.0002	–
220	76.8	7.56	272	0.336	0.0027	–	–	–
224	60.4	5.47	276	0.184	0.0013	–	–	–

Source: NASA/JPL Panel Evaluation No. 17 (Sander et al. 2011), <sup>a</sup>285 nm

The absorption cross sections of CF<sub>2</sub>ClBr and CF<sub>3</sub>Br are cited in Table 4.28. These absorption cross sections are extracted from NASA JPL Evaluation No. 17 (Sander et al. 2011) based on Gillotay and Simons (1989), Burkholder et al. (1991), Orkin and Kasimovskaya (1995), etc.

As the photolytic processes of CF<sub>2</sub>ClBr,



can be conceived and the measurements of Talukdar et al. (1996) gave the quantum yields for the production of Cl and Br atoms at 193, 222, and 248 nm as  $\Phi(\text{Cl}) = 1.03 \pm 0.14$ ,  $0.27 \pm 0.04$ , and  $0.18 \pm 0.03$ ,  $\Phi(\text{Br}) = 1.04 \pm 0.13$ ,  $0.86 \pm 0.11$ , and  $0.75 \pm 0.13$ , respectively. It is suggested that the simultaneous release of Cl and Br atoms by reaction (4.77) occurs at 193 nm, and reactions (4.75) and (4.76) take place with the total quantum yield of unity at the longer wavelengths than 200 nm.

As for CF<sub>3</sub>Br, the quantum yields of Br formation,  $\Phi(\text{Br}) = 1.12 \pm 0.16$ ,  $0.92 \pm 0.15$  at 193, and 222 nm, respectively, are reported by Talukdar et al. (1992), and the reaction,



is thought to take place with the quantum yield of unity.

## 4.4 Photolysis of Inorganic Halogens

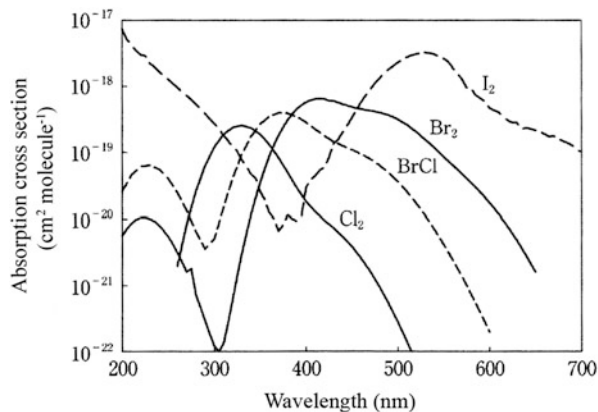
As a result of the photolyses of halogenated methane, CFCs, HCFCs, and halons, large amounts of Cl and Br atoms are released into the stratosphere, and chain reactions giving rise to ozone layer destruction are formed. Many inorganic halogen compounds formed as the chain carrier or chain terminating species in these chain reactions are photolyzed again in the stratosphere to regenerate halogen atoms or radicals. The calculations of the photolysis rates of these species are very important for determining the efficiency of the chain reactions. On the other hand, the same kinds of inorganic halogen compounds and radicals are formed in the troposphere from the photolysis or OH radical reactions of biogenic organic halogenated molecules and inorganic halogen molecules formed from heterogeneous reactions on sea salts. In this section, photolytic reactions of these inorganic halogen compounds which appear in common in the stratospheric and tropospheric chemistry will be summarized.

### 4.4.1 Chlorine ( $\text{Cl}_2$ ), Bromine Monochloride ( $\text{BrCl}$ ), Bromine ( $\text{Br}_2$ ), Iodine ( $\text{I}_2$ )

Chlorine  $\text{Cl}_2$ , and bromine monochloride  $\text{BrCl}$  are formed in the reactions of  $\text{ClONO}_2$ ,  $\text{BrONO}_2$ ,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HOCl}$ ,  $\text{HOBr}$  in the heterogeneous reaction in the polar stratospheric clouds (see Sect. 6.5), and their photolyses play an important role in the chain reactions of the ozone hole formation. In the troposphere,  $\text{Cl}_2$  is known to be produced in the heterogeneous reactions on sea salts, but observational data is still limited. Bromine  $\text{Br}_2$  is known to be produced by the heterogeneous chain reactions in the tropospheric ozone destruction in the arctic region. Meanwhile, iodine  $\text{I}_2$  is released from sea weeds in coastal regions.

Figure 4.36 illustrates absorption spectra of  $\text{Cl}_2$ ,  $\text{BrCl}$ ,  $\text{Br}_2$ , and  $\text{I}_2$ . As shown, the spectrum of  $\text{Cl}_2$  is a broad band extending from the ultraviolet region of 260 nm to visible region of 500 nm with a maximum at around 330 nm. Therefore,  $\text{Cl}_2$  can be photolyzed in the lower stratosphere at the altitude of ca. 20 km and in the troposphere by the photoabsorption in the near ultraviolet and visible light region at wavelengths longer than 290 nm. The absorption spectrum of  $\text{Br}_2$  consists of relatively weak bands in the 190–300 nm with a maximum at around 225 nm, and strong bands in the 300–650 nm with a maximum near 415 nm. Furthermore, the second and third bands can be seen as shoulders of the latter band at around 480 and 550 nm. Also, weak vibrational bands appear overlapping with the continuum at wavelengths longer than 510 nm, although it is not discernible in the logarithmic scale chart of Fig. 4.36.  $\text{Br}_2$  is photolyzed by visible light with large rate both in the stratosphere and troposphere. The spectrum of  $\text{BrCl}$  is similar to  $\text{Br}_2$  and consists of the 190–290 nm bands with a peak at around 230 nm and 290–600 nm bands with a peak at around 375 nm. Therefore,  $\text{BrCl}$  can be photolyzed in the

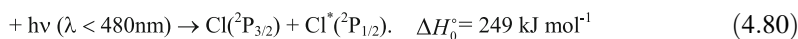
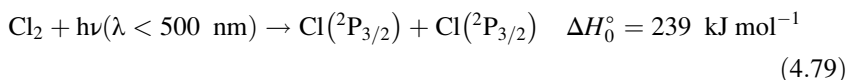
**Fig. 4.36** Absorption spectra of  $\text{Cl}_2$ ,  $\text{BrCl}$ ,  $\text{Br}_2$  and  $\text{I}_2$  (Constructed based on NASA/JPL Evaluation No. 17, Sander et al. 2011, and IUPAC Subcommittee Report Vol. III, Atkinson et al. 2007)



lower stratosphere at the atmospheric window region near 230 nm, but the photolysis rate at the visible radiation is much larger.  $\text{I}_2$  has a very strong absorption bands in the ultraviolet region of 200–300 nm and in the visible region of 450 – >700 nm, and easily photolyzed in the troposphere. Further distinct vibrational band structure can be seen (see Fig. 2.4) at the wavelengths longer than 500 nm in the visible spectrum although it is not shown in Fig. 4.36 with the vertical axis in the logarithmic scale.

Absorption cross sections of  $\text{Cl}_2$ ,  $\text{BrCl}$ ,  $\text{Br}_2$ , and  $\text{I}_2$  extracted from NASA/JPL Evaluation No. 17 (Sander et al. 2011) are cited in Table 4.29 that are based on Maric et al. (1993) for  $\text{Cl}_2$ , Maric et al. (1994) for  $\text{BrCl}$  and  $\text{Br}_2$ , and Saiz-Lopez et al. (2004) for  $\text{I}_2$ .

The absorption spectrum of  $\text{Cl}_2$  in the 250–450 nm is assigned to the transition from the ground  $X^1\Sigma_g$  state to the dissociative excited states  $^1\Pi_u$  and  $^3\Pi_u$ . From the  $^1\Pi_u$  state  $\text{Cl}(^2P_{3/2}) + \text{Cl}(^2P_{3/2})$  and from the  $^3\Pi_u$  state  $\text{Cl}(^2P_{3/2}) + \text{Cl}^*(^2P_{1/2})$  are thought to be formed (Matsumi et al. 1992) following the reactions,



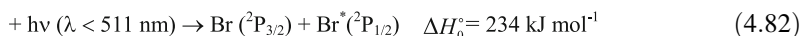
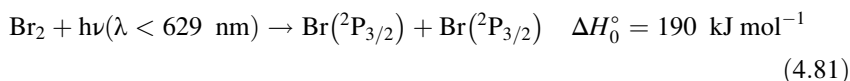
The formation ratio of the excited chlorine atom  $\text{Cl}^*(^2P_{1/2})$  is small 0.01 at wavelengths shorter than 350 nm, and increases to 0.47 at 475 nm, near the dissociation limit of reaction (4.80) (Park et al. 1991; Matsumi et al. 1992; Samartzis et al. 1997). The total photolysis quantum yields  $\Phi(\text{Cl}(^2P_{3/2})) + \Phi(\text{Cl}^*(^2P_{1/2}))$  are thought to be unity at the wavelengths shorter than 450 nm.

The photolytic processes of  $\text{Br}_2$  is thought to be similar to  $\text{Cl}_2$  (Lindeman and Wiesenfeld 1979).

**Table 4.29** Absorption cross sections of Cl<sub>2</sub>, BrCl, Br<sub>2</sub>

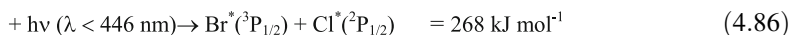
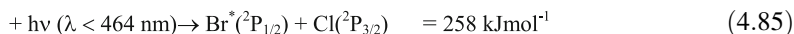
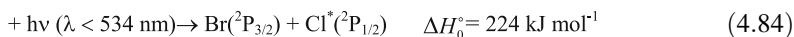
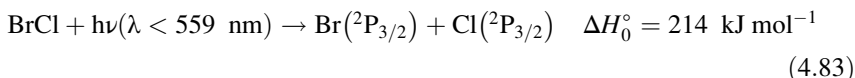
Wavelength (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )			Wavelength (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )		
	Cl <sub>2</sub>	BrCl	Br <sub>2</sub>		Cl <sub>2</sub>	BrCl	Br <sub>2</sub>
200	–	2.64	0.562	430	0.732	14.6	60.1
210	–	4.59	0.870	440	0.546	12.6	54.0
220	–	6.13	1.05	450	0.387	11.0	48.8
230	–	6.48	1.01	460	0.258	9.52	45.2
240	–	5.60	0.808	470	0.162	8.02	42.8
250	–	4.05	0.544	480	0.0957	6.47	40.3
260	0.198	2.50	0.316	490	0.0534	4.99	36.6
270	0.824	1.35	0.161	500	0.0283	3.68	31.8
280	2.58	0.653	0.0728	510	0.0142	2.59	26.2
290	6.22	0.357	0.0299	520	0.0068	1.74	20.6
300	11.9	0.504	0.0122	530	0.0031	1.13	15.7
310	18.5	1.47	0.0135	540	0.0014	0.700	11.7
320	23.7	4.08	0.0626	550	0.0006	0.419	8.68
330	25.6	9.25	0.300	560	–	0.243	6.43
340	23.5	17.2	1.14	570	–	0.136	4.77
350	18.8	26.7	3.49	580	–	0.0739	3.50
360	13.2	35.0	8.66	590	–	0.0390	2.52
370	8.41	39.6	17.8	600	–	0.0200	1.76
380	5.00	39.3	30.7	610	–	–	1.19
390	2.94	34.9	45.1	620	–	–	0.767
400	1.84	28.6	57.4	630	–	–	0.475
410	1.28	22.5	64.2	640	–	–	0.282
420	0.956	17.8	64.5	650	–	–	0.161

Source: NASA/JPL Panel Evaluation No. 17 (Sander et al. 2011)



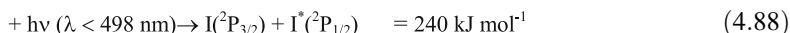
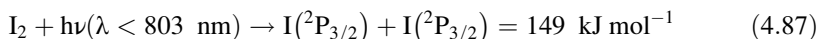
The formation quantum yields of the excited bromine atoms Br(<sup>3</sup>P<sub>1/2</sub>) increases from 0.4 at 444 nm to 0.89 at 510 nm close to the dissociation limit of reaction (4.82), and then decreases (Peterson and Smith 1978). As for the photolytic processes of Br<sub>2</sub>, several other studies have also been made (Haugen et al. 1985; Cooper et al. 1998), but no absolute photolytic quantum yields has been measured. For the purpose of atmospheric chemistry total photolytic quantum yields of Br<sub>2</sub> can be approximated to be unity for the wavelength region of 200–510 nm.

As for BrCl, the quantum yields for each of the processes,



are reported at 235 nm as  $\Phi[\text{Br}(^2\text{P}_{3/2}) + \text{Cl}(^2\text{P}_{3/2})] = 0.26 \pm 0.05$ ,  $\Phi[\text{Br}(^2\text{P}_{3/2}) + \text{Cl}^*(^2\text{P}_{1/2})] = 0.16 \pm 0.05$ , and  $\Phi[\text{Br}^*(^2\text{P}_{1/2}) + \text{Cl}(^2\text{P}_{3/2})] = 0.58 \pm 0.05$  (Park et al. 2000). The total quantum yields of photodissociation may be approximated to be unity.

The photolysis of  $\text{I}_2$  is similar to those of  $\text{Cl}_2$  and  $\text{Br}_2$ , and the reactions,



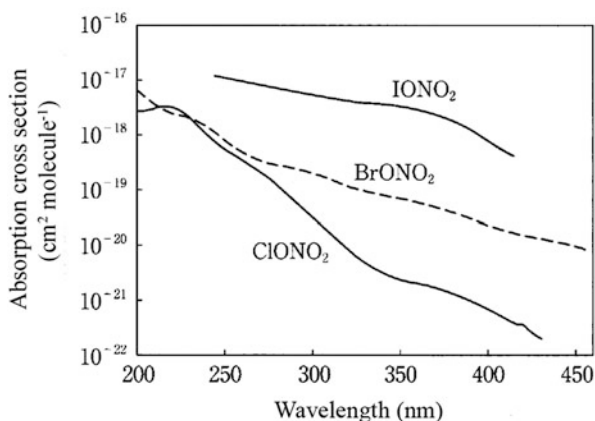
with the total photolytic quantum yields of 0.33–0.9 depending on the wavelengths at the 501–624 nm region, and of unity in the continuum at  $<500$  nm are reported (Brewer and Tellinghuisen 1972).

#### 4.4.2 Chlorine Nitrate ( $\text{ClONO}_2$ ), Bromine Nitrate ( $\text{BrONO}_2$ ), Iodine Nitrate ( $\text{IONO}_2$ )

Chlorine nitrate  $\text{ClONO}_2$  and bromine nitrate  $\text{BrONO}_2$  are important reservoir molecules formed by the chain termination reactions,  $\text{ClO} + \text{NO}_2$  and  $\text{BrO} + \text{NO}_2$ , in the  $\text{ClO}_x$  and  $\text{BrO}_x$  cycles in the stratosphere, respectively. Iodine nitrate  $\text{IONO}_2$  plays a similar role in the iodine chemistry in the troposphere.

As shown in Fig. 4.37, the absorption spectra of  $\text{ClONO}_2$  and  $\text{BrONO}_2$  have peaks in common in the stratospheric window region near 200 nm, and decreasing

**Fig. 4.37** Absorption spectra of  $\text{ClONO}_2$ ,  $\text{BrONO}_2$  and  $\text{IONO}_2$  (Constructed based on IUPAC Subcommittee Report Vol. III, Atkinson et al. 2007, and NASA/JPL Evaluation No. 17, Sander et al. 2011)



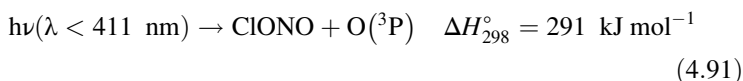
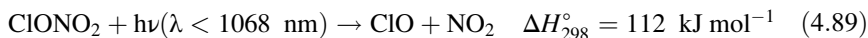
**Table 4.30** Absorption cross sections of ClONO<sub>2</sub><sup>a</sup>, BrONO<sub>2</sub><sup>a</sup>, IONO<sub>2</sub><sup>b</sup> (298 K)

Wavelength (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )			Wavelength (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )		
	ClONO <sub>2</sub>	BrONO <sub>2</sub>	IONO <sub>2</sub>		ClONO <sub>2</sub>	BrONO <sub>2</sub>	IONO <sub>2</sub>
200	282	680	–	330	0.466	9.32	380
205	284	520	–	335	0.367	8.62	374
210	314	361	–	340	0.302	8.06	360
215	342	292	–	345	0.258	7.57	348
220	332	256	–	350	0.229	7.01	334
225	278	230	–	355	0.208	6.52	316
230	208	205	–	360	0.200	5.99	294
235	148	175	–	365	0.180	5.43	270
240	105	140	–	370	0.159	4.89	242
245	76.4	106	1210	375	0.141	4.35	213
250	56.0	79.7	1170	380	0.121	3.85	184
255	43.2	60.0	1060	385	0.106	3.37	153
260	33.8	47.1	946	390	0.091	2.97	130
265	26.5	38.9	880	395	0.076	2.59	103
270	20.5	33.8	797	400	0.064	2.28	78.0
275	15.7	30.5	772	405	0.054	2.01	60.5
280	11.9	27.9	741	410	0.044	1.81	49.6
285	8.80	25.6	691	415	0.036	1.65	41.6
290	6.41	23.2	631	420	0.032	1.50	–
295	4.38	20.8	577	425	0.023	1.38	–
300	3.13	18.6	525	430	0.019	1.29	–
305	2.24	16.5	495	435	–	1.20	–
310	1.60	14.5	462	440	–	1.11	–
315	1.14	12.7	441	445	–	1.03	–
320	0.831	11.3	404	450	–	0.928	–
325	0.613	10.2	396	455	–	0.831	–

Source: <sup>a</sup>IUPAC Subcommittee Report Vol. III, <sup>b</sup>NASA/JPL Panel Evaluation No. 17 (Sander et al. 2011)

monotonically to 380 and 400 nm, respectively. The absorption spectrum of IONO<sub>2</sub> has been measured in the wavelength region of 240–415 nm, and is a broad continuum in the region. The absorption cross sections of ClONO<sub>2</sub> and BrONO<sub>2</sub> are compiled by IUPAC Subcommittee Report Vol. III (Atkinson et al. 2007) taking the average of Burkholder et al. (1994, 1995) and Deters et al. (1998), and those of IONO<sub>2</sub> by NASA/JPL Evaluation No. 17 (Sander et al. 2011) based on Mössinger et al. (2002)., Table 4.30 gives the values extracted from them.

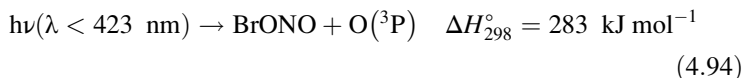
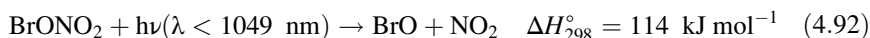
The photolytic processes of ClONO<sub>2</sub> are thought to be,





The quantum yields are recommended as  $\Phi(\text{Cl} + \text{NO}_3) = 0.6$  for  $\lambda < 308$  nm,  $7.143 \times 10^{-3} \lambda - 1.60$  for  $308 < \lambda < 364$  nm, 1.0 for  $\lambda > 364$  nm, and  $\Phi(\text{ClO} + \text{NO}_2) = 1 - \Phi(\text{Cl} + \text{NO}_3)$  by NASA/JPL Evaluation No. 17 (Sander et al. 2011) based on Goldfarb et al. (1997), Yokelson et al. (1997) and others.

As for  $\text{BrONO}_2$  the processes,



can be conceived by analogy to  $\text{ClONO}_2$  but experiments are sparse (Harwood et al. 1998; Soller et al. 2002). NASA/JPL Evaluation No. 17 (Sander et al. 2011) recommends  $\Phi(\text{total}) = 1$ ,  $\Phi(\text{Br} + \text{NO}_3) = 0.85$ , and  $\Phi(\text{BrO} + \text{NO}_2) = 0.15$  for  $\lambda > 300$  nm.

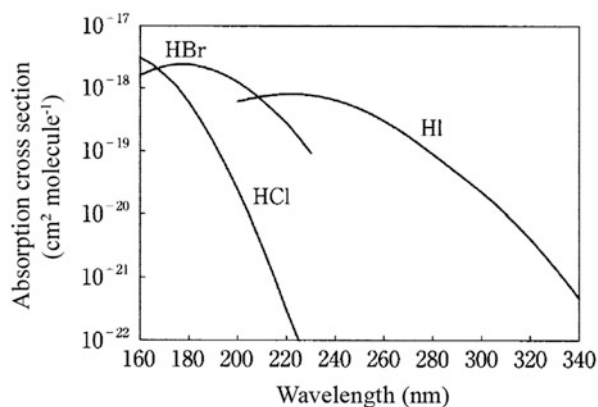
Although the photolytic processes and quantum yields of  $\text{IONO}_2$  are not studied well, the formation quantum yields of  $\text{IO}$  and  $\text{NO}_3$  are reported as  $\Phi(\text{IO}) \leq 0.02$ , and  $\Phi(\text{NO}_3) = 0.21 \pm 0.09$  at 248 nm by Joseph et al. (2007). From these results, the main photolytic pathway is presumed to be  $\text{I} + \text{NO}_3$  but the possibility of further decomposition of the formed  $\text{NO}_3$  to  $\text{NO}_2 + \text{O}$  is also suggested.

#### 4.4.3 Hydrogen Chloride (HCl), Hydrogen Bromide (HBr), Hydrogen Iodide (HI)

Hydrogen chloride HCl, hydrogen bromide HB, and hydrogen iodide HI are the reservoir molecules formed in the termination reactions of photochemical halogen chain in the troposphere and stratosphere together with  $\text{ClONO}_2$ ,  $\text{BrONO}_2$  and  $\text{IONO}_2$  mentioned in the previous section. Since their absorption spectra lie in the shorter wavelengths, and cross sections are much smaller than  $\text{ClONO}_2$ ,  $\text{BrONO}_2$  and  $\text{IONO}_2$ , their atmospheric photolysis rates are much smaller and lifetime is much longer as the reservoirs.

As shown in Fig. 4.38, the absorption spectra of HCl and HBr have peaks at 154 and 178 nm in the vacuum ultraviolet region, and decrease monotonically toward longer wavelengths extending to near 230 and 279 nm, respectively. Therefore, the photolyses of HCl and HBr are possible only in the stratosphere. The peak of the absorption band of HI is at 222 nm and the absorption extends to 340 nm so that it can be photolyzed in the troposphere, but the absorption cross sections in the tropospheric actinic flux region is as small as  $\leq 3 \times 10^{-20} \text{ cm}^2$ .

**Fig. 4.38** Absorption spectra of HCl, HBr, HI (Constructed based on NASA/JPL Evaluation No. 17, Sander et al. 2011)



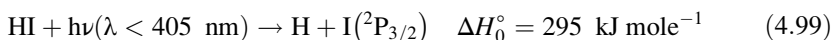
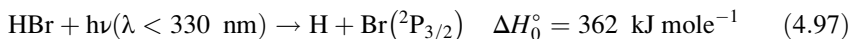
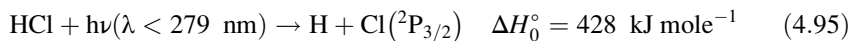
**Table 4.31** Absorption cross sections of HCl, HBr and HI (298 K)

Wavelength (nm)	$10^{20} \sigma$ ( $\text{cm}^2 \text{ molecule}^{-1}$ )			Wavelength (nm)	$10^{20} \sigma$ ( $\text{cm}^2 \text{ molecule}^{-1}$ )
	HCl	HBr	HI		HI
150	334	–	–	250	47.0
155	343	131	–	255	38.2
160	306	161	–	260	30.0
165	240	195	–	265	23.0
170	163	225	–	270	17.2
175	106	242	–	275	12.5
180	58.9	242	–	280	8.94
185	29.4	221	–	285	6.37
190	13.8	194	–	290	4.51
195	5.96	161	–	295	3.18
200	2.39	125	61.1	300	2.23
205	0.903	91.8	67.7	305	1.52
210	0.310	64.4	73.8	310	1.01
215	0.101	42.3	78.4	315	0.653
220	0.030	28.0	80.8	320	0.409
225	0.010	16.3	80.4	325	0.247
230	0.0034	9.32	77.4	330	0.145
235	–	–	71.9	335	0.083
240	–	–	64.6	340	0.047
245	–	–	56.1	345	–

Source: NASA/JPL Panel Evaluation No. 17 (Sander et al. 2011)

Table 4.31 cites absorption cross sections of HCl, HBr and HI extracted from NASA/JPL Evaluation No. 17 (Sander et al. 2011). These recommended values are based on Bahou et al. (2001) for HCl, Huebert and Martin (1968) and Nee et al. (1986) for HBr, and Campuzano-Jost and Crowley (1999) for HI.

Total photolytic quantum yields of HCl, HBr and HI in the wavelength region of tropospheric and stratospheric actinic fluxes are thought to be unity. The photolytic processes of each of them,



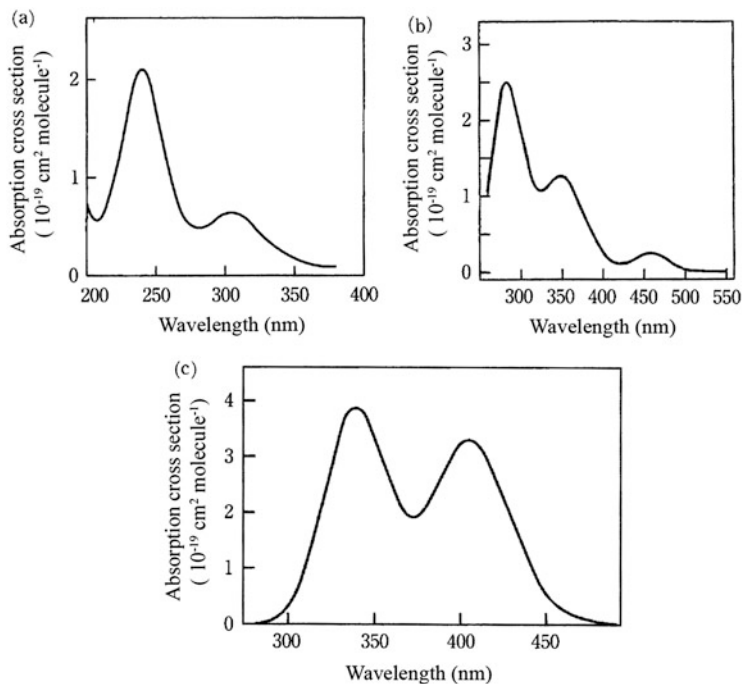
are known to produce both the ground states of Cl, Br and I atoms,  $\text{Cl}(^2\text{P}_{3/2})$ ,  $\text{Br}(^2\text{P}_{3/2})$ , and  $\text{I}(^2\text{P}_{3/2})$ , and the spin-orbit excited states of  $\text{Cl}^*(^2\text{P}_{1/2})$ ,  $\text{Br}^*(^2\text{P}_{1/2})$ , and  $\text{I}^*(^2\text{P}_{1/2})$ . The formation ratios of the excited and ground state atoms have been studied considerably well. For example,  $\Phi[\text{Cl}^*(^2\text{P}_{1/2})]/\Phi[\text{Cl}^*(^2\text{P}_{1/2}) + \text{Cl}(^2\text{P}_{3/2})] = 0.42\text{--}0.48$  at 201–210 nm for HCl (Regan et al. 1999a),  $\Phi[\text{Br}^*(^2\text{P}_{1/2})]/\Phi[\text{Br}^*(^2\text{P}_{1/2}) + \text{Br}(^2\text{P}_{3/2})] = 0.15\text{--}0.23$  at 201–253 nm for HBr (Regan et al. 1999b), and  $\Phi[\text{I}^*(^2\text{P}_{1/2})]/\Phi[\text{I}(^2\text{P}_{3/2})] = 0.2$  at 208 nm, 1.7 at 252 nm, and 0.1 at 303 nm for HI (Langford et al. 1998).

#### 4.4.4 Hypochlorous Acid (HOCl), Hypobromous Acid (HOBr), Hypoiodous Acid (HOI)

Hypochlorous acid HOCl, hypobromous acid HOBr, and hypoiodous acid HOI are formed in the chain termination reactions between ClO, BrO, IO radicals and HO<sub>2</sub> radicals. Since they have absorption spectra in the ultraviolet to visible region, the photolytic regeneration of the radicals has to be considered in the atmosphere.

As seen in Fig. 4.39(a), absorption spectrum of HOCl consists of a fairly strong continuum band with a peak at around 240 nm and a second continuum which appears as a shoulder at around 300 nm. These transitions have been assigned to  $2^1\text{A}' \leftarrow 1^1\text{A}'$ ,  $1^1\text{A}'' \leftarrow 1^1\text{A}'$ , respectively. Table 4.32 gives absorption cross sections of HOCl extracted from NASA/JPL Evaluation No. 17 (Sander et al. 2011) based on Burkholder (1993) and Barnes et al. (1998).

Considerable disagreement has been noted for the absorption spectrum of HBr due to impurities in samples (Finlayson-Pitts and Pitts 2000). Figure 4.39(b) shows the absorption spectrum by Ingham et al. (1998), and Table 4.32 gives the absorption cross sections recommended by Sander et al. (2011) based on Ingham et al. (1998). In the spectrum of HOBr a peak at 285 nm and a shoulder around 350 nm are seen corresponding to those of HOCl due to the same electronic

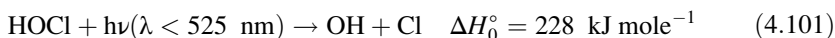


**Fig. 4.39** Absorption spectra of (a) HOCl, (b) HOBr, and (c) HOI (Adapted from Burkholder 1993 (HOCl); Ingham et al. 1998 (HOBr); Bauer et al. 1998 (HOI))

transition and shifted to longer wavelength. The absorption range at still longer wavelength is thought due to the forbidden transition to a triplet state (Francisco et al. 1996; Minaev 1999).

The absorption spectrum of HOI has been reported by Bauer et al. (1998) and Rowley et al. (1999). Figure 4.39(c) shows the absorption spectrum by Bauer et al. (1998), and Table 4.32 gives the absorption cross sections recommended by NASA/JPL Evaluation No. 17 (Sander et al. 2011) taking the average of above two studies. As can be seen in Fig. 4.39(c), the absorption spectrum of HOI consists of continuum bands with two peaks at 340 and 408 nm.

The photolyses of HOCl, HOBr and HOI proceeds via the pathways,



The quantum yields of unity for each reaction have been confirmed by the experiments of Schindler et al. (1997), Benter et al. (1995) and Bauer et al. (1998) for HOCl, HOBr, and HOI, respectively.

**Table 4.32** Absorption cross sections of HOCl, HOBr and HOI (298 K)

Wavelength (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )			Wavelength (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )		
	HOCl <sup>a</sup>	HOBr	HOI <sup>a</sup>		HOCl	HOBr	HOI
280	4.64	24.3	0.077	390	0.491	4.22	24.8
285	4.74	25.0	0.234	395	0.385	3.23	27.9
290	5.13	24.0	0.608	400	0.288	2.43	30.1
295	5.62	21.9	1.45	405	0.208	1.80	30.9
300	5.99	19.1	3.02	410	0.144	1.36	30.2
305	6.12	16.2	5.77	415	0.097	1.08	28.0
310	5.97	13.6	9.85	420	0.063	0.967	24.7
315	5.56	11.8	15.4	425	–	0.998	20.7
320	4.95	10.8	21.9	430	–	1.15	16.6
325	4.24	10.5	28.6	435	–	1.40	12.7
330	3.50	10.8	34.3	440	–	1.68	9.30
335	2.81	11.3	38.1	445	–	1.96	6.54
340	2.22	11.9	39.2	450	–	2.18	4.40
345	1.77	12.3	37.7	455	–	2.29	2.37
350	1.43	12.4	33.9	460	–	2.28	1.79
355	1.22	12.1	29.1	465	–	2.14	1.09
360	1.06	11.5	24.1	470	–	1.91	0.632
365	0.968	10.5	20.2	475	–	1.62	0.360
370	0.888	9.32	17.8	480	–	1.30	0.196
375	0.804	7.99	17.4	485	–	0.993	–
380	0.708	6.65	18.8	490	–	0.723	–
385	0.602	5.38	21.5	495	–	0.502	–

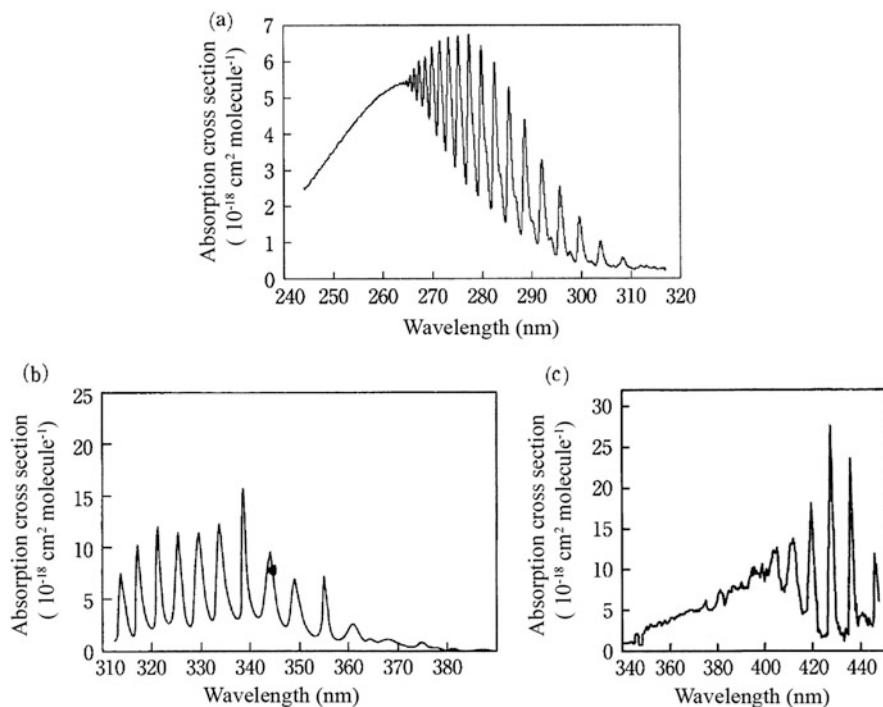
Source: NASA/JPL Panel Evaluation No. 17 (Sander et al. 2011)

<sup>a</sup>For example, the values at 285 nm, 295 nm are the average at 284 and 286 nm, and 294,296 nm, respectively

#### 4.4.5 Chlorine Monoxide (ClO), Bromine Monoxide (BrO), Iodine Monoxide (IO)

Chlorine monoxide ClO, bromine monoxide BrO, and iodine monoxide IO are the main chain carrier of stratospheric and tropospheric halogen chain reactions. ClO is partially photolyzed only in the stratosphere, and the photolytic rates of BrO and IO are large also in the troposphere. Their photolysis rates have to be considered in the evaluation of ozone depleting chain reactions.

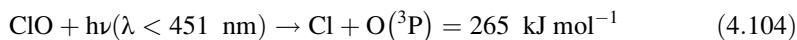
As shown in Fig. 4.40(a), the absorption spectrum of ClO consists of a continuum in the range of 210–265 nm, and vibrational-structured bands in the 265–315 nm (Sander and Friedl 1989; Sander et al. 2011). The absorption cross sections of ClO are dependent on spectral resolution and temperature. Table 4.28 cites the absorption cross sections with an averaged wavelength interval of 1 nm given in NASA/JPL Evaluation No. 17 (Sander et al. 2011) based on the measurement with spectral resolution of 0.3 nm by Sander and Friedl (1989). Although the



**Fig. 4.40** Absorption spectra of (a) ClO, (b) BrO, and (c) IO (Adapted from Sander and Friedl 1989 (ClO); Wahner et al. 1988 (BrO); Lasylo et al. 1995 (IO))

absorption cross sections of ClO at the peak of 265 nm is large,  $5.2 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ , the region overlaps with the absorption of  $\text{O}_3$  in the stratosphere, the photolysis of ClO is mainly brought by the absorption at the long-wavelength tail. Due to this reason, the loss of ClO by the photolysis is thought to be much smaller than the reactions with O atoms and NO (Langhoff et al. 1977).

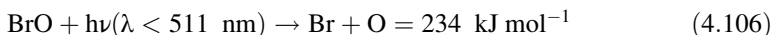
The quantum yields of the formation of  $\text{Cl}(2P_{3/2, 1/2})$  and  $\text{O}(^1\text{D})$  in the photolysis of ClO,



have been reported to be unity by Schmidt et al. (1998).

The absorption spectrum of BrO has banded structure in the ultraviolet region of 290–380 nm as shown in Fig. 4.40(b), and is assigned to  $\text{A}^2\Pi_{3/2} \leftarrow \text{X}^2\Pi_{3/2}$  transition (Wahner et al. 1988; Sander et al. 2011). The absorption cross sections of BrO depends on spectral resolution and temperature, and Table 4.28 gives the

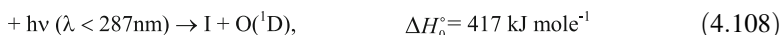
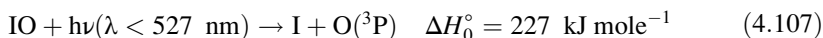
recommended values (Sander et al. 2011) based on Wilmouth et al. (1999). The photolysis of BrO,



is thought to occur with quantum yields of unity.

As for IO, the absorption bands corresponding to the  $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$  transition similar to BrO can be seen in the ultraviolet and visible region of 338–488 nm. The absorption maximum appears at around 400 nm, and the bands with a vibrational structure overlaps with a continuum at the wavelength side longer than 400 nm. The maximum of absorption cross sections appears for the A-X (4-0) band at 427.2 nm. Figure 4.40(c) depicts the absorption spectrum of IO (Lasylo et al. 1995; Harwood et al. 1997), and Table 4.33 gives the absorption cross sections of 1 nm intervals from NASA/JPL Evaluation No. 17 (Sander et al. 2011) based on Lasylo et al. (1995), Harwood et al. (1997), and Bloss et al. (2001).

Ingham et al. (2000) reported the quantum yields of  $\text{O}(^3\text{P})$  production in the photolysis of IO as 0.91 at 355 nm. Among the photolytic reactions of



the energetically possible process in the absorption spectrum region of Fig. 4.40(c) is only reaction (4.107), and the formation of I and  $\text{O}(^3\text{P})$  atoms by this reaction is thought to occur with quantum yields of unity.

#### 4.4.6 Chlorine Peroxide (ClOOCl)

Chlorine peroxide ClOOCl is formed by the termolecular recombination reaction of ClO radicals when the concentration of ClO radicals is high. Among the reservoir molecules in the stratosphere over the Antarctica in wintertime, ClOOCl has the highest concentration, and its photolysis in springtime is very important for the formation of the ozone hole.

Figure 4.41 shows the absorption spectrum by Papanastasiou et al. (2009). The absorption spectrum of ClOOCl has a valley at around 218 nm, maximum at 245 nm, and decreases monotonically toward the longer wavelengths side till near 400 nm. For the photochemistry in the lower stratosphere, absorption spectrum in the wavelength region longer than 290 nm is important. However, due to the impurity of  $\text{Cl}_2$  in the sample of ClOOCl in the laboratory, the disagreement of the absorption spectrum and cross sections have been much of concern until recently. In order to overcome this problem, Chen et al. (2009) used the molecular beam and measured the photolytic decay by mass spectrometry, and determined the absorption cross sections of ClOOCl. This method is supposed to exclude the effect of

Table 4.33 Absorption cross sections of ClO, BrO and IO (298 K)

Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )		Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )		Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )		Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )	
	ClO	BrO		ClO	BrO		BrO	IO		BrO	IO
250	352	-	300	133	275	335	652	-	400	671	1200
254	425	-	301	56.6	180	336	339	-	391	620	681
258	486	-	302	45.2	502	337	222	-	392	617	365
262	529	-	303	44.9	217	338	201	-	393	642	253
266	549	-	304	87.8	274	339	1296	-	394	684	204
270	574	-	305	45.5	466	340	445	118	395	694	205
271	489	-	306	33.2	221	341	243	100	396	709	302
272	532	-	307	33.1	407	342	235	107	397	701	2050
273	515	-	308	47.7	518	343	424	89	398	654	1370
274	470	-	309	45.5	227	344	968	96.2	399	671	543
275	507	-	310	28.7	396	345	542	86.2	400	671	309
276	456	-	311	27.3	659	346	226	126	401	700	208
277	418	-	312	33.1	294	347	146	112	402	765	173
278	501	-	313	32.5	197	348	258	108	403	859	166
279	283	-	314	28.9	901	349	748	142	404	864	177
280	538	-	315	27.8	443	350	499	160	400	787	653
281	329	-	316	26.8	232	351	272	154	401	667	1880
282	311	-	317	-	721	352	182	165	402	606	807
283	445	-	318	-	730	353	163	163	403	578	381
284	245	-	319	-	345	354	180	181	404	643	249
285	292	-	320	-	251	355	789	185	405	787	256
286	362	-	321	-	1138	356	276	194	406	667	219
287	200	107	322	-	677	357	120	207	407	606	168

(continued)

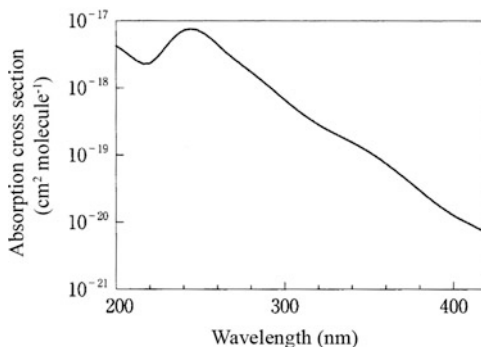


Table 4.33 (continued)

Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )		Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )		Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )		Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )	
	ClO	BrO		ClO	BrO		BrO	IO		IO	IO
288	197	95.0	323	301	358	408	223	578	443	183	
289	337	110	324	288	359	409	230	643	444	195	
290	165	184	325	983	360	410	242	813	445	957	
291	111	134	326	838	364	411	268	1010	446	805	
292	270	157	327	312	368	412	326	976	447	392	
293	161	248	328	223	372	413	360	786	448	214	
294	102	140	329	789	376	414	402	589	449	269	
295	94.5	294	330	1058	380	415	504	568	450	156	
296	206	164	331	453	384	416	523	414	451	96.9	
297	83.1	361	332	203	388	417	580	460	452	102	
298	65.1	193	333	260	392	418	617	734	453	87.3	
299	74.8	284	334	1294	396	419	709	1380	454	100	

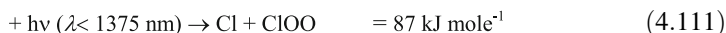
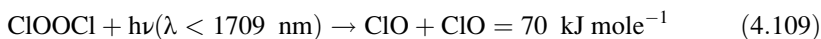
Source: NASA/JPL Panel Evaluation No. 17 (Sander et al. 2011)

**Fig. 4.41** Absorption spectrum of ClOOCl (Adapted from Papanastasiou et al. 2009)



photoabsorption of impurity  $\text{Cl}_2$ , and the values of 49.0, and  $11.2 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$  are reported at 308 nm, and 351 nm, respectively. These values agree well with those recently reported by Papanastasiou et al. (2009). Based on this data, NASA/JPL Evaluation No. 17 recommended the absorption cross sections averaged over 2 nm and estimated the error as  $\pm 35\%$  (Sander et al. 2011). Table 4.34 cites the recommended absorption cross sections at the temperature range of 190–250 K.

The photolytic pathways of ClOOCl can be conceived as,



According to the recent study of detecting Cl atoms and ClO radicals directly, the main product is Cl atoms by reaction (4.112) to form  $2\text{Cl} + \text{O}_2$  (Moore et al. 1999; Huang et al. 2011). NASA/JPL Evaluation No. 17 recommended  $\Phi(2\text{Cl} + \text{O}_2) = 0.8 \pm 0.1$ ,  $\Phi(2\text{ClO}) + \Phi(\text{ClO} + \text{Cl} + \text{O}) = 0.2 \pm 0.1$  with total quantum yield of unity for the whole spectral range of Fig. 4.44, and  $\Phi(\text{ClO} + \text{Cl} + \text{O}) = 0.0 \pm 0.1$  at  $\lambda > 300 \text{ nm}$ . Since the difference in the photolytic pathways can cause a big difference in the ozone destruction efficiency, the pathways of this reaction have attracted much interest.

#### 4.4.7 Chlorine Dioxide (ClO<sub>2</sub>)

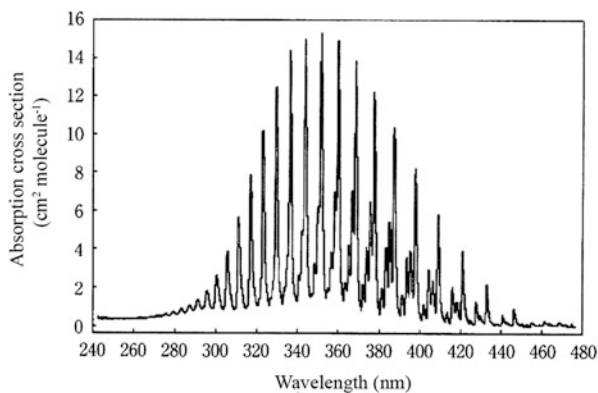
Chlorine dioxide ClO<sub>2</sub> is formed by the bimolecular cross reactions of ClO by themselves and is a reservoir molecule of chlorine in the stratosphere over winter-time Antarctica the same as ClOOCl. Since ClO<sub>2</sub> has the strong absorption in the visible region, it is photolyzed instantaneously when the solar light starts to irradiate in spring.

**Table 4.34** Absorption cross sections of ClOOCl (190–250 K)

Wave-length (nm)	$10^{20} \sigma$ ( $\text{cm}^2$ molecule $^{-1}$ )	Wave-length (nm)	$10^{20} \sigma$ ( $\text{cm}^2$ molecule $^{-1}$ )	Wave-length (nm)	$10^{20} \sigma$ ( $\text{cm}^2$ molecule $^{-1}$ )	Wave-length (nm)	$10^{20} \sigma$ ( $\text{cm}^2$ molecule $^{-1}$ )
200	423	260	445	320	28.2	380	2.97
204	362	264	360	324	24.7	384	2.45
208	303	268	294	328	21.9	388	2.04
212	255	272	246	332	19.5	392	1.71
216	228	276	206	336	17.3	396	1.47
220	232	280	173	340	15.4	400	1.26
224	277	284	144	344	13.6	404	1.11
228	366	288	119	348	11.9	408	0.988
232	488	292	98.2	352	10.3	412	0.878
236	618	296	80.5	356	8.82	416	0.778
240	719	300	66.1	360	7.43	420	0.712
244	758	304	54.4	364	6.24		
248	732	308	45.4	368	5.23		
252	651	312	38.2	372	4.35		
256	549	316	32.8	376	3.60		

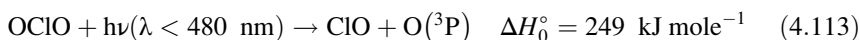
Source: NASA/JPL Panel Evaluation No. 17 (Sander et al. 2011)

**Fig. 4.42** Absorption spectrum of OClO (Adapted from Wahner et al. 1987)



The absorption spectrum consists of well-structured strong bands in the 280–480 nm region (Wahner et al. 1987) as shown in Fig. 4.42. This bands corresponds to the ClO stretching vibration ( $v' \leftarrow v'' = 0$ ) of electronic transition  $A^2A_2 \leftarrow X^2B_1$ . As expected from the banded structure, the shape and cross sections of absorption depends on spectroscopic resolution. The measurements of Wahner et al. (1987) was at 0.25 nm, and those at higher resolution of 0.01–0.02 nm and middle resolution of 0.2–0.4 nm has been made later by Kromminga et al. (2003). NASA/JPL Evaluation No. 17 gives the absorption cross sections averaged over 1 nm interval, and those at the peak of each vibrational band at different temperatures (Sander et al. 2011). Table 4.35 cites the absorption cross sections at the 1 nm interval at 204 K extracted from them.

The photolytic pathways of OClO are known to be



The production of  $\text{O}(^3\text{P})$  is reported to be the main process in the 350–475 nm region including photofragment spectroscopic study (Lawrence et al. 1990; Davis and Lee 1992, 1996; Delmdahl et al. 1998). Although the formation of Cl atoms is also reported at the shorter wavelengths region, it is presumed that the formation of  $\text{O}(^3\text{P})$  by reaction (4.113) occurs with quantum yields of unity and the formation of Cl atoms is less than 4 % at the wavelength region longer than 350 nm, which is effective in the photolysis of lower stratosphere (Sander et al. 2011).

#### 4.4.8 Nitrosyl Chloride (ClNO), Nitryl Chloride (ClNO<sub>2</sub>)

Nitrosyl chloride ClNO and nitryl chloride ClNO<sub>2</sub> are both formed by the heterogeneous reactions of NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> on the solid sea salt surface. These are

**Table 4.35** Absorption cross sections of OCIO (averaged over 1 nm interval, 204 K)

Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )	Wave-length (nm)	$10^{20} \sigma$ (cm <sup>2</sup> molecule <sup>-1</sup> )
270	44.3	300	226	330	782	360	1210	390	71.4	420	81.4
271	45.7	301	222	331	285	361	477	391	123	421	323
272	49.9	302	143	332	155	362	173	392	109	422	151
273	49.1	303	95.3	333	147	363	179	393	203	423	50.0
274	48.1	304	96.1	334	208	364	207	394	270	424	23.8
275	54.8	305	276	335	335	365	361	395	285	425	23.3
276	58.3	306	328	336	1090	366	403	396	275	426	14.5
277	52.5	307	190	337	782	367	625	397	370	427	43.8
278	54.3	308	116	338	266	368	919	398	53	428	99.5
279	67.4	309	85.4	339	155	369	903	399	225	429	46.9
280	67.2	310	168	340	167	370	268	400	70.1	430	44.3
281	58.3	311	511	341	250	371	107	401	45.6	431	23.3
282	65.4	312	338	342	414	372	180	402	96.9	432	47.0
283	82.4	313	174	343	925	373	170	403	56.3	433	173
284	77.6	314	107	344	1090	374	364	404	196	434	69.6
285	67.2	315	94.2	345	388	375	376	405	194	435	24.6
286	77.7	316	239	346	176	376	554	406	185	436	11.2
287	100	317	686	347	161	377	718	407	160	437	7.68
288	93.7	318	360	348	258	378	881	408	158	438	9.09
289	79.4	319	176	349	320	379	278	409	493	439	5.13
290	90.5	320	114	350	581	380	92.4	410	210	440	12.5
291	127	321	125	351	1100	381	135	411	71.6	441	47.8
292	116	322	279	352	993	382	148	412	34.0	442	23.2
293	90.9	323	873	353	330	383	266	413	46.8	443	14.7

294	94.1	324	443	354	164	384	298	414	44.6	444	7.59
295	147	325	192	355	190	385	440	415	30.0	445	3.96
296	172	326	121	356	276	386	345	416	164	446	46.8
297	122	327	147	357	343	387	762	417	100	447	55.2
298	92.0	328	221	358	597	388	388	418	107	448	18.4
299	106	329	838	359	830	389	173	419	75.1	449	7.17

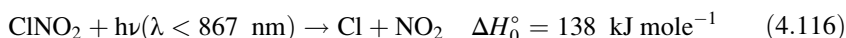
Source: NASA/JPL Panel Evaluation No. 17 (Sander et al. 2011)

thought to be formed mainly in the marine boundary layer affected by urban polluted plumes, and their photolyses are considered in the halogen chemistry in the troposphere.

As depicted in Fig. 4.43, the ultraviolet and visible spectrum of ClNO has strong absorption maximum at around 200 nm and has very broad continuum extending toward longer wavelength till over 600 nm in the visible region. The evaluation of absorption cross sections by NASA/JPL Evaluation No. 17 (Sander et al. 2011) is based on the data of Tyndall et al. (1987) (190–350 nm) and Roehl et al. (1992) (350–650 nm), and Table 4.36 gives those extracted from it for the 200–500 nm region. The absorption spectrum drawn using these cross sections is shown in Fig. 4.43 for the tropospheric actinic flux region.

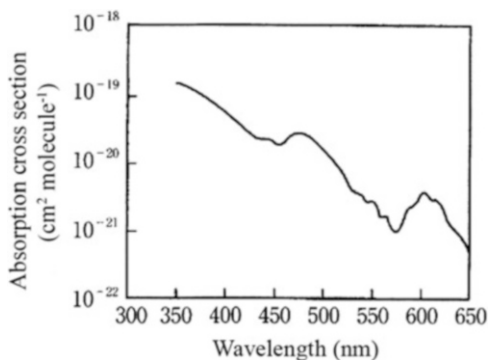
The absorption spectrum of ClNO<sub>2</sub> also has the maximum at around 215 nm in the ultraviolet region and a broad continuum extends toward visible region as shown in Fig. 4.44. The decay of cross sections are larger than ClNO, and the spectrum terminates at around 400 nm. The absorption cross sections of NASA/JPL Evaluation No. 17 (Sander et al. 2011) takes the average of Illies and Takacs (1976) and Furlan et al. (2000). Table 4.36 cites those extracted from the evaluation together with ClNO. As for the absorption spectrum of ClNO<sub>2</sub>, new measurement data was reported recently by Ghosh et al. (2011), which gives values somehow different from the above.

The photolyses of ClNO and ClNO<sub>2</sub> are confirmed to proceed,



by Calvert and Pitts (1966) and Nelson and Johnston (1981). As expected from the absorption spectra, their quantum yields are thought to be unity. As for ClNO, the relative yields of different spin-orbit states of the formed Cl atoms  $\Phi[\text{Cl}^*(^2\text{P}_{1/2})]/\Phi[\text{Cl}^*(^2\text{P}_{1/2}) + \text{Cl}(^2\text{P}_{3/2})]$  are also measured. For example, the ratio is reported to be  $0.90 \pm 0.10$  at 351 nm, thus Cl<sup>\*</sup>(<sup>2</sup>P<sub>1/2</sub>) atoms are mostly formed at this wavelength (Chichinin 1993).

**Fig. 4.43** Absorption spectrum of ClNO (Adapted from Roehl et al. 1992)

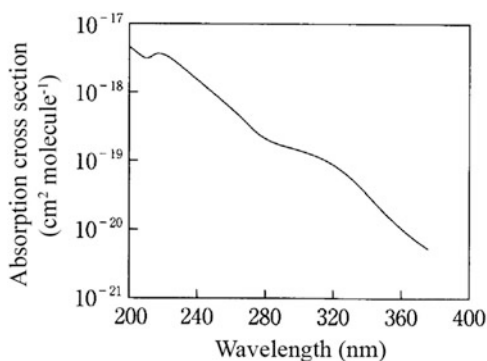


**Table 4.36** Absorption cross sections of ClNO and ClNO<sub>2</sub> (298 K)

Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )		Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )		Wave-length (nm)	10 <sup>20</sup> σ (cm <sup>2</sup> molecule <sup>-1</sup> )
	ClNO	ClNO <sub>2</sub>		ClNO	ClNO <sub>2</sub>		ClNO
200	5860	445	310	11.5	12.1	420	2.89
210	2630	321	320	13.4	9.40	430	2.21
220	896	325	330	14.7	6.79	440	2.20
230	266	221	340	15.2	4.62	450	1.87
240	82.5	132	350	14.2	3.05	460	1.95
250	31.7	90.9	360	12.9	1.86	470	2.50
260	17.5	58.7	370	11.0	1.12	480	2.53
270	12.9	33.7	380	8.86	0.772	490	2.07
280	10.6	20.7	390	6.85	0.475	500	1.50
290	9.64	16.3	400	5.13	0.327		
300	10.0	14.1	410	3.83	–		

Source: NASA/JPL Panel Evaluation No. 17 (Sander et al. 2011)

**Fig. 4.44** Absorption spectrum of ClNO<sub>2</sub> (Adapted from Ganske et al. 1992)



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## Chapter 5

# Homogeneous Elementary Reactions in the Atmosphere and Rate Constants

Atmospheric chemical systems consist of numerous chemical reactions. Fundamental reactions that can be considered with interests in microscopic processes focusing on the changes of chemical bonds among atoms, molecules and free radicals, are often called elementary reactions. Homogeneous elementary reactions are the subjects of theoretical analysis, for example by the transition state theory described in Chap. 2, and also the subjects of research on molecular dynamics. In this chapter, among the gas phase homogeneous reactions related to atmospheric chemistry, basic elementary reactions are picked up, and their reaction products and rate constants are presented including brief information on quantum chemical knowledge on reaction pathways and reaction rates.

Sequential oxidation reaction mechanisms of many organic molecules emitted into the atmosphere and the overall reaction system with HO<sub>x</sub> chain reaction mechanism in the troposphere are treated in Chap. 7, and the HO<sub>x</sub>, NO<sub>x</sub>, ClO<sub>x</sub> chain reaction systems in the stratosphere are described in Chap. 8.

Regarding the reaction rate constants, evaluation by the NASA/JPL panel has been conducted from 1977, and the recommended rate constants have been renewed every few years. The most recent evaluation was obtained in Evaluation 17 (Sander et al. 2011). Another evaluation has been reported by the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry as Vol. I Inorganic Species, Vol. II Organic Species, Vol. III Inorganic Halogen Species, Vol. IV Organic Halogen Species in 2004, 2006, 2007 and 2008, separately (Atkinson et al. 2004, 2006, 2007, 2008). More recent data was updated on a web page (Wallington et al. 2012). These recommend values are extremely useful for atmospheric chemistry research, and those values are fully quoted in this chapter. In principle, the temperature ranges to be applied for temperature dependent rate constant formulas are taken from the IUPAC subcommittee report, and the values of enthalpy of reactions  $\Delta H^\circ$  are given at 298 K calculated from the heat of formation given in Table 2.5 at the end of this book.

## 5.1 Reactions of O(<sup>3</sup>P) and O(<sup>1</sup>D) Atoms

Reactions of oxygen atoms formed in the photolysis of atmospheric O<sub>2</sub>, O<sub>3</sub>, NO<sub>2</sub> are initial triggers to drive stratospheric and tropospheric chemistry system. Oxygen atoms targeted in the stratospheric and tropospheric chemistry are O(<sup>3</sup>P) in the ground state, and O(<sup>1</sup>D) in the lowest excited state at 190 kJ mol<sup>-1</sup> higher than the ground state.

O(<sup>3</sup>P) can react with many organic and inorganic molecules but the reactivity is much lower than O(<sup>1</sup>D). Thus, although hydrocarbons existing in the clean and polluted troposphere can all react with O(<sup>3</sup>P), the reactions can in general be neglected as compared to those with OH radicals when atmospheric concentrations of O(<sup>3</sup>P) and reaction rates are considered, and only the reaction with the atmospheric main species O<sub>2</sub> is necessary to be considered as the O(<sup>3</sup>P) reaction in the troposphere. In the stratosphere, reactions with O<sub>2</sub> and O<sub>3</sub> are predominant, but those with OH, HO<sub>2</sub>, NO<sub>2</sub>, ClO are also important in the chain reaction system.

On the other hand, O(<sup>1</sup>D) is much more reactive than O(<sup>3</sup>P), and reacts with many atmospheric trace molecules that do not react with O(<sup>3</sup>P). Among them, the most important is the reaction with water vapor (H<sub>2</sub>O) to form OH radicals. As for the O(<sup>1</sup>D) reactions, it is necessary to consider only this reaction in the troposphere, other reactions with N<sub>2</sub>O, CH<sub>4</sub>, CFC are also important in the stratosphere.

Table 5.1 gives reaction rate constants of O(<sup>3</sup>P) and O(<sup>1</sup>D) with atmospheric species, that are excerpted from the NASA/JPL panel evaluation No. 17 (Sander et al. 2011) and the IUPAC subcommittee report (Atkinson et al. 2004). In this section, reactions of O(<sup>3</sup>P) with O<sub>2</sub>, O<sub>3</sub>, OH, HO<sub>2</sub>, NO<sub>2</sub>, ClO, and those of O(<sup>1</sup>D) with H<sub>2</sub>O, N<sub>2</sub>O, CH<sub>4</sub>, CFC that are particularly important in atmospheric chemistry, are described.

### 5.1.1 O(<sup>3</sup>P) + O<sub>2</sub> + M

The reaction of O(<sup>3</sup>P) and O<sub>2</sub> is a typical termolecular reaction (see 2.3.1) forming ozone O<sub>3</sub>,



The slightly different low pressure limit rate constant  $k_0$  of reaction (5.1) has been obtained in laboratory for O<sub>2</sub> and N<sub>2</sub> acting as M (Lin and Leu 1982; Hippler et al. 1990). The recommended values of the IUPAC subcommittee (Atkinson et al. 2004) are,

Table 5.1 Rate constants at 298 K and Arrhenius parameters for the reactions of O(<sup>3</sup>P) and O(<sup>1</sup>D) atoms

Reactions	$k$ (298 K) (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	A Factor (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$E_a/R$ (K)	Ref.
O( <sup>3</sup> P) + O <sub>2</sub> + M → O <sub>3</sub> + M	$6.0 \times 10^{-34}$ [O <sub>2</sub> ] ( $k_0$ ) $5.6 \times 10^{-34}$ [N <sub>2</sub> ] ( $k_0$ )	$6.0 \times 10^{-34}$ (T/300) <sup>-2.6</sup> [O <sub>2</sub> ] ( $k_0$ ) $5.6 \times 10^{-34}$ (T/300) <sup>-2.6</sup> [N <sub>2</sub> ] ( $k_0$ )		(a1)
O( <sup>3</sup> P) + O <sub>3</sub> → 2 O <sub>2</sub>	$8.0 \times 10^{-15}$	$8.0 \times 10^{-12}$	2060	(a1)
O( <sup>3</sup> P) + OH → H + O <sub>2</sub>	$3.5 \times 10^{-11}$	$2.4 \times 10^{-11}$	-110	(a1)
O( <sup>3</sup> P) + HO <sub>2</sub> → OH + O <sub>2</sub>	$5.8 \times 10^{-11}$	$2.7 \times 10^{-11}$	-220	(a1)
O( <sup>3</sup> P) + NO <sub>2</sub> → NO + O <sub>2</sub>	$1.0 \times 10^{-11}$	$5.5 \times 10^{-12}$	-190	(a1)
O( <sup>3</sup> P) + NO <sub>2</sub> + M → NO <sub>3</sub> + M	$1.3 \times 10^{-31}$ [N <sub>2</sub> ] ( $k_0$ ) $2.3 \times 10^{-11}$ ( $k_\infty$ )	$1.3 \times 10^{-31}$ (T/300) <sup>-1.5</sup> [N <sub>2</sub> ] ( $k_0$ ) $2.3 \times 10^{-11}$ (T/300) <sup>-0.24</sup> ( $k_\infty$ )		(a1)
O( <sup>3</sup> P) + ClO → Cl + O <sub>2</sub>	$3.7 \times 10^{-11}$	$2.5 \times 10^{-11}$	-110	(a2)
O( <sup>3</sup> P) + BrO → Br + O <sub>2</sub>	$4.1 \times 10^{-11}$	$1.9 \times 10^{-11}$	-230	(a2)
O( <sup>1</sup> D) + N <sub>2</sub> + M → N <sub>2</sub> O + M	$2.8 \times 10^{-36}$ [N <sub>2</sub> ] ( $k_0$ )	$2.8 \times 10^{-36}$ (T/300) <sup>-0.9</sup> [N <sub>2</sub> ] ( $k_0$ )		(a1, b)
O( <sup>1</sup> D) + N <sub>2</sub> → O( <sup>3</sup> P) + N <sub>2</sub>	$3.1 \times 10^{-11}$	$2.2 \times 10^{-11}$	-110	(b)
+ O <sub>2</sub> → O( <sup>3</sup> P) + O <sub>2</sub>	$4.0 \times 10^{-11}$	$3.3 \times 10^{-11}$	-60	(b)
O( <sup>1</sup> D) + H <sub>2</sub> → OH + H	$1.2 \times 10^{-10}$	$1.2 \times 10^{-10}$	0	(b)
O( <sup>1</sup> D) + H <sub>2</sub> O → 2OH	$2.0 \times 10^{-10}$	$1.6 \times 10^{-10}$	-60	(b)
O( <sup>1</sup> D) + N <sub>2</sub> O → overall	$1.3 \times 10^{-10}$	$1.2 \times 10^{-10}$	-20	(b)
→ N <sub>2</sub> + O <sub>2</sub>	$5.0 \times 10^{-11}$	$4.6 \times 10^{-11}$	-20	(b)
→ 2 NO	$7.8 \times 10^{-11}$	$7.3 \times 10^{-11}$	-20	(b)
O( <sup>1</sup> D) + CH <sub>4</sub> → overall	$1.8 \times 10^{-10}$	$1.8 \times 10^{-10}$	0	(b)
→ CH <sub>3</sub> + OH	$1.3 \times 10^{-10}$	$1.3 \times 10^{-10}$	0	(b)
→ CH <sub>2</sub> OH + H	$0.35 \times 10^{-10}$	$0.35 \times 10^{-10}$	0	(b)
→ HCHO + H <sub>2</sub>	$0.09 \times 10^{-10}$	$0.09 \times 10^{-10}$	0	(b)
O( <sup>1</sup> D) + CCl <sub>3</sub> F → overall	$2.3 \times 10^{-10}$	$2.3 \times 10^{-10}$	0	(b)
O( <sup>1</sup> D) + CCl <sub>2</sub> F <sub>2</sub> → overall	$1.4 \times 10^{-10}$	$1.4 \times 10^{-10}$	0	(b)

(continued)

Table 5.1 (continued)

Reactions	$k$ (298 K) ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	A Factor ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	$E_a/R$ (K)	Ref.
$\rightarrow \text{ClO} + \text{CClF}_2$	$1.2 \times 10^{-10}$	$1.2 \times 10^{-10}$	0	(a3)
$\rightarrow \text{O}(^3\text{P}) + \text{CCl}_2\text{F}_2$	$2.4 \times 10^{-11}$	$2.4 \times 10^{-11}$	0	(a3)
$\text{O}(^1\text{D}) + \text{CClF}_3 \rightarrow \text{overall}$	$8.7 \times 10^{-11}$	$8.7 \times 10^{-11}$	0	(b)

(a1, a2, a3) IUPAC subcommittee report Vol. I, III, IV (Atkinson et al. 2004, 2007, 2008), respectively

(b) NASA/JPL panel evaluation No.17 (Sander et al. 2011)

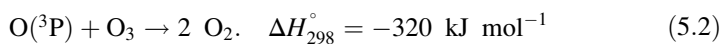
$$k_{0,5.1}(T, N_2) = 5.6 \times 10^{-34} [N_2] \left(\frac{T}{300}\right)^{-2.6} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (100 - 300\text{K})$$

$$k_{0,5.1}(T, O_2) = 6.0 \times 10^{-34} [O_2] \left(\frac{T}{300}\right)^{-2.6} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (100 - 300\text{K})$$

Under atmospheric conditions, reaction (5.1) is in the low-pressure limit, where the rate constants are proportional to pressure, and the apparent bimolecular rate constant at 298 K and 1 atm ( $M = 2.69 \times 10^{19}$  molecules  $\text{cm}^{-3}$ ) is  $1.6 \times 10^{-14}$   $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

### 5.1.2 O(<sup>3</sup>P) + O<sub>3</sub>

The reaction of (<sup>3</sup>P) and O<sub>3</sub> are typical bimolecular reaction with large exothermicity.



Wine et al. (1983) determined the rate constants of reaction (5.2) at 237–477 K by direct measurement of time decay of O(<sup>3</sup>P) using a resonance fluorescence method. These values agreed well with previous experiments, and the IUPAC subcommittee (Atkinson et al. 2004) recommends the rate constant at 298 K as  $k(298 \text{ K}) = 8.0 \times 10^{-15}$   $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and the Arrhenius's formula for temperature dependence as,

$$k_{5.2}(T) = 8.0 \times 10^{-12} \exp\left(-\frac{2060}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (200 - 400 \text{ K}).$$

The activation energy of reaction (5.2) is considerably large, 17.1  $\text{kJ mole}^{-1}$ , so that it is necessary to use proper values considering the temperature conditions in the stratosphere.

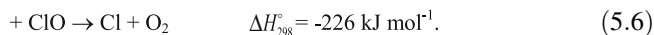
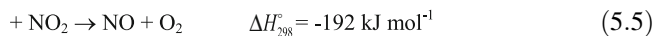
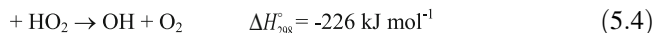
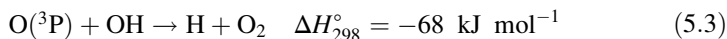
Quantum chemical calculation of transition state theory for reaction (5.2) has been reported by Balakrishnan and Billing (1996), and the obtained theoretical value agreed with the above experimental value reasonably well. According to the theoretical calculation, excess energy released by the large exothermicity is retained in one of the produced O<sub>2</sub> exclusively, which is formed as vibrationally highly excited molecule with up to  $v = 27$ .

### 5.1.3 O(<sup>3</sup>P) + OH, HO<sub>2</sub>, NO<sub>2</sub>, ClO

Reactions of O(<sup>3</sup>P) with OH, HO<sub>2</sub>, NO<sub>2</sub>, and ClO are important in the upper troposphere where the concentration of O(<sup>3</sup>P) is high enough to constitute ozone dissipation cycles (Sect. 8.2).



These reactions have common characteristics that the reaction partners are all radicals with unpaired electron. Each reaction is an oxygen atom transfer reaction expressed as,



Since the reactions form atoms and radicals as products, they play a role as propagation reaction of ozone destruction chain reactions in the stratosphere (see Sect. 8.2).

The atom-radical reactions such as those of O(<sup>3</sup>P) with OH, HO<sub>2</sub>, NO<sub>2</sub>, and ClO, have characteristics of very large rate constants with nearly zero activation energy. The rate constants of reactions (5.3), (5.4), (5.5), and (5.6) at 298 K are known to be 3.5, 5.8, 1.0,  $3.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively, all having similar magnitude (Atkinson et al. 2004, 2007). The recommended values of the IUPAC subcommittee including temperature dependences are,

$$k_{5.3}(T) = 2.4 \times 10^{-11} \exp\left(\frac{110}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (150 - 500 \text{ K})$$

$$k_{5.4}(T) = 2.7 \times 10^{-11} \exp\left(\frac{224}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (220 - 400 \text{ K})$$

$$k_{5.5}(T) = 5.5 \times 10^{-12} \exp\left(\frac{188}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (220 - 420 \text{ K})$$

$$k_{5.6}(T) = 2.5 \times 10^{-11} \exp\left(\frac{110}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (150 - 500 \text{ K}),$$

and all have small negative temperature dependence. Recommended temperature dependence of rate constants are based on O(<sup>3</sup>P) + OH: Lewis and Watson (1980), Howard and Smith (1981), O(<sup>3</sup>P) + HO<sub>2</sub>: Keyser (1982), Nicovich and Wine (1987), O(<sup>3</sup>P) + NO<sub>2</sub>: Ongstad and Birks (1986), Geers-Müller and Stuhl (1987), Gierczak et al. (1999), O(<sup>3</sup>P) + ClO: Ongstad and Birks (1986), Nicovich et al. (1988), Goldfarb et al. (2001), and previous experiments.

As for the O(<sup>3</sup>P) + NO<sub>2</sub> reaction, termolecular process,



is known to occur in addition to above reaction (5.5). Since this reaction is in fall-off region between the low- and high-pressure limit under the atmospheric conditions, the following formula described in Chap. 2 (Eq. (2.54)),

$$k_{ter}([M], T) = \left[ \frac{k_0(T)[M]}{1 + \frac{k_0(T)[M]}{k_\infty(T)}} \right] F_c \left\{ 1 + \left[ \log_{10} \left( \frac{k_0(T)[M]}{k_\infty(T)} \right)^2 \right] \right\}^{-1} \quad (5.8)$$

has to be applied to the temperature and pressure dependence. The recommended parameters by IUPAC subcommittee (Atkinson et al. 2004) are by taking  $F_c = 0.6$ ,

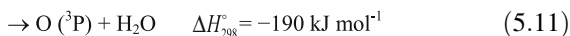
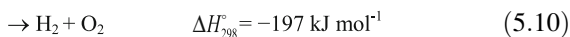
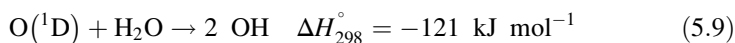
$$k_{0,5.5b}(T) = 1.3 \times 10^{-31} \left( \frac{T}{300} \right)^{-1.5} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} (200 - 400 \text{ K})$$

$$k_{\infty,5.5b}(T) = 2.3 \times 10^{-11} \left( \frac{T}{300} \right)^{-0.24} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (200 - 400 \text{ K}),$$

which are based on Burkholder and Ravishankara (2000), Hahn et al. (2000) and previous data.

### 5.1.4 O(<sup>1</sup>D) + H<sub>2</sub>O

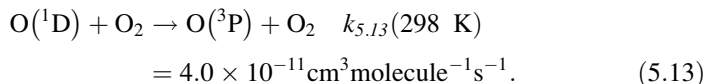
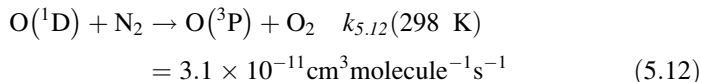
As for the reaction pathways of the reaction of O(<sup>1</sup>D) and H<sub>2</sub>O, other than the formation of OH, the formation of H<sub>2</sub>+O<sub>2</sub> and the deactivation (also called quenching) can also be conceived.



However, the reaction ratio of (5.10) and (5.11) has been reported to be 0.6 % (Glinski and Birks 1985), and 0.3 % (Carl 2005), respectively, and almost negligible against reaction (5.9).

The recent measurement of rate constant for the reaction O(<sup>1</sup>D) + H<sub>2</sub>O at 298 K by Dunlea and Ravishankara (2004b) agreed well with previous values, and the NASA/JPL panel evaluation No. 17 (Sander et al. 2011) recommends  $k_{5,9}(298 \text{ K}) = 2.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  based on these values. The IUPAC subcommittee report Vol. I (Atkinson et al. 2004) recommends temperature independent value of  $k_{5,9} = 2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 200–350 K, which agreed with the above value within 10 %. More recent measurements by Vranckx et al. (2010) for wider temperature range also agreed well with previous results.

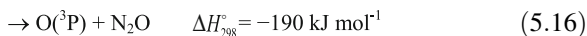
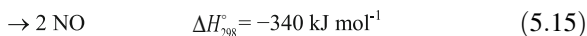
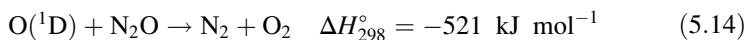
Thus, reaction (5.9) is the very fast reaction that is close to collision frequency with nearly zero activation energy. For this reason, this reaction can produce OH radicals under the condition with enough concentration of H<sub>2</sub>O in the troposphere competing well with the deactivation reactions (Sander et al. 2011),



The quantum chemical calculation of potential surface of the  $\text{O}({}^1\text{D}) + \text{H}_2\text{O}$  reaction has been conducted by Sayós et al. (2001). The lowest energy pathway for the main reaction channel to form  $\text{OH} + \text{OH}$  have no energy barrier agreeing with the experimental results.

### 5.1.5 $\text{O}({}^1\text{D}) + \text{N}_2\text{O}$

For the reaction of  $\text{O}({}^1\text{D})$  and  $\text{N}_2\text{O}$ , three pathways,



can be conceived. Although the formation ratio of  $\text{O}({}^3\text{P})$  by reaction (5.16) is  $<0.01$  and can be neglected in general (Vranckx et al. 2008a), the reaction pathways, (5.14) and (5.15), are known to be both important. In atmospheric chemistry, reaction (5.15) is important as the formation of reactive nitrogen (also called odd nitrogen) in the stratosphere, and the overall reaction rate constant combining reaction (5.14) and (5.15) is important for the estimation of atmospheric lifetime of  $\text{N}_2\text{O}$ .

Many measurements of rate constants of the reaction of  $\text{O}({}^1\text{D})$  and  $\text{N}_2\text{O}$  have been made mostly before 2000 (Blitz et al. 2004; Dunlea and Ravishankara 2004a; Carl 2005; Takahashi et al. 2005; Vranckx et al. 2008a), and the NASA/JPL panel evaluation No. 17 recommends  $k_{5.10}(298 \text{ K}) = 1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  based on these values (Sander et al. 2011). The recommended rate constant by the IUPAC subcommittee agrees well with this value. Similar to the reaction of  $\text{O}({}^1\text{D})$  and  $\text{H}_2\text{O}$ , this reaction also has nearly zero activation energy and there is no temperature dependence in the range of 200–350 K.

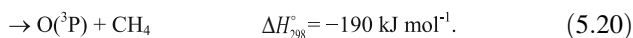
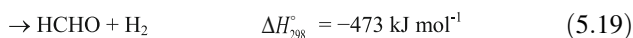
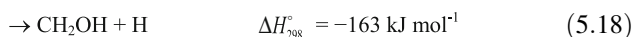
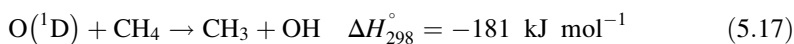
As for the ratio of reaction (5.15), it is recommended the value of  $k_{5.15}/k_{5.10} = 0.61$  based on Cantrell et al. (1994), and reaction rate constant for the NO formation reaction is  $k_{5.15} = 7.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Sander et al. 2011). Reaction (5.15) has a large exothermicity and it is known experimentally that the formed NO is in vibrationally and rotationally excited. Akagi et al. (1999) found from the experiments of  ${}^{18}\text{O}({}^1\text{D}) + \text{N}_2{}^{16}\text{O} \rightarrow \text{N}^{18}\text{O} + \text{N}^{16}\text{O}$  using the oxygen isotopes that the  $\text{N}^{16}\text{O}$  in the original  $\text{N}^{16}\text{O}$  molecule is formed mostly in  $v=0$ ,

1 without vibrational excitation and the newly formed N<sup>18</sup>O is produced in highly vibrationally excited levels in  $v=4-15$ . Further, Tokel et al. (2010) recently reported in the molecular beam experiment that the NO vibrational levels ( $v=0-9$ ) showed inverted population, which suggests that there are two reaction pathways, one gives the statistical distribution and another gives the inverted distribution.

Quantum chemical theoretical calculations for this reaction have been conducted by several groups. Takayanagi and Wada (2001) showed that the exothermic energy is mainly distributed in the vibrational energy of the newly formed NO and not in the NO in the original N<sub>2</sub>O, but the latter NO is not a complete spectator but a part of excess energy is also distributed in the old NO. This result of theoretical calculation agrees well with the above experimental results using the oxygen isotopes. According to the trajectory calculation on the potential energy surface by Takayanagi and Akagi (2002), the ratio of reactions (5.15) forming 2NO and (5.14) forming N<sub>2</sub> + O<sub>2</sub> is affected by the collision energy of O(<sup>1</sup>D) and approaching angle of O(<sup>1</sup>D) toward N – N – O.

### 5.1.6 O(<sup>1</sup>D) + CH<sub>4</sub>

The pathways of the reaction of O(<sup>1</sup>D) and CH<sub>4</sub> has been thought to be,



Overall reaction rate constant is recommended as  $k_{5.17-5.20}(298 \text{ K}) = 1.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  by the NASA/JPL panel evaluation No. 17 (Sander et al. 2011), and as  $k_{5.11-5.20}(298 \text{ K}) = 1.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with no temperature dependence for 200–350 K by the IUPAC subcommittee report Vol. II (Atkinson et al. 2006) based on experiments by Davidson et al. (1977), Blitz et al. (2004), Dillon et al. (2007), Vranckx et al. (2008b) et al. Similar to the reaction of O(<sup>1</sup>D) with H<sub>2</sub>O and N<sub>2</sub>O, this reaction is also a very fast reaction with nearly collisional frequency and near zero activation energy.

As for the ratio of reaction pathways of (5.17) (5.18) and (5.19), spectroscopic studies have been conducted using molecular beams (Casavecchia et al. 1980; Lin et al. 1999; Matsumi et al. 1993; Chen et al. 2005). The branching ratios and rate constants of each reaction pathway at 298 K are,

$$\begin{aligned} \frac{k_{5.17}}{k_{5.17-5.20}} &= 0.75 \pm 0.15, & k_{5.17} &= 1.31 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\ \frac{k_{5.18}}{k_{5.17-5.20}} &= 0.20 \pm 0.10, & k_{5.18} &= 1.35 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\ \frac{k_{5.19}}{k_{5.17-5.20}} &= 0.05 \pm 0.05, & k_{5.19} &= 0.09 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \end{aligned}$$

For reaction (5.18) it has been shown from a crossed molecular beam experiment that the main process is  $\text{CH}_2\text{OH} + \text{H}$ , and the process of  $\text{CH}_3\text{O} + \text{H}$  is not important (Lin et al. 1998). Also for the physical deactivation pathway (5.20), Wine and Ravishankara (1982) and Takahashi et al. (1996) reported that the ratio is less than a few%, while the recent high precision experiment of Vranckx et al. (2008b) by using the chemiluminescence method showed that it is  $0.2 \pm 0.3\%$  and that it is negligible as an atmospheric reaction.

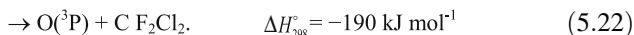
Regarding the reaction of oxygen atoms with  $\text{CH}_4$  and other alkanes, in contrast to that, the reactions of  $\text{O}({}^3\text{P})$  that is an H atom abstraction, the reactions of  $\text{O}({}^1\text{D})$  have been discussed to be mainly insertion to C-H bonds. Lin et al. (1999) showed from an angular distribution of products in the crossed molecular beam experiment, that H atom forming pathway (5.18) and  $\text{H}_2$  molecule forming pathway (5.19) both go through reaction intermediate  $\text{CH}_3\text{OH}^\ddagger$  with a rather long lifetime. Also, the relative distribution of vibrational levels of the OH radical formed in reaction (5.17) has been shown by LIF experiment to be 0.18, 0.29, 0.37, 0.15 and 0.01 for  $v = 0, 1, 2, 3$  and 4, respectively, and an inversion from the statistical distribution has been known for  $v = 0, 1$  and 2 (Cheskis et al. 1989). Furthermore, from the experiment of changing the collision energy of  $\text{O}({}^1\text{D})$  by González et al. (2000), it has been shown that the inversion of the vibrational levels of OH are observed reflecting the insertion reaction when the collision energy of less than  $57.8 \text{ kJ mol}^{-1}$  (0.6 eV), but the inversion is not seen for the higher collision energy. From the trajectory calculation on the potential surface it has also been shown that insertion is the main reaction when the collision energy is small and abstraction reaction increases as the collision energy increases, which agrees well with experimental evidence (Sayós et al. 2002). Theoretical calculation by Yu and Muckerman (2004) considering configuration interaction, give the ratios of pathways of (5.17) (5.18) and (5.19) to form OH, H and  $\text{H}_2$ , respectively, as 0.725, 0.186 and 0.025, respectively, reproducing well the experimental results, and also suggested that the reaction pathway,  $\text{CH}_2 + \text{H}_2\text{O}$  exists in the ratio of 0.064.

### 5.1.7 $\text{O}({}^1\text{D}) + \text{CFCs}$

The reactions of  $\text{O}({}^1\text{D})$  with CFCs (chlorofluorocarbons) and halons are known to have large rate constants in the order of  $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and could possibly affect the stratospheric lifetime of these ozone layer depleting substances. However, decomposition rates of CFCs and halons in the stratosphere are in general

determined mainly by photolysis rate, and the reaction with  $O(^1D)$  is almost negligible for  $CFCl_3$  (CFC – 11) and halons whose photolysis rates are high. However, as the photolysis rate decreases for such as  $CF_2Cl_2$  (CFC – 12),  $CF_3Cl$  (CFC – 13), the importance of  $O(^1D)$  reaction increases.

The pathways of the reactions of  $O(^1D)$  and CFCs can be conceived as ClO radical formation and physical deactivation. For example, for  $CCl_2F_2$  the following reaction pathways are known to be,



The measurements of rate constants for the reaction of  $O(^1D)$  with  $CFCl_3$  and  $CF_2Cl_2$  are made by Davidson et al. (1978) and Force and Wiesenfeld (1981), and with  $CF_3Cl$  by Ravishankara et al. (1993), which all showed no temperature dependence. Table 5.1 shows the recommended values by the NASA/JPL panel and the IUPAC subcommittee based on these experiments. The ratio for the production of ClO against quenching are obtained to be  $88 \pm 18$ ,  $87 \pm 18$  and  $85 \pm 18$  % for  $CFCl_3$ ,  $CF_2Cl_2$  and  $CF_3Cl$ , respectively, by Takahashi et al. (1996).

Although  $O(^1D)$  also reacts with halons to form BrO, FO is not formed from the reaction with CFC and PFCs (perfluoro carbons).

## 5.2 Reactions of OH Radicals

OH radicals react with almost all trace molecules in the atmospheric excluding  $CO_2$ ,  $N_2O$ , CFC, etc., and drives atmospheric photochemical reaction system while the atmospheric lifetime of most of chemical species are determined by the reaction rate with OH, so that OH is the most important reactive species in the troposphere. In this sense, the rate constants of atmospheric molecules and OH are of unequivocal importance. In the stratosphere, inorganic reactions of OH in the  $HO_x$  cycle and in the cross chain reactions with  $NO_x$  and  $ClO_x$  cycles are also important. The OH reaction rate constants and their temperature dependence with almost all molecules of atmospheric interest have been measured in laboratory.

In this section, among the numerous atmospheric OH reactions, those with interest as elementary reactions are selected and explained. Table 5.2 gives the rate constants and their temperature dependence of particular importance in the atmosphere are excerpted from the recommendation by the IUPAC subcommittee (Atkinson et al. 2004, 2006) and the NASA/JPL panel (Sander et al. 2011). The equilibrium constants of typical reversible reactions in the atmosphere are shown in Table 5.3.

Table 5.2 Rate constants at 298 K and Arrhenius parameters for the reactions of OH radicals

Reactions	$k(298\text{ K})$ ( $\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ )	A Factor ( $\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ )	$E_d/R$ (K)	Ref.
$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	$7.3 \times 10^{-14}$	$1.7 \times 10^{-12}$	940	(a1)
$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	$1.1 \times 10^{-10}$	$4.8 \times 10^{-11}$	-250	(a1)
$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	$1.7 \times 10^{-12}$	$2.9 \times 10^{-12}$	160	(a1)
$\text{OH} + \text{CO} \rightarrow$ overall	$2.3 \times 10^{-13}$ (1 atm)	$1.4 \times 10^{-13}$ ( $1 + [\text{N}_2]/4.2 \times 10^{19}$ )		(a2)
$\rightarrow \text{H} + \text{CO}_2$	$1.5 \times 10^{-13}$	$1.5 \times 10^{-13}$ ( $T/300$ ) <sup>0.6</sup> ( $k_0$ )		(b)
$+ \text{M} \rightarrow \text{HOCO} + \text{M}$		$5.9 \times 10^{-33}$ ( $T/300$ ) <sup>-1.4</sup> [ $\text{N}_2$ ] ( $k_0$ )		(b)
		$1.1 \times 10^{-12}$ ( $T/300$ ) <sup>1.3</sup> ( $k_\infty$ )		
$\text{OH} + \text{NO} + \text{M} \rightarrow \text{HONO} + \text{M}$	$7.4 \times 10^{-31}$ [ $\text{N}_2$ ] ( $k_0$ )	$7.4 \times 10^{-31}$ ( $T/300$ ) <sup>-2.4</sup> [ $\text{N}_2$ ] ( $k_0$ )		(a1)
	$3.3 \times 10^{-11}$ ( $k_\infty$ )	$3.3 \times 10^{-11}$ ( $T/300$ ) <sup>0.3</sup> ( $k_\infty$ )		
$\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HOOH} + \text{M}$	$1.2 \times 10^{-11}$ (1 atm)	$1.8 \times 10^{-30}$ ( $T/300$ ) <sup>-3.0</sup> [ $\text{M}$ ] ( $k_0$ )		(b)
$\rightarrow \text{HOONO} + \text{M}$		$2.8 \times 10^{-11}$ ( $T/300$ ) <sup>0</sup> ( $k_\infty$ )		
	$1.2 \times 10^{-12}$ (1 atm)	$9.1 \times 10^{-32}$ ( $T/300$ ) <sup>-3.9</sup> [ $\text{M}$ ] ( $k_0$ )		(b)
		$4.2 \times 10^{-11}$ ( $T/300$ ) <sup>-0.5</sup> ( $k_\infty$ )		
$\text{OH} + \text{HONO} \rightarrow \text{H}_2\text{O} + \text{NO}_2$	$6.0 \times 10^{-12}$	$2.5 \times 10^{-12}$	-260	(a1)
$\text{OH} + \text{HONO}_2 \rightarrow \text{H}_2\text{O} + \text{NO}_3$	$1.5 \times 10^{-13}$ (1 atm)	$2.4 \times 10^{-14}$	-460	(a1) (b)
$\text{OH} + \text{HO}_2\text{NO}_2 \rightarrow$ products	$4.6 \times 10^{-12}$	$1.3 \times 10^{-12}$	-380	(b)
$\text{OH} + \text{NH}_3 \rightarrow \text{H}_2\text{O} + \text{NH}_2$	$1.6 \times 10^{-13}$	$1.7 \times 10^{-12}$	710	(b)
$\text{OH} + \text{SO}_2 + \text{M} \rightarrow \text{HOSO}_2 + \text{M}$	$1.1 \times 10^{-12}$ (1 atm)	$4.5 \times 10^{-31}$ ( $T/300$ ) <sup>-3.9</sup> [ $\text{N}_2$ ] ( $k_0$ )		(a1)
		$1.3 \times 10^{-12}$ ( $T/300$ ) <sup>0.7</sup> ( $k_\infty$ )		
$\text{OH} + \text{OCS} \rightarrow$ products	$2.0 \times 10^{-15}$	$1.1 \times 10^{-13}$	1200	(a1)
$\text{OH} + \text{CS}_2 + \text{M} \rightarrow \text{HOCS}_2 + \text{M}$	$1.2 \times 10^{-12}$ (1 atm)	$4.9 \times 10^{-31}$ ( $T/300$ ) <sup>-3.5</sup> [ $\text{N}_2$ ] ( $k_0$ )		(b)
		$1.4 \times 10^{-11}$ ( $T/300$ ) <sup>-1</sup> ( $k_\infty$ )		
$\text{OH} + \text{H}_2\text{S} \rightarrow \text{SH} + \text{H}_2\text{O}$	$4.7 \times 10^{-12}$	$6.1 \times 10^{-12}$	80	(b)

OH + CH <sub>3</sub> SH → CH <sub>3</sub> S + H <sub>2</sub> O	$3.3 \times 10^{-11}$	$9.9 \times 10^{-12}$	-360	(b)
OH + CH <sub>3</sub> SCH <sub>3</sub> → CH <sub>3</sub> SCH <sub>2</sub> + H <sub>2</sub> O	$3.1 \times 10^{-11}$	$1.2 \times 10^{-11}$	280	(b)
OH + CH <sub>3</sub> SCH <sub>3</sub> + M → (CH <sub>3</sub> ) <sub>2</sub> SOH + M	$5.7 \times 10^{-12}$ (1 atm)	$2.9 \times 10^{-31} (T/300)^{-6.2} [M] (k_0)$		(a1) (b)
OH + CH <sub>3</sub> SSCH <sub>3</sub> → products	$2.3 \times 10^{-10}$	$6.0 \times 10^{-11}$	-400	(b)
OH + CH <sub>4</sub> → CH <sub>3</sub> + H <sub>2</sub> O	$6.4 \times 10^{-15}$	$1.9 \times 10^{-12}$	1690	(a2)
OH + C <sub>2</sub> H <sub>6</sub> → C <sub>2</sub> H <sub>5</sub> + H <sub>2</sub> O	$2.4 \times 10^{-13}$	$6.9 \times 10^{-12}$	1000	(a2)
OH + C <sub>3</sub> H <sub>8</sub> → C <sub>3</sub> H <sub>7</sub> + H <sub>2</sub> O	$1.1 \times 10^{-12}$	$7.6 \times 10^{-12}$	590	(a2)
OH + C <sub>2</sub> H <sub>4</sub> + M → HOCH <sub>2</sub> CH <sub>2</sub> + M	$7.9 \times 10^{-12}$ (1 atm)	$8.6 \times 10^{-29} (T/300)^{-3.1} [N_2] (k_0)$		(a2)
		$9.0 \times 10^{-12} (T/300)^{-0.85} (k_{\infty})$		
OH + C <sub>3</sub> H <sub>6</sub> + M → HOC <sub>3</sub> H <sub>6</sub> + M	$2.9 \times 10^{-11}$ (1 atm)	$8 \times 10^{-27} (T/300)^{-3.5} [N_2] (k_0)$		(a2)
		$3.0 \times 10^{-11} (T/300)^{-1} (k_{\infty})$		
OH + C <sub>5</sub> H <sub>8</sub> (isoprene) → products	$1.0 \times 10^{-10}$	$3.1 \times 10^{-11}$	-350	(b)
OH + C <sub>10</sub> H <sub>16</sub> (α-pinene) → products	$5.3 \times 10^{-11}$	$1.2 \times 10^{-11}$	-440	(a2)
OH + C <sub>2</sub> H <sub>2</sub> + M → HOCHCH + M	$7.8 \times 10^{-13}$ (1 atm)	$5.5 \times 10^{-30} (T/300)^0 [N_2] (k_0)$		(a2) (b)
		$8.3 \times 10^{-13} (T/300)^2 (k_{\infty})$		
OH + HCHO → H <sub>2</sub> O + HCO	$8.5 \times 10^{-12}$	$5.4 \times 10^{-12}$	-140	(a2)
OH + CH <sub>3</sub> CHO → H <sub>2</sub> O + CH <sub>3</sub> CO	$1.5 \times 10^{-11}$	$4.4 \times 10^{-12}$	-370	(a2)
OH + (CHO) <sub>2</sub> → H <sub>2</sub> O + CH(O)CO	$1.1 \times 10^{-11}$	-	-	(a2)
OH + CH <sub>3</sub> C(O)CH <sub>3</sub> → H <sub>2</sub> O + CH <sub>2</sub> C(O)CH <sub>3</sub>	$1.8 \times 10^{-13}$	$8.8 \times 10^{-12}$	1320	(a2)
OH + CH <sub>3</sub> OH → products	$9.0 \times 10^{-13}$	$2.9 \times 10^{-12}$	350	(a2)
OH + CH <sub>3</sub> OOH → products	$5.5 \times 10^{-12}$	$2.9 \times 10^{-12}$	-190	(a2)
OH + HC(O)OH → products	$4.5 \times 10^{-13}$	$4.5 \times 10^{-13}$	0	(a2)
OH + CH <sub>3</sub> ONO <sub>2</sub> → products	$2.3 \times 10^{-14}$	$4.0 \times 10^{-13}$	850	(a2)
OH + HCl → H <sub>2</sub> O + Cl	$7.8 \times 10^{-13}$	$1.8 \times 10^{-12}$	250	(b)
OH + CH <sub>3</sub> Cl → H <sub>2</sub> O + CH <sub>2</sub> Cl	$3.6 \times 10^{-14}$	$2.4 \times 10^{-12}$	1250	(b)
OH + CH <sub>3</sub> CCl <sub>3</sub> → H <sub>2</sub> O + CH <sub>2</sub> CCl <sub>3</sub>	$1.0 \times 10^{-14}$	$1.6 \times 10^{-12}$	1520	(b)

(continued)



Table 5.2 (continued)

Reactions	$k(298\text{ K})$ ( $\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ )	A Factor ( $\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ )	$E_d/R$ (K)	Ref.
$\text{OH} + \text{CHF}_2\text{Cl} \rightarrow \text{H}_2\text{O} + \text{CF}_2\text{Cl}$	$4.8 \times 10^{-15}$	$1.1 \times 10^{-12}$	1600	(b)
$\text{OH} + \text{HBr} \rightarrow \text{H}_2\text{O} + \text{Br}$	$1.1 \times 10^{-11}$	$5.5 \times 10^{-12}$	-200	(b)
$\text{OH} + \text{CH}_3\text{Br} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{Br}$	$3.0 \times 10^{-14}$	$2.4 \times 10^{-12}$	1300	(b)
$\text{OH} + \text{HI} \rightarrow \text{H}_2\text{O} + \text{I}$	$7.0 \times 10^{-11}$	$1.6 \times 10^{-11}$	-440	(a,3)
$\text{OH} + \text{CH}_3\text{I} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{I}$	$7.2 \times 10^{-14}$	$2.9 \times 10^{-12}$	1100	(b)

(a1, a2, a3) IUPAC subcommittee report Vol. I, II, III (Atkinson et al. 2004, 2006, 2007), respectively

(b) NASA/JPL panel evaluation No. 17 (Sander et al. 2011)

**Table 5.3** Equilibrium constants at 298 K and temperature dependence parameters for reversible reactions

Reactions	$K_{\text{eq}}$ (298 K) ( $\text{cm}^3 \text{ molecule}^{-1}$ )	A ( $\text{cm}^3 \text{ molecule}^{-1}$ )	B ( $^{\circ}\text{K}$ )
$\text{HO} + \text{NO}_2 \rightleftharpoons \text{HOONO}$	$2.2 \times 10^{-12}$	$3.5 \times 10^{-27}$	10140
$\text{HO}_2 + \text{NO}_2 \rightleftharpoons \text{HO}_2\text{NO}_2$	$1.6 \times 10^{-11}$	$2.1 \times 10^{-27}$	10900
$\text{HO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HO}_2 \cdot \text{H}_2\text{O}$	$5.2 \times 10^{-19}$	$2.4 \times 10^{-25}$	4350
$\text{NO}_2 + \text{NO}_3 \rightleftharpoons \text{N}_2\text{O}_5$	$2.9 \times 10^{-11}$	$2.7 \times 10^{-27}$	11000
$\text{CH}_3\text{O}_2 + \text{NO}_2 \rightleftharpoons \text{CH}_3\text{O}_2\text{NO}_2$	$2.2 \times 10^{-12}$	$9.5 \times 10^{-29}$	11230
$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2 \rightleftharpoons \text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$	$2.3 \times 10^{-8}$	$9.0 \times 10^{-29}$	14000
$\text{OH} + \text{CS}_2 \rightleftharpoons \text{CS}_2\text{OH}$	$1.4 \times 10^{-17}$	$4.5 \times 10^{-25}$	5140
$\text{CH}_3\text{S} + \text{O}_2 \rightleftharpoons \text{CH}_3\text{SOO}$	$2.2 \times 10^{-19}$	$1.8 \times 10^{-25}$	5550
$\text{Cl} + \text{O}_2 \rightleftharpoons \text{ClOO}$	$2.9 \times 10^{-21}$	$6.6 \times 10^{-25}$	2500
$\text{ClO} + \text{ClO} \rightleftharpoons \text{Cl}_2\text{O}_2$	$6.9 \times 10^{-15}$	$1.7 \times 10^{-27}$	8650

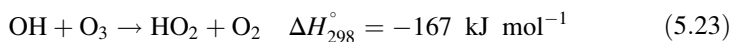
$K_{\text{eq}}(T) (\text{cm}^3 \text{ molecule}^{-1}) = A \exp(B/T) (200 < T < 300 \text{ K})$

Source: NASA/JPL panel evaluation No.17 (Sander et al. 2011)

### 5.2.1 OH + O<sub>3</sub>

The reaction of OH radicals and O<sub>3</sub> is an important reaction that converts OH to HO<sub>2</sub> in the HO<sub>x</sub> cycle of the ozone dissipating chain process in the lower stratosphere (Sect. 8.2.1). In the troposphere, HO<sub>2</sub> is reproduced via the OH + CO reaction even in the clean atmosphere, the contribution of OH + O<sub>3</sub> reaction for the reproduction of HO<sub>2</sub> is small.

The reaction of OH with O<sub>3</sub> proceeds,



to form a HO<sub>2</sub> radical. The IUPAC subcommittee (Atkinson et al. 2004) recommends the rate constants of this reaction at 298 K as  $k_{5,23}(298 \text{ K}) = 7.3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and the temperature dependence as,

$$k_{5,23}(T) = 1.7 \times 10^{-12} \exp\left(-\frac{940}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

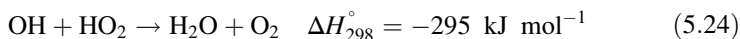
based on Ravishankara et al. (1979), Nickolaisen et al. (2000), etc. Thus, the reaction of OH and O<sub>3</sub> has the activation energy, 7.8 kJ mol<sup>-1</sup>, and is not very fast at near room temperature.

Meanwhile, according to quantum chemical calculations, this reaction has one or two transition states depending on the level of calculation, and the calculated activation barrier is larger than experimental values (Peiró-García and Nebot-Gil, 2003a) so that further theoretical study is needed.

### 5.2.2 $OH + HO_2$

The reaction of HO and HO<sub>2</sub> forms stable molecules from two radicals acting as a termination reaction of the HO<sub>x</sub> cycle in the middle to upper stratosphere, which is important as affecting the efficiency of the ozone destruction process (Sect. 8.2.1).

The reaction of OH and O<sub>3</sub> proceeds as,



to form H<sub>2</sub>O and O<sub>2</sub>. The measurement of this reaction rate had been difficult experimentally, and previously measured values had large uncertainty. Keyser (1988) identified that the cause of the uncertainty is due to side reactions by H and O atoms formed secondarily, and reported more accurate values by the using chemical model analysis. The recommended value at 298 K by the IUPAC subcommittee is  $k_{5.24}(298 \text{ K}) = 1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson et al. 2004). Thus, it is a very fast radical-radical reaction. The temperature dependence is recommended in the Arrhenius equation,

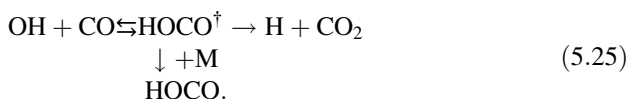
$$k_{5.14}(T) = 4.8 \times 10^{-11} \exp\left(\frac{250}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with a small negative activation energy (Atkinson et al. 2004). It has also been confirmed that there is no pressure dependence in the range of 1–1000 torr (Keyser 1988).

This reaction has been concerned from the perspective of combustion chemistry and rate constants at high temperature have been measured. Anomalous temperature dependence, decrease of rate constant at 1100 K, has been reported by Hippler et al. (1995), and the possibility of existence of intermediate complex has been suggested.

### 5.2.3 $OH + CO$

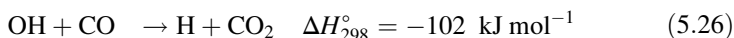
The reaction of OH and CO is important for OH radical as the main reaction in the clean troposphere (Sect. 7.1), and for CO to determine its atmospheric lifetime. There are many studies on the rate constants of this reaction, and it has been revealed that the reaction proceeds via a process,



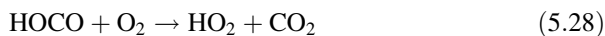
The reaction scheme involving the intermediate HOCO has been proposed from the experimental evidence that the rate constants of OH + CO reaction increase with

pressure (Smith 1977). Later, HOCO has been detected directly by infrared absorption (Petty et al. 1993), and photoionization spectrometer (Miyoshi et al. 1994), and confirmed theoretically as described below.

According to the above scheme, the rate constants of OH + CO reaction can be described by the following two processes,



The HOCO formed in reaction (5.27) reacts with O<sub>2</sub>,



with a rate constant,  $\sim 1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Miyoshi et al. 1994). The H atom formed in the reaction (5.26) reacts exclusively with O<sub>2</sub> under the atmospheric conditions and also gives HO<sub>2</sub>. Thus, the products of OH + CO can be thought as HO<sub>2</sub> + CO<sub>2</sub> in the atmosphere regardless either of pathway, (5.26) or (5.27) is taken.

Recent measurements of the reaction rate constants following the above scheme have been conducted by Golden et al. (1998), McCabe et al. (2001), etc., and the data including these studies have been compiled by the NASA/JPL evaluation No. 17 (Sander et al. 2011). At the low-pressure limit, the reaction proceeds via the path (5.26), and the bimolecular reaction rate constant is recommended as,

$$k_{5.26}(T) = 1.5 \times 10^{-13} \left( \frac{T}{300} \right)^{0.6} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

and the temperature dependence is small. On the other hand, reaction (5.27) is a termolecular reaction and Eq. (5.7) is applied for the temperature and pressure dependences of the rate constant. The recommended low-pressure and high-pressure limit values with  $F_c = 0.6$  (Sander et al. 2011) are,

$$k_{0,5.27}(T) = 5.9 \times 10^{-33} \left( \frac{T}{300} \right)^{-1.4} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

$$k_{\infty,5.27}(T) = 1.1 \times 10^{-12} \left( \frac{T}{300} \right)^{-1.3} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Under the atmospheric conditions, reaction (5.27) is in the intermediate region between the low-pressure and high-pressure limit, and the pressure dependence has to be calculated by using Eq. (5.7). The IUPAC subcommittee report Vol. II proposed the approximate equation for the overall rate constants combining reaction (5.26) and (5.27),

$$k_{5.26-5.27} = 1.44 \times 10^{-33} \left( 1 + \frac{[N_2]}{4.2 \times 10^{19}} \right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

for the pressure range of 0–1 atm (N<sub>2</sub>), and temperature range 200–300 K where the temperature dependence is small (Atkinson et al. 2006). From these results, the rate

constant at 298 K and 1 atm is obtained as  $k_{5.26-5.27}$  (298 K, 1 atm)  $\approx 2.4 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

This reaction has attracted interest from a theoretical point of view as a four-centered reaction model involving three heavy atoms, and many studies have been conducted. The calculations of the potential energy surface of the association reaction of OH+CO have been conducted by several groups (Yu et al. 2001; Zhu et al. 2001; Valero et al. 2004), and the reaction of OH+CO is thought to initially form trans-HOCO, and it decomposes into H+CO<sub>2</sub> after trans- to cis- isomerization. Theoretical calculations of the reaction rate constants have been performed using such potential surface (Valero et al. 2004; Medvedev et al. 2004), and unimolecular decomposition theory (see Sect. 2.3.2) applying to HOCO<sup>†</sup> (Trope 1998; Zhu et al. 2001; Senosiain et al. 2003; Chen and Marcus 2005; Joshi and Wang 2006). Other than atmospheric chemistry, the reaction of OH+CO is also important in combustion chemistry, so that studies have been conducted in wide temperature range in 80–2800 K. The temperature dependence of the obtained bimolecular rate constant is known to show large deviation from the Arrhenius plot between, below and above 500 K. Although the temperature dependence is very small below 300 K as noted above, the temperature dependence, pressure dependence, and isotope effects cannot be reproduced well with recent theoretical studies, and the discussion is still going on the energy height of the transition states (TS<sub>1</sub>, TS<sub>2</sub>) of decomposition pathways of HOCO and the existence of the tunneling effect.

### 5.2.4 OH + NO<sub>2</sub> + M

The recombination reaction of OH radical and NO<sub>2</sub> is the most important as HO<sub>x</sub> chain termination reaction in the troposphere (Sect. 7.3.2). The reaction of OH + NO<sub>2</sub> used to be described as a termolecular reaction forming nitric acid (HONO<sub>2</sub>) (although nitric acid is usually written as HNO<sub>3</sub>, it is written as HONO<sub>2</sub> in this chapter for helping to understand the reaction path more easily). However, in the measurements of reaction rate constant of this reaction using pulse photolysis, the time profile of HO shows double exponential decay, and the pathway to form HOONO (peroxynitrous acid) in addition to HONO<sub>2</sub> has been suggested (Burkholder et al. 1987; Hippler et al. 2002), and Golden and Smith (2000) proposed the importance of this reaction pathway.

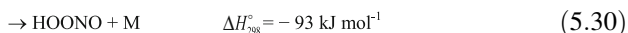
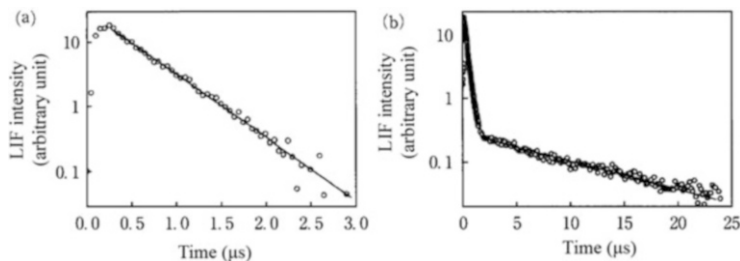


Figure 5.1 shows an example of time profile of OH signal intensity in the reaction of OH+NO<sub>2</sub> by Hippler et al. (2002). As shown in Fig. 5.1, the OH decay is single exponential at 300 K, but shows apparent double exponential at 340 K suggesting



**Fig. 5.1** Decay curves of OH signals in the experiments of OH + NO<sub>2</sub> reaction (a) 300 K, (b) 430 K (Adapted from Hippler et al. 2002)

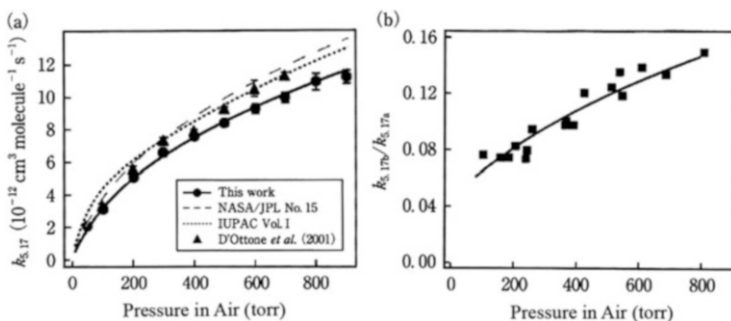
the existence of the equilibrium reaction, OH + NO<sub>2</sub>  $\rightleftharpoons$  HOONO experimentally. The existence of reaction (5.30) confirmed by such experimental evidence and theoretical consideration implies that the rate constant used for OH + NO<sub>2</sub> for a long time was supposed to be overestimation as a rate of reaction (5.29), which may affect model calculation of ozone formation, etc. (Golden and Smith 2000). The spectroscopic detection of HOONO has been reported by using infrared spectroscopy (Nizkorodov and Wennberg 2002; Pollack et al. 2003), and cavity ring-down spectroscopy (Bean et al. 2003).

The NASA/JPL panel evaluation No. 17 (Sander et al. 2011) recommends the low-pressure and high-pressure limit rate constants of reaction (5.29) and (5.30) as,

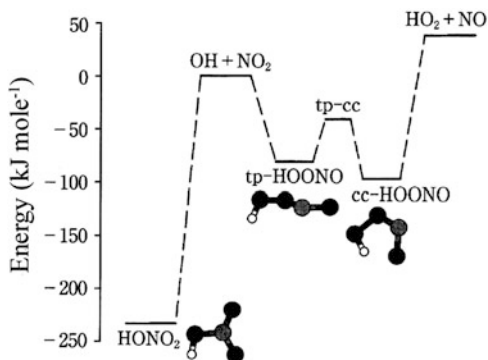
$$\begin{aligned}
 k_{0,5.29}(T) &= 1.8 \times 10^{-30} \left(\frac{T}{300}\right)^{-3.0} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \\
 k_{\infty,5.29}(T) &= 2.8 \times 10^{-11} \left(\frac{T}{300}\right)^0 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\
 k_{0,5.30}(T) &= 9.1 \times 10^{-32} \left(\frac{T}{300}\right)^{-3.9} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \\
 k_{\infty,5.30}(T) &= 4.2 \times 10^{-11} \left(\frac{T}{300}\right)^{-0.5} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},
 \end{aligned}$$

based on studies by Brown et al. (1999), D’Ottone et al. (2001), Hippler et al. (2002) and others. The formation rate constant of HONO<sub>2</sub> at 298 K, and 1 atm using the recommended value is  $k_{5.29} = 1.1 \times 10^{-11} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ , and the formation ratio of HOONO is 5 – 15 %.

Recently, Mollner et al. (2010) reported more accurate values of overall rate constant of  $k_{5.29} + k_{5.30}$  at 20–900 torr by high sensitivity LIF, and branching ratio of reaction (5.29) and (5.30) by detecting HONO<sub>2</sub> and HOONO individually using cavity ring-down spectroscopy. From these results, there is some difference in the efficiency of N<sub>2</sub> and O<sub>2</sub> as a third body M, and the collisional efficiency of air is 94 % of N<sub>2</sub>. The rate constants of reaction (5.29) and (5.30) at 298 K in air are reported as  $k_{0,5.29} = 1.51 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ ,  $k_{\infty,5.29} = 1.84 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_{0,5.30} = 6.2 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ , and  $k_{\infty,5.30} = 8.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . According to these results, formation rate constant of HONO<sub>2</sub> under atmospheric pressure is  $k_{5.29} = 9.2 (\pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and the branching ratio of the formation of HOONO is  $k_{\infty,5.30}/k_{\infty,5.29} = 0.142 (\pm 0.012)$ . The HONO<sub>2</sub> formation rate constant obtained here is 14 %



**Fig. 5.2** Pressure dependence of the rate constants for the reaction of OH + NO<sub>2</sub>: (a)  $k_{17}(\text{OH} + \text{NO}_2)$ ; (b)  $k_{17a}/k_{17b}$  (Adapted from Mollner et al. 2010)



**Fig. 5.3** Schematic diagram of potential energy surface for the reaction of OH + NO<sub>2</sub> (Adapted from Pollack et al. 2003)

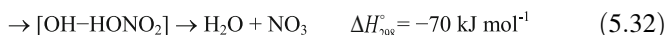
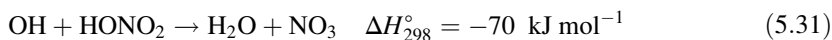
lower than the recommended value of the NASA/JPL evaluation No. 17 (Sander et al. 2011). Figure 5.2 shows the pressure dependence of the rate constants,  $k(\text{OH} + \text{NO}_2)$ ,  $k_{5,29}$ , and the branching ratio  $k_{5,30}/k_{5,29}$ .

Figure 5.3 depicts potential energy surface of OH + NO<sub>2</sub> reaction obtained by quantum chemical calculation (Pollack et al. 2003). Reaction rate constants calculated by RRKM calculation using the electronic structure of the transition state has been compared with the observed values (Sumathi and Peyerimhoff 1997; Chakraborty et al. 1998), and Golden et al. (2003) reported that recently calculated rate constants reproduced well the temperature and pressure dependence obtained by experiments. It has not been elucidated yet, however, if the reaction intermediate HOONO isomerizes to HONO<sub>2</sub> or it regenerates more reactive chemical species by photolysis or reaction with other reactive species in the atmosphere, which would affect the ozone formation efficiency in the troposphere.

### 5.2.5 OH + HONO<sub>2</sub> (HNO<sub>3</sub>)

The reaction of OH radical with nitric acid (HONO<sub>2</sub>, HNO<sub>3</sub>) in the stratosphere is important as it reproduces active nitrogen from the reservoir molecule HONO<sub>2</sub> in the NO<sub>x</sub> cycle. Although in the troposphere, water-soluble nitric acid is mainly removed by wet deposition into cloud and fog, and dry deposition on earth's surface, the OH reaction as well as photolysis are also important as removal processes and as active nitrogen regenerating process in the upper troposphere where clouds are not abundant.

It has been known experimentally that the rate constants of the OH and HONO<sub>2</sub> reaction show pressure dependence and negative temperature dependence deviating largely from Arrhenius plot (Margitan and Watson 1982; Smith et al. 1984; Devolder et al. 1984; Stachnik et al. 1986; Brown et al. 1999). From this experimental evidence, it has been suggested that the reaction proceeds through two paths, one through a reaction intermediate OH – HONO<sub>2</sub>, and another by a direct reaction (Smith et al. 1984; Brown et al. 1999).



The existence of OH – HONO<sub>2</sub> has been confirmed theoretically as a six-membered ring molecule (Xia and Lin 2001), and experimentally by direct detection with infrared spectroscopy (O'Donnell et al. 2008). The pathways of reaction (5.32) can be expressed as,

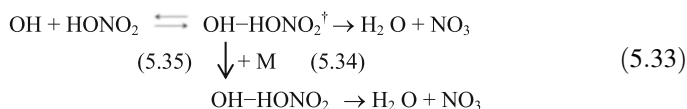
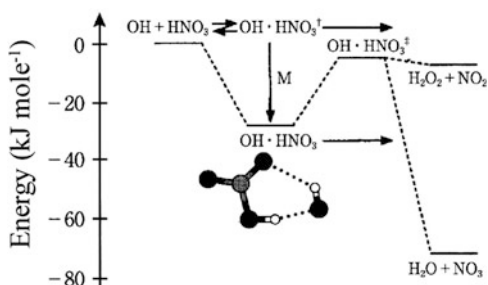


Figure 5.4 shows the energy scheme of the reaction (Brown et al. 1999).

From these considerations, the overall reaction rate constants of the OH + HONO<sub>2</sub> can be expressed by the sum of pressure-independent  $k_{5.31}$  and pressure-dependent  $k_{5.32}$  described by the Lindeman mechanism formula,

**Fig. 5.4** Schematic diagram of potential energy surface for the reaction of OH + HONO<sub>2</sub> (Adapted from Brown et al. 1999)





$$k_{5.33} = k_{5.31}(T) + k_{5.32}([M], T) \quad (5.36)$$

$$k_{5.32}(M, T) = \frac{k_{5.35}[M]}{1 + \frac{k_{5.35}[M]}{k_{5.34}}} \quad (5.37)$$

Recommended values by the NASA/JPL panel evaluation No. 17 (Sander et al. 2011) for rate parameters are,

$$\begin{aligned} k_{5.31}(T) &= 2.4 \times 10^{-14} \exp\left(\frac{460}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \\ k_{5.34}(T) &= 2.7 \times 10^{-17} \exp\left(\frac{2199}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \\ k_{5.35}(T) &= 6.5 \times 10^{-34} \exp\left(\frac{1335}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}, \end{aligned}$$

and the same values are adopted by the IUPAC subcommittee report (Atkinson et al. 2004). Since the same products are given by either of the reaction path (5.31) and (5.32), the reaction yield of  $\text{NO}_3$  is unity. From the above reaction rate parameters, it can be seen that the pathway via  $\text{OH} - \text{HONO}_2$  gets more important as the temperature goes down.

### 5.2.6 $\text{OH} + \text{SO}_2 + \text{M}$

The main atmospheric reactions of  $\text{SO}_2$  are homogenous gas phase oxidation reaction by OH radicals and liquid phase oxidation reaction by  $\text{H}_2\text{O}_2$  and  $\text{O}_3$  in water droplets of cloud and fog. In this paragraph, the reaction with OH is described an important homogeneous gas phase reaction.

The reaction of OH and  $\text{SO}_2$  is the termolecular reaction expressed by,



As for the rate constant of reaction (5.38), the low-pressure and high-pressure limit equations given by Wine et al. (1984) adopting  $F_c = 0.525$ ,

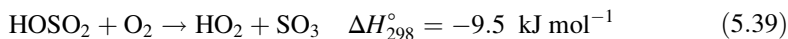
$$\begin{aligned} k_{0,5.22}(T) &= 4.5 \times 10^{-31} [\text{N}_2] \left(\frac{T}{300}\right)^{-3.9} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \\ k_{\infty,5.22}(T) &= 1.3 \times 10^{-12} \left(\frac{T}{300}\right)^{-0.7} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \end{aligned}$$

are recommended by the IUPAC subcommittee (Atkinson et al. 2004). The value at 298 K and 1 atm is  $\sim 1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which is nearly one order of magnitude smaller than the rate constant for the reaction of  $\text{NO}_2$  by OH.

Quantum chemical calculations for the pathways of reaction (5.38) and the product  $\text{HOSO}_2$  have been conducted by Li and McKee (1997), Somnitz (2004)

and others. The exact thermochemical values for the HOSO<sub>2</sub> radical was not obtained experimentally, Klopper et al. (2008) recently reported the heat of formation as  $\Delta H_{f,0}^{\circ}(\text{HOSO}_2) = -366.6 \pm 2.5$  and  $\Delta H_{f,298}^{\circ}(\text{HOSO}_2) = -374.1 \pm 3.0$  kJ mol<sup>-1</sup>.

The HOSO<sub>2</sub> radicals formed in the reaction of OH and SO<sub>2</sub> are thought to react with O<sub>2</sub> in the atmosphere,

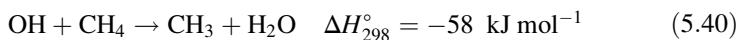


to form HO<sub>2</sub> and SO<sub>3</sub>. The enthalpy of the reaction was obtained from the above value of heat of formation as  $\Delta H_{f,0}^{\circ} = -8.5 \pm 3.0$ ,  $\Delta H_{f,298}^{\circ} = -9.5 \pm 3.0$  kJ mol<sup>-1</sup>. Experimentally, HOSO<sub>2</sub> has been detected in the gas phase (Egsgaard and Carlsen 1988) and in the low temperature matrix (Hashimoto et al. 1984; Kuo et al. 1991).

### 5.2.7 OH + CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>

Although the OH radicals react with all alkanes, methane (CH<sub>4</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), and propane (C<sub>3</sub>H<sub>8</sub>) are picked up here as typical alkanes. Since the atmospheric lifetimes of alkanes are determined by the reaction rates with OH, for example the accurate rate constant of OH + CH<sub>4</sub> is important for the evaluation of global warming.

The reactions of OH with alkanes are H-atom abstraction such as,



Many measurements OH and CH<sub>4</sub> reaction have been reported within the temperature range of 200–420 K, and the IUPAC subcommittee report Vol. II (Atkinson et al. 2006) cited the value at 298 K,  $k_{5,40}(298 \text{ K}) = 6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and the temperature dependence as,

$$k_{5,40}(T) = 1.85 \times 10^{-12} \exp\left(-\frac{1690}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

The NASA/JPL panel evaluation No. 17 (Sander et al. 2011) recommends more detailed formula with three parameters,

$$k_{5.40}(T) = 2.80 \times 10^{-14} T^{0.667} \exp\left(-\frac{1575}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

for applying to model calculation in the lower and upper troposphere. Recent values of the rate constant of the OH and CH<sub>4</sub> reaction reported by Gierczak et al. (1997) and Bonard et al. (2002) agree with previous values.

Similarly, many studies on measurements for rate constants of the reaction of OH with C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> has been reported, and the recommended values by the IUPAC subcommittee report Vol. II (Atkinson et al. 2006) based on these are  $k_{5.41} = 2.4 \times 10^{-13}$ ,  $k_{5.42+5.53} = 1.1 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  at 298 K and the temperature dependences are,

$$k_{5.41}(T) = 6.9 \times 10^{-12} \exp\left(-\frac{1000}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

$$k_{5.42+5.43}(T) = 7.6 \times 10^{-12} \exp\left(-\frac{585}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}.$$

Comparing at 298 K, the rate constants for C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> are by one and two orders of magnitude larger than for CH<sub>4</sub>, respectively. The difference is found to be due to the difference in the activation energy of each reaction.

For the reaction of alkanes of >C<sub>3</sub>, hydrogen atom abstraction by OH can occur either from the primary (one adjacent carbon atom), secondary (two adjacent carbon atoms), and tertiary (three adjacent carbon atoms) carbon atom. In case of C<sub>3</sub>H<sub>8</sub>, the temperature dependence for the two reaction paths (5.42) and (5.43) are given by Droege and Tully (1986) as,

$$k_{5.42}(T) = 6.3 \times 10^{-12} \exp\left(-\frac{1050}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

$$k_{5.43}(T) = 6.3 \times 10^{-12} \exp\left(-\frac{580}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1},$$

and the ratio of hydrogen abstraction from the primary and secondary carbon atoms are 0.17:0.83 at 298 K. It has been known that the hydrogen atoms on tertiary, secondary, and primary are easier to be abstracted in this order, and the reason is due to the difference in the activation energy as seen in the above equation.

The difference in reactivity of OH for different alkanes has long been discussed in terms of physical parameters of molecules, and it has been known that the ionization potentials (IP) have good correlation with the rate constants (Grosjean 1990) as in the reaction of OH, O<sub>3</sub> and NO<sub>3</sub> with olefins described below. Furthermore, comparison of rate constants using the calculated  $\Delta S^\ddagger$  and  $\Delta H^\ddagger$  by conventional transition state theory with experimental values has also been made (Cohen 1982).

### 5.2.8 $OH + C_2H_4 + M$

Alkenes such as ethylene (ehene,  $C_2H_4$ ) have large reaction rate constants with OH among hydrocarbons, and have large contribution to photochemical ozone formation in urban air considering their mixing ratios.

The reactions of OH with alkenes are in general addition, and the reaction of OH and  $C_2H_4$  is expressed by termolecular reaction such as,



Many experiments on the temperature and pressure dependence of reaction (5.44) have been reported. The IUPAC subcommittee report Vol. II (Atkinson et al. 2006) recommends the low-pressure and high-pressure limit rate constants in 200–300 K as,

$$k_{0,5.44}(T) = 8.6 \times 10^{-29} \left(\frac{T}{300}\right)^{-3.1} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

$$k_{\infty,5.44}(T) = 9.0 \times 10^{-12} \left(\frac{T}{300}\right)^{-0.85} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

based on Zellner and Lorenz (1984), Klein et al. (1984), Kuo and Lee (1991), Fulle et al. (1997), Vakhtin et al. (2003), etc. As seen in the above formula, this reaction has large temperature dependence at low-pressure limit while there is almost no temperature dependence at the high-pressure limit. Quantum chemical calculation has been made for the  $OH + C_2H_4$  reaction, and used for the analysis of experimental values (Cleary et al. 2006; Taylor et al. 2008).

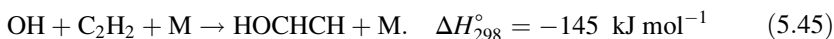
The  $OH + C_2H_4$  reaction is nearly in the high-pressure limit at the atmospheric condition of 1 atm, but it is in the intermediate region between the low- and high-pressure limit in the upper atmosphere, and the rate constants have to be calculated by Eq. (5.8). The  $HOCH_2CH_2$  radicals formed in reaction (5.44) are stabilized in the atmospheric conditions, and react with  $O_2$  to form peroxy-radicals (see Chap. 7).

The reaction of OH with higher alkenes with more carbon atoms are almost in the high-pressure limit, and the IUPAC subcommittee report Vol. II recommends the rate constants at 298 K and 1 atm as  $7.9 \times 10^{-12}$ ,  $2.9 \times 10^{-11}$  and  $1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $C_2H_4$ ,  $C_3H_6$  and  $C_5H_8$  (isoprene), respectively (Atkinson et al. 2006). Thus, the reaction rate constants of OH and alkenes increases significantly with carbon number in general. The correlation of rate constants of the OH-alkene reactions with parameters of electronic structure of molecules has been studied, and it has been shown that the ionization potential (Grosjean 1990) and the highest occupied orbit (HOMO) energy (King et al. 1999) have a very good correlation.

### 5.2.9 $\text{OH} + \text{C}_2\text{H}_2 + \text{M}$

Alkynes represented by acetylene ( $\text{C}_2\text{H}_2$ ) are chain hydrocarbons containing a triple bond in a molecule. Although the reaction rate of alkynes with OH is smaller than alkenes,  $\text{C}_2\text{H}_2$  in particular has relatively high mixing ratio in the polluted atmosphere and its reaction cannot be ignored for the photochemical ozone production in general.

The reactions of OH with alkynes are addition reactions near at the room temperature and atmospheric pressure similar to alkenes, and the reaction of OH and  $\text{C}_2\text{H}_2$  can be written as the termolecular reaction,



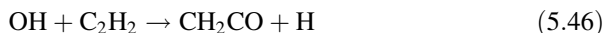
The rate constants of reaction (5.45) have been measured experimentally, and the IUPAC subcommittee report Vol. II recommends based on Bohn et al. (1996), Fulle et al. (1997) and other previous studies,

$$\begin{aligned} k_{0,5.45}(T, N_2) &= 5 \times 10^{-30} [N_2] \left(\frac{T}{300}\right)^{-1.5} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\ k_{\infty,5.45}(298 \text{ K}) &= 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \end{aligned}$$

for the low-pressure limit at 300–800 K and high-pressure limit at 298 K, respectively (Atkinson et al. 2006). This reaction does not reach to the high-pressure limit under the atmospheric pressure, and the recommended value of the rate constant at room temperature and 1 atm. is

$$k_{5.45}(298 \text{ K}, 1 \text{ atm}) = 7.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Quantum chemical calculation for the OH and  $\text{C}_2\text{H}_2$  reaction has recently been made by Senosiain et al. (2005) and the theoretical rate constants has been obtained. According to the calculation, it has been concluded that the reaction pathway to form ketene,

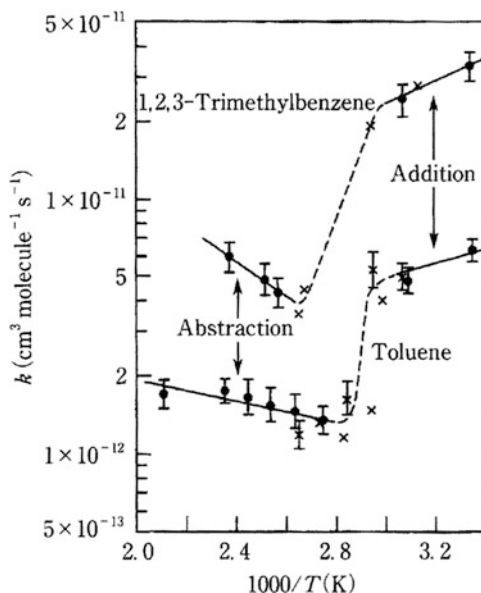


is predominant rather than the hydrogen atom abstraction at high temperature, and collisional stabilization of HOCHCH formed in the reaction (5.45) is the main path at low temperature.

### 5.2.10 $\text{OH} + \text{C}_6\text{H}_6, \text{C}_6\text{H}_5\text{CH}_3$

The reaction of OH with a typical aromatic hydrocarbon, benzene ( $\text{C}_6\text{H}_6$ ), is known to be addition to the benzene ring (Atkinson and Arey 2003),

**Fig. 5.5** Arrhenius plots of rate constants for the reactions of OH + toluene and 1,2,3 trimethylbenzene (Adapted from Perry et al. 1977)



For aromatic hydrocarbons with side chain alkyl group such as toluene ( $\text{C}_6\text{H}_5\text{CH}_3$ ), the addition reaction to the benzene ring and hydrogen atom abstraction reaction from the alkyl group can occur simultaneously.

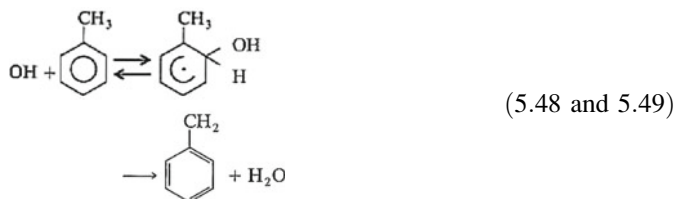


Figure 5.5 shows the Arrhenius plots for the reaction of OH and toluene and 1,2,3-trimethylbenzene (Perry et al. 1977). From this figure, it can be seen that at the high temperature regime of  $> \sim 350$  K for toluene and  $> 380$  K for trimethylbenzene, their Arrhenius plots show normal negative slope (positive activation energy), but at the low temperature regime of  $< \sim 330$  K for both compounds they give positive slope (negative activation energy) and there a big gap in rate constants between both temperature regimes. Furthermore, it is reported that the logarithmic plot of the decay rate of OH is linear with time in the high- and low-temperature range, where the Arrhenius plot is linear, non-exponential decay is seen in the gap region (Perry et al. 1977). This implies that the initial reactions between OH and aromatic hydrocarbons are hydrogen abstraction and addition reactions in the high- and low-temperature range, respectively, and both processes are important in the

intermediate temperature range, where OH radicals are regenerated at certain time delay causing nonexponential decay of OH. Also, the reason that the hydrogen atom abstraction can be seen exclusively from the side chain rather than the benzene ring reflects the fact that the C-H bond energy of the alkyl group ( $360 \text{ kJ mol}^{-1}$ ) is much smaller than the benzene ring ( $460 \text{ kJ mol}^{-1}$ ) (Uc et al. 2006).

The adduct radical formed by the OH addition to the benzene ring in reactions (5.47) and (5.48) are called cyclohexadienyl radicals, and their existence has been confirmed experimentally by their UV absorption spectrum (Grebekin and Krasnoperov 2004; Johnson et al. 2005).

The addition of OH to toluene can be thought to occur at the position of ipso (carbon atom bonded to the methyl group), ortho (carbon atom adjacent to the methyl group), meta (one carbon apart from the methyl group), and para (opposite carbon to the methyl group). Actually, the OH addition reaction occurs predominantly to the ortho position followed by to the para position (ortho-para orientation), which has been confirmed by the yields of cresol isomers (Smith et al. 1998; Klotz et al. 1998), and also by supported by theoretical calculations (Bartolotti and Edney 1995; Suh et al. 2002). The reaction of cyclohexadienyl radicals with  $\text{O}_2$  in the atmosphere will be described in Sect. (7.2.8).

The rate constants of the reaction of OH and benzene has been measured by Perry et al. (1977), Tully et al. (1981), Goumri et al. (1991), Bohn and Zetzsch (1999), etc. They showed that the reaction is in the high-pressure limit where the OH adduct radicals are stabilized by collision at the pressure of  $>100$  torr, and in the fall-off region at the lower pressure than this. The IUPAC subcommittee (Wallington et al. 2012) recommends the temperature dependence of the rate constant at atmospheric pressure (high-pressure limit) at 230–350 K,

$$k_{5.47}(T) = 2.3 \times 10^{-12} \exp\left(-\frac{190}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1},$$

and the value at 298 K,

$$k_{5.47}(298 \text{ K}) = 1.2 \times 10^{-12} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}.$$

The rate constants for reaction of OH and toluene has also been measured by Perry et al. (1977), Tully et al. (1981), Bohn (2001), and others. Based on these studies, the IUPAC subcommittee (Wallington et al. 2012) recommends the overall rate constant for the reactions (5.48 and 5.49) at 210–350 K and at 298 K,

$$k_{5.48+5.49}(T) = 1.8 \times 10^{-12} \exp\left(-\frac{340}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

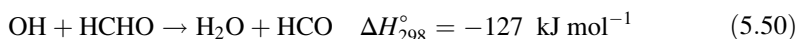
$$k_{5.48+5.49}(298 \text{ K}) = 5.6 \times 10^{-12} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}.$$

The ratio of abstraction reaction (5.49) is given as  $k_{5.49}/(k_{5.48+5.49}) = 0.063$  at 298 K, reflecting the results of product analysis obtained by the experiments (Smith et al. 1998; Klotz et al. 1998).

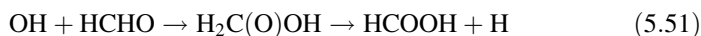
### 5.2.11 OH + HCHO, CH<sub>3</sub>CHO

The reaction of OH and aldehydes are thought to be H atom abstraction from the aldehyde group in general. The reactions of HCHO and CH<sub>3</sub>CHO are described here as one of typical atmospheric reaction of the OH with organic compounds, in parallel with the H atom abstraction reactions from alkyl groups of alkanes and addition reactions to C-C double bonds of alkenes taken up so far.

The reaction of OH and HCHO has been confirmed to be H atom abstraction from aldehyde group,

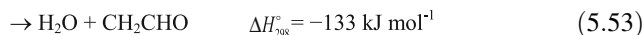


base on experimental evidence (Niki et al. 1984; Butkovskaya and Setser 1998; Sivakumaran et al. 2003). For this reaction, theoretical consideration for the possibility of addition reaction to form HCOOH (formic acid),



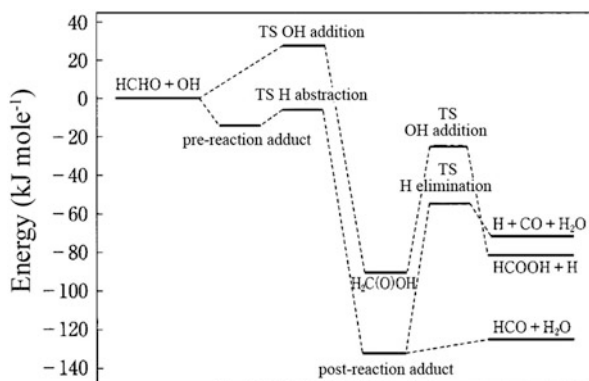
has been made (D'Anna et al. 2003). Figure 5.6 depicts the energy diagram for the OH and HCHO obtained by quantum chemical calculation of D'Anna et al. (2003). According to this calculation, there is no energy barrier for the transition state of the H atom abstraction reaction of OH and HCHO, while the transition state of the addition reaction has a positive barrier of 30 kJ mol<sup>-1</sup>, agreeing with the experimental evidence that HCOOH is not seen in the product.

In the case of the reaction of OH and CH<sub>3</sub>CHO, two possibilities of H atom abstraction,



can be conceived, but it has been known that a major process is the H atom abstraction from aldehyde group given in (5.52). Cameron et al. (2002) reported

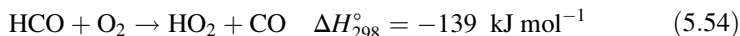
**Fig. 5.6** Energy diagram for the reaction system of OH + HCHO (Adapted from D'Anna et al. 2003)





the yield of this reaction as  $(93 \pm 18)\%$  based on the direct measurement of  $\text{CH}_3\text{CO}$  radicals. Furthermore, the ratio of H atom abstraction from  $\text{CH}_3$  group expressed by the reaction of (5.53) has been reported as ca. 5.1 % based on the direct measurement of  $\text{CH}_2\text{CHO}$  radicals by Butkovskaya et al. (2004).

The  $\text{HCO}$ ,  $\text{CH}_3\text{CO}$ , and  $\text{CH}_2\text{CHO}$  radicals formed in the reactions (5.50), (5.52), and (5.53) react with  $\text{O}_2$  in the atmosphere to form peroxy radicals,



Here, acetylperoxy radicals formed in the reaction (5.55) reacts with  $\text{NO}_2$  in polluted atmosphere to give peculiar compound called peroxyacetyl nitrate (PAN)  $\text{CH}_3\text{C(O)O}_2\text{NO}_2$  (see Sect. 7.2.9).

The temperature dependence of the reaction rate constant of OH and HCHO has been measured by Atkinson and Pitts (1978), Stief et al. (1980), Sivakumaran et al. (2003), etc. and the IUPAC subcommittee (Atkinson et al. 2006) recommends the Arrhenius formula based on these results,

$$k_{5.50}(T) = 5.4 \times 10^{-12} \exp\left(\frac{135}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}. \quad (200 - 300 \text{ K})$$

As seen in the above formula, small negative activation energy is obtained agreeing with the result of theoretical calculation for the abstraction reaction (D'Anna et al. 2003). However, it should be noted that the rate constants deviate from the above Arrhenius formula toward the positive activation energy at higher temperature than 330 K, and the above formula should be applied only at atmospheric conditions (Atkinson et al. 2006).

The similar Arrhenius formula for the reaction of  $\text{CH}_3\text{CHO}$  is recommended as,

$$k_{5.52+5.53}(T) = 4.6 \times 10^{-12} \exp\left(\frac{350}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}. \quad (200 - 300 \text{ K})$$

by the IUPAC subcommittee (Atkinson et al. 2006) based on Sivakumaran and Crowley (2003), etc. This value agrees well with the recommendation by NASA/JPL panel evaluation No. 17 which includes the recent result of Zhu et al. (2008).

There are no large differences in the pre-exponential factor and small negative activation energy in the reaction rate constants of OH with  $\text{C}_1$  and  $\text{C}_2$  aldehydes, which is very much different from the case of OH reaction with alkanes and alkenes. The rate constants for HCHO and  $\text{CH}_3\text{CHO}$  at 298 K are given as  $k_{5.50}(298 \text{ K}) = 8.5 \times 10^{-12}$ ,  $k_{5.52+5.53}(298 \text{ K}) = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively, both by the IUPAC subcommittee report Vol. II (Atkinson et al. 2004) and NASA/JPL panel evaluation No. 17 (Sander et al. 2011). Therefore, the

reaction of OH with aldehydes has large rate constants at room temperature even for HCHO with the least carbon number.

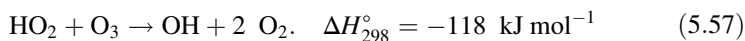
### 5.3 Reactions of HO<sub>2</sub>, CH<sub>3</sub>O<sub>2</sub> Radicals

HO<sub>2</sub> radicals are one of the major chemical species constituting chain reaction cycles, together with OH radicals in the troposphere and stratosphere. In the troposphere, other than HO<sub>2</sub>, organic peroxy radicals RO<sub>2</sub> are also important chain propagation intermediates. In this section, among the reactions of peroxy radicals, the reaction of HO<sub>2</sub> and O<sub>3</sub>, which affects formation and dissipation of O<sub>3</sub> in the stratosphere and troposphere, HO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub> with NO, which is directly related to the tropospheric ozone formation, and radical-radical reaction of HO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub>, are taken up. Table 5.4 cites rate constants and their temperature dependence for the reactions HO<sub>2</sub>, CH<sub>3</sub>O<sub>2</sub> and other organic radicals extracted from the IUPAC subcommittee report Vol. II (Atkinson et al. 2004), and the NASA/JPL panel evaluation No. 17 (Sander et al. 2011).

#### 5.3.1 HO<sub>2</sub> + O<sub>3</sub>

The reaction of HO<sub>2</sub> and O<sub>3</sub> is important in the stratosphere as a reaction to convert HO<sub>2</sub> to OH in the HO<sub>x</sub> cycle. In the troposphere, it is a main reaction to convert HO<sub>2</sub> to OH in the marine boundary layer and free troposphere where the concentration of NO is low.

The pathway of the HO<sub>2</sub> + O<sub>3</sub> reaction is,



As for the reaction rate constants, the NASA/JPL panel evaluation No. 17 (Sander et al. 2011) recommends the Arrhenius formula,

$$k_{5.38}(T) = 1.0 \times 10^{-14} \exp\left(-\frac{490}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1},$$

and the IUPAC subcommittee (Atkinson et al. 2004) recommends the temperature dependent rate formula,

$$k_{5.38}(T) = 2.0 \times 10^{-16} \left(\frac{T}{300}\right)^{4.57} \exp\left(\frac{693}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \quad (250 - 340 \text{ K})$$

based on the measurements by Zahniser and Howard (1980), Sinha et al. (1987),

**Table 5.4** Rate constants at 298 K and Arrhenius parameters for the reactions of HO<sub>2</sub> and organic radicals

Reactions	$k(298\text{ K})$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	A Factor (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$E_a/R$ (K)	Ref.
HO <sub>2</sub> + O <sub>3</sub> → OH + 2O <sub>2</sub>	$1.9 \times 10^{-15}$	$1.0 \times 10^{-14}$	490	(b)
HO <sub>2</sub> + NO → OH + NO <sub>2</sub>	$8.0 \times 10^{-12}$	$3.3 \times 10^{-12}$	-270	(b)
CH <sub>3</sub> O <sub>2</sub> + NO → CH <sub>3</sub> O + NO <sub>2</sub>	$7.7 \times 10^{-12}$	$2.3 \times 10^{-12}$	360	(a)
HO <sub>2</sub> + NO <sub>2</sub> + M → HO <sub>2</sub> NO <sub>2</sub> + M	$2.0 \times 10^{-31} [\text{N}_2] (k_0)$	$2.0 \times 10^{-31} (T/300)^{-3.4} [\text{N}_2] (k_0)$		(b)
	$2.9 \times 10^{-12} (k_\infty)$	$2.9 \times 10^{-12} (T/300)^{-1.1} (k_\infty)$		
HO <sub>2</sub> + HO <sub>2</sub> → H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub> + M → HO <sub>2</sub> NO <sub>2</sub> + M	$1.4 \times 10^{-12}$	$3.0 \times 10^{-13}$	-460	(b)
	$4.6 \times 10^{-32} [\text{M}]$	$2.1 \times 10^{-33} [\text{M}]$	-920	
HO <sub>2</sub> + CH <sub>3</sub> O <sub>2</sub> → CH <sub>3</sub> OOH + O <sub>2</sub>	$5.2 \times 10^{-12}$	$4.1 \times 10^{-13}$	-750	(b)
CH <sub>3</sub> O <sub>2</sub> + CH <sub>3</sub> O <sub>2</sub> → products	$3.5 \times 10^{-13}$	$1.0 \times 10^{-13}$	-370	(a)
HCO + O <sub>2</sub> → HO <sub>2</sub> + CO	$5.1 \times 10^{-12}$	$5.1 \times 10^{-12}$	0	(a)
CH <sub>3</sub> CO + O <sub>2</sub> + M → CH <sub>3</sub> C(O)O <sub>2</sub> + M	$5.1 \times 10^{-12} (k_\infty)$	$5.1 \times 10^{-12}$	0	(a)
CH <sub>2</sub> OH + O <sub>2</sub> → HCHO + HO <sub>2</sub>	$9.7 \times 10^{-12}$	-	-	(a)
CH <sub>3</sub> O + O <sub>2</sub> → HCHO + HO <sub>2</sub>	$1.9 \times 10^{-15}$	$7.2 \times 10^{-14}$	1080	(a)
CH <sub>3</sub> O + NO + M → CH <sub>3</sub> ONO + M	$2.6 \times 10^{-29} [\text{N}_2] (k_0)$	$2.6 \times 10^{-29} (T/300)^{-2.8} [\text{N}_2] (k_0)$		(a)
	$3.3 \times 10^{-11} (k_\infty)$	$3.3 \times 10^{-11} (T/300)^{-0.6} (k_\infty)$		
CH <sub>3</sub> O + NO <sub>2</sub> + M → CH <sub>3</sub> ONO + M	$8.1 \times 10^{-29} [\text{N}_2] (k_0)$	$8.1 \times 10^{-29} (T/300)^{-4.5} [\text{N}_2] (k_0)$		(a)
	$2.1 \times 10^{-11} (k_\infty)$	$2.1 \times 10^{-11} (k_\infty)$		

(a) IUPAC subcommittee report Vol. II (Atkinson et al. 2006)

(b) NASA/JPL panel evaluation No. 17 (Sander et al. 2011)

Wang et al. (1988), Herndon et al. (2001), etc. The rate constants at 298 K is  $k_{5.57}$  (298 K) =  $2.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which is relatively slow as compared to the reaction of OH + O<sub>3</sub> (see 5.2.1) by an order of magnitude. Furthermore, the Arrhenius plot shows a curved feature as shown in the above formula, which is more pronounced under 250 K. This implies the activation energy decreases at low temperature.

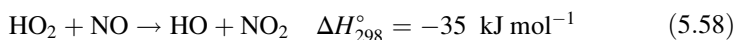
As for the reaction mechanism this reaction, Sinha et al. (1987) detected OH by LIF in the experiments using isotope labeled H<sup>18</sup>O<sub>2</sub> and <sup>16</sup>O<sub>3</sub>, and found that most of OH (75 ± 10 %) is <sup>16</sup>OH. This means that the hydrogen abstraction by O<sub>3</sub> is the main reaction. Nelson and Zahniser (1994) determined the formation ratio of <sup>16</sup>OH and <sup>18</sup>OH by LIF in a similar experiment, which showed the H-atom abstraction by O<sub>3</sub> occurs 94 ± 5 and 85 ± 5 % at 226 K and 355 K, respectively, indicating that the temperature dependence is small.

Quantum chemical calculation for the reaction of HO<sub>2</sub> and O<sub>3</sub> has been performed to show that the energy barrier for the pathway of H-atom abstraction by forming HO<sub>3</sub> via O<sub>3</sub> – HO<sub>2</sub> complex is lower than that of O-atom abstraction via O<sub>3</sub> – O<sub>2</sub>H, which agrees well with the branching, ratio obtained by the experiments (Xu and Lin 2007; Varandas and Viegas 2011).

### 5.3.2 HO<sub>2</sub> + NO

The reaction of HO<sub>2</sub> and NO to form OH and NO<sub>2</sub> is the important reaction to complete the OH – HO<sub>2</sub> chain reaction in the troposphere and stratosphere. Particularly in the troposphere, it is the fundamental reaction to produce photochemical ozone together with the reaction of RO<sub>2</sub> and NO that will be described later (see Sect. 7.3.1 and 7.3.2).

The rate constants of the reaction of HO<sub>2</sub> + NO,

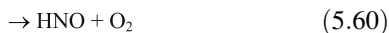


have been measured in many studies since the first measurement of absolute rate using LMR (Laser Magnetic Resonance) by Howard and Evenson (1977). The studies after 1990 are Jemi-Alade and Thrush (1990), Seeley et al. (1996a), Bohn and Zetzsch (1997), Bardwell et al. (2003) and others. The NASA/JPL panel evaluation No. 17 (Sander et al. 2011) recommends the value at 298 K as  $k_{5.58}$  (298 K) =  $8.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and the temperature dependence as,

$$k_{5.58}(T) = 3.3 \times 10^{-12} \exp\left(\frac{270}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The IUPAC subcommittee recommends a 10 % larger value at 200–400 K (Atkinson et al. 2004). It has been known that the reaction has negative activation energy and does not have pressure dependence.

Studies on potential energy surface of the reaction of HO<sub>2</sub> and NO by quantum chemical calculation has been made by Sumathi and Peyerimhoff (1997), Chakraborty et al. (1998), Zhang and Donahue (2006), etc. According to these studies, the reaction of HO<sub>2</sub> and NO proceeds the HOONO intermediate, and the possibilities of reaction pathways other than reaction (5.58) to form HONO<sub>2</sub>, and HNO,



are also suggested. Particularly concerned is that the pernitric acid (HOONO) is a common intermediate with the reaction of OH and NO<sub>2</sub> described in Sect. (5.2.4), and it is interesting to see if the reaction of HO<sub>2</sub> + NO partially leads to formation of nitric acid (HONO<sub>2</sub>).

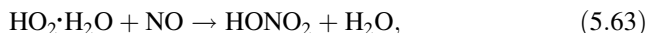
In this regard, Butkovskaya et al. (2005, 2007, 2009) reported the formation of HONO<sub>2</sub> in the HO<sub>2</sub> + NO reaction experimentally. Butkovskaya et al. (2009) detected HONO<sub>2</sub> by using chemical ionization mass spectrometer, and showed that the reaction rate to form HONO<sub>2</sub> increases with the decrease of temperature and the increase of pressure in the range of 223–323 K, and 72–600 Torr, respectively, in the absence of water vapor. The ratio of reaction (5.58) in the absence of water vapor,  $\alpha(T, P) = k_{5.59}/k_{5.58}$ , is given, by,

$$\alpha(T, P) = \frac{k_{5.59}}{k_{5.58}} = \frac{530}{T} + 6.4 \times 10^{-4}P(\text{torr}) - 1.731. \quad (5.61)$$

In the presence of water vapor, the increase ratio  $f$  of HONO<sub>2</sub> formation is represented as,

$$f = (1 + 2 \times 10^{-17}[\text{H}_2\text{O}]) \quad (5.62)$$

where the unit of [H<sub>2</sub>O] is molecule cm<sup>-3</sup>. From this equation the yield of HONO<sub>2</sub> under the relative humidity of 50 % at 298 K ([H<sub>2</sub>O] = 4 × 10<sup>17</sup> molecule cm<sup>-3</sup>) increases by a factor of 8 as compared to the case of [H<sub>2</sub>O] = 0. If the increase of the reaction by water vapor is considered to be due to the reaction involving HO<sub>2</sub>·H<sub>2</sub>O complex,



the rate constant of reaction (5.63) is deduced to be  $k_{5.63} = 6 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K and 1 atm., which is larger than the rate constant of , CH<sub>3</sub>O<sub>2</sub> Radicals reaction (5.59) in the absence of water vapor by a factor of 40. Butkovskaya et al. (2009) discussed the possibility of contribution of heterogeneous

reaction is low, and suggested that the formation of HONO<sub>2</sub> could be important in the reaction of HO<sub>2</sub>· H<sub>2</sub>O complex with NO in the lower troposphere.

Quantum chemical calculation for the HO<sub>2</sub> + NO reaction has also been reported by Zhu and Lin (2003a) and the major reaction pathway is the OH + NO<sub>2</sub> by the direct decomposition of HOONO, and the isomerization of HOONO to HONO<sub>2</sub> is disadvantageous energetically by 21.7 kJ mol<sup>-1</sup>. The theoretical calculation shows that there is no pressure dependence for the OH + NO<sub>2</sub> reaction under 10 atm, agreeing with experimental results.

### 5.3.3 CH<sub>3</sub>O<sub>2</sub> + NO

The reactions of CH<sub>3</sub>O<sub>2</sub> and other organic peroxy radicals with NO are also important in tropospheric chemistry as HO<sub>x</sub> chain propagation reaction together with HO<sub>2</sub> and NO mentioned in the previous paragraph. Particularly in urban and forest air where anthropogenic and biogenic hydrocarbon concentration is high, the contribution of the reaction of RO<sub>2</sub> + NO is large for local photochemical ozone formation. Here, CH<sub>3</sub>O<sub>2</sub> is picked up as a representative organic peroxy radical, and other alkyl peroxy radicals will be mentioned where appropriate.

The products, of the reaction of CH<sub>3</sub>O<sub>2</sub> and NO is known to be CH<sub>3</sub>O and NO<sub>2</sub> (Ravishankara et al. 1981; Zellner et al. 1986; Bacak et al. 2004), so that the main reaction path is,



Many measurements of the, rate constants of this reaction has been reported, and the IUPAC subcommittee (Atkinson et al. 2006) recommends  $k_{5.64}$  (298 K) =  $7.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K and temperature dependent formula,

$$k_{5.64}(T) = 2.3 \times 10^{-12} \exp\left(\frac{360}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

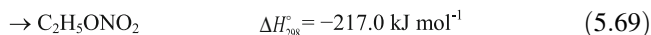
based on Scholtens et al. (1999), Bacak et al. (2004) and previous values. As shown in the above formula, this reaction has negative activation energy and the rate constants are known to increase with pressure a low temperature. From these evidence, the pathways of this reaction is thought to be similar to the HO<sub>2</sub> + NO reaction (Scholtens et al. 1999),



The scheme, of isomerization reaction of CH<sub>3</sub>OONO to CH<sub>3</sub>ONO<sub>2</sub> is also expected from the quantum chemical calculation by Zhang et al. (2004). However, the

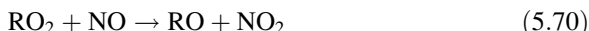
formation of  $\text{CH}_3\text{ONO}_3$  is not seen experimentally, and the upper limit is given as 0.3 % by Scholtens et al. (1999).

The yields of nitric ester (alkyl nitrate) in the above scheme is known to become larger as the number of carbon atoms in the alkyl radical increases. For example, the reaction of ethyl peroxy radical,  $\text{C}_2\text{H}_5\text{O}_2$  and  $\text{NO}$ ,

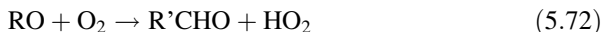


gives the yield of  $\text{C}_2\text{H}_5\text{ONO}_2$  as  $k_{5.69}/k_{5.68}+k_{5.69} \leq 0.014$  at 298 K (Ranschaert et al. 2000), and the yields of  $n\text{-C}_3\text{H}_7\text{ONO}_2$  and  $i\text{-C}_3\text{H}_7\text{ONO}_2$  for  $n\text{-C}_3\text{H}_7\text{O}_2$  and  $i\text{-C}_3\text{H}_7\text{O}_2$  as 0.020 and 0.042, respectively (Carter and Atkinson 1989) as recommended by the IUPAC subcommittee report Vol. II (Atkinson et al. 2006). The production yield of  $\text{RONO}_2$  for each alkane has been tabulated in Lightfoot et al. (1992), Tyndall et al. (2001) and Finlayson-Pitts and Pitts (2000). The production ratios increase for higher than  $\text{C}_4$  alkanes, and reach over 0.3 for  $\text{C}_7$  and  $\text{C}_8$ .

In general, the reaction of  $\text{RO}_2$  and  $\text{NO}$ ,



forms  $\text{RO}$  radicals and  $\text{RONO}_2$ . From the  $\text{RO}$  radicals  $\text{HO}_2$  is regenerated by



to propagate the chain reaction, while the formation of  $\text{RONO}_2$  act as the termination of the chain reaction. Therefore, the production yield of  $\text{RONO}_2$  in the reaction of  $\text{RO}_2$  and  $\text{NO}$  is a very important parameter affecting the photochemical production efficiency of each hydrocarbon.

Quantum chemical calculation for the reaction of  $\text{RO}_2$  ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, i\text{-C}_3\text{H}_7, 2\text{-C}_5\text{H}_{11}$ ) +  $\text{NO}$  has been conducted by Lohr et al. (2003) and Barker et al. (2003). According to these theoretical calculations, the main products of the reaction are  $\text{RO} + \text{NO}_2$ , and the energy barrier for the isomerization from  $\text{ROONO}$  to  $\text{RONO}_2$  is very high and could not explain the experimentally obtained yield of  $\text{RONO}_2$ .

### 5.3.4 $\text{HO}_2 + \text{NO}_2 + \text{M}$

The production of peroxy nitric acid ( $\text{HO}_2\text{NO}_2$ ) by the reaction of  $\text{HO}_2$  and  $\text{NO}_2$  has a possibility to act as the termination reaction of  $\text{OH} - \text{HO}_2$  radical chain reaction, but since  $\text{HO}_2\text{NO}_2$  is thermally unstable and decomposes back to  $\text{HO}_2$  and  $\text{NO}_2$  at around the room temperature, it generally does not affect the formation of ozone

near the surface. However, when HO<sub>2</sub>NO<sub>2</sub> is formed in the troposphere at low temperature, it acts as a reservoir species to transport NO<sub>x</sub> to long distance so that it is important to include this reaction in chemical transport models.

The reaction of HO<sub>2</sub> and NO<sub>2</sub> is in the thermal equilibrium,



The reaction (5.73) is the termolecular reaction, and the low- and high-pressure limit rate constants have been described by Eq. (5.6) taking e.g.  $F_c = 0.6$ . The NASA/JPL evaluation No. 17 (Sander et al. 2011) recommends,

$$k_{0,5.73}(T) = 2.0 \times 10^{-31} \left(\frac{T}{300}\right)^{-3.4} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

$$k_{\infty,5.73}(T) = 2.9 \times 10^{-12} \left(\frac{T}{300}\right)^{-1.1} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

based on the data of Christensen et al. (2004). Meanwhile for the reverse reaction the IUPAC subcommittee (Atkinson et al. 2004) recommends,

$$k_{0,5.74}(T, N_2) = 4.1 \times 10^{-5} [N_2] \left(-\frac{10650}{T}\right) \text{ s}^{-1}$$

$$k_{\infty,5.74}(T) = 4.8 \times 10^{15} \exp\left(-\frac{11170}{T}\right) \text{ s}^{-1}$$

for the temperature range in 260–300 K based on the data of Graham et al. (1977) and Zabel (1995). The values at 298 K are  $k_{0,5.74} = 1.3 \times 10^{-20} [N_2] \text{ s}^{-1}$  and  $k_{\infty,5.74} = 0.25 \text{ s}^{-1}$ , and from these values the atmospheric lifetime of HO<sub>2</sub>NO<sub>2</sub> can be estimated to be a few seconds. From the rate constants of these reverse reactions and reaction (5.38), the NASA/JPL panel (Sander et al. 2011) recommends the equilibration constant of reaction (5.73) and (5.74) as,

$$k_{5.73/5.74}(T) = 2.1 \times 10^{-27} \exp\left(-\frac{10900}{T}\right) \text{ cm}^3 \text{ molecule}^{-1}$$

and the equilibrium constant  $K_{5.73/5.74}(298 \text{ K}) = 1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$  at 298 K.

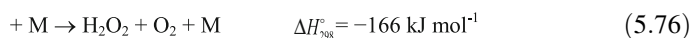
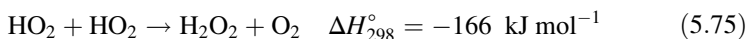
Although quantum chemical calculation by Bai et al. (2005) suggested the formation pathway of HONO, the production of HONO in this reaction has not been confirmed experimentally (Dransfield et al. 2001).



### 5.3.5 $HO_2 + HO_2 (+ M)$

The self-reaction of  $HO_2$  is important in the radical chain reaction in the troposphere and stratosphere since the concentration of  $HO_2$  is in general the highest among atmospheric radicals.  $H_2O_2$  formed in this reaction act as an important oxidizing agent in the liquid phase oxidation reaction of  $SO_2$  in cloud and fog (see Sect. 7.6.2).

The self-reaction of  $HO_2$  is known to proceed both via bimolecular and termolecular reaction in parallel (Kircher and Sander 1984; Kurylo et al. 1986; Takacs and Howard 1986; Lightfoot et al. 1988),



The recommended values of rate constants at 298 K by the IUPAC subcommittee (Atkinson et al. 2004) is  $k_{5.75}$  (298 K) =  $1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the bimolecular reaction and  $k_{5.76}$  (298 K) =  $5.2 \times 10^{-32} [\text{N}_2]$ ,  $4.6 \times 10^{-32} [\text{O}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the termolecular reaction. The NASA/JPL panel evaluation (Sander et al. 2011) recommends  $k_{5.75}$  (298 K) =  $1.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the bimolecular reaction, and  $k_{5.76}$  (298 K) =  $4.6 \times 10^{-32} [M] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the termolecular reaction in common for  $\text{N}_2$ ,  $\text{O}_2$  as the third body. They also recommend the temperature dependent rate equation for the bimolecular and termolecular reaction as,

$$k_{5.75}(T) = 3.0 \times 10^{-13} \exp\left(\frac{460}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{5.76}(T) = 2.1 \times 10^{-33} [M] \exp\left(\frac{920}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

respectively. Thus, this reaction has negative activation energy and is not very fast as a radical-radical reaction.

The rate constants of this reaction is known to increase in the presence of water vapor. The effect of water vapor for this reaction was found by Hamilton (1975) for the first time, and reaction rate equation including the temperature dependence has been given by Lii et al. (1981) and Kircher and Sander (1984). The increasing factor  $f_{5.50}$  in the presence of water vapor given by Kircher and Sander (1984) is,

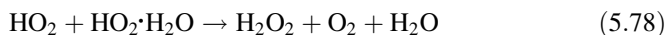
$$f_{5.75+5.76}(T) = 1 + 1.4 \times 10^{-21} [H_2O] \exp\left(\frac{2200}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

which is also recommended by the IUPAC subcommittee (Atkinson et al. 2004).

The effect of water vapor for the  $HO_2 + HO_2$  reaction has been studied in detail both theoretically and experimentally, and it has been revealed that  $HO_2$  forms a complex  $HO_2 - H_2O$  with  $H_2O$  as,



and the reaction rate constant of this complex with HO<sub>2</sub>,



is faster than the rate constant of HO<sub>2</sub> + HO<sub>2</sub> (Aloisio and Francisco 1998; Aloisio et al. 2000; Zhu and Lin 2002). Kanno et al. (2005, 2006) determined the equilibrium constant for HO<sub>2</sub> and HO<sub>2</sub> – H<sub>2</sub>O from the decrease of infrared absorption of HO<sub>2</sub> radicals in the presence of H<sub>2</sub>O and obtained the temperature dependent rate constant of reaction (5.78),

$$k_{5.52}(T) = 5.4 \times 10^{-11} \exp\left(-\frac{410}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

from the experimental decay rate of HO<sub>2</sub> by subtraction the contribution due to reaction (5.50). The value of  $k_{5.78}$  at 298 K is  $1.4 \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ , which is one order of magnitude larger than the rate constant of reaction (5.50) without H<sub>2</sub>O. The NASA/JPL panel (Sander et al. 2011) recommends this value for the rate constant of reaction (5.78).

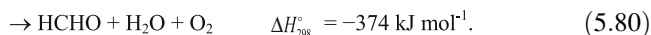
The enthalpy  $\Delta H_{298}^\circ$  and entropy  $\Delta S_{298}^\circ$  of the reaction (5.78), calculated from the equilibrium constant obtained by Kanno et al. (2006) are  $-31 \pm 4 \text{kJ mol}^{-1}$  and  $-83 \pm 14 \text{mol}^{-1} \text{K}^{-1}$ , respectively, agreeing well with previous experimental (Aloisio et al. 2000) and theoretical (Hamilton and Naleway 1976; Aloisio and Francisco 1998) values. From the obtained equilibrium constant, the concentration ratio of [HO<sub>2</sub> – H<sub>2</sub>O]/[HO<sub>2</sub>] is estimated as  $0.19 \pm 0.11$  at a relative humidity of 50 % at 297 K (Kanno et al. 2005).

The quantum chemical calculation for the self-reaction of HO<sub>2</sub> has been reported by Zhu and Lin (2002). They showed the pathways though both of singlet and triplet potential surface are possible and a H<sub>2</sub>O molecule decreases the potential barrier in both paths.

### 5.3.6 HO<sub>2</sub> + CH<sub>3</sub>O<sub>2</sub>

In the free troposphere with low NO<sub>x</sub> concentration, the chain termination reaction by the cross radical reaction between HO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub> formed in the oxidation of CH<sub>4</sub> is important in addition to the self-reaction of HO<sub>2</sub>. In the polluted atmosphere where concentrations of organic peroxy radicals (RO<sub>2</sub>) are high, their cross radical reactions with HO<sub>2</sub> also need to be considered in the model calculation of photochemical ozone formation. Here, as a representative radical-radical reaction of RO<sub>2</sub>, the reaction of HO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub> is described.

The two reaction pathways of HO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub> are known to be,



The scatters of previous experimental values of the rate constants of this reaction were mainly due to the scatters of UV absorption cross-section of the reactant radicals. The IUPAC subcommittee (Atkinson et al. 2006) and NASA/JPL panel (Sander et al. 2011) recommends the rate constant at 298 K and temperature dependence equation based on Cox and Tyndall (1980), Dagaut et al. (1988), Lightfoot et al. (1991), Boyd et al. (2003), etc., and a review of Tyndall et al. (2001). The recommended value by the both evaluation for 298 K is  $k_{5.79+5.80}$  (298 K) =  $5.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The reaction rate constant at 298 K is shown to be pressure independent in the range of 13–1013 hPa by Lightfoot et al. (1990), etc.

The recommended Arrhenius formula by the NASA/JPL panel (Sander et al. 2011) is

$$k_{5.79+5.80}(T) = 4.1 \times 10^{-13} \exp\left(\frac{750}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

which agrees with the recommended parameters by the IUPAC subcommittee (Atkinson et al. 2006) within 10 %.

The branching ratio of the two reaction paths has been obtained by Wallington and Japar (1990) and Elrod et al. (2001). The yield of reaction (5.80) is small at 298 K,  $k_{5.80}/k_{5.53}$  (298 K) = 0.1. However, the branching ratio has been found to be temperature dependent (Elrod et al. 2001), and the IUPAC subcommittee (Atkinson et al. 2006) recommends the temperature dependent ratio as,

$$\frac{k_{5.80}}{k_{5.79+5.80}} = \frac{1}{1 + 498 \exp(-1160/T)}$$

Thus, the branching ratio of reaction (5.80) increases with decreasing temperature and is 0.31 at 218 K.

According to the quantum chemical calculation for this reaction, there are singlet and triplet paths involving a complex CH<sub>3</sub>OOOOH, which are related to the formation of singlet and triplet O<sub>2</sub> in reaction (5.79) (Zhou et al. 2006).

## 5.4 Reactions of O<sub>3</sub>

Although ozone (O<sub>3</sub>) is a reactive species among stable molecules in the atmosphere, partner molecules of homogeneous gas phase reaction are not so many. Important atmospheric reactions are reactions with halogen atoms in the

**Table 5.5** Rate constants at 298 K and Arrhenius parameters for the reactions of ozone

Reactions	$k(298\text{ K})$	$A$ Factor	$E_a/R$	Ref.
	(cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	(cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	(K)	
O <sub>3</sub> + NO → NO <sub>2</sub> + O <sub>2</sub>	1.8 × 10 <sup>-14</sup>	1.0 × 10 <sup>-12</sup>	1310	(a1)
O <sub>3</sub> + NO <sub>2</sub> → NO <sub>3</sub> + O <sub>2</sub>	3.5 × 10 <sup>-17</sup>	1.4 × 10 <sup>-13</sup>	2470	(a1)
O <sub>3</sub> + C <sub>2</sub> H <sub>2</sub> → products	1.0 × 10 <sup>-20</sup>	1.0 × 10 <sup>-14</sup>	4100	(b)
O <sub>3</sub> + C <sub>2</sub> H <sub>4</sub> → products	1.7 × 10 <sup>-18</sup>	1.2 × 10 <sup>-14</sup>	2630	(b)
O <sub>3</sub> + C <sub>3</sub> H <sub>6</sub> → products	1.1 × 10 <sup>-17</sup>	6.5 × 10 <sup>-15</sup>	1900	(b)
O <sub>3</sub> + <i>i</i> -C <sub>4</sub> H <sub>8</sub> → products	1.1 × 10 <sup>-17</sup>	2.7 × 10 <sup>-15</sup>	1630	(a2)
O <sub>3</sub> + 1-C <sub>4</sub> H <sub>8</sub> → products	9.6 × 10 <sup>-18</sup>	3.6 × 10 <sup>-15</sup>	1750	(a2)
O <sub>3</sub> + <i>cis</i> -2-C <sub>4</sub> H <sub>8</sub> → products	1.3 × 10 <sup>-16</sup>	3.2 × 10 <sup>-15</sup>	970	(a2)
O <sub>3</sub> + <i>trans</i> -2-C <sub>4</sub> H <sub>8</sub> → products	1.9 × 10 <sup>-16</sup>	6.6 × 10 <sup>-15</sup>	1060	(a2)
O <sub>3</sub> + C <sub>5</sub> H <sub>8</sub> (isoprene) → products	1.3 × 10 <sup>-17</sup>	1.0 × 10 <sup>-14</sup>	1970	(b)
O <sub>3</sub> + C <sub>10</sub> H <sub>16</sub> (α-pinene) → products	9.0 × 10 <sup>-17</sup>	6.3 × 10 <sup>-16</sup>	580	(a2)

(a1, a2) IUPAC subcommittee report Vol. I, V (Atkinson et al. 2004; Wallington et al. 2012), respectively

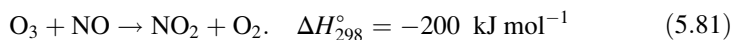
(b) NASA/JPL panel evaluation No. 17 (Sander et al. 2011)

stratosphere, NO, NO<sub>2</sub>, OH and HO<sub>2</sub> in both troposphere and stratosphere, and alkenes (olefins), dienes (diolefines), and biogenic cyclic hydrocarbons, etc. in the troposphere. Among these, the reactions with NO, NO<sub>2</sub>, and C<sub>2</sub>H<sub>4</sub> as a typical alkene are described in detail in this section, and the reaction with Cl atom, and biogenic hydrocarbons will be described in Sects. (5.6.1) and (7.2.6), respectively. The reactions with OH and HO<sub>2</sub> have already given in Sects. (5.2.1 and 5.3.1). Rate constants of fundamental O<sub>3</sub> reactions are summarized in Table 5.5.

### 5.4.1 O<sub>3</sub> + NO

The reaction of O<sub>3</sub> and NO in the troposphere dissipate O<sub>3</sub> temporarily, and is known as a “titration reaction,” which is important at near NO<sub>x</sub> sources and in urban air. In the stratosphere, it is important as a reaction to constitute NO<sub>x</sub> cycle to bring about the net destruction of O<sub>3</sub> (see Sect. 8.2.2).

The reaction of O<sub>3</sub> and NO can be written as,



The rate constant of this reaction has been measured by many studies including Lippmann et al. (1980), Ray and Watson (1981), Borders and Birks (1982), Moonen et al. (1998). Based on these, the IUPAC subcommittee report Vol. I (Atkinson et al. 2004) and the NASA/JPL panel evaluation No. 17 (Sander et al. 2011) gives the rate constants and their temperature dependence. The IUPAC subcommittee

recommends the overall reaction rate constants adding reaction (5.81) and (5.82) described below as  $k_{5.81+5.82}(298\text{ K}) = 1.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K, and Arrhenius formula as,

$$k_{5.81+5.82}(T) = 1.4 \times 10^{-12} \exp\left(-\frac{1310}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

in the temperature range of 195–308 K (Atkinson et al. 2004).

Meanwhile, this reaction has been known to be a chemiluminescent reaction (Clyne et al. 1964; Clough and Thrush 1967),



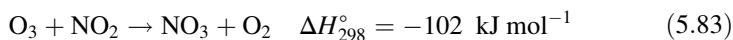
and the activation energy of reaction (5.82) has been shown to be larger than reaction (5.81) (Michael et al. 1981; Schurath et al. 1981). The quantum yield of  $\text{NO}_2^*$  is obtained as 0.20 at 290 K by Schurath et al. (1981). As for the atmospheric reaction, only the overall reaction rate combining reaction (5.81) and (5.82) is important, since almost all of  $\text{NO}_2^*$  is deactivated to the ground state  $\text{NO}_2$ . The chemiluminescence by reaction (5.82) has been utilized for an instrument measuring  $\text{O}_3$  in the atmosphere (Fontijn et al. 1970).

Quantum chemical calculation for the  $\text{O}_3 + \text{NO}$  reaction has been made by classical trajectory method on potential surfaces by Viswanathan and Raff (1983), and reaction cross section and internal energy distribution among products was obtained, although no recent study has been reported.

## 5.4.2 $\text{O}_3 + \text{NO}_2$

The reaction of  $\text{O}_3$  and  $\text{NO}_2$  is important as an  $\text{NO}_3$  radical forming reaction in tropospheric chemistry. The reactions of  $\text{NO}_3$  with other atmospheric species are described in Sect. (5.5).

The reaction pathway of  $\text{O}_3 + \text{NO}_2$  is,



to form  $\text{NO}_3$ . The rate constants of this reaction at 298 K and an Arrhenius formula have been recommended by the IUPAC subcommittee (Atkinson et al. 2004) as  $k_{5.54}(298\text{ K}) = 3.5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}$ , and

$$k_{5.83}(T) = 1.4 \times 10^{-13} \exp\left(-\frac{2470}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \quad (230 - 360\text{ K})$$

respectively, based on the measurements of Davis et al. (1974), Graham and Johnston (1974), Huie and Herron (1974) and Cox and Coker (1983). This reaction has an activation energy of  $20.5 \text{ kJ mole}^{-1}$  and is rather slow at room temperature.

Quantum chemical calculation has been reported by Peiró-García and Nebot-Gil (2003b), and activation energy, reaction enthalpy, and reaction rate constants have been obtained, agreeing well with experiments.

### 5.4.3 O<sub>3</sub> + C<sub>2</sub>H<sub>4</sub>

Important reactions of O<sub>3</sub> in the polluted atmosphere are those with organic compounds with double bonds such as alkenes, dienes, terpenes, etc. Here, the most fundamental elemental reactions with ethylene (C<sub>2</sub>H<sub>4</sub>) are described. Reactions with other alkenes and biogenic hydrocarbons are treated in Sects. (7.2.4) and (7.2.6).

The rate constants of the reaction of O<sub>3</sub> and C<sub>2</sub>H<sub>4</sub>,



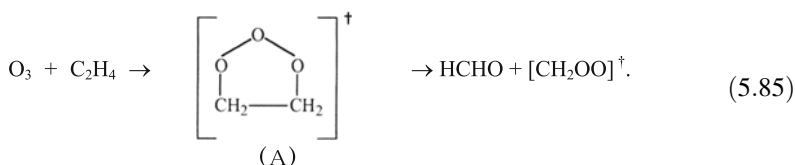
have been measured in wide range of temperature. The IUPAC subcommittee (Atkinson et al. 2006) recommends the Arrhenius formula,

$$k_{5.56}(T) = 9.1 \times 10^{-15} \exp\left(-\frac{2580}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \quad (180 - 360\text{K})$$

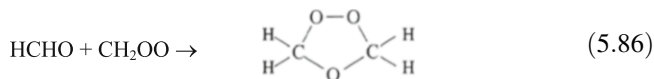
and rate constant at 298 K as  $k_{5.84}(298 \text{ K}) = 1.6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1}$  based on measurements of Bahta et al. (1984) and Treacy et al. (1992). Thus, although the reaction of O<sub>a</sub> and C<sub>2</sub>H<sub>4</sub> is a relatively slow reaction with activation energy of 21.5 kJ mol<sup>-1</sup>, it is important as a dissipation process of C<sub>2</sub>H<sub>4</sub> and also as a radical forming reaction as described below in the polluted atmosphere where the concentrations of O<sub>3</sub> and C<sub>2</sub>H<sub>4</sub> are high.

The activation energy of O<sub>3</sub> and the alkene reaction decreases with the increase of the number of carbon atoms, and reaction rate constants increase rapidly. For example, the activation energy for the reaction with propylene (C<sub>3</sub>H<sub>6</sub>) and α-pinene (C<sub>10</sub>H<sub>16</sub>) decreases to 15.6 and 4.8 kJ mol<sup>-1</sup>, and the rate constants are  $1.0 \times 10^{-17}$  and  $9.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}$ , respectively, which are 1–2 orders of magnitude larger than compared to with ethylene (Atkinson et al. 2006).

The initial reaction of O<sub>3</sub> and alkenes are known to be the formation of carbonyl compounds and carbonyl oxide via primary ozonide formed by cyclic addition of O<sub>3</sub> to double bond. In the case of ethylene, the reaction formula can be represented as,



Historically, this type of reaction was first proposed to interpret the formation of secondary ozonide in solvent cage in the liquid phase (Criegee 1975),

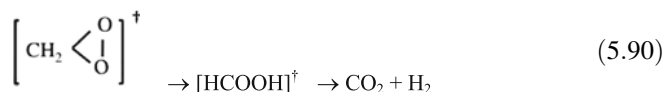
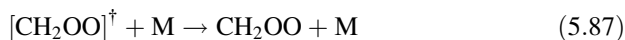


and now recognized well also in the gas phase ozone-alkene reactions (Finlayson-Pitts and Pitts 2000). The formation of primary ozonide (A) in the gas phase reaction of ethylene has been confirmed by micro-wave spectroscopy and its molecular structure has been determined (Gillies et al. 1988, 1989). Also, quantum chemical calculation for the primary ozonide has been made by McKee and Rohlfling (1989) and obtained geometrical molecular structure agrees very well with experiments. From these experimental and theoretical studies, the structure of the primary ozonide has confirmed that two methylene planes of  $\text{C}_2\text{H}_4$  and O-O-O plane of  $\text{O}_3$  have parallel conformation. Taking the theoretical value for the heat of formation of primary ozonide, as  $-51 \text{ kJ mole}^{-1}$  (Olzmann et al. 1997), reaction (5.85) is exothermic by  $246 \text{ kJ mol}^{-1}$  and it is expected that the formed primary ozonide has excess energy to decompose to HCHO and  $\text{CH}_2\text{OO}$  as shown in reaction (5.85). Experimentally, the production yield of HCHO is known to be unity (Grosjean and Grosjean 1996).

The RR'COO type species ( $\text{CH}_2\text{OO}$  in case of  $\text{C}_2\text{H}_4$ ) formed by the decomposition of primary ozonide in the reaction of ozone-olefin reactions are in general called carbonyl oxide or Criegee intermediate after the name of Criegee who first proposed the mechanism. As for the Criegee intermediate, although the existence of the species has been well recognized, including in theoretical studies, direct measurement has not been made in the gas phase for a long time. Very recently, Taatjes et al. (2008) and Welz et al. (2012) detected  $\text{CH}_2\text{OO}$  (formaldehyde oxide) by photoionization mass spectrometer in use of synchrotron radiation directly, and its UV and IR absorption spectrum has been reported (Bearnès et al. 2012; Su et al. 2013).

In liquid phase,  $\text{CH}_2\text{OO}$  is recognized as in zwitterion structure  $^+\text{CH}_2\text{OO}^-$  from its reactivity. Meanwhile, there has been a long discussion about whether  $\text{CH}_2\text{OO}$  in gas phase is in either biradical  $\cdot\text{CH}_2\text{OO}\cdot$  or zwitterion structure (Wald and Goddard III 1975; Johnson and Marston 2008), and recent quantum chemical calculation showed it is a biradical with iconicity (Sander 1990; Cremer et al. 1993). Heat of formation of the ground state  $\text{CH}_2\text{OO}$  ( $1A'$ ) has been reported as,  $\Delta H_{f, 298}^\circ = 1.2$  and  $\Delta H_{f, 0}^\circ = 12.5 \text{ kJ mol}^{-1}$  from a theoretical study (Nguyen et al. 2007).

The  $\text{CH}_2\text{OO}$  produced in reaction (5.85) is known to be vibrationally excited, and partially undergoes unimolecular decomposition and partially participates bimolecular reaction with other molecules under the atmospheric conditions (Atkinson et al. 2006).



The yield of CH<sub>2</sub>OO stabilized under the atmospheric conditions has been previously obtained as  $\Phi(\text{CH}_2\text{OO}) = 0.35\text{--}0.39$  from experiments by capturing it by HCHO, SO<sub>2</sub> and other molecules at 1 atm and room temperature (Niki et al. 1981; Kan et al. 1981; Hatakeyama et al. 1984, 1986; Hasson et al. 2001), while recent experiments give larger values,  $\Phi(\text{CH}_2\text{OO}) = 0.47\text{--}0.50$  (Horie and Moortgat 1991; Neeb et al. 1996, 1998; Horie et al. 1999; Alam et al. 2011). The yield of stabilized CH<sub>2</sub>OO is thought to be pressure dependent. Hatakeyama et al. 1986 reported  $\Phi(\text{CH}_2\text{OO}) = 0.20 \pm 0.03$  even at extrapolated zero pressure, which implies that a part of CH<sub>2</sub>OO is formed without excess energy in reaction (5.85).

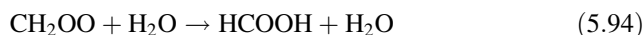
Decomposition products of vibrationally excited CH<sub>2</sub>OO are known to include OH radicals and H atoms in addition to CO<sub>2</sub>, H<sub>2</sub>, CO, H<sub>2</sub>O (Atkinson et al. 2006; Finlayson-Pitts and Pitts 2000). Many theoretical studies on the decomposition path of CH<sub>2</sub>OO presume that the decomposition occurs from vibrationally excited formic acid, HCOOH, formed via dioxirane, a cyclic isomer as shown in reactions (5.90), (5.91), (5.92), and (5.93) (Anglada et al. 1996; Gutbrod et al. 1996; Olzmann et al. 1997; Qi et al. 1998).

Among these decomposition processes, formation of OH radicals and H atoms are important in atmospheric chemistry. The yield of OH has been obtained by experiments with tracers or direct measurements with LIF method (Paulson et al. 1999; Rickard et al. 1999; Kroll et al. 2001), and the IUPAC subcommittee recommends  $\Phi(\text{OH}) = 0.16$  (Atkinson et al. 2006). A recent value by the LIF detection using the EUPHORE chamber (see column in page 278) is  $\Phi(\text{OH}) = 0.17 \pm 0.09$  agreeing with the above recommendation (Alam et al. 2011). As for the reaction pathway of HCO + OH, existence of a direct decomposition path, reaction (5.89) has also been suggested in addition to the path via dioxirane mentioned above (Alam et al. 2011). Information on the OH yields in the reactions of OH with alkene other than C<sub>2</sub>H<sub>4</sub> will be described in Sect. (7.2.4).



As for the yields of H atoms, they have been obtained as the yields of HO<sub>2</sub> since H atoms formed in reaction (5.92) react with O<sub>2</sub> to be transformed into HO<sub>2</sub> under atmospheric conditions. However, the HCO radicals formed in reaction (5.93) also produce HO<sub>2</sub> via reaction with O<sub>3</sub> by reaction (5.35), measured yields of HO<sub>2</sub> corresponds to the sum,  $2\Phi_{5.92} + \Phi_{5.93}$ . Also under certain experimental conditions, formed OH also gives HO<sub>2</sub> by its reaction with O<sub>3</sub> via reaction (5.13), which could give error to the initial yields of HO<sub>2</sub>. The yields of HO<sub>2</sub> have been reported to be  $0.39 \pm 0.03$  (Mihelcic et al. 1999),  $0.38 \pm 0.02$  (Qi et al. 2006),  $0.27 \pm 0.07$  (Alam et al. 2011) by the methods of low temperature matrix, chemical amplification method (PERCA), etc.

As for the stabilized CH<sub>2</sub>OO formed in reaction (5.87), bimolecular reactions with other atmospheric molecules can occur. The bimolecular reactions so far conceived are,



The reported rate constants of these reactions, however, used to have large uncertainties since they were indirect values assuming the above reaction mechanism for CH<sub>2</sub>OO. Recently, Welz et al. (2012) and Stone et al. (2014) reported the following values based on the direct measurement of CH<sub>2</sub>OO as: SO<sub>2</sub>:  $3.9 \times 10^{-11}$ ,  $3.4 \times 10^{-11}$ ; NO<sub>2</sub>:  $7 \times 10^{-12}$ ,  $1.5 \times 10^{-12}$ ; NO:  $< 6 \times 10^{-14}$ ,  $< 2 \times 10^{-13}$ ; H<sub>2</sub>O:  $< 4 \times 10^{-15}$ ,  $< 9 \times 10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively. The values for SO<sub>2</sub> and NO<sub>2</sub> are large enough for these reactions to affect in the polluted atmosphere.

The reaction of O<sub>3</sub> with other alkenes and derived carbonyl oxides are described in Sect. (7.2.4).

## 5.5 Reactions of NO<sub>3</sub> Radicals

Nitrate radicals (NO<sub>3</sub>) are formed by the reaction of O<sub>3</sub> and NO<sub>2</sub> (Sect. 5.4.2) and play an important role in atmospheric chemistry at nighttime in polluted air. NO<sub>3</sub> has an absorption spectrum in the visible region as seen in Sect. (4.2.4) so that daytime concentration is very low since it is easily photodecomposed by sun light. Simultaneously, since the reaction rate constant of NO<sub>3</sub> with NO is large, it returns easily to NO<sub>2</sub> by NO so that its concentration near NO sources is also very low. NO<sub>3</sub> reacts with alkenes and aldehydes to form dinitrates and OH/HO<sub>2</sub> radicals at nighttime. Rate constants of fundamental reactions of atmospheric NO<sub>3</sub> and related N<sub>2</sub>O<sub>5</sub> are cited in Table 5.6.

**Table 5.6** Rate constants at 298 K and Arrhenius parameters for the reactions of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>

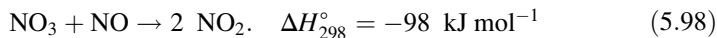
Reactions	k(298 K) (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	A Factor (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	E <sub>a</sub> /R (K)	Ref.
NO <sub>3</sub> + NO → 2 NO <sub>2</sub>	$2.6 \times 10^{-11}$	$1.8 \times 10^{-11}$	-110	(a1)
NO <sub>3</sub> + NO <sub>2</sub> + M → N <sub>2</sub> O <sub>5</sub> + M	$3.6 \times 10^{-30} [N_2] (k_0)$ $1.9 \times 10^{-12} (k_{\infty})$	$3.6 \times 10^{-30} (T/300)^{-4.1} [N_2] (k_0)$ $1.9 \times 10^{-12} (T/300)^{0.2} (k_{\infty})$		(a1)
N <sub>2</sub> O <sub>5</sub> + M → NO <sub>3</sub> + NO <sub>2</sub>	$1.2 \times 10^{-19} [N_2] (k_0/s^{-1})$ $6.9 \times 10^{-2} (k_{\infty}/s^{-1})$	$1.3 \times 10^{-3} (T/300)^{-3.5} \times \exp(-11000/T) [N_2] (k_0/s^{-1})$ $9.7 \times 10^{14} (T/300)^{0.1} \times \exp(-11080/T) (k_{\infty}/s^{-1})$		(a1)
N <sub>2</sub> O <sub>5</sub> + H <sub>2</sub> O → 2 HONO <sub>2</sub>	$2.5 \times 10^{-22}$	—	—	(a1)
N <sub>2</sub> O <sub>5</sub> + 2 H <sub>2</sub> O → 2 HONO <sub>2</sub> + H <sub>2</sub> O	$1.8 \times 10^{-39}$ (b)	—	—	(a1)
NO <sub>3</sub> + C <sub>2</sub> H <sub>4</sub> → products	$2.1 \times 10^{-16}$	$3.3 \times 10^{-12}$	2880	(a2)
NO <sub>3</sub> + C <sub>3</sub> H <sub>6</sub> → products	$9.5 \times 10^{-15}$	$4.6 \times 10^{-13}$	1160	(a2)
NO <sub>3</sub> + i-C <sub>4</sub> H <sub>8</sub> → products	$3.4 \times 10^{-13}$	—	—	(a3)
NO <sub>3</sub> + 1-C <sub>4</sub> H <sub>8</sub> → products	$1.3 \times 10^{-14}$	$3.2 \times 10^{-13}$	950	(a3)
NO <sub>3</sub> + cis-2-C <sub>4</sub> H <sub>8</sub> → products	$3.5 \times 10^{-13}$	—	—	(a3)
NO <sub>3</sub> + trans-2-C <sub>4</sub> H <sub>8</sub> → products	$3.9 \times 10^{-13}$	—	—	(a3)
NO <sub>3</sub> + C <sub>5</sub> H <sub>8</sub> (isoprene) → products	$7.0 \times 10^{-13}$	$3.2 \times 10^{-12}$	450	(a2)
NO <sub>3</sub> + C <sub>10</sub> H <sub>16</sub> (α-pinene) → products	$6.2 \times 10^{-12}$	$1.2 \times 10^{-12}$	-490	(a2)
NO <sub>3</sub> + n-C <sub>4</sub> H <sub>10</sub> → products	$4.6 \times 10^{-17}$	$2.8 \times 10^{-12}$	3280	(a3)
NO <sub>3</sub> + i-C <sub>4</sub> H <sub>10</sub> → products	$1.1 \times 10^{-16}$	$3.0 \times 10^{-12}$	3050	(a3)
NO <sub>3</sub> + HCHO → HONO <sub>2</sub> + HCO	$5.6 \times 10^{-16}$	—	—	(a2)
NO <sub>3</sub> + CH <sub>3</sub> CHO → HONO <sub>2</sub> + CH <sub>3</sub> CO	$2.7 \times 10^{-15}$	$1.4 \times 10^{-12}$	1860	(a2)
NO <sub>3</sub> + C <sub>2</sub> H <sub>5</sub> CHO → HONO <sub>2</sub> + C <sub>2</sub> H <sub>5</sub> CO	$6.4 \times 10^{-15}$	—	—	(a2)
NO <sub>3</sub> + pinonaldehyde → products	$2.0 \times 10^{-14}$	—	—	(a3)

(a1, a2, a3) IUPAC subcommittee report Vol. I, II (Atkinson et al. 2004, 2006), and Wallington et al. 2012), respectively

(b) Unit: cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>

### 5.5.1 $\text{NO}_3 + \text{NO}$

The reaction of  $\text{NO}_3$  and  $\text{NO}$  is a simple oxygen atom transfer reaction,



Measured values for reaction (5.98) by Hammer et al. (1986), Sander and Kircher (1986), Tyndall et al. (1991), Brown et al. (2000) agree very well, and based on these values the IUPAC subcommittee (Atkinson et al. 2004) recommends  $k_{5,98}$  (298 K) =  $2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ , and an Arrhenius formula,

$$k_{5,98}(T) = 1.8 \times 10^{-11} \exp\left(\frac{110}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (220 - 420 \text{ K})$$

in the above temperature range. Thus, the reaction of  $\text{NO}_3$  and  $\text{NO}$  is a fast reaction with negative activation energy and frequency factor of one tenth of collisional frequency.

### 5.5.2 $\text{NO}_3 + \text{NO}_2 + \text{M}$

The reaction of  $\text{NO}_3$  radicals and  $\text{NO}_2$  in the nighttime polluted atmosphere removes  $\text{NO}_3$  to form  $\text{N}_2\text{O}_5$ , which is transformed into nitric acid,  $\text{HONO}_2$ , by reacting with  $\text{H}_2\text{O}$ . Therefore, this reaction is important as a process removing  $\text{NO}_x$  from the chain reaction system and forms a  $\text{HONO}_2$  reservoir together with the daytime reaction of  $\text{OH} + \text{NO}_2 + \text{M}$  (Sect. 5.2.4).

The reaction of  $\text{NO}_3$  and  $\text{NO}_2$  is an equilibrium reaction,



and the IUPAC subcommittee (Atkinson et al. 2004) recommends low- and high-pressure limit formulas of the  $\text{NO}_3 + \text{NO}_2 + \text{M}$  reaction as,

$$k_{0,5.99}(T, N_2) = 3.6 \times 10^{-30} [N_2] \left(-\frac{T}{300}\right)^{-4.1} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (200 - 300 \text{ K})$$

$$k_{\infty,5.99}(T) = 1.9 \times 10^{-12} \left(\frac{T}{300}\right)^{0.2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \quad (200 - 400 \text{ K})$$

respectively, by taking  $F_c = 0.35$  based on Orlando et al. (1991), Hahn et al. (2000), and other previous data. Also, the recommended low- and high-pressure limit formulas of the  $\text{N}_2\text{O}_5 + \text{M}$  reaction (5.100) are,

$$k_{0,5.100}(T, N_2) = 1.3 \times 10^{-3} [N_2] \left(-\frac{T}{300}\right)^{-3.5} \exp\left(-\frac{11000}{T}\right) \text{s}^{-1} \quad (200 - 400 \text{ K})$$

$$k_{\infty,5.100}(T) = 9.7 \times 10^{14} \left(\frac{T}{300}\right)^{0.1} \exp\left(-\frac{11000}{T}\right) \text{s}^{-1}, \quad (200 - 400 \text{ K})$$

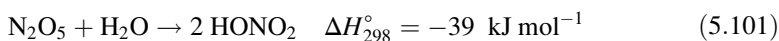
respectively, based on Cantrell et al. (1993). The NASA/JPL pane evaluation No. 17 (Sander et al. 2011) recommends the equilibrium constants of reaction (5.99) and (5.100),

$$K_{5.99/5.100}(T) = 2.7 \times 10^{-27} \exp\left(-\frac{11000}{T}\right) \text{cm}^3 \text{molecule}^{-1}$$

$$K_{5.99/5.100}(298 \text{ K}) = 2.9 \times 10^{-11} \text{cm}^3 \text{molecule}^{-1}$$

as cited in Table 5.3.

The atmospheric lifetimes of N<sub>2</sub>O<sub>5</sub> at room temperature and atmospheric pressure is calculated from the above formula as about 10 s, and during this lifetime N<sub>2</sub>O<sub>5</sub> is converted to HONO<sub>2</sub> either by homogeneous reaction with H<sub>2</sub>O molecule,



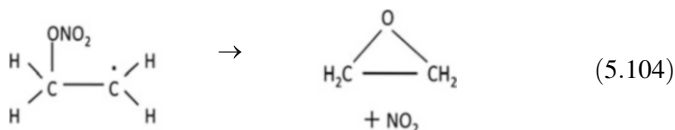
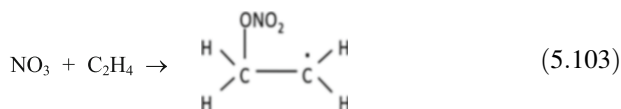
or by heterogeneous reaction on aerosols. The homogeneous rate constants of reactions (5.101) and (5.102) are recommended as  $k_{5.101}(290 \text{ K}) = 2.5 \times 10^{-22} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  and  $k_{5.102}(290 \text{ K}) = 1.8 \times 10^{-39} \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$  by IPAC subcommittee based on the measurement of Wahner et al. (1998). In real polluted atmosphere, heterogeneous reaction is in general thought to be more important for the formation of HONO<sub>2</sub>. The conversion of N<sub>2</sub>O<sub>5</sub> to HONO<sub>2</sub> by heterogeneous reaction is treated in Chap. 6.

Quantum chemical theoretical calculations for the equilibrium reaction between NO<sub>3</sub>, NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> have been made by Jitariu and Hirst (2000), Glendening, and Halpern (2007). Jitariu and Hirst (2000) obtained the molecular structure of N<sub>2</sub>O<sub>5</sub> and transition state of the unimolecular decomposition, and suggested that the NO<sub>3</sub>-NO<sub>2</sub> reaction could lead to decomposition into NO<sub>2</sub>+NO+O<sub>2</sub> via peroxy type complex, ONO---ONOO. Experimentally, however, the importance of the process to form NO<sub>2</sub>+NO+O<sub>2</sub> has not been confirmed (Sander et al. 2011). Glendening and Halpern (2007) obtained  $\Delta H^\circ$ ,  $\Delta G^\circ$ ,  $\Delta S^\circ$  for the reactions (5.99), (5.100) and other equilibrium reactions of nitrogen oxides by theoretical calculations, and compared with the values in NIST/JANAF (1988). As for the hydrolysis reaction (5.101) and (5.102), Hanway and Tao (1998) made theoretical calculations, and showed that there are two low-energy reaction pathways, one involves one H<sub>2</sub>O molecule and another with two H<sub>2</sub>O molecules. According to this calculation, it has been shown that the activation energy for the reaction with one H<sub>2</sub>O molecule is 84 kJ mol<sup>-1</sup>, while it reduces to nearly a half value for the reaction involving two H<sub>2</sub>O molecules, and the heterogeneous hydrolysis process proceeds more efficiently than the homogeneous process.

### 5.5.3 $\text{NO}_3 + \text{C}_2\text{H}_4$

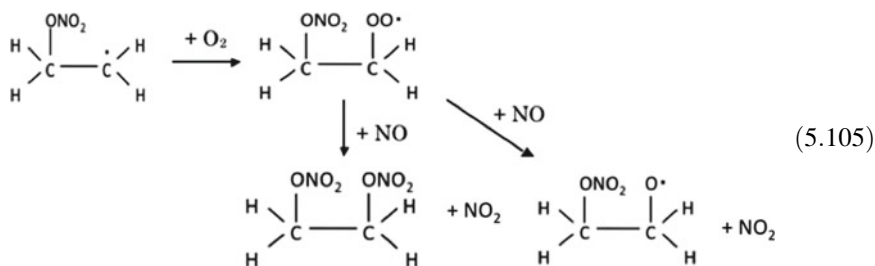
$\text{NO}_3$  radicals are known to react with alkenes and aldehydes among organic compounds. Here the reaction with  $\text{C}_2\text{H}_4$  is described as a representative of the reactions with alkenes.

The reactions of  $\text{NO}_3$  with  $\text{C}_2\text{H}_4$  and other alkenes are known to be initiated by the addition, and proceed as,



Thus, epoxides (epoxyethane in the case of  $\text{C}_2\text{H}_4$ ) are formed from the  $\text{NO}_3$ -alkene adducts (Benter et al. 1994; Skov et al. 1994). The lifetime of the adduct is long enough to allow molecular rotation around C-C bond, and cis- and trans-epoxides are formed in the same ratio irrespective of starting with either cis- or trans-asymmetrical alkenes such as cis- and trans-2-butenes (Benter et al. 1994). The yields of epoxides are reported to be 0.50, 0.95, 0.20 for cis-, tran-2-butene. The yields of epoxides are 0.50, 0.95 and 0.20 for 2,3-dimethyl-2-butene, and isoprene, respectively (Skov et al. 1994).

Meanwhile, the  $\text{NO}_3$ -alkene adduct reacts with  $\text{O}_2$  in the atmosphere to form peroxy radical, from which dinitrate is formed,



As for the rate constants of the reaction of  $\text{NO}_3$  and  $\text{C}_2\text{H}_4$ , the IUPAC subcommittee report Vol. II (Atkinson et al. 2006) recommends the Arrhenius formula,

$$k_{5.103}(T) = 3.3 \times 10^{-12} \exp\left(-\frac{2880}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (270 - 340 \text{ K})$$

and the rate constant at 298 K,  $k_{5.103}(298 \text{ K}) = 2.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  based on Canosa-Mas et al. (1988a, b) and others. Although the reaction of  $\text{NO}_3$  and

C<sub>2</sub>H<sub>4</sub> is addition reaction as described above, pressure dependence is not seen in this reaction implying the reaction is in the high-pressure limit under the atmospheric conditions. Although the reaction rate constants of NO<sub>3</sub> and C<sub>2</sub>H<sub>4</sub> reaction is rather small with relatively high activation energy of 23.9 kJ mol<sup>-1</sup>, the activation energy decreases with the increase of carbon number and the rate constants at 298 K become large as  $3.5 \times 10^{-13}$ ,  $5.7 \times 10^{-11}$  and  $7.0 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, for cis-2-butene, 2,3-dimethyl-2-butene and isoprene, respectively (Atkinson et al. 2006).

Quantum chemical calculation for the reaction of NO<sub>3</sub> and C<sub>2</sub>H<sub>4</sub> was made by Nguyen et al. (2011). They confirmed the picture that the initial pathway is the electrophilic addition of O atom of NO<sub>3</sub> to C-C double bond to form an open-chain adduct, as shown in reaction (5.103). From this calculation, 80-90 % of the formed adduct is stabilized in this form, and the remaining 10-20 % forms epoxyethane. The calculated rate constants agreed well with the experimental values.

### 5.5.4 NO<sub>3</sub> + HCHO

NO<sub>3</sub> reacts with aldehydes other than alkenes among organic compounds. Since HO<sub>2</sub> radicals are formed from acyl radicals (RCO) generated in the reaction, the NO<sub>3</sub>-aldehydes reactions are important as HO and HO<sub>2</sub> radical source at nighttime. In this paragraph, the reactions of NO<sub>3</sub> with HCHO and CH<sub>3</sub>CHO are described as representative example of aldehydes.

The reactions of NO<sub>3</sub> and aldehydes are H atom abstraction from aldehyde group. In the case of HCHO and CH<sub>3</sub>CHO, the reactions proceed as,



to produce formyl and acetyl radicals, HCO and CH<sub>3</sub>CO, respectively, from which peroxy radicals, HO<sub>2</sub> and CH<sub>3</sub>C(O)OO are generated with the reaction with O<sub>2</sub> as seen in reaction (5.54), (5.55), and (5.56) (Sect. 5.2.11).

Measurements of rate constants of the reaction of NO<sub>3</sub> with HCHO and CH<sub>3</sub>CHO are scarce. The IUPAC subcommittee (Atkinson et al. 2006) recommends the rate constants at 298 K for the reactions of HCHO and CH<sub>3</sub>CHO as  $k_{5.106}$  (298 K) =  $5.6 \times 10^{-16}$ , and  $k_{5.107}$  (298 K) =  $2.7 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively, based on Cantrell et al. (1985) using DOAS for the direct measurement of NO<sub>3</sub>. The measurement of temperature dependence has been made only for reaction (5.107) with CH<sub>3</sub>CHO, and the IUPAC subcommittee (Atkinson et al. 2006) recommends

$$k_{5.107}(T) = 1.4 \times 10^{-12} \exp\left(-\frac{1860}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

based on Dlugokencky and Howard (1989). The activation energy given here is  $15.6 \text{ kJ mol}^{-1}$ . Measurement of temperature dependence of rate constants for the reaction with HCHO has not been reported, and if the similar value is assumed for the pre-exponential factor as the reaction of  $\text{CH}_3\text{CHO}$ , the Arrhenius formula for HCHO is assumed to be  $k_{5.106}(T) = \sim 2 \times 10^{-12} \exp(-2440/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with larger activation energy of  $20.3 \text{ kJ mol}^{-1}$  (Atkinson et al. 2006).

Quantum chemical calculations for the reactions of  $\text{NO}_3$  with HCHO and  $\text{CH}_3\text{CHO}$  has been made by Mora-Diez and Boyd (2002), and the transition states and their energy levels for the H-atom abstraction reaction (5.106) and (5.107) has been obtained. The activation energy for the reaction of  $\text{CH}_3\text{CHO}$  obtained theoretically is  $18.5 \text{ kJ mol}^{-1}$ , which agrees reasonably well with the experimental value of  $15.6 \text{ kJ mol}^{-1}$ .

## 5.6 Reactions of Cl Atoms and ClO Radicals

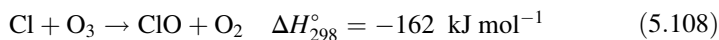
The reactions of halogen atoms and radicals are of fundamental importance in stratospheric chemistry (see Sects. 4.4 and 8.2, 8.3, and 8.4), and the halogen cycle is also of interest in the marine boundary layer in the troposphere (see Sect. 7.5). In this section, among the atmospheric reactions of halogen atoms and radicals, fundamental homogeneous reactions of Cl atoms and ClO radicals are described, and the reactions of bromine and iodine atoms and radicals are discussed in the more phenomenological discussions in Chaps. 7 and 8.

Table 5.7 cites the rate constants and their temperature dependence for the reactions of Cl, ClO and other halogen atoms and radicals excerpted from the NASA/JPL panel evaluation No. 17 (Sander et al. 2011), and the IUPAC subcommittee reports Vol. III (Atkinson et al. 2007).

### 5.6.1 $\text{Cl} + \text{O}_3$

The reaction of Cl atoms and  $\text{O}_3$  is the direct dissipation reaction of  $\text{O}_3$  molecules in the  $\text{ClO}_x$  cycle (Sect. 8.2.3), and is important as a rate-determining step to reduce the equilibrium concentration of ozone by  $\text{CH}_3\text{Cl}$  in the natural stratosphere.

The reaction of Cl and  $\text{O}_3$ ,



is known to produce chlorine oxide (ClO) radical with the yield of nearly unity

**Table 5.7** Rate constants and Arrhenius parameters for the reactions of halogen atoms and radicals

Reactions	$k(298\text{ K})$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	A Factor ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	$E_d/R$ (K)	References
$\text{F} + \text{O}_2 + \text{M} \rightarrow \text{FOO} + \text{M}$	$5.8 \times 10^{-33} [\text{N}_2] (k_0)$ $1.2 \times 10^{-10} (k_\infty)$	$5.8 \times 10^{-33} (\text{T}/300)^{-3.9} [\text{N}_2] (k_0)$ $1.2 \times 10^{-10} (k_\infty)$		(a)
$\text{Cl} + \text{O}_2 + \text{M} \rightarrow \text{ClOO} + \text{M}$	$1.4 \times 10^{-33} [\text{N}_2] (k_0)$ $1.6 \times 10^{-33} [\text{O}_2] (k_0)$	$1.4 \times 10^{-33} (\text{T}/300)^{-3.9} [\text{N}_2] (k_0)$ $1.6 \times 10^{-33} (\text{T}/300)^{-2.9} [\text{O}_2] (k_0)$		(a)
$\text{F} + \text{O}_3 \rightarrow \text{FO} + \text{O}_2$	$1.0 \times 10^{-11}$	$2.2 \times 10^{-11}$	230	(b)
$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	$1.2 \times 10^{-11}$	$2.3 \times 10^{-11}$	200	(b)
$\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2$	$1.2 \times 10^{-12}$	$1.6 \times 10^{-11}$	780	(b)
$\text{I} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2$	$1.2 \times 10^{-12}$	$2.3 \times 10^{-11}$	870	(b)
$\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$	$2.6 \times 10^{-11}$	$1.4 \times 10^{-10}$	500	(b)
$\text{F} + \text{CH}_4 \rightarrow \text{HF} + \text{CH}_3$	$6.7 \times 10^{-11}$	$1.6 \times 10^{-10}$	260	(b)
$\text{F} + \text{H}_2\text{O} \rightarrow \text{HF} + \text{OH}$	$1.4 \times 10^{-11}$	$1.4 \times 10^{-11}$	0	(b)
$\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$	$1.0 \times 10^{-13}$	$7.3 \times 10^{-12}$	1280	(b)
$\text{FO} + \text{O} \rightarrow \text{F} + \text{O}_2$	$2.7 \times 10^{-11}$	—	—	(a)
$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$	$3.7 \times 10^{-11}$	$2.8 \times 10^{-11}$	-90	(b)
$\text{BrO} + \text{O} \rightarrow \text{Br} + \text{O}_2$	$4.1 \times 10^{-11}$	$1.9 \times 10^{-11}$	-230	(b)
$\text{IO} + \text{O} \rightarrow \text{I} + \text{O}_2$	$1.2 \times 10^{-10}$	—	—	(b)
$\text{ClO} + \text{OH} \rightarrow \text{HO}_2 + \text{Cl}$	$1.8 \times 10^{-11}$	$7.4 \times 10^{-12}$	-270	(b)
$\rightarrow \text{HCl} + \text{O}_2$	$1.3 \times 10^{-12}$	$6.0 \times 10^{-13}$	-230	(b)
$\text{BrO} + \text{OH} \rightarrow \text{products}$	$3.9 \times 10^{-11}$	$1.7 \times 10^{-12}$	-250	(b)
$\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$	$6.9 \times 10^{-12}$	$2.6 \times 10^{-12}$	-290	(b)
$\text{BrO} + \text{HO}_2 \rightarrow \text{HOBr} + \text{O}_2$	$2.1 \times 10^{-11}$	$4.5 \times 10^{-12}$	-460	(b)
$\text{IO} + \text{HO}_2 \rightarrow \text{HOI} + \text{O}_2$	$8.4 \times 10^{-11}$	—	—	(b)
$\text{FO} + \text{NO} \rightarrow \text{NO}_2 + \text{F}$	$2.2 \times 10^{-11}$	$8.2 \times 10^{-12}$	-300	(b)
$\text{ClO} + \text{NO} \rightarrow \text{NO}_2 + \text{Cl}$	$1.7 \times 10^{-11}$	$6.4 \times 10^{-12}$	-290	(b)

(continued)



Table 5.7 (continued)

Reactions	$k(298\text{ K})$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	A Factor ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	$E_d/R$ (K)	References
$\text{BrO} + \text{NO} \rightarrow \text{NO}_2 + \text{Br}$	$2.1 \times 10^{-11}$	$8.8 \times 10^{-12}$	-260	(b)
$\text{IO} + \text{NO} \rightarrow \text{NO}_2 + \text{I}$	$2.0 \times 10^{-11}$	$9.1 \times 10^{-12}$	-240	(b)
$\text{FO}_2 + \text{NO} \rightarrow \text{FNO} + \text{O}_2$	$7.5 \times 10^{-13}$	$7.5 \times 10^{-12}$	690	(b)
$\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}$	$1.8 \times 10^{-31} [\text{M}] (k_0)$	$1.8 \times 10^{-31} (\text{T}/300)^{-3.4} [\text{M}] (k_0)$		(b)
	$1.5 \times 10^{-11} (k_\infty)$	$1.5 \times 10^{-11} (\text{T}/300)^{-1.9} (k_\infty)$		
$\text{BrO} + \text{NO}_2 + \text{M} \rightarrow \text{BrONO}_2 + \text{M}$	$5.2 \times 10^{-31} [\text{M}] (k_0)$	$5.2 \times 10^{-31} (\text{T}/300)^{-3.2} [\text{M}] (k_0)$		(b)
	$6.9 \times 10^{-12} (k_\infty)$	$6.9 \times 10^{-12} (\text{T}/300)^{-2.9} (k_\infty)$		
$\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M}$	$1.6 \times 10^{-32} [\text{M}] (k_0)$	$1.6 \times 10^{-32} (\text{T}/300)^{-4.5} [\text{M}] (k_0)$		(b)
	$3.0 \times 10^{-12} (k_\infty)$	$3.0 \times 10^{-12} (\text{T}/300)^{-2.0} (k_\infty)$		
$\text{ClO} + \text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2$	$4.8 \times 10^{-15}$	$1.0 \times 10^{-12}$	1590	(a)
$\rightarrow \text{Cl} + \text{ClOO}$	$8.0 \times 10^{-15}$	$3.0 \times 10^{-11}$	2450	
$\rightarrow \text{Cl} + \text{OCIO}$	$3.5 \times 10^{-15}$	$3.5 \times 10^{-13}$	1370	
$\text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{OCIO}$	$6.0 \times 10^{-12}$	$9.5 \times 10^{-13}$	-550	(b)
$\rightarrow \text{Br} + \text{ClOO}$	$5.5 \times 10^{-12}$	$2.3 \times 10^{-12}$	-260	
$\rightarrow \text{BrCl} + \text{O}_2$	$1.1 \times 10^{-12}$	$4.1 \times 10^{-13}$	-290	
$\text{BrO} + \text{BrO} \rightarrow \text{products}$	$3.2 \times 10^{-12}$	$1.5 \times 10^{-12}$	-230	(b)
$\text{BrO} + \text{IO} \rightarrow \text{products}$	$6.9 \times 10^{-11}$	-	-	(b)
$\text{IO} + \text{IO} \rightarrow \text{products}$	$8.0 \times 10^{-11}$	$1.5 \times 10^{-11}$	-500	(b)

(a) IUPAC subcommittee report Vol. III (Atkinson et al. 2007)

(b) NASA/JPL panel evaluation No. 17 (Sander et al. 2011)

(Atkinson et al. 2007; Sander et al. 2011). Numerous measurements of the rate constants of reaction (5.108) have been made due to its importance related to ozone layer destruction by CFCs. The NASA/JPL panel evaluation No. 17 (Sander et al. 2011) recommends the Arrhenius formula,

$$k_{5.108}(T) = 2.3 \times 10^{-11} \exp\left(\frac{200}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \quad (180 - 300 \text{ K})$$

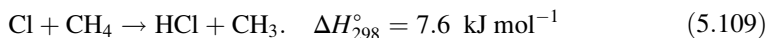
and the value at 298 K,  $k_{5.108}(298 \text{ K}) = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  based on relatively recent measurements by Nicovich et al. (1990), Seeley et al. (1996b), Beach et al. (2002), and other previous data. The recommended value of  $k_{5.108}(298 \text{ K})$  by the IUPAC subcommittee (Atkinson et al. 2008) is the same as above and the Arrhenius parameters are consistent with the above formula within an error range.

Reaction (5.108) is an exothermic reaction with large excess energy, and Matsumi et al. (1996) showed the vibrationally excited ClO is formed with inverse distribution of 0.8 : 1.0 : 1.3 : 2.4 : 2.9 : 2.7 for  $v'' = 1, 2, 3, 4, 5$ . Castillo et al. (2011) determined potential energy surface of this reaction by quantum chemical calculation, and showed that the energy level of the transition state is lower than the reactants, which agrees well with the experimental evidence that the reaction has small negative activation energy with no energy barrier. The calculated reaction rate constants and strongly inverted distribution of vibrationally excited levels obtained by the theoretical calculation agrees reasonably well with the experiments.

### 5.6.2 Cl + CH<sub>4</sub>

Although the CH<sub>4</sub> dissipation reaction by Cl atoms has an important role not only in the stratosphere but also possibly in the troposphere, the ratio of its importance relative to OH reaction has not been estimated quantitatively since the global emissions of inorganic chlorine from sea salt has not been evaluated yet.

The reaction of Cl and CH<sub>4</sub> is a simple H-atom abstraction,



The measurements of rate constant of this reaction have been made extensively including relatively recent measurements for temperature dependence (Seeley et al. 1996b; Pilgrim et al. 1997; Wang and Keyser 1999; Bryukov et al. 2002). Based on these and other measurements at 298 K, the NASA/JPL panel evaluation No. 17 (Sander et al. 2011) recommends,

$$k_{5.109}(T) = 7.3 \times 10^{-12} \exp\left(-\frac{1280}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \quad (200 - 300 \text{ K})$$

and the value at 298 K,  $k_{5.109}(298 \text{ K}) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Recommended value of  $k_{5.109}(298 \text{ K})$  by the IUPAC subcommittee (Atkinson et al. 2006) is the same as above and the Arrhenius parameters are also consistent within error range. The activation energy of this reaction is reported to be different at below and above 300 K, and the above formula is recommended for conditions at lower than room temperature.

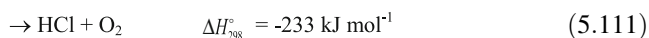
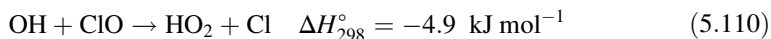
Although the reaction of  $\text{Cl} + \text{CH}_4$  is slightly endothermic, its rate constant at 298 K is larger than that of the  $\text{OH} + \text{CH}_4$  reaction (5.40) described in Sect. (5.2.7) by a factor of 15 since the activation energy is smaller by 3.4 kJ and the pre-exponential is larger by a factor of 4 than the latter. Thus, this reaction may not be negligible even though the concentration of Cl is lower than OH.

The  $\text{Cl} + \text{CH}_4$  reaction has been attracted much interest theoretically, and the effect of excitation of inner-vibrational mode of  $\text{CH}_4$  and difference of spin-orbit state of Cl atoms ( $^2\text{P}_{3/2}$ ,  $^2\text{P}_{1/2}$ ) on reactivity, and the distribution of internal energy of formed HCl have been studied by molecular dynamic experiments using crossed molecular beams (Yoon et al. 2002; Bechtel et al. 2004; Zhou et al. 2004; Bass et al. 2005). Many studies on quantum chemical calculations for the potential energy surface, rate constants, molecular dynamic parameters have been made, and comparisons with experiments have been discussed (Corchado et al. 2000; Troya et al. 2002; Yang et al. 2008).

### 5.6.3 *ClO + OH*

The reaction of ClO and OH is a cross reaction between the  $\text{ClO}_x$  and  $\text{HO}_x$  cycles together with the reaction of Cl and  $\text{HO}_2$  described in the next paragraph.

For the ClO and OH reaction, two reaction pathways,



have been confirmed experimentally. Reaction (5.110) is a chain propagating reaction by regenerating Cl atoms while reaction (5.111) is a chain termination reaction by forming metastable HCl molecules so that their function in the chain reaction is quite different. The branching ratio of these reactions has been obtained based on the direct measurements of products by Bedjanian et al. (2001), Wang and Keyser (2001a) and Lipson et al. (1999), and the temperature independent ratio for reaction (5.111) has been reported to be  $0.035 \pm 0.010$ ,  $0.07 \pm 0.03$  and  $0.090 \pm 0.04$ , respectively. The IUPAC subcommittee recommends the ratio of

the formation of  $\text{HCl} + \text{O}_2$  as 0.06 by taking the average of these values (Atkinson et al. 2007).

Many measurements of the rate constant of the  $\text{ClO} + \text{OH}$  reaction have been reported, and studies after the 1990s are by Lipson et al. (1999), Kegley-Owen et al. (1999), Bedjanian et al. (2001), Wang and Keyser (2001b). Based on these and previous studies, the NASA/JPL panel evaluation No. 17 recommends,

$$k_{5.110}(T) = 7.4 \times 10^{-12} \exp\left(\frac{270}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \quad (200 - 380 \text{ K})$$

$$k_{5.111}(T) = 6.0 \times 10^{-13} \exp\left(\frac{230}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \quad (200 - 380 \text{ K})$$

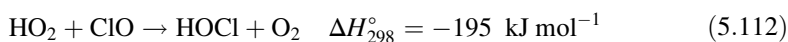
and  $k_{5.110}(298 \text{ K}) = 1.8 \times 10^{-11}$ ,  $k_{5.111}(298 \text{ K}) = 1.3 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  (Sander et al. 2011). The recommendation by the IUPAC subcommittee matches well these values (Atkinson et al. 2007).

Quantum chemical calculations for the reaction of  $\text{ClO} + \text{OH}$  has been reported by Zhu et al. (2002). According to the study, this reaction proceeds mainly on the singlet potential energy surface and forms  $\text{HO}_2 + \text{Cl}$  and  $\text{HCl} + \text{O}_2$  ( $^1\Delta$ ) according to reaction path (5.110) and (5.111), and the formation ratio of  $\text{HCl} + \text{O}_2$  is 0.073, agreeing well with the experimental values.

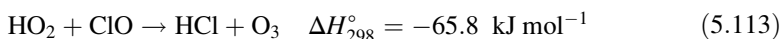
### 5.6.4 $\text{ClO} + \text{HO}_2$

The reaction of  $\text{ClO}$  and  $\text{HO}_2$  is also a cross reaction of  $\text{ClO}_x$  and  $\text{HO}_x$  cycles in the stratosphere as well as the reaction with  $\text{OH}$  in the previous paragraph.

As for the pathway of the  $\text{ClO}$  and  $\text{HO}_2$  reaction,



is the sole path substantially. Other than the above pathway,



has been considered, but several experiments have reported that the formation of  $\text{HCl}$  by reaction (5.113) has not been observed including recent study of Knight et al. (2000). Theoretical study by Nickolaisen et al. (2000) also concluded that the contribution of this reaction is zero.

The measurements of the rate constant of reaction (5.78) have been reported rather recently by Nickolaisen et al. (2000), Knight et al. (2000) and Hickson et al. (2007). The recommended Arrhenius formula and value at 298 K by the NASA/JPL panel evaluation No. 17 (Sander et al. 2011) based on these and previous studies are,

$$k_{5.112}(T) = 2.6 \times 10^{-12} \exp\left(\frac{290}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (230 - 300 \text{ K})$$

and  $k_{5.78}(298 \text{ K}) = 6.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The recommendations by the IUPAC subcommittee agree mostly with the above (Atkinson et al. 2007). Thus, this reaction has nearly the same small negative activation energy and pre-exponential factor, and the rate constant at 298 K is about 50 % as compared to the ClO + OH reaction.

According to the quantum chemical calculations (Nickolaisen et al. 2000; Kaltsoyannis and Rowley 2002; Xu et al. 2003), the ClO + HO<sub>2</sub> reaction proceeds on a singlet potential energy surface as,



This reaction forms an adduct which is more stable than the reactants by 64 kJ mol<sup>-1</sup>, and since there are large potential barrier to decompose into either HOCl + O<sub>2</sub> (<sup>1</sup>Δ) or HCl + O<sub>3</sub>, it has been suggested that HOOCl can have relatively long lifetime in the atmosphere. On the other hand, a reaction along the triplet energy surface gives HOCl + O<sub>2</sub>(<sup>3</sup>Σ) as shown in reaction (5.112) and the small negative activation energy of 10 kJ mol<sup>-1</sup> is given. These theoretical results agree well with the experimental evidence that this reaction has small negative activation energy and the reaction path is solely (5.112) and the path (5.113) for HCl + O<sub>3</sub> is not seen.

### 5.6.5 ClO + NO<sub>2</sub>

The formation of ClONO<sub>2</sub> by the reaction of ClO and NO<sub>2</sub> is the termination reaction of the ClO<sub>x</sub> radical chain. The reaction is also a cross reaction of ClO<sub>x</sub> and NO<sub>x</sub> cycles in the stratospheric ozone dissipation reaction (see Sect. 8.2.3).

The reaction of ClO + NO<sub>2</sub> is a termolecular recombination reaction similar to OH + NO<sub>2</sub>,



and the rate constant is in the fall-off region under the atmospheric pressure. The measurements of the rate constants of this reaction were made mostly prior to the 1990s, and the NASA/JPL panel evaluation (Sander et al. 2011) recommends the low- and high-pressure limit formulas as,

$$k_{0,5.115}(T) = 1.8 \times 10^{-31} \left(\frac{T}{300}\right)^{-3.4} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1},$$

$$k_{\infty,5.115}(T) = 1.5 \times 10^{-11} \left(\frac{T}{300}\right)^{-1.9} \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1},$$

respectively, based on Handwerk and Zellner (1984), Wallington and Cox (1986), Percival et al. (1997) and more previous studies. However, the high-pressure limit equation has not been obtained directly from experiments under high pressure, but from the curvilinear regression value based on the measurement under 1 atm using Eq. (5.7) with  $F_c = 0.6$ . The IUPAC subcommittee (Atkinson et al. 2007) recommends the temperature independent high pressure limit value,  $k_{\infty, 5.115} = 7 \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ , using more plausible value of  $F_c = 0.4$  based on Cobos and Troe (2003).

Quantum chemical calculations for the reaction of ClO + NO<sub>2</sub> have been performed by Kovacic et al. (2005), Zhu and Lin (2005). According to these theoretical calculations, this reaction forms ClONO<sub>2</sub> by the association of the O atom of ClO and N atom of NO<sub>2</sub> without energy barrier. Also, although the formation of cis-ClOONO and trans-ClOONO which correspond to HOONO in the reaction of OH + NO<sub>2</sub> is thermo-neutral or slightly exothermic, there is a large energy barrier for the isomerization from ClOONO to ClONO<sub>2</sub>, and it was concluded that ClONO<sub>2</sub> may not be formed by this process.

### 5.6.6 ClO + ClO

The self-reaction of ClO becomes important under the condition of very high concentration of ClO such as in the stratospheric ozone hole.

The most important pathway of the ClO + ClO reaction is,



to form dichlorine peroxide, ClOOCI, a dimer of ClO by the termolecular association reaction (Birk et al. 1989; Troler et al. 1990). This termolecular reaction is in the fall-off region under the stratospheric conditions, and the low- and high-pressure expressions has been obtained by the curvilinear regression using equation (5.7). The NASA/JPL panel evaluation (Sander et al. 2011) recommends the rate equations by taking  $F_c = 0.6$ ,

$$k_{0,5.116}(T) = 1.6 \times 10^{-32} \left(\frac{T}{300}\right)^{-4.5} \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$$

$$k_{\infty,5.116}(T) = 3.0 \times 10^{-12} \left(\frac{T}{300}\right)^{-2.0} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

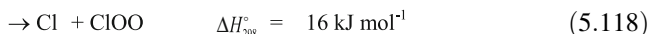
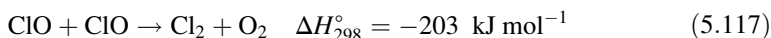
based on Troler et al. (1990), Nickolaisen et al. (1994), Bloss et al. (2001), Boakes et al. (2005), and others. Meanwhile, the IUPAC subcommittee report (Atkinson et al. 2007) recommends,

$$k_{0,5.116}(T) = 2.0 \times 10^{-32} \left(\frac{T}{300}\right)^{-4} \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1} \quad (190 - 300 \text{ K})$$

$$k_{\infty,5.116} = 1.0 \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \quad (190 - 300 \text{ K})$$

based on Trolier et al. (1990) and Bloss et al. (2001). Particularly, they presented the pressure independent value by taking  $F_c = 0.45$  as above.

As for the ClO + ClO reaction, other than the above pathway, bimolecular processes,



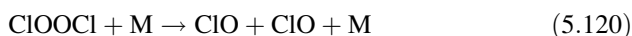
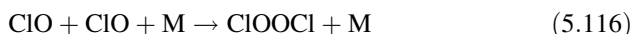
are known, and the NASA/JPL panel and the IUPAC subcommittee recommends the measured values by Nikolaisen et al. (1994) (Sander et al. 2011; Atkinson et al. 2007) as,

$$k_{5.117}(T) = 1.0 \times 10^{-12} \exp\left(-\frac{1590}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \quad (260 - 390 \text{ K})$$

$$k_{5.118}(T) = 3.0 \times 10^{-11} \exp\left(-\frac{2450}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \quad (260 - 390 \text{ K})$$

$$k_{5.119}(T) = 3.5 \times 10^{-13} \exp\left(-\frac{1370}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \quad (260 - 390 \text{ K})$$

The rate constants at 298 K are 4.8, 8.0, and  $3.5 \times 10^{-15} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  for  $k_{5.117}$ ,  $k_{5.118}$  and  $k_{5.119}$ , respectively, and the branching ratios of reaction (5.117), (5.118) and (5.119) are 0.39, 0.41 and 0.20, respectively. Since these bimolecular reactions have large activation energy, the rate constants are very small as a radical-radical reaction, and the termolecular reaction (5.116) is predominant by far under the stratospheric conditions. However, the ClOOCl molecule formed by the termolecular reaction is thermally unstable, and is in equilibrium with ClO,



with the equilibrium constant (Sander et al. 2011)

$$K_{5.116/5.120}(T) = 1.72 \times 10^{-27} \exp(-8650/T) \text{cm}^3 \text{molecule}^{-1}.$$

Thus, the termolecular reaction (5.116) becomes less important above 285 K (Atkinson et al. 2007).

According to the quantum chemical calculation, this reaction process mainly along the singlet energy surface. As for the structure of the dimer, ClOOCl, ClOCIO and ClCIOO are conceived, but ClOOCl is the most stable energetically, agreeing

with the experimental results (Lee et al. 1992; Zhu and Lin 2003b; Liu and Barker 2007).

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## Chapter 6

# Heterogeneous Reactions in the Atmosphere and Uptake Coefficients

Although most of chemical processes constituting a chemical system in the atmosphere consist of the photolysis of gaseous molecules, and gas phase homogeneous reactions that are described in Chaps. 4 and 5, there are some phenomena in which multiphase processes, such as uptake of atmospheric molecules on the solid and liquid surface, heterogeneous reactions on the surface, reactions in the bulk liquids, etc. are important. In the stratosphere, chemical reactions on the polar stratospheric clouds (PSC) are the most prominent example, and are of essential importance in the formation of the “ozone hole”. In the troposphere, multiphase reactions in clouds and fog have long been investigated as being related to acid rain historically. Recently, the surface reactions on sea salt in the marine boundary layer and on snow and ice related to tropospheric halogen chemistry, and the uptake and heterogeneous reactions of HO<sub>2</sub> radicals and nitrogenous compounds on aerosols related to tropospheric ozone chemistry, and heterogeneous oxidation reactions of organic aerosols related to their aging process are paid attention. In this chapter, uptake coefficients of atmospheric species on water droplet, sea salt, mineral particle and soot as important surfaces for tropospheric heterogeneous processes, and reactive uptake on PSC important in the stratosphere are described. The roles of multiphase reactions in the troposphere and stratosphere are described in Chaps. 7 and 8, respectively.

Since most homogeneous reaction processes have already been well established in principle, much attention has recently been focused on chemical processes at the gas-solid and gas-liquid interfaces in the atmosphere and studies are now going on intensively. However, such heterogeneous processes have a problem that the uptake coefficients and reaction probabilities are not unequivocally determined as a constant, being different from homogeneous processes, due to the diversity of chemical and morphological structure of surfaces. The constant to describe loss rate of gas phase molecules on liquid and solid particle surfaces can be expressed as,

$$J_{het} = \frac{1}{4} \gamma u_{av} N_g \quad (6.1)$$

as described by Eq. (2.84) in Sect. 2.4. Here,  $J$  (molecules  $\text{cm}^{-2} \text{s}^{-1}$ ) is the dissipation flux,  $\gamma$  is the uptake coefficient (the ratio of the loss number of gaseous molecule to the number of colliding molecule to the particles (see Eq. (2.81)),  $N_g$  (molecules  $\text{cm}^{-3}$ ) is a molecular density (molecules  $\text{cm}^{-3}$ ) and  $u_{av}$  ( $\text{cm s}^{-1}$ ) is the average kinetic velocity of gaseous molecules. In general, the loss process of gaseous molecules on the liquid and solid surfaces is the combined process of gas phase diffusion, accommodation coefficient, Henry's law constant, interaction at the interface, reaction in the bulk liquid, and so on, and the uptake coefficient  $\gamma$  contains their simultaneous equations. Since the general solution of such equations cannot be obtained, approximate equation based on a resistant model is used for expressing  $\gamma$  (see Sect. 2.4). The  $\gamma$  for the case of uptake accompanying heterogeneous reactions which are treated in this chapter can be expressed as shown by Eq. (2.88) before,

$$\frac{1}{\gamma} = \frac{1}{\Gamma_g} + \frac{1}{\alpha} + \frac{1}{\Gamma_{sol} + \Gamma_{rxn}}. \quad (6.2)$$

Here,  $\alpha$  is the mass accommodation coefficient expressing the probability of a gaseous molecule to stay on the surface when it collides with the particle surface, and  $\Gamma_g$ ,  $\Gamma_{sol}$ , and  $\Gamma_{rxn}$  are conductance corresponding to the gas phase diffusion, liquid phase diffusion and chemical reaction, respectively. When we neglect  $\Gamma_g$ , and  $\Gamma_{sol} + \Gamma_{rxn}$  are expressed as  $\Gamma_{rs}$ , Eq. (6.2) can be simplified as,

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{1}{\Gamma_{rs}} \quad (6.3)$$

In this chapter, the experimental values of  $\gamma$  and  $\alpha$  defined by the above formula are treated.

However, in some literature, the values under the conditions where  $\Gamma_g$  cannot be neglected, have been reported as they are, as  $\gamma$  and  $\alpha$ . Discussion will be made for some heterogeneous processes in such a case. Meanwhile, for example, for the reactions of PSCs, it is thought that  $\alpha = 1$  and  $\gamma$  is almost determined by the  $\Gamma_{rs}$ . Furthermore,  $\gamma$  is in general dependent on the density of coexisting molecules which have been taken to the surface in the past and are therefore dependent on the reaction time, initial and stationary state uptake coefficients are expressed as  $\gamma_0$  and  $\gamma_{ss}$ , respectively, and  $\gamma$  is simply used when they are not distinguished. However, the time for reaching the stationary state depends on the surface process of each reaction and molecular density, it is not necessarily clear whether  $\gamma_0$  or  $\gamma_{ss}$  should be used in the model for the actual atmosphere. Moreover, in the case of porous surface many orders of magnitude difference appears whether geometric or BET (Brunauer-Emmett-Teller) surface area is used for the calculation of  $\gamma$ . Further, reactive uptake coefficient  $\gamma_r$  is used when the uptake of a molecule

accompanies reactions on the surface or in bulk liquid and formation rate of reaction products are concerned.

As for the heterogeneous processes, the NASA/JPL panel evaluation No. 17 (Sander et al. 2011), and Report V (Crowley et al. 2010) and Data Sheet (Wallington et al. 2012) of the IUPAC Subcommittee on Gas Kinetics Data Evaluation for Atmospheric Chemistry provide useful reviews. Due to the above reasons, however, there are many cases in which the recommended values of uptake coefficients are not given since they are still in process of research. Table 6.1 gives the (reactive) uptake coefficients taken from the above evaluations or recent literature on the heterogeneous processes treated in this chapter. In Table 6.1, the values of  $\alpha$ ,  $\gamma$ ,  $\gamma_0$ , or  $\gamma_{0, BET}$  are given on a case by case basis, according to each literature. There are high possibilities that they will be renewed in the future, and this chapter will have to be revised. The heterogeneous processes of organic molecules that are now under the progress of research are not included in this book, being related to aging of organic aerosols.

## 6.1 Uptake on Water Droplet

The uptake coefficients of gaseous molecules into water  $\text{H}_2\text{O}(\text{l})$  are an important constant that determines their removal process on clouds and fogs, and removal rates by deposition over the ocean. The measurements of uptake coefficients for water surface have been made for  $\text{O}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{NO}_2$ ,  $\text{HONO}$ ,  $\text{HNO}_3$ , and many water soluble organic molecules among atmospheric species. Table 6.1 cites accommodation coefficients or uptake coefficients of typical inorganic atmospheric molecules for water surface. Simulation of transport through the gas-liquid interface of water has been interested theoretically, and a recent review is available in Garrett et al. (2006).

### 6.1.1 $\text{H}_2\text{O}$

Since the uptake and evaporation of gaseous  $\text{H}_2\text{O}$  molecules (water vapor) are very important as a microscopic process of cloud physics, many measurements and theoretical studies have been made from this viewpoint. From the perspective of atmospheric chemistry, it is worthy of study as a most fundamental process of uptake to the water surface among other many atmospheric molecules.

Recent measurements of accommodation coefficients of  $\text{H}_2\text{O}(\text{g})$  to  $\text{H}_2\text{O}(\text{l})$  have been made mainly using a liquid droplet train flow reactor or liquid droplet growth method. Although the obtained values converge within  $0.1 < \alpha < 1$ , it has been pointed out that there is some discrepancy between the values obtained by both methods. For example, the values of  $\alpha$  obtained by the liquid droplet train method of Li et al. (2001) are  $0.17 \pm 0.03$  and  $0.32 \pm 0.04$  at 280 and 258 K, while the value by



**Table 6.1** Uptake coefficients on water droplet, sea salt, soil and mineral dust, and soot

Gas phase molecules	Surface	Products	Uptake (accommodation) coefficients	Temperature (K)	References
H <sub>2</sub> O	Water	–	$\alpha > 0.3$	250–290	(c)
OH	Water	–	$\alpha > 0.1$	275–310	(a)
HO <sub>2</sub>	Water	–	$\alpha > 0.5$	270–300	(a)
	Water	–	$\gamma = 0.1$	290–300	(a)
O <sub>3</sub>	Water	–	$\alpha \geq 0.04$	195–262	(b)
	NaCl (s)	–	$\gamma < 1 \times 10^{-2}$	223–300	(b)
	Natural Salt	–	$\gamma = 10^{-3} - 10^{-2}$	~298	(d)
	Al <sub>2</sub> O <sub>3</sub>	–	$\gamma_{0, BET} = (1.2 \pm 0.4) \times 10^{-4}$	296	(e)
	Soil	–	$\gamma_{0, BET} = (3-6) \times 10^{-5}$	296	(e)
	Soot	–	$\gamma_0 = 10^{-4} - 10^{-3}$	298	(f)
NO <sub>2</sub>	Soot	HONO, NO	$\gamma_{0, BET} = (3-5) \times 10^{-5}$	240–350	(g)
N <sub>2</sub> O <sub>5</sub>	Water	HNO <sub>3</sub>	$\gamma = 0.01-0.06$	260–295	(b)
	NaCl (s)	ClNO <sub>2</sub> , HNO <sub>3</sub>	$\gamma_0 = 0.005$	~ 298	(h)
	NaCl (aq)	–	$\gamma_0 = 0.02$	260–300	(a)
	Synthetic Salt	ClNO <sub>2</sub>	$\gamma_0 = 0.02-0.03$	~ 298	(h)
	Soil	–	$\gamma_{ss} = 0.01-0.04$	296	(i)
	Soot	HNO <sub>3</sub>	$\gamma = (4 \pm 2) \times 10^{-4}$	294	(j)
	Soot	NO + NO <sub>2</sub>	$\gamma_{ss} = 5.0 \times 10^{-3}$	298	(k)
HNO <sub>3</sub>	Water	–	$\alpha \geq 0.05$	250–300	(b)
	NaCl (s)	NaNO <sub>3</sub>	$\gamma_0 = 0.002$	295–298	(b)
	Synthetic Salt	NaNO <sub>3</sub>	$\gamma_0 = 0.07-0.75$	298	(l)
	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	–	$\gamma_0 < 0.2$	295–300	(b)
	Soil	–	$\gamma_0 \approx 0.1$	298	(m)
	Soot	NO, NO <sub>2</sub>	$\gamma_0 = (2.0 \pm 0.1) \times 10^{-2}$	298	(n)
ClONO <sub>2</sub>	NaCl (s)	–	$\gamma_0 = 0.23 \pm 0.06$	298	(o)
	Synthetic Salt	–	$\gamma_0 = 0.42$	298	(o)

(continued)

**Table 6.1** (continued)

Gas phase molecules	Surface	Products	Uptake (accommodation) coefficients	Temperature (K)	References
SO <sub>2</sub>	Water	–	$\alpha \geq 0.12$	260–298	(b)
	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	–	$\gamma_0 > 5 \times 10^{-3}$	298	(b)
	Soil	–	$\gamma_0 = (7.6 \pm 0.5) \times 10^{-2}$	298	(b)
	Soot	–	$\gamma \approx 2 \times 10^{-3}$	298	(q)

(a) IUPAC Subcommittee Report Sheet (Wallington et al. 2012)

(b) NASA/JPL Panel Evaluation No.17 (Sander et al. 2011)

(c) Voiglander et al. (2007)

(d) Mochida et al. (2000)

(e) Michel et al. (2003)

(f) Fendel et al. (1995) and Rogaski et al. (1997)

(g) Lelievre et al. (2004)

(h) Thornton and Abbatt (2005)

(i) Wagner et al. (2008, 2009)

(j) Saathoff et al. (2001)

(k) Kargulian and Rossi (2007)

(l) De Haan and Finlayson-Pitts (1997)

(m) Seisel et al. (2004)

(n) Salgado-Muñoz and Rossi (2002)

(o) Gebel and Finlayson-Pitts (2001)

(p) Seisel et al. (2006)

(q) Koehler et al. (1999)

liquid droplet evaporation method of Smith et al. (2006) is  $0.62 \pm 0.09$  at 255–295 K. Meanwhile, Laaksonen et al. (2005), Winkler et al. (2006) reported the values,  $0.4 < \alpha < 1$ , obtained by the liquid droplet growth rate in the expansion chamber and recommended  $\alpha \approx 1$ . The discussion on the discrepancy between the values obtained by those methods has been given by Davidovits et al. (2004). In turn, a recent study, combining the liquid droplet growth experiment, by the fluid mechanics model calculation of Voigländer et al. (2007)  $\alpha$  is given as close to unity, and the lower limit is reported as 0.3, taking into consideration experimental error. The recommended value by the NASA/JPL panel evaluation No. 17 is  $\alpha > 0.1$  (Sander et al. 2011).

The uptake of an H<sub>2</sub>O molecule to the liquid H<sub>2</sub>O surface has been attracted interest from the molecular dynamics point of view and theoretical analysis has been made (Morita et al. 2003, 2004b; Viececi et al. 2004). From these theoretical analysis,  $\alpha \approx 1$  has been obtained and the reason that experiments by the droplet train method gives the smaller values has been ascribed to the diffusion effect in the gas phase.

In the case that water droplet is coated by organic compounds,  $\alpha$  is known to be decreased (Chakraborty and Zachariah 2011; Takahama and Russell 2011; Sakaguchi et al. 2012), which is paid attention to from the point of indirect effect of climate sensitivity of aerosols.

### 6.1.2 OH

Uptake of OH and HO<sub>2</sub> on H<sub>2</sub>O(l) has attracted interest and been investigated from a theoretical point of view since they are the main free radicals carrying the most important HO<sub>x</sub> chain reaction in the troposphere as well as being hydrophilic. Since the uptake rate of OH and HO<sub>2</sub> are thought to be dependent on how quickly they are removed from the interface by self-reactions on the H<sub>2</sub>O(l) surface, uptake coefficients are conceived to be dependent on contact time of the radicals to the interface, pH of water, co-existing substances, etc. Therefore, values obtained directly by experiments are those under the specific experimental conditions, and it is necessary to convert them by simulation taking into account these interface reactions in order to obtain the accommodation coefficient  $\alpha$ .

As for the uptake of OH on H<sub>2</sub>O(l), Hanson et al. (1992a) gave  $\gamma > 3.5 \times 10^{-3}$  for pure water at 275 K by the measurement using wetted wall flow tube reactor. Takami et al. (1998) obtained  $\gamma = (4.2 \pm 2.8) \times 10^{-3}$  for pure water at 293 K by the impinging flow method, and reported that the value decreases with gas-liquid contact time and increases by a factor of 2–3 for the acidic and alkaline water with pH = 1 and 11. They estimated that the accommodation coefficient  $\alpha$  is close to unity by the simulation using the rate constant of OH in the aqueous phase and Henry's law constants, which agrees with the result of  $\alpha = 0.83$  (300 K) by molecular dynamics calculation by Roeselová et al. (2004). The recommended values of the IUPAC subcommittee and the NASA/JPL panel are  $\alpha > 0.1$  and 0.02, respectively (Wallington et al. 2012; Sander et al. 2011).

### 6.1.3 HO<sub>2</sub>

As for the uptake of HO<sub>2</sub> into pure water, Hanson et al. (1992) reported an accommodation coefficient  $\alpha > 0.01$  at 275 K by the measurement with the wetted wall flow reactor. Meanwhile, Mozurkewich et al. (1987) reported  $\alpha > 0.2$  by taking the obtained value by a fine particle flow system using concentrated NH<sub>4</sub>HSO<sub>4</sub> solution doped with Cu<sup>2+</sup> to facilitate the uptake as an accommodation coefficient. Morita et al. (2004a) obtained  $\alpha \approx 1$  by molecular dynamics calculation and deduced that the upper limit of uptake coefficient  $\gamma$  is close to unity. The recommended values by the IUPAC subcommittee and the NASA/JPL panel are  $\alpha > 0.5$  and  $\alpha > 0.02$ , respectively (Wallington et al. 2012; Sander et al. 2011).

### 6.1.4 O<sub>3</sub>

The uptake rate of O<sub>3</sub> at the surface of pure water is very small and cannot be directly measured by experiments, so that all the measurements of the

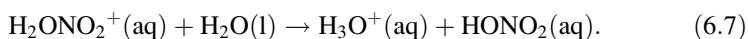
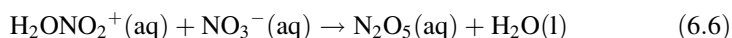
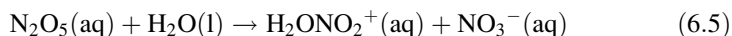
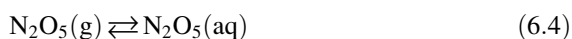
accommodation coefficient have so far been made on aqueous solution containing ions e.g.  $\text{I}^-$  as  $\text{O}_3$  scavenger. From these measurements, it has been known that the accommodation coefficient of  $\text{O}_3$  to  $\text{H}_2\text{O}$  (l) has negative temperature dependence, and  $\alpha$  becomes larger at the lower temperature between 275 and 300 K. Measured values by Magi et al. (1997) are in the range of  $0.92 \times 10^{-2}$  to  $2.08 \times 10^{-2}$  between 281 and 261 K. Measurements by Müller and Heal (2002) using the wetted wall reactor gave the value of  $\alpha = 4 \times 10^{-3}$  at 293 K. They proposed an estimate of  $\alpha \geq 0.01$  or the possibility of even larger value considering the experimental errors, while Schutze and Herrmann (2002) reported a value of  $\alpha \geq 0.02$  at 298 K by using the single drops flow tube reactor.

From the theoretical calculation of molecular dynamics,  $\alpha \approx 0.1$ , and 0.047 are given by Roeselová et al. (2003), and Vieseli et al. (2005), respectively. In these studies, they made a comparison between the collisions of OH and  $\text{O}_3$  on  $\text{H}_2\text{O}$  (l) surface and showed that OH stays on the surface for 100 ps while  $\text{O}_3$  stays less than 50 ps when they collide with thermal energy at room temperature, reflecting the difference in affinity to  $\text{H}_2\text{O}$  (l). The value recommended by the NASA/JPL panel is  $\alpha \geq 0.04$  (Sander et al. 2011).

### 6.1.5 $\text{N}_2\text{O}_5$

The uptake of  $\text{N}_2\text{O}_5$  to water droplets and aerosols forms nitric acid  $\text{HONO}_2$  ( $\text{HNO}_3$ ), which removes  $\text{NO}_x$  from the gas phase. Since the process could have large effects on the production rate of  $\text{O}_3$  and OH in the troposphere, many studies have been conducted recently.

The reactive uptake processes of  $\text{N}_2\text{O}_5$  on pure water and salt solutions have been summarized by Bertram and Thornton (2009) as follows,



Succeeding to the absorptive dissolution process (6.4) of  $\text{N}_2\text{O}_5$  on  $\text{H}_2\text{O}$  (l), the formation of protonated nitric acid  $\text{H}_2\text{ONO}_2^+$  (aq) by the reaction of  $\text{N}_2\text{O}_5$  (aq) and  $\text{H}_2\text{O}$  (l) is assumed (Eq. 6.5), and  $\text{H}_2\text{ONO}_2^+$  (aq) forms  $\text{HONO}_2$  (aq) by the reaction with  $\text{H}_2\text{O}$  (l). Also, it is thought that the presence of  $\text{NO}_3^-$  (aq) increases  $\text{N}_2\text{O}_5$  (aq) and decreases the uptake rate of  $\text{N}_2\text{O}_5$  (g).

Van Doren et al. (1990) found that the uptake coefficients of  $\text{N}_2\text{O}_5$  onto the surface of pure water have negative temperature dependence such that

$\gamma = 0.057 \pm 0.003$  at 271 K and  $0.036 \pm 0.004$  at 282 K by using the droplet train flow reactor method. George et al. (1994) gave similar values of  $0.030 \pm 0.002$  (262 K),  $0.013 \pm 0.008$  (277 K) by using the same experimental methodology. Schütze and Herrmann (2002) obtained  $\alpha = 0.011$  (293 K) after the correction of gas phase diffusion by using the single drops flow tube reactor.

On the other hand, many measurements have been made for the uptake of  $\text{N}_2\text{O}_5$  on aqueous solutions of inorganic salts. The NASA/JPL panel evaluation No. 17 mentions that the reported values are in good agreement within the range of  $\gamma = 0.02\text{--}0.04$  at room temperature considering the temperature and humidity effects including pioneering study of Mozurkewich and Calvert (1988) for  $\text{NH}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  and more recent studies of Hallquist et al. (2003) ( $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NaNO}_3$ ) and Griffiths et al. (2009) (organic acid +  $(\text{NH}_4)_2\text{SO}_4$ ). Bertram and Thornton (2009) proposed a new parameterization for the uptake of  $\text{N}_2\text{O}_5$  on a mixed droplet according to the reaction scheme (6.4)–(6.7) based on the experiment using the chemical ionization mass spectrometer for the mixed solution droplets of  $\text{H}_2\text{O}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and organic acid showing that the inhibition effect by  $\text{NO}_3^-$  is negated by the co-existence of  $\text{Cl}^-$ .

It has been known that the uptake coefficient of  $\text{N}_2\text{O}_5$  decreases when the water droplet surface is coated by organics, as in the case of the uptake of  $\text{H}_2\text{O}$  on  $\text{H}_2\text{O}$  (l) (Folkers et al. 2003; Anttila et al. 2006; Park et al. 2007), and theoretical and model analyses have been made by Anttila et al. (2006) and Riemer et al. (2009).

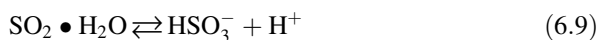
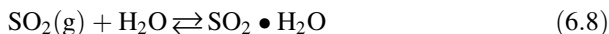
### 6.1.6 $\text{HNO}_3$

$\text{HNO}_3$  has a large affinity for  $\text{H}_2\text{O}$  (l), and it has been known that the accommodation coefficient rather than solubility or bulk reaction in the liquid phase, is the rate-determining step for the removal process from the gas phase.

As for the uptake coefficient of  $\text{HNO}_3$  on  $\text{H}_2\text{O}$  (l), Van Doren et al. (1990) showed that  $\gamma$  has negative temperature dependence such that  $0.19 \pm 0.02$  at 268 K and  $0.071 \pm 0.02$  at 293 K, from the experiment of mono-disperse droplet train in a flow reactor. As seen in Sect. 6.1.1, this experimental method underestimates the accommodation coefficient due to the effect of gas phase diffusion (Garrett et al. 2006). Using the similar experimental method Ponche et al. (1993) obtained the values of  $0.11 \pm 0.01$  at 298 K, and Schütze and Herrman (2002) reported the values of  $\alpha \geq 0.03$  after the correction for the effect of gas phase diffusion. The recommended value of the NASA/JPL panel is  $\alpha \geq 0.05$  (Sander et al. 2011). In general it is thought that the diffusion in the gas phase is rate determining for the uptake of gaseous molecules when  $\alpha \geq 10^{-3}$ .

### 6.1.7 SO<sub>2</sub>

When SO<sub>2</sub> contacts with the surface of H<sub>2</sub>O (l) and is taken into the aqueous phase, SO<sub>2</sub> react with water molecule as,



and reaches to the chemical equilibrium (Wallington et al. 2012). Thus, SO<sub>2</sub> in the interface can be quickly removed by reactions (6.9) and (6.10) when a water droplet is alkaline, but the uptake rate is dependent on contact time for the range of low pH. Jane et al. (1990) reported that the uptake is governed by the formation rate of HSO<sub>3</sub><sup>-</sup> from the reaction of SO<sub>2</sub> with H<sub>2</sub>O for pH > 5 and is determined by Henry's law solubility for the low pH. In either of the case, however, the uptake coefficients for the experiments changing the pH and the gas-liquid contact time by using the droplet flow method, are larger than those expected from the known constants. Donaldson et al. (1995) detected the chemisorbed SO<sub>2</sub>•H<sub>2</sub>O on water surface spectroscopically which was assumed by Jane et al. (1990).

The values of  $\gamma$  have been obtained by the experiment of Boniface et al. (2000) as  $0.43 \pm 0.01$ , and  $0.175 \pm 0.015$  at 263 and 291 K, respectively showing the negative temperature dependence. Other values are  $\gamma = 0.13 \pm 0.01$  with the low pressure reactor by Ponche et al. (1993), and  $\gamma = 0.2$  with the liquid impinging method by Shimono and Koda (1996). The recommended value of the NASA/JPL evaluation No. 17 is  $\alpha \geq 0.12$  (Sander et al. 2011). The IUPAC subcommittee proposed the bulk accommodation coefficient  $\alpha_b$  and recommends  $\alpha_b = 0.11$  (Wallington et al. 2012).

A series of multiphase reactions after SO<sub>2</sub> is taken into fog and rain droplets followed by liquid phase oxidation processes by O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> are described in Chap. 7, Sect. 7.6.2.

## 6.2 Uptake and Surface Reactions on Sea Salt and Alkaline Halides

The interface reactions of O<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, etc. on sea salt is important heterogeneous reactions that have a possibility of releasing inorganic molecules containing Cl, Br, etc. However, those reaction processes have not been fully elucidated and are still important themes of research experimentally and theoretically. Furthermore, uptake of HO<sub>2</sub> radicals on sea salt is an important process having a large effect on the efficiency of HO<sub>x</sub> cycle and ozone formation in the troposphere, together with the uptake on soil and mineral dust which will be described in the next section. In

addition, when nitric acid is converted to  $\text{NaNO}_3$  by the reaction with sea salt, it can be transported to far longer distance than  $\text{HNO}_3$  and has a large influence on nitrogen budget in the troposphere, since the surface deposition rate of  $\text{NaNO}_3$  is much smaller than  $\text{HNO}_3$ . The reaction of  $\text{ClONO}_2$  with sea salt, which will be described in the last paragraph of this section, is important as a process in the tropospheric halogen cycle in the troposphere. As for the uptake and reactions of atmospheric species on sea salt and alkali halide salts, reviews have been given by Finlayson-Pitts (2003) and Rossi (2003).

The efflorescence and deliquescence point of  $\text{NaCl}$  is relative humidity of 43 % and 75 %, respectively. It is thought that water is adsorbed on the solid surface at above the efflorescence point, and salt is liquefied above the deliquescence point. In this section, uptake and heterogeneous reactions of atmospheric molecules on the surface of sea salts and halogenated alkali salts as their surrogate compounds are described. In general the surfaces of inorganic salts are not porous so that the adsorption surface area by the BET method agree with those of geometrical surface area.

### 6.2.1 $\text{O}_3$

The uptake coefficients of  $\text{O}_3$  on the solid surface of pure  $\text{NaCl}$ ,  $\text{NaBr}$ , etc. are very small ( $\gamma \approx 10^{-6}$ ) and the decay of  $\text{O}_3$  cannot be observed experimentally (Alebic-Juretic et al. 1997; Mochida et al. 2000). However, when water vapor is adsorbed or other ions coexist as in the case of actual sea salts, it has been known that the value of  $\gamma$  increases largely and  $\text{Cl}_2$  and/or  $\text{Br}_2$  are released.

Sadanaga et al. (2001) reported that the values of  $\gamma$  increases greatly from  $<10^{-5}$  to  $3.5 \times 10^{-2}$  when  $\text{Fe}^{3+}$  coexists in  $\text{NaCl}$  more than 0.1 %, and under the condition that the ratio of  $\text{Fe}^{3+}$  increased to 0.5–1 %, the release of  $\text{Cl}_2$  is observed in the dark reaction. In the experiment using synthetic sea salt, release of only  $\text{Br}_2$  is observed and suggested that  $\text{Cl}_2$  could be released after  $\text{Br}_2$  is depleted in the reaction on actual sea salt. Hirokawa et al. (1998) reported that the uptake of  $\text{O}_3$  and the formation of  $\text{Br}_2$  were observed on the surface of  $\text{NaBr}$  only when the relative humidity was increased to near the deliquescence point. Similar uptake of  $\text{O}_3$  and the release of  $\text{Br}_2$  have been confirmed on Pyrex glass surfaces (Anastasio and Mozurkewich 2002) and in aerosol chambers (Hunt et al. 2004). Furthermore, Oum et al. (1998b) reported that  $\text{Br}_2$  is released from the dark reaction of  $\text{O}_3$  on sea ice surface, and Mochida et al. (2000) reported that the formation of  $\text{Br}_2$  with  $\gamma \sim 10^{-3} - 10^{-2}$  from synthetic and natural sea salt in the Knudsen cell experiment, which are three orders of magnitude larger than those estimated in the reaction in the bulk solution of bromides.

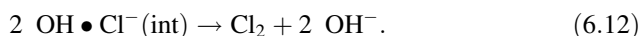
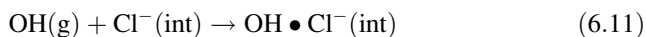
Several studies have been made experimentally and theoretically seeking for the reason of preferential release of  $\text{Br}_2$  in the reaction of  $\text{O}_3$  with sea salt in spite of the fact that the ratio of  $\text{Cl} : \text{Br}$  is 660:1. Ghosal et al. (2000) showed experimentally by X-ray photoelectron spectroscopy that  $\text{Br}^-$  is aggregated on the surface of  $\text{NaCl}$

doped with small amount of  $\text{Br}^-$  under the exposure of water vapor. Zangmeister et al. (2001) found by use of a spectroscopic method, that the ratio of Br at the surface of mixed salt which has the same Br: Cl ratio as the sea salt is 4–5 %, that is higher than the ratio in the bulk crystal by a factor of 35. Similarly, it has been shown that Br aggregation occurs on the surface of NaCl single crystal doped with Br when the relative humidity increased to 50–65 % by Hess et al. (2007) using the Rutherford backward scattering spectroscopy. It is suggested that the Br/Cl ratio is increased to 0.2 if the results are applied to natural sea salt. On the other hand, from the theoretical molecular dynamics calculation, it has been shown that polar ions such as  $\text{Br}^-$  and  $\text{I}^-$  float up to the surface in the presence of water molecules (Jungwirth and Tobias 2002).

### 6.2.2 OH

Although the uptake coefficient of the OH radical on sea salt has not been measured directly, it has been reported that active chlorine species are formed by the irradiation of  $\text{O}_3$  under the coexistence of sea salt particles in a chamber (Behnke et al. 1995). Oum et al. (1998a) confirmed that  $\text{Cl}_2$  is released to the gas phase by the irradiation of UV at 254 nm to the deliquescent sea salt in the coexistence of  $\text{O}_3$ , and proposed the formation of  $\text{Cl}_2$  by the surface reaction of sea salt and OH produced by the photolysis of  $\text{O}_3$  in the presence of water vapor (reaction 4.3).

Detailed analysis has been made for a chamber experiment with the use of molecular dynamics calculation by Knipping et al. (2000), and this reaction has been confirmed to occur on pure NaCl and sea salt without the existence of other metal ions. From the molecular dynamics calculations, it has become clear that  $\text{Na}^+$  is buried into bulk water by solvation through hydrogen bonds on the deliquescent NaCl surface while  $\text{Cl}^-$  with large molecular diameter is pushed to the liquid surface resulting higher probability of surface reaction, and the affinity energy between OH and Cl is  $4.0 \text{ kJ mol}^{-1}$  which is much larger than the value  $1.2 \text{ kJ mol}^{-1}$  for  $\text{H}_2\text{O}$  to allow easier formation of an  $\text{OH} \bullet \text{Cl}^-$  complex. Based on these results, Knipping et al. (2000) proposed the formation mechanism of  $\text{Cl}_2$  from OH and sea salt as,



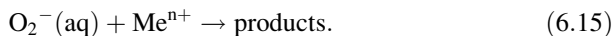
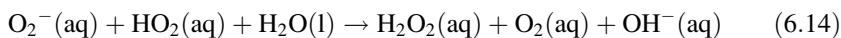
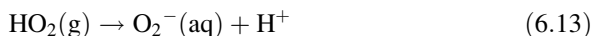
Here,  $\text{Cl}^-(\text{int})$  and  $\text{OH} \bullet \text{Cl}^-(\text{int})$  stands for the species on interface surface. Furthermore, it has been shown from kinetic analysis that the experimental results can be reproduced by this mechanism, while they cannot be explained by the known liquid phase reactions unless a strong acidic solution is postulated.



### 6.2.3 HO<sub>2</sub>

Uptake of HO<sub>2</sub> radicals to sea salt has attracted interest as a loss process of HO<sub>2</sub> in the marine boundary layer. Experimentally, the formation of H<sub>2</sub>O<sub>2</sub> has been reported by a self-reaction of HO<sub>2</sub> on the surface under the conditions with the radical concentration of a few 100 times higher than in the atmosphere. Recently, Taketani et al. (2008, 2009) reported the experimental uptake coefficient  $\gamma$  under the condition of comparable concentration of HO<sub>2</sub> to the atmosphere by direct measurement of HO<sub>2</sub> using a chemical conversion LIF method used in the atmospheric detection of the radicals. According to their results, the values of  $\gamma$  for dry NaCl and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> are small, 0.04–0.05 (RH = 20–45 %) and 0.01–0.02 (RH = 20–55 %), respectively, but they increase to 0.11–0.19 (RH = 44–75 %) and 0.09–0.11 (RH = 53–75 %) under increased humidity higher than deliquescence point, and they further increase distinctly to  $0.53 \pm 0.12$  and  $0.65 \pm 0.17$ , respectively, with the dope of Cu(II). Thus, it is known that uptake coefficient of HO<sub>2</sub> to sea salt increases with the existence of H<sub>2</sub>O(l) molecules and metal ions such as Cu(II) at the surface. Taketani et al. (2009) also reported that  $\gamma$  for synthetic sea salt and natural sea salt crystallized from sea water is 0.07–0.13 and 0.10–0.11, respectively, under the condition of RH = 35–75 %. Based on these results, the IUPAC subcommittee recommends 0.1 for the uptake coefficient for sea salt to be used in atmospheric models (Wallington et al. 2012). Negative temperature dependences for the reaction of HO<sub>2</sub> on sea salt, NaCl, NaBr and MgCl<sub>2</sub> · 6H<sub>2</sub>O have been reported by Loukhovitskaya et al. (2009).

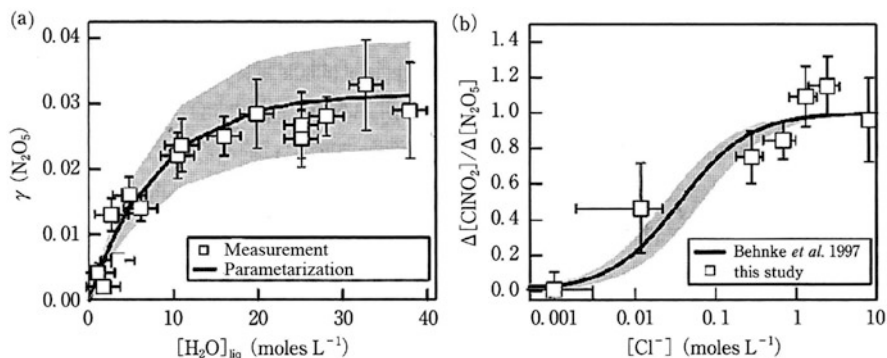
From these results, the uptake of HO<sub>2</sub> on sea salt does not have direct chemical interaction with Cl<sup>-</sup> and Br<sup>-</sup> being different from the case of O<sub>3</sub> and OH, and the following processes are thought if as processes at the interface with water solution (Wallington et al. 2012),



Here, Me<sup>n+</sup> stands for metal ions such as Cu(II).

### 6.2.4 N<sub>2</sub>O<sub>5</sub>

The reactions of N<sub>2</sub>O<sub>5</sub> with sea salt has attracted interest since they are important as a loss process of N<sub>2</sub>O<sub>5</sub> in the marine boundary layer, and also as a trigger for tropospheric halogen chemistry by forming photochemically active ClNO<sub>2</sub> in the marine boundary layer in urban coasts.



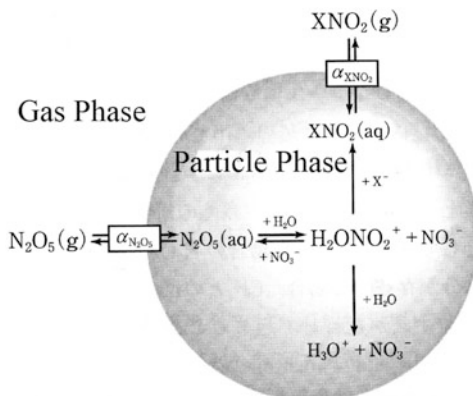
**Fig. 6.1** Uptake of  $\text{N}_2\text{O}_5$  on NaCl particles. (a) Dependence of  $\gamma(\text{N}_2\text{O}_5)$  on surface water concentration, (b) Dependence of production yields of  $\text{ClNO}_2$ , ( $\Delta[\text{ClNO}_2]/\Delta[\text{N}_2\text{O}_5]$ ), on surface concentration of  $\text{Cl}^-$  (Adapted from Bertram and Thornton 2009)

In the surface reactions of  $\text{N}_2\text{O}_5$  with NaCl, a surrogate species for sea salt, the formation of  $\text{ClNO}_2$  by the reaction with  $\text{Cl}^-$  and formation of  $\text{HNO}_3$  by the hydrolysis reaction are known to occur simultaneously under the condition of the presence of water on the solid surface. Based on many measurements, Bertram and Thornton (2009) compiled the concentration dependence on  $\text{H}_2\text{O}(\text{l})$  and  $\text{Cl}^-$  for the surface reactions of  $\text{N}_2\text{O}_5$  with dissolved NaCl, and showed that uptake coefficient  $\gamma$  increases with water concentration on the NaCl surface (Fig. 6.1a). The ratio of the formation yield of  $\text{ClNO}_2$ ,  $\Delta(\text{ClNO}_2)$ , to the decreased amount of  $\text{N}_2\text{O}_5$ ,  $\Delta(\text{N}_2\text{O}_5)$ , increases with the increase of the concentration of  $\text{Cl}^-$ , and the yield of  $\text{ClNO}_2$ ,  $\Delta(\text{ClNO}_2)/\Delta(\text{N}_2\text{O}_5)$  is unity for  $[\text{Cl}^-] > 1 \text{ M}$  (Fig. 6.1b).

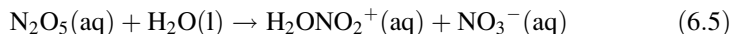
The experiments of Hoffman et al. (2003) gave  $\gamma = 0.0029 \pm 0.0017(2\sigma)$  for the overall reactive uptake for the  $\text{ClNO}_2$  and  $\text{HNO}_3$  formation, and the branching ratio of  $\text{ClNO}_2$  formation reaction is  $0.73 \pm 0.28$ . Thornton and Abbatt (2005) reported  $\gamma = 0.005 \pm 0.004$  for NaCl crystal under the humidity lower than the deliquescence point, which agrees with those of Hoffman et al. (2003). For the deliquescent sea salt,  $\gamma$  is one order of magnitude larger,  $\gamma = 0.03 \pm 0.008$  ( $\text{RH} = 65\%$ ), agreeing well with the result of Stewart et al. (2004), 0.025 ( $\text{RH} > 40\%$ ). Recently, Roberts et al. (2009) obtained  $0.2 < \Delta(\text{ClNO}_2)/\Delta(\text{N}_2\text{O}_5) < 0.8$  for  $0.02 < [\text{Cl}^-] < 0.5 \text{ M}$  in the experiments of changing the concentration of NaCl in the aqueous solution. These values agree well with the uptake coefficient and the formation yield of  $\text{ClNO}_2$  as a function of  $[\text{H}_2\text{O}(\text{l})]$  and  $[\text{Cl}^-]$  shown in Fig. 6.1a, b, respectively.

It has been reported by Hoffman et al. (2003) that for the experiments using synthetic sea salt, the value of  $\gamma$  is one order of magnitude larger,  $0.034 \pm 0.08$ , and the formation yield of  $\text{ClNO}_2$  is 100%. The value of  $\gamma$  by Stewart et al. (2004) is  $\gamma = 0.025$  is independent of humidity under the condition of relative humidity larger than 30%, and those by Thornton and Abbatt (2005) is  $\gamma = 0.02\text{--}0.03$  under the relative humidity of 43–70%.

**Fig. 6.2** Schematic diagram of uptake on an NaCl particle and reactions of  $N_2O_5$  in liquid particles (Adapted from Bertram and Thornton 2009)



Based on these many experiments, the process for the reaction of  $N_2O_5$  with the surface of dissolved sea salt has been proposed as,

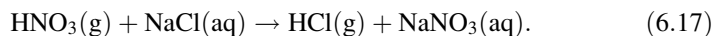


to form  $ClNO_2$  (Bertram and Thornton 2009). Figure 6.2 shows schematic picture of the processes in a liquid droplet including these reactions.

### 6.2.5 $HNO_3$

The reaction of  $HNO_3$  with sea salt is an important heterogeneous process in the troposphere for converting gaseous nitric acid to particulate sodium nitrate  $NaNO_3$ . Since the uptake coefficient of this reaction is large, most  $HNO_3$  is transported from the coastal terrestrial boundary layer in polluted areas to the marine boundary layer is converted to  $NaNO_3$  in a few hours. The deposition rate of  $HNO_3$  to the ground surface is very large and the atmospheric lifetime in the boundary layer is short, while the deposition rate of  $NaNO_3$  is much smaller. This means that  $NO_3^-$  is transported long distances by the conversion of  $HNO_3$  to  $NaNO_3$ , and has a large impact on  $NO_3^-$  in remote areas. On the other hand, since there is a possibility that  $NaCl$  and other salts could be injected to the stratosphere, this heterogeneous reaction is also interested in the stratospheric chemistry.

Many studies have been conducted on the uptake of  $HNO_3$  on  $NaCl$  particles and deliquescent salts (Rossi 2003), and the uptake is known to be facilitated by the substitution reaction on the  $NaCl$  surface,



This reaction is dependent strongly on the adsorbed amount of water, and Ghosal and Hemminger (2004), and Davies and Cox (1998) showed adsorbed water at the

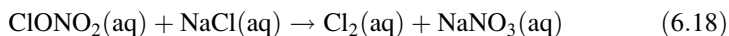
surface of NaCl increases mobility of ions and increases the uptake coefficient even below the deliquescent point. The NASA/JPL panel (Sander et al. 2011) recommends the initial uptake coefficient  $\gamma_0$  as 0.002, based on the above measurements and those of Hoffman et al. (2003) and Leu et al. (1995).

The value of the uptake coefficient of HNO<sub>3</sub> on NaCl differs largely by the surface conditions and  $\gamma_0$  is as large as  $0.5 \pm 0.2$  for deliquescent salt under RH of 60 %, but the uptake coefficient decreases by a factor of 5–50 when the surface is coated by long-chain fatty acid (Stemmler et al. 2008). Saul et al. (2006) reported that the uptake coefficient becomes as large as  $>0.1$  under the co-existence of MgCl<sub>2</sub> even under the low humidity of RH = 10 %.

De Haan and Finlayson-Pitts (1997) reported  $\gamma_0 = 0.07\text{--}0.75$  and the value at the stationary state  $\gamma_{ss} = 0.03\text{--}0.2$  by the experiments of using the synthetic sea salt, showing that the uptake coefficient becomes large for sea salt as compared with pure salt similar to the reaction with O<sub>3</sub> mentioned in Sect. 6.2.1. Similarly, the uptake coefficient is very large,  $0.5 \pm 0.2$  for the deliquescent sea salt (RH 55 %) in the experiment of Guimbaud et al. (2002).

### 6.2.6 ClONO<sub>2</sub>

In the tropospheric halogen chemistry, ClONO<sub>2</sub> is a quasi-stable compound formed in the chain termination reaction of ClO in the urban coastal area where NO<sub>x</sub> concentration is relatively high. The reaction of ClONO<sub>2</sub> with sea salt results in photochemically active Cl<sub>2</sub> as in the process,



and facilitates halogen chain reaction in the troposphere (Finlayson-Pitts et al. 1989) (see Sect. 7.5.2). This reaction may have a role as a source of the Cl<sub>2</sub> which is episodically observed in the marine boundary layer.

Several measured values have been reported for the uptake coefficient of ClONO<sub>2</sub> on NaCl crystals. Very large values such as  $\gamma_0 = 0.23 \pm 0.06$ , (Caloz et al. 1996),  $0.10 \pm 0.05$  (Aguzzi and Rossi 1999),  $0.23 \pm 0.06$  (Gebel and Finlayson-Pitts 2001) have been reported for the initial uptake coefficient, while Hoffman et al. (2003) reported the stationary state value as  $\gamma_{ss} = 0.024 \pm 0.012$  after the correction by a model. Deiber et al. (2004) obtained an accommodation coefficient  $\alpha = 0.108 \pm 0.03$  from an experiment using the droplet train method with NaCl aqueous solution. As for the product, well-agreed results that the yield of Cl<sub>2</sub> is unity in the reaction (6.18) have been obtained in these experiments.

Similar experiments for NaBr and KBr have been conducted, and large uptake coefficients similar to NaCl described above, and the formation of BrCl as a product has been reported (Caloz et al. 1996; Aguzzi and Rossi 1999; Deiber et al. 2004). Furthermore, Gebel and Finlayson-Pitts (2001) conducted an experiment using

synthetic sea salt, and obtained the initial uptake coefficient of 0.42, stationary state uptake coefficient of 0.16, and the yield of  $\text{Cl}_2$  as  $0.78 \pm 0.13$ .

### 6.3 Uptake and Surface Reactions on Soil Dust and Mineral Particles

Soil dust blown up from the desert of Sahara, Gobi, etc. is an important constituent of the troposphere, and uptake of  $\text{O}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_3$ ,  $\text{SO}_2$ , etc. on the particle surface can have a large impact on tropospheric chemistry (Bauer et al. 2004). The soil dust consists of chemical components of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaCO}_3$ ,  $\text{NaCl}$ ,  $\text{MgCO}_3$ , etc. The main components of typical aeolian dust are oxides of silicone and aluminum e.g. 60 %  $\text{SiO}_2$ , 10–15 %  $\text{Al}_2\text{O}_3$  and the ratio of minerals containing other elements varies widely by location (Usher et al. 2003). Therefore,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , etc. are often used as surrogates of dust particles in laboratory experiments. Since the surfaces of mineral dust are in general porous, different from inorganic salt crystals described in the previous section, it should be noted that the value of uptake coefficient differs largely before and after the correction for BET surface.

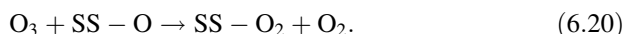
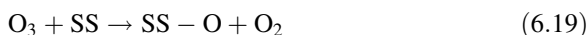
Chemical reactions on mineral dust have been reviewed by Usher et al. (2003), and the impacts on global tropospheric chemistry have been discussed using global chemical transport models by Bian and Zender (2003), Bauer et al. (2004), Evans and Jacob (2005), and other studies.

#### 6.3.1 $\text{O}_3$

The decrease of  $\text{O}_3$  concentration under aeolian dust has been found in field observations, and the causes have been discussed as due to the decomposition of  $\text{O}_3$  on the dust surface, uptake of  $\text{N}_2\text{O}_5$ , the removal of  $\text{NO}_x$  from gas phase due to the conversion to  $\text{HNO}_3$ , etc. (Usher et al. 2003).

Many measurements of the uptake coefficient of  $\text{O}_3$  on the surface of actual soil particles such as Saharan dust, and surrogates such as  $\text{SiO}_2$  have been made studying the dependences on exposure time and on water molecules.

From these results, the following scheme for surface decomposition process has been proposed (Li et al. 1998),



Here, SS expresses reactive sites on the surface of e.g.  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  particles. The uptake of  $\text{O}_3$  on mineral surface is irreversible, and the desorption of  $\text{O}_3$  from

the surface has not been observed (Crowley et al. 2010). From the above scheme, it is expected that the uptake of  $O_3$  is large initially, decreases later and reach to a stationary state after all of the SS are oxidized to SS- $O_2$ . The presence of water molecule is supposed to either inhibit the uptake of  $O_3$  by covering SS competitively or facilitate by reactivating SS-O or SS- $O_2$ , so that the uptake coefficient would have positive or negative humidity effect depending on which process is predominate (Sullivan et al. 2004; Mogili et al. 2006). The presence of SS-O on  $Al_2O_3$  surface has been confirmed by the experiment of Roscoe and Abbatt (2005) using infrared spectroscopy.

Initial uptake coefficients  $\gamma_0$  have been reported by Michel et al. (2003) in the experiments with a Knudsen cell at 296 K as  $(1.2 \pm 0.4) \times 10^{-4}$ ,  $(2.0 \pm 0.3) \times 10^{-4}$  and  $(6.3 \pm 0.9) \times 10^{-5}$  for  $\alpha-Al_2O_3$ ,  $\alpha-Fe_2O_3$  and  $SiO_2$ , and  $(2.7 \pm 0.8) \times 10^{-5}$  and  $(6 \pm 2) \times 10^{-5}$  for yellow dust and Saharan dust, respectively, after the BET surface correction. Meanwhile, stationary state uptake coefficients are  $\gamma_{ss, BET} = 2.2 \times 10^{-5}$  for  $\alpha-Fe_2O_3$  and  $6 \times 10^{-6}$  for Saharan dust. Sullivan et al. (2004) obtained  $\gamma_{0, BET} = 1.0 \times 10^{-5}$  and  $6 \times 10^{-6}$  for  $\alpha-Al_2O_3$  and Saharan dust at the low mixing ratio (ppmv) region of  $O_3$  by using a coated wall flow reactor. Hanisch and Crowley (2003) showed that the uptake coefficients for Saharan dust are dependent on the mixing ratio of  $O_3$ , and gave  $\gamma_{0, BET} \sim 3 \times 10^{-5}$ ,  $\gamma_{ss, BET} = \sim 7 \times 10^{-6}$  at 30 ppbv of  $O_3$ . From these measurements, it has been revealed that  $\gamma_{0, BET}$  and  $\gamma_{ss, BET}$  are  $\approx 10^{-5}$  and  $\approx 10^{-6}$ , respectively, for actual soil dust and  $SiO_2$ , and the values for pure  $Al_2O_3$  and  $\alpha-Fe_2O_3$  are one order of magnitude larger than these.

### 6.3.2 $HO_2$

A measurement of uptake coefficient of  $HO_2$  on soil dust particles has been made recently and its temperature dependence has been reported. Bendjiamian et al. (2013) obtained the reactive uptake coefficient of  $HO_2$  on the membrane coated with Arizona desert dust by using the combined method of low-pressure flow system and molecular beam mass spectrometer. They reported  $\gamma_0 = 1.2 / (18.7 + RH^{1.1})$  at  $RH = 0.02-94\%$  independent of temperature (275–320 K) and photo-irradiation, and the upper limit of the formation yield of  $H_2O_2$  on the surface is 5%. Taketani et al. (2012) measured the uptake coefficients of  $HO_2$  on the particles field-sampled at Mt. Tai (Shandong Province) and Mt. Meng (Beijing City) in China by using a LIF method, and reported the values of 0.13–0.34 and 0.09–0.40, respectively. These values are very large compared to those for single component particles and sea salt, and they suggest the enhancement of uptake coefficient of  $HO_2$  on atmospheric aerosols due to the effect of co-existent trace metal ions and/or organic materials.

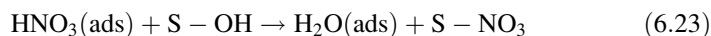
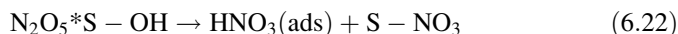
### 6.3.3 $N_2O_5$

The uptake of  $N_2O_5$  on soil dust is thought to have the largest impact on the decrease of tropospheric ozone by aeolian dust. Although several experimental studies in laboratories have been made, there are still large discrepancies in the measured uptake coefficients. A recent review on heterogeneous reactions of  $N_2O_5$  is given by Chang et al. (2011), including field observations and model calculations.

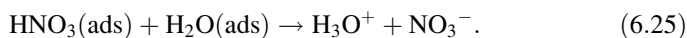
In the experiments using a Knudsen cell for Saharan dust, Seisel et al. (2005) and Karagulian et al. (2006) reported  $\gamma_{ss}$  (RH = 0 %) as  $0.008 \pm 0.003$  and  $0.2 \pm 0.05$ , respectively, which are different by more than an order of magnitude. The reason is thought to be the difference in the concentration of  $N_2O_5$  (the uptake coefficient increases at lower concentration) and in the estimated surface area of particles. Recently, Wagner et al. (2008, 2009) obtained the uptake coefficient (RH = 0) as  $\gamma = 0.013 \pm 0.002$  for Saharan dust by using a particle flow reactor simultaneously obtained by Knudsen cell experiments which gave the upper limit,  $\gamma_0 = \gamma_{ss} = 0.037 \pm 0.012$  and  $0.022 \pm 0.00$  for Saharan and Arizona dust, respectively.

As for the reaction products after  $N_2O_5$  is taken up on particles, Karagulian et al. (2006) reported that the yield of  $HNO_3$  is large for Arizona test dust and Kaolinite (silicate mineral including Al), but the yield is small for Saharan dust and  $CaCO_3$ , and  $CO_2$  is produced with the yield of 42–50 % particularly for  $CaCO_3$ .

Seisel et al. (2005) proposed a mechanism for the reaction of  $N_2O_5$  with mineral dust particles as,



to convert  $N_2O_5$  (g) to  $HNO_3$  (ads). Here, S-OH is the OH group existing on the surface site. When adsorbed water exists on the surface, it is thought that  $HNO_3$  is formed directly as,



### 6.3.4 $HNO_3$

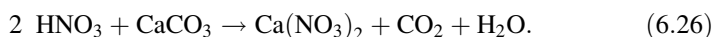
The uptake of gaseous nitric acid  $HNO_3$  into atmospheric dust and mineral aerosols is thought to be an important process resulting in the removal of  $HNO_3$  from the gas phase, and thus affects tropospheric  $O_3$  formation by decreasing the supply of  $NO_x$  by the photolysis in the upper troposphere (Bian and Zender 2003; Bauer et al. 2004). On the other hand, the mineral dust coated by  $HNO_3$  is interested from the viewpoint of climate impact since the optical property is changed and it

could act as condensation nuclei by changing the particles to hydrophilic (Lohmann et al. 2004).

Although many studies has been reported on the measurements of uptake coefficients of  $\text{HNO}_3$  on mineral dust, there are large scatter of values, whose cause is thought to be due to the uncertainty in estimation of surface area of samples. In general, the corrected values for diffusion into surface holes and the BET surface area are smaller than those for the geometric surface area by orders of magnitude. Hanisch and Crowley (2001a, 2001b) gave the uncorrected values  $0.13 \pm 0.033$ ,  $0.10 \pm 0.025$ ,  $0.11 \pm 0.03$  for  $\text{Al}_2\text{O}_3$ ,  $\text{CaCO}_3$ , and Sahara Dust, respectively, by use of a Knudsen cell. Also by using a Knudsen cell, Seisel et al. (2004) obtained  $\gamma_0 \approx 0.1$  for Saharan, Chinese and Arizona dust. Vlasenko et al. (2006) reported the uptake coefficient increases from  $0.022 \pm 0.007$  (RH 12 %) to  $0.113 \pm 0.017$  (RH73 %) with the increase of humidity for the Arizona dust using a flow system experiment. Smaller values  $2.5 \pm 0.1 \times 10^{-4}$  (Goodman et al. 2000) and  $2 \pm 1 \times 10^{-3}$  (Johnson et al. 2005) are reported for  $\text{CaCO}_3$  corrected with the BET surface area. The NASA/JPL panel evaluation No. 17 recommends  $\gamma_0 < 0.2$  for  $\alpha\text{-Al}_2\text{O}_3$  base on the measurements by Hanisch and Crowley (2001a, b) and Seisel et al. (2004).

As for the uptake process of  $\text{HNO}_3$  on mineral dust, Seisel et al. (2004) proposed the two step mechanism of initial surface adsorption of  $\text{HNO}_3$  (g) succeeded by a surface reaction of  $\text{HNO}_3$  (ads) based on the experimental evidence that initial uptake coefficient is as large as  $\sim 0.1$  whereas  $\gamma$  for the formation of  $\text{NO}_3^-$  at the surface is much smaller,  $8 \times 10^{-3} < \gamma < 5.4 \times 10^{-2}$ .

Overall reaction of  $\text{HNO}_3$  and  $\text{CaCO}_3$  is expressed as



but the yields of  $\text{CO}_2/\text{HNO}_3$  and  $\text{H}_2\text{O}/\text{HNO}_3$  are much smaller than the stoichiometric values, which suggests that the actual process is more complex (Goodman et al. 2000).

### 6.3.5 $\text{SO}_2$

The uptake of  $\text{SO}_2$  on soil dust has been interested in relating to the observational evidence that negative correlation is seen between the concentrations of  $\text{SO}_2$ , and Saharan and Chinese dust (yellow sand) in the field measurement (Hanke et al. 2003), surface of mineral particles is in general coated by nss- $\text{SO}_4^{2-}$  (Kojima et al. 2006), and positive correlation is seen between the concentration of nss- $\text{SO}_4^{2-}$  and mineral particles in aerosols (Carmichael et al. 1996). The existence of the oxidation process on aerosol surface in addition to the gas phase reaction and liquid phase oxidation in water droplets has also been suggested by Kasibhatla et al. (1997) since the overestimation of  $\text{SO}_2$  and underestimation of  $\text{SO}_4^{2-}$  is seen systematically in the comparison between the global model calculation and observation.



The values of the uptake coefficient of  $\text{SO}_2$  on mineral particle surfaces scatter largely as they are dependent on the preparation and processing methods of samples, method of estimation of surface area, humidity and  $\text{SO}_2$  concentrations in the gas phase, and other factors. The values of  $\gamma_{0,BET}$  are reported as  $(9.5 \pm 0.3) \times 10^{-5}$  (Goodman et al. 2001),  $(1.6 \pm 0.5) \times 10^{-4}$  (Usher et al. 2002) for  $\text{Al}_2\text{O}_3$ , and  $\sim 10^{-6}$  (Ullerstam et al. 2003),  $(6.6 \pm 0.8) \times 10^{-5}$  (Adams et al. 2005) for Saharan dust. Without BET correction, large values of  $\gamma_0$  are reported by Seisel et al. (2006) as  $(7.4 \pm 0.9) \times 10^{-3}$ ,  $(8.8 \pm 0.4) \times 10^{-2}$ ,  $(7.6 \pm 0.5) \times 10^{-2}$  for  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Al}_2\text{O}_3$ , and Saharan dust, respectively.

When  $\text{SO}_2$  is taken into the surface of mineral dust, it is known to be oxidized to  $\text{SO}_4^{2-}$  and  $\text{HOSO}_3^-$  in the presence of  $\text{O}_3$  (Usher et al. 2002; Ullerstam et al. 2003). Wu et al. (2011) studied the temperature dependence of the uptake coefficient of  $\text{SO}_2$  to form  $\text{SO}_4^{2-}$  on  $\text{CaCO}_3$  in the presence of  $\text{O}_3$ , and showed that the formation rate of  $\text{SO}_4^{2-}$  increases with temperatures between 230 and 250 K, but decreases with temperatures between 250 and 298 K. The apparent activation energy between 230 and 245 K is relatively large,  $14.6 \pm 0.2 \text{ KJ mole}^{-1}$ . The measured  $\gamma_{0,BET}$  value is  $1.27 \times 10^{-7}$  at 298 K, agreeing well with  $1.4 \times 10^{-7}$  on  $\text{CaCO}_3$  previously obtained by Li et al. (2006). Meanwhile, the value using geometrical surface area instead of the BET area is  $(7.7 \pm 1.6) \times 10^{-4}$ , which is nearly four orders of magnitude larger. The value of  $\gamma_{0,BET}$  for Saharan dust by Ullerstam et al. (2002) is  $5 \times 10^{-7}$ , three times larger than for  $\text{CaCO}_3$ , but the value of using the geometrical area is  $\sim 10^{-3}$ , which is in the same orders of magnitude as Li et al. (2006). The NASA/JPL panel recommends  $\gamma_0 > 5 \times 10^{-3}$  for  $\gamma\text{-Al}_2\text{O}_3$  (Sander et al. 2011).

From these results uptake of  $\text{SO}_2$  in the presence of  $\text{O}_3$  is thought to occur in two steps, adsorption on the mineral particle surface and succeeding oxidation (Ullerstam et al. 2002; Li et al. 2006). The rate-determining step is the adsorption on the mineral particle surface, and in the case of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , etc., physisorption and  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$  formation by dissolution to  $\text{H}_2\text{O}$  (l) are thought to occur in the presence of water. In case of  $\text{CaCO}_3$  reactions,



have been proposed as reaction processes (Al-Hosney and Grassian 2004; Santschi and Rossi 2006).

## 6.4 Uptake and Surface Reactions on Soot

Soot is emitted by incomplete combustion of fossil fuel and biomass. It is also called black carbon since it strongly absorbs the solar and terrestrial radiation in all of ultraviolet, visible and infrared regions, and attention is paid as one of the radiatively active species from the climate change point of view. As reactions on

soot surface, uptake and dissipation of  $O_3$  by soot emitted from aircrafts into upper troposphere and lower stratosphere, impact on photochemical budget of  $O_3$  by the reactive uptake of  $NO_2$ ,  $N_2O_5$ ,  $HNO_3$  in the boundary layer have been discussed. Particularly, formation of HONO by the reaction of  $NO_2$  on soot has been of much concern since it gives important contribution to the formation of OH in polluted atmosphere. Although the fresh surface of soot is hydrophobic, it becomes hydrophilic by taking up  $H_2SO_4$  and  $HNO_3$  in the gas phase, and by the formation of  $H_2SO_4$  in the surface reaction of  $SO_2$ . It is thus activated as cloud condensation nuclei and is interested in from a viewpoint of cloud physics.

The components of soot is mainly amorphous carbon containing polycyclic aromatic hydrocarbons and oxygen containing polycyclic aromatic hydrocarbons giving the elemental composition of C:  $\sim 95\%$ , H:  $\sim 1\%$ , O:  $\sim 1\text{--}5\%$ , N:  $< 1\%$  (Chughtai et al. 1998; Stadler and Rossi 2000). The existence of various functional groups such as the carbonyl group has been known by infrared spectroscopy (Kirchner et al. 2000; Liu et al. 2010), etc., and the types and amounts of the functional group have important effects on the uptake and reaction of gaseous molecules. The types of functional group on the surface is very much dependent on fuel types, combustion conditions, and sampling location of soot in the flame. As a soot for the use of laboratory experiments on uptake coefficients and surface reactions, samples taken from combustion flame of n-hexane and diesel fuel, and from the spark generators of diesel engines of automobiles are often used. International Steering Committee for Black Carbon Reference Materials recommends those from the n-hexane flame as the standard soot (Sander et al. 2011).

Even though the mass ratio of soot in aerosol is small, its surface area ratio is much larger than the mass ratio since soot has an amorphous and fractal structure, and it has the similar importance for the heterogeneous reactions in the atmosphere as other aerosols. The uptake coefficients of soot obtained so far has an uncertainty of a few orders of magnitude, and the causes are thought to be largely ascribed to the difference in the type and amount of surface functional groups due to the difference in formation methods, and the estimate of surface area. It has been known that there are at least two reactive sites on soot, and the fresh soot near the emission source has sites with large reaction rates, but changes to less reactive site for the aged soot in the atmosphere. The actual values of uptake coefficients of soot in the atmosphere is thus thought to be affected by the difference in the gas-solid contact time resulting in the chemical transformation of the soot surface.

### 6.4.1 $O_3$

It has been suggested that the uptake and decomposition of  $O_3$  on soot particles contribute to the loss of  $O_3$  due to the emission from aircraft in the lower stratosphere and upper troposphere (Lary et al. 1997) and nighttime loss of  $O_3$  in the urban atmosphere (Berkowitz et al. 2001), and many measurement have been made (Sander et al. 2011).

The uptake process of  $O_3$  by the new soot causes very large initial loss of  $O_3$ , but the uptake rate decreases drastically as the reaction proceeds or for the pre-treated soot. The initial uptake coefficients are reported as  $\gamma_0 = 10^{-4}$ – $10^{-3}$  (Fendel et al. 1995; Rogaski et al. 1997), while they decrease to  $10^{-6}$ – $10^{-7}$  with the progress of the time (Kamm et al. 1999; Pöschl et al. 2001). Longfellow et al. (2000) showed that the value of  $\gamma_0$  gets smaller by a factor of 30 depending on the estimate of the surface area. From these values, discussion has been made that the importance of the process for  $O_3$  loss on soot is limited.

### 6.4.2 $NO_2$

The uptake and reaction of  $NO_2$  on soot is very important as a process to release nitrous acid (HONO) into the gas phase. The formation of HONO by the heterogeneous surface reaction and its enhancement by light irradiation has been found for the first time by Akimoto et al. (1987) relevant to the “unknown radical source” in a smog chamber (see column on p.278). The uptake of  $NO_2$  and photocatalytic reaction on soot has been interested in as a model reaction of such heterogeneous process to elucidate the characteristics of HONO formation in the atmosphere.

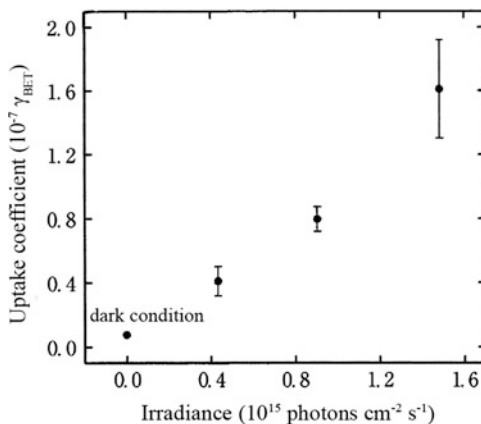
In the polluted atmosphere, HONO has been measured at far higher concentrations than expected from the production rate by the homogeneous gas phase reaction,  $OH + NO + M \rightarrow HONO + M$  (Sect. 5.2.4), and the discussions on the contribution other than the homogeneous reaction have been made in model analysis studies (Gonçalves et al. 2012; Elshorbany et al. 2012).

The uptake of  $NO_2$  is composed of two processes, fast initial uptake and succeeding slow process as in the case of  $O_3$ , and many measurements have been made for  $\gamma_0$  and  $\gamma_{aged}$ . The NASA/JPL panel compiled a large range of values,  $\gamma_0 \approx 10^{-1}$ – $10^{-4}$  and  $\gamma_{aged} \approx 10^{-4}$ – $10^{-6}$  for soot prepared by various methods (Sander et al. 2011). Recently reported values are  $\gamma_{0, BET} \sim 10^{-5}$  (Lelievre et al. 2004) and  $\gamma_{aged, BET} \sim 10^{-8}$  (Prince et al. 2002), which are smaller than before and the discussion was made that the process cannot be a source of high concentration of HONO in the polluted atmosphere. However, it has also been pointed out that there is enough possibility to contribute if the photo-enhancement effect on the heterogeneous HONO formation process is considered.

As for the reaction products of  $NO_2$  uptake on soot, the release of HONO into the gas phase is well known. The formation of NO is reported depending on the conditions, but the formation of  $HNO_3$  has not been found (Arens et al. 2001). The yield of HONO is about 100 % for the soot from the flame of high fuel/oxygen ratio, while the yield is lower for soot from lean flame (Stadler and Rossi 2000; Khalizov et al. 2010). Also the uptake coefficients of  $NO_2$  and the yields of HONO are known to be affected by the coating of the surface of soot by  $H_2SO_4$  or organics (Aubin and Abbatt 2007; Khalizov et al. 2010).

Recently, Monge et al. (2010) found that the formation of HONO by the reaction of  $NO_2$  on soot is accelerated by the irradiation of light in the range of 300–420 nm,

**Fig. 6.3** Dependence on the irradiated light intensity of the uptake coefficients  $\gamma$  of  $\text{NO}_2$  on soot (Adapted from Monge et al. 2010)



the HONO formation rate does not decrease with time under the irradiation, and the uptake coefficient of  $\text{NO}_2$  keeps the value of  $(2.0 \pm 0.6) \times 10^{-6}$ . Figure 6.3 shows the dependence of  $\gamma$  on light intensity of irradiation. As shown in the figure, the values of  $\gamma$  is proportional to the light intensity. This is thought to be an important experimental results suggesting the importance of the photocatalytic reaction of  $\text{NO}_2$  as a source of high concentration of HONO at daytime. The photo-enhancement of HONO formation by the heterogeneous surface reaction has been found in the smog chamber (Akimoto et al. 1987; Rohrer et al. 2005) as noted above and on the thin layer of PAH, pyrene (Brignite et al. 2008), so that the reaction is supposed to occur on various surfaces.

### 6.4.3 $\text{N}_2\text{O}_5$

The reaction of  $\text{N}_2\text{O}_5$  on soot has been studied considering the possibility of heterogeneous reaction to convert  $\text{N}_2\text{O}_5$  to  $\text{HNO}_3$  effectively alternative to the very slow gas phase bimolecular reaction,  $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3$ . According to the measurement by Longfellow et al. (2000), release of  $\text{NO}_2$  into gas phase has been found, and the upper limit of uptake coefficient using the geometrical surface area,  $\gamma = 0.016$  has been reported. The measurement by Saathoff et al. (2001) gave  $\gamma = (4 \pm 2) \times 10^{-5}$  for the  $\text{N}_2\text{O}_5 + \text{soot} \rightarrow 2 \text{HNO}_3$  reaction under dry conditions,  $(2 \pm 1) \times 10^{-4}$  for RH 50 %, and  $\gamma = (4 \pm 2) \times 10^{-6}$  for the  $\text{N}_2\text{O}_5 + \text{soot} \rightarrow \text{NO} + \text{NO}_2 + \text{prod.}$  reaction under dry conditions. Kargulian and Rossi (2007) reported the large reactive uptake coefficient for the  $\text{NO} + \text{NO}_2$  formation,  $\gamma_{r, \text{ss}} = 5.0 \times 10^{-3}$  by extrapolating  $\text{N}_2\text{O}_5$  concentration to zero.

### 6.4.4 $\text{HNO}_3$

The reaction of  $\text{HNO}_3$  with soot is expected to solve the discrepancy between the model and observation for the  $\text{HNO}_3/\text{NO}_2$  ratio by converting  $\text{HNO}_3$  to  $\text{NO}$  and  $\text{NO}_2$  on the surface of soot emitted from aircrafts in the lower stratosphere and upper troposphere (Lary et al. 1997), and several measurements have been made.

According to the measurements of Kirchner et al. (2000), the uptake of  $\text{HNO}_3$  on soot particles consists of fast and slow processes as in the uptake of  $\text{O}_3$  and  $\text{NO}_2$  on soot. For the soot prepared from spark generator,  $\gamma = 10^{-3}$ – $10^{-6}$  and  $\gamma = 10^{-6}$ – $10^{-8}$  have been reported for the fast and slow process, respectively. For the soot from diesel engine exhaust, one order of magnitude smaller values are reported. The functional group such as  $-\text{C}=\text{O}$ ,  $-\text{NO}_2$ ,  $-\text{ONO}_2$ ,  $-\text{ONO}$ , etc. are known to be formed on the surface of soot which takes up  $\text{HNO}_3$  by using Fourier transform infrared spectroscopy (FTIR), which suggests  $\text{HNO}_3$  reacts on the soot surface. Longfellow et al. (2000) reported that the uptake of  $\text{HNO}_3$  is reversible at 298 K, and the formation of  $\text{NO}_2$  and  $\text{NO}$  was not observed by the chamber experiment using a flow tube/chemical ionization mass spectrometry (CIMS). On the other hand, Disselkamp et al. (2000) reported the formation of  $\text{NO}_2$  by the chamber experiment with a long-path infrared spectrometer. They showed the yield of  $\text{NO}_2$  to the decrease of  $\text{HNO}_3$  is dependent on the type of soot, but the active points on the surface to form  $\text{NO}_2$  are not reproduced leaving the unreacted  $\text{HNO}_3$  on the surface. Similarly, Saathoff et al. (2001) reported the formation of  $\text{NO}_2$  with  $\gamma_{\text{BET}} \leq 3 \times 10^{-7}$  in a chamber experiment and Salgado-Muñoz and Rossi (2002) obtained the  $\text{NO}_2$  forming uptake coefficients of  $\gamma_0 = (2.0 \pm 0.1) \times 10^{-2}$  and  $\gamma_{\text{ss}} = (4.6 \pm 1.6) \times 10^{-3}$  for geometric surface area using a Knudsen cell for the soot from lean decane flame.

Thus, the formation of  $\text{NO}_2$  in the heterogeneous reaction on soot has been confirmed for the atmospheric concentration of  $\text{HNO}_3$ , but the uptake coefficient  $\gamma_r$  is different by the type and formation method of soot, and the uncertainty is still large as for the importance of this reaction in the atmosphere.

### 6.4.5 $\text{SO}_2$

The uptake and reaction of  $\text{SO}_2$  on soot has been discussed as one of the heterogeneous oxidation process of  $\text{S(IV)} \rightarrow \text{S(VI)}$  together with the oxidation of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  in liquid droplet and on mineral particles, but the measurements of the uptake coefficient are scarce.

Rogaski et al. (1997) and Koehler et al. (1999) reported the initial uptake coefficients of  $\gamma \leq (3 \pm 1) \times 10^{-3}$  (298 K), and  $(2 \pm 1) \times 10^{-3}$  (173 K), respectively, for geometric surface area using the combustion flame soot. The value decreases to one thirty-third when the roughness of the surface is considered (Koehler et al. 1999). However, since the uptake coefficient decreases with

exposure time to nearly zero in a short time, the contribution of the reaction of  $\text{SO}_2$  on soot to the formation of  $\text{H}_2\text{SO}_4$  in the atmosphere is thought to be small. Meanwhile, it has been reported that when metal oxides such as  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{V}_2\text{O}_5$ , etc. are present on the soot surface, the formation rate of  $\text{H}_2\text{SO}_4$  increases significantly as compared to simple substance of soot or metal oxide (Chughtai et al. 1993).

## 6.5 Reactions on Polar Stratospheric Cloud (PSC)

While the many heterogeneous reactions in the troposphere so far described plays a complementary role to the homogeneous gas phase reactions, heterogeneous reactions on polar stratospheric cloud (PSC) are of primary importance for the formation of stratospheric ozone hole.

When the temperature decreases to lower than 200 K in the lower stratosphere of the polar regions, so-called PSC, clouds consisting of aerosols, appears (Brasseur and Solomon, 2005). The aerosols consist of  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{O}$  in general and it is known that their mixing ratios are known to change according to the thermodynamic stability (Koop et al. 1997). In the stratosphere there is sulfuric acid aerosol of 40–80 wt %  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  (l) (SSA, stratospheric sulfate aerosols) as liquid droplet by nature (see Sect. 8.5), gas phase molecules of  $\text{HNO}_3$  and  $\text{H}_2\text{O}$  are taken into the sulfuric acid droplet as temperature decreases, and becomes diluted acids consisting of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  about 30 % each. When the temperature decreases further, sulfuric acid is further diluted by  $\text{HNO}_3$  and  $\text{H}_2\text{O}$ , and becomes a liquid particle almost consisting of nitric acid and water at around 195 K. From this state nitric acid trihydrate (NAT)  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$  freezes out as thermodynamically most stable form (Molina et al. 1993; Voight et al. 2000), and it is called type Ia particles from the viewpoint of LIDAR observation, which accompany depolarization. At the temperature 3–4 K still lower than the NAT formation, super-cooled ternary solution (STS) consisting of  $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ , or type Ib particles are formed, which does not depolarize LIDAR beam. Furthermore, at temperatures less than 188 K, the freezing temperature of  $\text{H}_2\text{O}$ , large particle of ice consisting of  $\text{H}_2\text{O}(s)$  is formed, which is called type II PSC. Other than this sulfuric acid tetrahydrate (SAT)  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  is known to be frozen out as solid particles from the  $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$  solution. Although still other particles with different constituents are thought as PSC, three solid particles, ice, NAT and SAT, and two liquid particles, SSA and STS are describe in this section as the most typical PSCs. Table 6.2 shows the characteristics of these main PSCs.

On the other hand, reactions between  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HCl}$ ,  $\text{HOCl}$  and  $\text{ClONO}_2$  on PSC are described in this section. The reason that PSC plays a primary role in the formation of Antarctic and Arctic ozone hole is that visible light absorbing species like  $\text{Cl}_2$ ,  $\text{HOCl}$  and  $\text{ClONO}_2$  are formed by the reactions on PSC, and they are promptly photolyzed to generate Cl atoms right after the polar night to cause rapid ozone destruction (see Sect. 8.4). Although similar reactions are known for

**Table 6.2** Typical particles constituting polar stratospheric clouds (PSC)

Particle names	Chemical composition	Shape · Phase	Particle diameter (μm)	Threshold temperature (K)
Stratospheric sulfate aerosols(SSA)	H <sub>2</sub> SO <sub>4</sub> /H <sub>2</sub> O	Fine liquid droplet	0.1–5	T < 261
Sulfuric acid tetrahydrate(SAT)	H <sub>2</sub> SO <sub>4</sub> · 4H <sub>2</sub> O	Fine solid crystals	<1	T < 213
Nitric acid trihydrate (NAT)	HNO <sub>3</sub> · 3H <sub>2</sub> O	Solid crystals	1–5	T < 196
Super cooled ternary solution(STS)	H <sub>2</sub> SO <sub>4</sub> /HNO <sub>3</sub> /H <sub>2</sub> O	Liquid droplet	<1	T < 192
Ice	H <sub>2</sub> O	Large solid crystals	5–50	T < 189

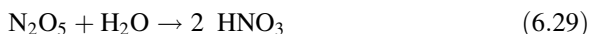
Based on Brasseur and Solomon (2005)

Br-containing species (Finlayson-Pitts and Pitts 2000), only the Cl-containing species are described in this chapter as heterogeneous halogen reactions on PSC.

As for the heterogeneous reaction on PSC, the review have been made in the NASA/JPL panel evaluation No. 17 (Sander et al. 2011), and the IPAC subcommittee report Vol. V (Crowley et al. 2010) and data sheet (Wallington et al. 2012), and recommended values for many reactive uptake coefficients are given. Table 6.3 shows the values of reactive uptake coefficients  $\gamma_r$  for Cl-compounds on PSC based on these evaluation reports.

### 6.5.1 N<sub>2</sub>O<sub>5</sub> + H<sub>2</sub>O

The reaction of N<sub>2</sub>O<sub>5</sub> and H<sub>2</sub>O on PSC is the process,



to form nitric acid on the particle. This reaction is important for the formation of the ozone hole, as it removes reactive NO<sub>x</sub> from the gas phase during polar night and accelerates the ozone destruction in spring by negating the ClO<sub>x</sub> chain termination reaction ClO + NO<sub>2</sub> + M → ClONO<sub>2</sub> + M. Furthermore, when N<sub>2</sub>O<sub>5</sub> is taken into big ice particles, nitric acid is removed from the stratosphere by gravitational sedimentation, which is called denitrification, and the ozone destruction proceeds even more effectively since NO<sub>2</sub> is no more supplied by the photolysis of HNO<sub>3</sub>.

The measurements of uptake coefficients of N<sub>2</sub>O<sub>5</sub> on ice particles at 188 K by Leu (1988), and Hanson and Ravishankara (1991b, 1993a) using a coated wall flow reactor, and by Quinlan et al. (1990) and Seisel et al. (1998) using a Knudsen cell agreed well. The NASA/JPL panel (Sander et al. 2011) and the IUPAC subcommittee (Wallington et al. 2012) both recommend  $\gamma = 0.02$ .

**Table 6.3** Reactive uptake coefficients ( $\gamma_r$ ) on polar stratospheric clouds under typical polar night conditions

Polar stratospheric clouds (a)					
Reactions	Solid ice	Solid NAT nitrogen trihydrate	Solid SAT sulfuric acid tetrahydrate	Liquid SSA stratospheric sulfate aerosols	Liquid STS supercooled ternary solution
$N_2O_5 + H_2O \rightarrow 2HNO_3$	0.02 (b)	$4 \times 10^{-4}$ (b)	$6 \times 10^{-3}$ (b)	0.05–0.20 (b)	0.09 (218 K) (c) 0.02–0.03 (195 K) (c)
$N_2O_5 + HCl \rightarrow ClNO_2 + HNO_3$	0.03 (b)	$3 \times 10^{-3}$ (b)	$<1 \times 10^{-4}$ (SAM) (b)	–	---
$HOCl + HCl \rightarrow Cl_2 + H_2O$	0.2 (b)	0.1 (b)	–	0.15 (58 wt % $H_2SO_4$ $1 \times 10^{-8}$ atm HCl, 220 K) (d) Decrease with $H_2SO_4$ Concentration Increase with HCl Partial Pressure (e)	–
$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$	0.3 (b)	0.004 (b)	0.01 (RH100 %) (f)	0.038 (45 wt % $H_2SO_4$ , 230 K) (g) $1.1 \times 10^{-5}$ (75 wt % $H_2SO_4$ , 230 K) (g)	0.019 (4.6 % $HNO_3$ ) 44 % $H_2SO_4$ , 205K) (g)
			Increase with RH in the second order (f)	Rapidly decrease with $H_2SO_4$ concentration (e)	Decrease with $HNO_3$ concentration (g)

(continued)



Table 6.3 (continued)

Reactions	Polar stratospheric clouds (a)			
	Solid ice	Solid NAT nitrogen trihydrate	Solid SAT sulfuric acid tetrahydrate	Liquid SSA stratospheric sulfate aerosols
$\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3$	0.3 (b)	0.2 (b)	$\geq 0.1$ (RH100 %) (f)	Liquid STS supercooled ternary solution
	0.2 (b)		0.0035 (RH 18 %) (f)	0.18 (4.4 % $\text{HNO}_3$ )
			Increase with RH in the second order (f)	44 % $\text{H}_2\text{SO}_4$ , 205 K (g)
				Decrease with $\text{HNO}_3$ Concentration (g)
				Rapidly decrease with $\text{H}_2\text{SO}_4$ concentration
				Increase with HCl partial pressure (e)

Temperature range is in general 180–220 K. Refer to the sources except noted

(a) ice =  $\text{H}_2\text{O}$ , NAT (nitric trihydrate) =  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ , SAT (sulfuric acid tetrahydrate) =  $\text{H}_2\text{SO}_7 \cdot 4\text{H}_2\text{O}$ , SSA (stratospheric sulfate aerosols)/LBA (liquid binary sulfate aerosol) =  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ , STS (Supercooled ternary solution) =  $\text{H}_2\text{SO}_2/\text{HNO}_3/\text{H}_2\text{O}$ , SAM (sulfuric acid monohydrate) =  $\text{H}_2\text{SO}_2 \cdot \text{H}_2\text{O}$

(b) NASA/JPL panel evaluation No. 17 (Sander et al. 2011)

(c) Zhang et al. (1995)

(d) Donaldson et al. (1997)

(e) Shi et al. (2001)

(f) Zhang et al. (1994b)

(g) Hanson (1998)

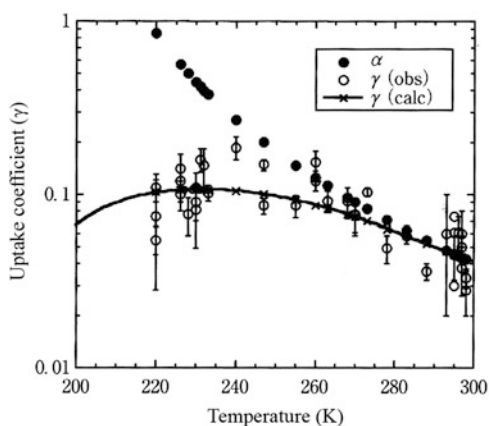
As for the uptake coefficient of  $\text{N}_2\text{O}_5$  on NAT, the NASA/JPL panel recommends  $\gamma = 4 \times 10^{-4}$  based on the measurement of Hanson and Ravishankara (1993a), which is much smaller than for ice particles.

The uptake coefficients of  $\text{N}_2\text{O}_5$  on SAT surface are recommended as  $\gamma = 6 \times 10^{-3}$  by the NASA/JPL panel (Sander et al. 2011), and as  $\gamma = 6.5 \times 10^{-3}$  for RH 22–100 % at 195–205 K by the IUPAC subcommittee (Wallington et al. 2012).

Compared to these reactions on solid PSCs, many more measurements have been conducted for the reaction of  $\text{N}_2\text{O}_5$  on the liquid sulfuric acid  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  surface in the wide temperature range of from 195 K to room temperature. The measurements at low temperature assuming PSC have been made with the use of an aerosol flow reactor (Fried et al. 1994; Hanson and Lovejoy 1994), a wet wall flow reactor (Zhang et al. 1995), Knudsen cell (Beichert and Finlayson Pitts 1996), droplet train method (Robinson et al. 1997), and chamber method (Wagner et al. 2005). The obtained values for 40–80 %  $\text{H}_2\text{SO}_4$  agree fairly well in the range of  $\gamma_r = 0.05$ –0.20. Robinson et al. (1997) presumed that the uptake of  $\text{N}_2\text{O}_5$  is controlled by the hydrolysis rate of  $\text{N}_2\text{O}_5$  in the bulk liquid and proposed a parameterized formula for the temperature and concentration dependence. The IUPAC subcommittee report recommends  $\gamma_r = [(7353/T) - 24.83]^{-1}$  as an equation for the uptake coefficient of  $\text{N}_2\text{O}_5$  in the temperature range of 210–300 K (Wallington et al. 2012). Figure 6.4 depicts the temperature dependence of the uptake coefficients of  $\text{N}_2\text{O}_5$  on  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  aerosols summarized in the report. In the figure,  $\alpha$  is the physical accommodation coefficient,  $\gamma_r$  is the reactive uptake coefficient of  $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3$ , and the solid line is the calculated values by the above equation.

As  $\text{N}_2\text{O}_5$  is taken into  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ , the sulfuric acid aqueous solution is diluted by nitric acid  $\text{HNO}_3$  and the PSC changes to super-cooled ternary solution (STS),  $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ . The uptake coefficient of  $\text{N}_2\text{O}_5$  on STS has been shown to decrease as the concentration of  $\text{HNO}_3$  increases (Hanson 1997). From the experiments of Zhang et al. (1995) and Wagner et al. (2005), this nitrate effect gets larger

**Fig. 6.4** Temperature dependence of uptake coefficient of  $\text{N}_2\text{O}_5$  on SAA ( $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ ) surface (Adapted from the IUPAC subcommittee evaluation data sheet, Wallington et al. 2012)



as the temperature decreases, and under the stratospheric condition of  $P(\text{H}_2\text{O}) = 3.8 \times 10^{-4} - 1.0 \times 10^{-3}$  Torr,  $\gamma_r$  decreases from 0.09 at 195 K to 0.02–0.03 at 218 K by a factor of 2–5 (Zhang et al. 1995).

### 6.5.2 $\text{N}_2\text{O}_5 + \text{HCl}$

The reaction of  $\text{N}_2\text{O}_5 + \text{HCl}$  on PSC proceeds as,



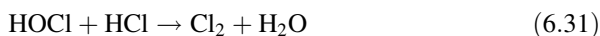
to convert metastable HCl to photochemically active  $\text{ClONO}_2$  which is released to the gas phase, and to convert  $\text{NO}_x$  to  $\text{HNO}_3$  to remove  $\text{NO}_2$  from the gas phase. Both processes accelerate the destruction of polar stratospheric ozone in springtime.

For the reaction of  $\text{N}_2\text{O}_5 + \text{HCl}$  on the surface of ice particles  $\text{H}_2\text{O}(\text{s})$ , it has been reported by Seisel et al. (1998) that the uptake coefficient of  $\text{N}_2\text{O}_5$  is  $\gamma_r = 0.03$  with the  $\text{ClONO}_2$  yield of 63 % for the consumed  $\text{N}_2\text{O}_5$ . The NASA/JPL panel recommends this value. Hanson and Ravishankara (1991a), however, pointed out that this reaction forms NAT layer on the ice surface, which decreases the uptake coefficient, and the measurement of reactive uptake coefficient for pure  $\text{H}_2\text{O}(\text{s})$  is difficult.

The uptake coefficient  $3.2 \times 10^{-3}$  of this reaction on NAT particle has been recommended by the NASA/JPL panel (Sander et al. 2011) based on the measurement by Hanson and Ravishankara (1991a). The measurement on SAT has not been made and a small value of  $\gamma_r = 1 \times 10^{-4}$  has been reported for  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  (SAM, sulfuric acid monohydrate) by Zhang et al. (1995). The IUPAC subcommittee (Wallington et al. 2012) recommends the upper limit value of  $\gamma_r < 1 \times 10^{-4}$  based on this value.

### 6.5.3 $\text{HOCl} + \text{HCl}$

The reaction of HOCl and HCl on PSC particles forms  $\text{Cl}_2$  as follows.



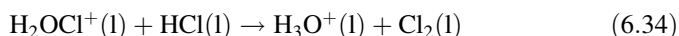
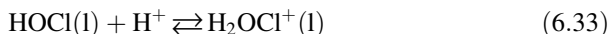
This reaction and those of  $\text{ClONO}_2$  described in the following Sects. 6.5.4 and 6.5.5 are called chlorine activation since they convert metastable HCl and  $\text{ClONO}_2$  stored in polar night of the stratosphere to photochemically active  $\text{Cl}_2$  and HOCl to be released into the gas phase. As shown in Fig. 4.38 in Sect. 4.4.3, HCl only has an absorption spectrum shorter than 200 nm, whereas HOCl has an absorption spectrum longer than 300 nm, as shown in Fig. 4.38 (Sect. 4.4.4), and can be photolyzed by the low altitude sunlight of early polar spring in the stratosphere.  $\text{Cl}_2$

has much larger absorption cross-sections in the visible region as shown in Fig. 4.36 (Sect. 4.4.1) so that it can be photolyzed more effectively to release two Cl atoms.

It has been known that the reaction of HOCl and HCl has a large reactive uptake coefficient of  $\gamma_r > 0.1$  on either PSCs of ice particle, NAT, SAT and SSA (Hanson and Ravishankara 1992; Abbatt and Molina 1992a). McNeill et al. (2006) deduced that the presence of HCl in the gas phase causes surface disorder by the dissolution of ice surface layer, and induces quasi liquid layer (QLL) at stratospheric temperature (188–203 K), which accelerate heterogeneous reaction of HOCl and ClONO<sub>2</sub> with HCl on ice surface. For this reason, the uptake coefficient of HOCl on the ice surface doped with HCl is very large, and the NASA/JPL panel recommends  $\gamma_r = 0.2$  (uncertainty by a factor of 2) taking the average of the values reported by Hanson and Ravishankara (1992), Abbatt and Molina (1992a), and Chu et al. (1993). Meanwhile, this value is reported to decrease by a factor of 3–4 if the surface area of porosity is considered (Chu et al. 1993). The products of this reaction are reported to be Cl<sub>2</sub> and H<sub>2</sub>O as seen in reaction (6.31). The production yield of Cl<sub>2</sub> for the loss of HOCl is reported to be  $0.87 \pm 0.20$  by Abbatt and Molina (1992a), and it is generally thought this reaction forms Cl<sub>2</sub> and H<sub>2</sub>O with the yields of unity (Sander et al. 2011).

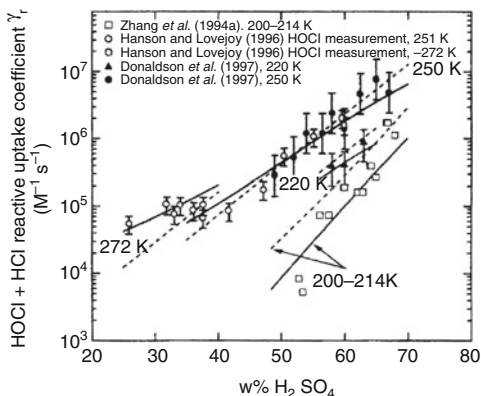
The  $\gamma_r$  for the reaction of HOCl and HCl on NAT particles is known to increase with water vapor and reaches a constant value at more than a certain vapor pressure. The average of measured values by Hanson and Ravishankara (1992) and Abbatt and Molina (1992a) is  $\gamma_r = 0.135 \pm 0.049$  without considering the porosity of the surface. The  $\gamma_r$  decreases to one tenth when water vapor is not present (Abbatt and Molina 1992a). The recommended values by the NASA/JPL panel is  $\gamma = 0.1$  with an uncertainty by a factor of 2 (Sander et al. 2011).

Many measurements have been made for the reaction of HOCl and HCl on sulfuric acid liquid droplets H<sub>2</sub>SO<sub>4</sub> · nH<sub>2</sub>O (l). The uptake coefficient of this reaction is dependent on temperature, water vapor, and concentration ratio of H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O. The reason is thought to be that the solubility of HOCl and HCl is affected largely by these parameters. The experimental results of the reaction of HCl with HOCl and with ClONO<sub>2</sub> in sulfuric acid droplets described in Sect. 6.5.5 has been proposed to be explained by the following acid-catalyzed protonation reaction pathways,



Shi et al. (2001) modeled the reaction considering this scheme in the temperature range of 185–260 K, and showed that the measured values of  $\gamma_r$  by Donaldson et al. (1997), Hanson and Lovejoy (1996) and Zhang et al. (1994a) can be reproduced well by the model as shown in Fig. 6.5. As seen in the figure, the value of  $\gamma_r$  increases with the increase of partial pressure of HCl, and H<sub>2</sub>O ratio in sulfuric acid. It decreases with the increase of temperature, and Zhang et al. (1994a)

**Fig. 6.5** Dependence of reactive uptake coefficients for the reaction of HOCl and HCl on sulfuric acid liquid droplet on temperature and sulfuric acid concentration (Adapted from Shi et al. 2001)



reported that  $\gamma_r$  decreases by a factor of 50 when the temperature increases from 198 K to 208 K. The rate of the reaction HOCl + HCl is very fast in the cold stratosphere at  $T < 199$  K, and it decreases as HCl is depleted.

#### 6.5.4 $\text{ClONO}_2 + \text{H}_2\text{O}$

The formation of HOCl in the reaction of  $\text{ClONO}_2$  and  $\text{H}_2\text{O}$  on PSC,



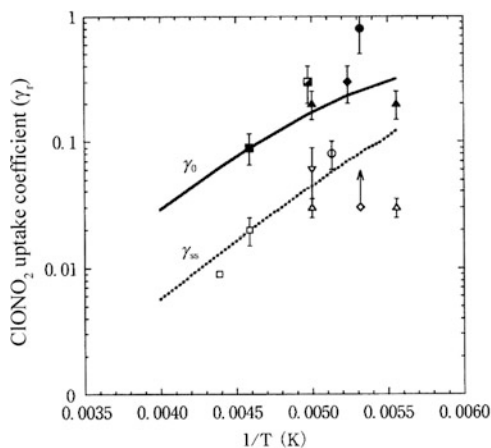
is an important chlorine activation reaction (see the previous paragraph) together with the  $\text{Cl}_2$  production in the reaction of  $\text{ClONO}_2$  and HCl described in the following paragraph. In the polar night with no solar irradiation, most ClO radicals are converted to metastable chlorine nitrate  $\text{ClONO}_2$  by the reaction with  $\text{NO}_2$ . The absorption spectrum of  $\text{ClONO}_2$  has large absorption cross-sections only at wavelengths shorter than 300 nm, as seen in Fig. 4.37 (Sect. 4.4.2), so that if  $\text{ClONO}_2$  stays as it is during the polar night, release of active chlorine by the photolysis does not occur effectively by the solar irradiation with relatively long wavelength in early spring at the lower altitude of sun, and the rapid ozone depletion producing the ozone hole cannot be not caused. Only in the presence of PSC at polar night, the conversion of  $\text{ClONO}_2$  to HOCl occurs. Since the HOCl has absorption in the range of 300–350 nm as shown in Fig. 4.39a (Sect. 4.4.4), the release of Cl atoms by the low altitude sunlight is possible, and the formation of ozone hole results.

The uptake of  $\text{ClONO}_2$  on ice surface followed by the reaction with  $\text{H}_2\text{O}$  is thought to form HOCl and  $\text{HNO}_3$ . At the stratospheric temperature, the product HOCl is released to the gas phase, and  $\text{HNO}_3$  stays on the ice surface to form NAT. The accumulation of  $\text{HNO}_3$  on the ice surface decreases the number of  $\text{H}_2\text{O}$  molecules that can participate the surface reaction, and interfere with the total reaction. Therefore, the uptake coefficient of this reaction decreases in general with time, and the evidence is more distinct for the experiments using high

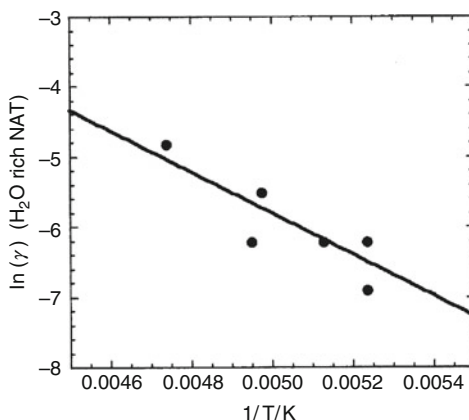
concentration of  $\text{ClONO}_2$  (Sander et al. 2011; Wallington et al. 2012). The NASA/JPL panel (Sander et al. 2011) recommends the reactive uptake coefficient  $\gamma_r = 0.3$  at 180–200 K for the geometrical surface area, based on the experiments by Hanson and Ravishankara (1991a, 1992), Oppliger et al. (1997) and Fernandez et al. (2005) using relatively low concentrations of  $\text{ClONO}_2$ . The IUPAC subcommittee (Wallington et al. 2012) gives the negative temperature dependence of this reaction as depicted in Fig. 6.6 and temperature parameters based on the result of Fernandez et al. (2005).

The reactive uptake coefficient of the reaction  $\text{ClONO}_2$  and  $\text{H}_2\text{O}$  on NAT has been measured by Hanson and Ravishankara (1991a, 1992, 1993b), Abbatt and Molina (1992b), Zhang et al. (1994b), Barone et al. (1997), etc., and shown that  $\gamma_r$  is larger under the higher water vapor pressure (Wallington et al. 2012). Sander et al. (2011) presented the average value of  $\gamma_r = 0.0043 \pm 0.0021$  for  $\text{RH} \geq 90\%$ . This reaction is known to have positive temperature dependence as shown in Fig. 6.7 conversely to the reaction on ice particles, and  $\gamma_r = 7.1 \times 10^{-3} \exp(-2940/T)$  is given for the Arrhenius plot of  $\gamma_r$  at 100% RH.

**Fig. 6.6** Temperature dependence of reactive uptake coefficients for the reaction  $\text{ClONO}_2$  and  $\text{H}_2\text{O}$  on PSC ice surface (Adapted from IUPAC subcommittee evaluation data sheet, Wallington et al. 2012). Refer to the original literature for the source of each experimental point. *Solid and dotted lines* are calculated values by the model for  $\gamma_0$  and  $\gamma_{ss}$ , respectively



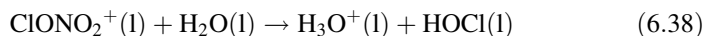
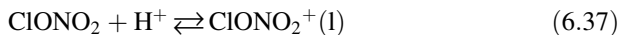
**Fig. 6.7** Temperature dependence of reactive uptake coefficients for the reaction  $\text{ClONO}_2$  and  $\text{H}_2\text{O}$  on NAT (Adapted from the IUPAC subcommittee evaluation data sheet, Wallington et al. 2012)



The relative humidity dependence of the reactive uptake coefficient for the reaction,  $\text{ClONO}_2$  and  $\text{H}_2\text{O}$ , on SAT has been measured by Hanson and Ravishankara (1993b), and Zhang et al. (1994b) for the temperature range 192–205 K. From these results,  $\gamma_r$  of this reaction increases rapidly with the increase of RH. The measurement of Zhang et al. (1994b) gave  $\gamma_r = 0.016$  at 195 K, which is in between ice particles and  $\text{H}_2\text{O}$ -rich NAT. It decreases rapidly with the decrease of RH to  $5 \times 10^{-4}$  at RH 8 %. Based on these data, the IUPAC subcommittee recommends the dependence of  $\gamma_r$  on relative humidity as  $\gamma_r = 1 \times 10^{-4} + 1 \times 10^{-4} [\text{RH}] + 1 \times 10^{-7} [\text{RH}]^2$  (192–205 K) (Crowley et al. 2010; Wallington et al. 2012).

Many measurements have been made for the reaction of  $\text{ClONO}_2 + \text{H}_2\text{O}$  on SSA, sulfuric acid liquid droplets  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}(\text{l})$ , as compared to the solid PSCs mentioned above, and the dependence on temperature, humidity, and sulfuric acid composition has been investigated. The reaction products of  $\text{ClONO}_2 + \text{H}_2\text{O}$  on the sulfuric acid liquid droplets are  $\text{HOCl}$  and  $\text{HNO}_3$  that are the same for the solid PSCs, but  $\text{HNO}_3$  are released to the gas phase being different from the cases of the solid surface. The reactive uptake coefficient is known to be strongly dependent on the  $\text{H}_2\text{O}$  content in sulfuric acid, and increases with the  $\text{H}_2\text{O}$  in the range of 20–70 % wt %  $\text{H}_2\text{SO}_4$ , and it increases with the decrease of temperature (Hanson and Ravishankara 1991b; Zhang et al. 1995; Ball et al. 1998; Hanson 1998). For example,  $\gamma_r$  is close to 0.1 for 40 % wt %  $\text{H}_2\text{SO}_4$ , but decreases to  $\sim 10^{-5}$  for 75 wt %  $\text{H}_2\text{SO}_4$  (Hanson 1998) at around 200 K.

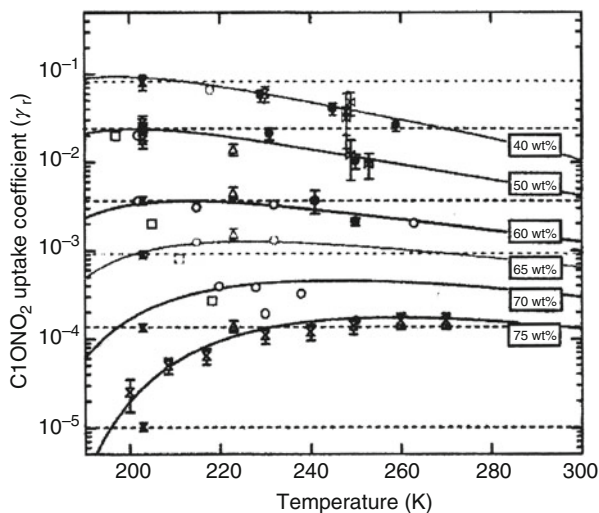
Shi et al. (2001) analyzed the reaction rate of this reaction based on the assumption that both of direct reaction (6.36) and the acid-catalyzed reactions proposed similarly for the reaction of  $\text{HOCl}$  and  $\text{HCl}$  (Sect. 6.5.3),



occurs simultaneously. Figure 6.8 depicts the dependence of the reactive uptake coefficients of the  $\text{ClONO}_2 + \text{H}_2\text{O}$  reaction on temperature and sulfuric acid concentration to compare the experimental data and model equation of Shi et al. (2001) based on the above mechanism. The detailed parameters of the model equation are given in the IUPAC subcommittee data sheet (Wallington et al. 2012).

The uptake coefficient of this reaction is smaller for the nitric acid co-existing sulfuric acid water droplets,  $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}(\text{l})$ . The values of  $\gamma_r$  under the typical condition of gas phase concentration  $\sim 5$ ppb  $\text{HNO}_3$  in the polar lower stratosphere are reported to be one half of the reaction on  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}(\text{l})$  (Zhang et al. 1995; Hanson 1998).

**Fig. 6.8** Temperature and sulfuric acid concentration dependence of reactive uptake coefficients for the reaction of  $\text{ClONO}_2$  and  $\text{H}_2\text{O}$  on sulfuric acid liquid droplet (Adapted from Shi et al. 2001). Refer to original literature for the source of each experimental point



### 6.5.5 $\text{ClONO}_2 + \text{HCl}$

The reaction of  $\text{ClONO}_2$  and  $\text{HCl}$  on PSC,

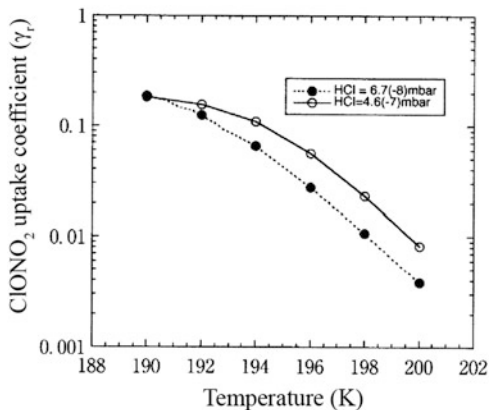


is a main reaction for the formation of the polar ozone hole together with the reaction of  $\text{ClONO}_2$  and  $\text{H}_2\text{O}$  described in the previous paragraph. Particularly, reaction (6.39) forms photochemically active  $\text{Cl}_2$  containing two chlorine atoms each from metastable  $\text{ClONO}_2$  and  $\text{HCl}$ . Since the absorption spectrum of  $\text{Cl}_2$  extends to the visible region, as seen in Fig. 4.35 (Sect. 4.4.1), so that  $\text{Cl}_2$  can release  $\text{Cl}$  atoms more effectively than  $\text{HOCl}$  under the low altitude sun, and brings rapid ozone destruction in the polar stratosphere in early spring.

The heterogeneous reaction of  $\text{ClONO}_2 + \text{HCl}$  occurs rapidly on the ice  $\text{H}_2\text{O}$  (s) surface and the product  $\text{Cl}_2$  is released to the gas phase immediately (Oppliger et al. 1997). According to the measurement by McNeill et al. (2006) using a Knudsen cell, the uptake coefficient of this reaction  $\gamma_r$  has large values of  $\geq 0.3$  being independent on  $p_{\text{HCl}}$  under the condition that partial pressure of  $\text{HCl}$  ( $p_{\text{HCl}}$ ) is larger than  $\text{ClONO}_2$  ( $p_{\text{ClONO}_2}$ ). The NASA/JPL panel (Sander et al. 2011) recommends  $\gamma_r = 0.3$  at 180–200 K based on this value and other measurements (Leu 1988; Hanson and Ravishankara 1991a; Chu et al. 1993; Lee et al. 1999; Fernandez et al. 2005). The  $\gamma_r$  of this reaction decreases under the condition of  $p_{\text{HCl}} \leq p_{\text{ClONO}_2}$  (Oppliger et al. 1997), and also decreases as the ice surface is coated by  $\text{HNO}_3$ , the same as for the reaction of  $\text{ClONO}_2$  and  $\text{H}_2\text{O}$  in the previous paragraph (Fernandez et al. 2005).



**Fig. 6.9** Temperature dependence of reactive uptake coefficients for the reaction of ClONO<sub>2</sub> and HCl on NAT (adapted from the IUPAC subcommittee evaluation data sheet, Wallington et al. 2012)

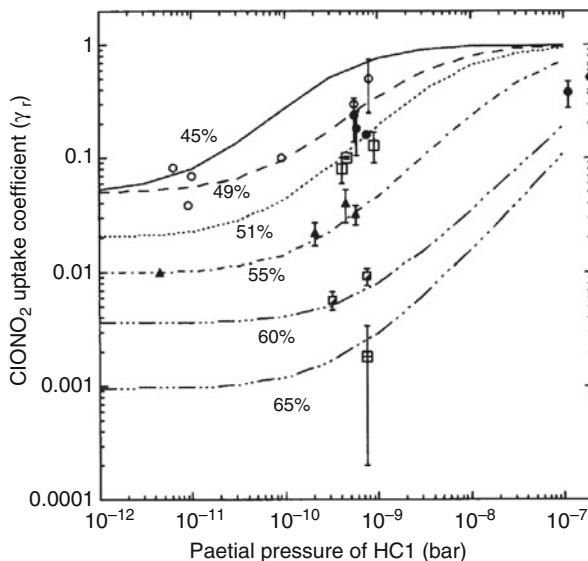


The reactive uptake coefficients for the reaction of ClONO<sub>2</sub> and HCl on NAT have been measured by Hanson and Ravishankara (1991a, 1992, 1993b), Leu et al. (1991), and Abbatt and Molina (1992b), and agreed well with  $\gamma_r > 0.1$ . The recommended value by the NASA/JPL panel based on these is  $\gamma_r = 0.2$  at 185–210 K. According to Abbatt and Molina (1992b),  $\gamma_r$  of this reaction is  $>0.2$  at RH 90 %, about the same as on H<sub>2</sub>O(s) mentioned above. It decreases rapidly to 0.002 at RH 20 %, and it is suggested that solvation is necessary for this reaction to occur. Figure 6.9 shows the reactive uptake coefficients on H<sub>2</sub>O-rich NAT as a function of temperature as compiled by the data sheets of IPAC subcommittee (Wallington et al. 2012), demonstrating that they decrease with temperature in the range of 190–202 K. Meanwhile, the reactive uptake coefficient on the HNO<sub>3</sub>-rich NAT increases with the partial pressure of HCl, and it has been shown that HCl is the limiting factor of this reaction (Abbatt and Molina 1992b). The HCl dependence of this reaction has been modeled by Carslaw and Peter (1997).

The reactive uptake coefficient of the reaction ClONO<sub>2</sub> and HCl on SAT has been measured by Hanson and Ravishankara (1993b), and Zhang et al. (1994b), and is known to be strongly dependent on temperature and water vapor pressure. The  $\gamma_r$  of this reaction has a large value of 0.12 at around RH 100 %, but decreases rapidly with the decrease of RH to give 0.0035 at RH 18 % in the similar way as on NAT. A parameterized equation of the RH-dependence of  $\gamma_r$  has been presented by Zhang et al. (1994b).

Many more measurements for the ClONO<sub>2</sub> + HCl reaction on SSA, sulfuric acid liquid particle under the stratospheric condition of polar night, have been made as compared to those on solid PSCs similar to the case of the ClONO<sub>2</sub> + H<sub>2</sub>O reaction (Tolbert et al. 1988; Hanson and Ravishankara 1991b, 1994; Zhang et al. 1994a; Elrod et al. 1995; Hanson 1998). The reaction products are Cl<sub>2</sub> and HNO<sub>3</sub> as shown in reaction (6.39), both of which are released to the gas phase. Alike the reaction of ClONO<sub>2</sub> and H<sub>2</sub>O described in a precedent paragraph, this reaction depends on temperature, humidity and composition of sulfuric acid, and has a complex dependence on the partial pressure of HCl. The  $\gamma_r$  of this reaction has a large value of

**Fig. 6.10** Dependence of reactive uptake coefficients for the reaction of ClONO<sub>2</sub> and HCl on sulfuric acid liquid on gas phase HCl partial pressure for different H<sub>2</sub>SO<sub>4</sub> wt % (Adapted from the IUPAC subcommittee evaluation data sheet, Wallington et al. 2012)



$\gamma_r = 0.6$  at 202 K when the HCl partial pressure is relatively high and decreases to 0.01 as  $p(\text{HCl})$  decreases. The  $\gamma_r$  has a negative temperature dependence, which is thought to reflect the fact solubility of HCl to sulfuric acid decreases with the increase of temperature.

Shi et al. (2001) assumed the acid-catalyzed reaction by  $\text{H}^+$  for this reaction similar to the  $\text{ClONO}_2 + \text{H}_2\text{O}$  reaction in the preceding paragraph, and presented a modeling equation for the dependence of  $\gamma_r$  on temperature, humidity and composition of sulfuric acid by evaluating the available experimental data. The IUPAC subcommittee report sheet adopted the parameters given by Shi et al. (2001), and Fig. 6.10 depicts the dependence of  $\gamma_r$  on  $p_{\text{HCl}}$  at 200 K for the different sulfuric acid concentration wt % given in the sheet (Wallington et al. 2012). The  $\gamma_r$  of this reaction is also known to decrease with the increase of the concentration of  $\text{HNO}_3$  in  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}(\text{l})$  (Zhang et al. 1994b; Hanson 1998).

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# Chapter 7

## Tropospheric Reaction Chemistry

About 90 % of the main constituents of earth's atmosphere (nitrogen and oxygen), and most atmospheric trace constituents exist in the troposphere. Almost all trace species found in the troposphere are substances emitted from anthropogenic and/or natural sources on the ground, and from volcanoes and aircraft into the free troposphere. The exceptions are O<sub>3</sub> and other secondary products formed by the chemical reactions in the atmosphere, or produced by lightning such as NO. Tropospheric chemistry is a research field for studying a series of processes as a system, including the identification and quantification of emission sources, chemical reactions and transport in the atmosphere, transformation from the gas phase molecules to liquid and/or solid particles, and deposition to clouds and fog, raindrops, and earth surface. Tropospheric chemistry is the most important fundamental discipline for various air pollution issues on the global, regional and urban scales that affect the social life of human beings. For the integrated management of air pollution global warming/climate change, atmospheric chemistry, particularly tropospheric chemistry, provides important scientific knowledge together with atmospheric physics and meteorology. As for atmospheric /tropospheric chemistry as a holistic system science, many textbooks have been published in recent decades (for example, Jacob 1999; Finlayson-Pitts and Pitts 2000; Wayne 2000; Akimoto et al. 2002; Brasseur et al. 1999, 2003; Seinfeld and Pandis 2006). This chapter provides specialized descriptions of the chemical reaction system in the troposphere, one of the main elements of tropospheric chemistry.

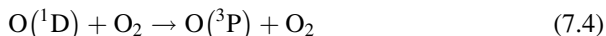
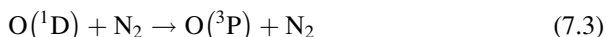
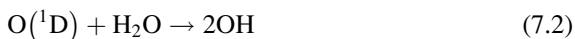
### 7.1 Oxidation of Methane in the Natural Atmosphere and OH Radical Chain Reaction

As described in Chap. 1, in contrast to stratospheric chemistry that can be traced back to the 1930s when the chemical theory of ozone layer formation was published by Chapman (1930), research on chemical reaction system in the tropospheric

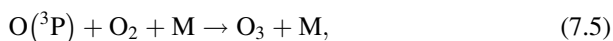
chemistry started only after the end of the 1960s to the early 1970s when the OH/HO<sub>2</sub> radical chain reaction system was proposed (Crutzen 1973). This era overlaps with the era of elucidation of the chain reactions of HO<sub>x</sub>, NO<sub>x</sub> and ClO<sub>x</sub>, which modified the Chapman theory in the stratospheric chemistry (see Chap. 8). This section describes the oxidation reaction mechanism of methane in the natural atmosphere, which provided the opportunity for the proposal of the chain mechanism with OH and HO<sub>2</sub> radicals as chain carriers. The column 1 on page 288 provides a historical story when the OH chain reaction mechanism was proposed.

As for the primary trace chemical species in the remote natural atmosphere where there is no influence of anthropogenic activities, methane (CH<sub>4</sub>) emitted from lakes and marshes, biogenic volatile organic compounds (BVOCs), nitric oxide (NO) from natural soils and lightning, dimethyl sulfide (DMS) from marine organisms, O<sub>3</sub> descended from the stratosphere can be conceived. Among them, the most important chemical species that is subjected to photolysis by the actinic flux (see Sect. 3.5) in the troposphere is O<sub>3</sub> and NO<sub>2</sub> (see Sects. 4.2.1 and 4.2.2).

The OH radicals formed by the reaction of water vapor H<sub>2</sub>O with excited oxygen atoms O(<sup>1</sup>D) produced by the photolysis of O<sub>3</sub> (Sects. 4.2.1 and 5.1.4), play an unequivocally important role in tropospheric chemistry.

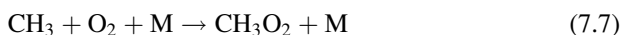


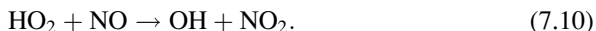
Among the O(<sup>1</sup>D) formed in the photolysis (7.1), the ratio of reacting with H<sub>2</sub>O to form OH depends on the humidity. For example, under the condition of RH = 50 % at 298 K, it is about 10 % against the deactivation (also called quenching) by reactions (7.3) and (7.4) referring to the rate constants given in Table 5.1. The ratio of OH formation by this reaction decreases with the altitude due to the decrease of humidity. Meanwhile, the ground state oxygen atoms O(<sup>3</sup>P) formed by the deactivation, react with O<sub>2</sub> returning to O<sub>3</sub> (Sect. 5.1.1),



so that they hardly play a role in tropospheric chemistry.

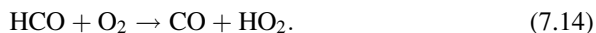
The OH radicals formed in reaction (7.2), react with CH<sub>4</sub> (Sect. 5.2.7) in the natural atmosphere followed by a series of reactions under the condition of low concentration of NO (Levy 1971; Warneck 1988),





A fundamentally important processes in tropospheric chemistry is the formation of  $\text{HO}_2$  in a series of reactions initiated by the reaction of OH with  $\text{CH}_4$ , and the regeneration of OH by reaction (7.10) (Sect. 5.3.2). Thus, this series of reactions (7.6, 7.7, 7.8, 7.9 and 7.10), forms a chain reaction with OH and  $\text{HO}_2$  as chain carriers. This chain reaction is called the  $\text{HO}_x$  chain cycle, but is often called the OH radical chain reaction since the reaction of OH with  $\text{CH}_4$  is the rate-determining step. Including stratospheric chemistry, described in the following chapter, the fundamental aspect of atmospheric chemical reaction system is chain reactions where ultra-trace levels of radicals act as catalysis, which enables loss and formation of trace species whose concentrations are much higher than these radicals.

In the oxidation processes of  $\text{CH}_4$  in the troposphere, formaldehyde (HCHO) is formed by reaction (7.9). The HCHO further reacts with OH (Sect. 5.2.11) or photolyses (Sect. 4.2.5 to form CO,  $\text{H}_2\text{O}$  and  $\text{H}_2$ ,

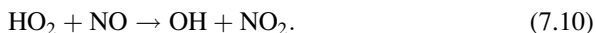


The CO reacts with OH (Sect. 5.2.3) to give  $\text{CO}_2$  as a final product,



Since these reactions of HCHO and CO with OH forms  $\text{HO}_2$  by reactions (7.14) and (7.16) and OH is regenerated by reaction (7.10), they form  $\text{HO}_x$  chain cycle, just the same as the case of  $\text{CH}_4$ .

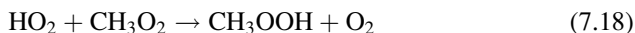
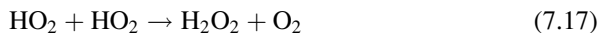
Here, referring to CO, the  $\text{HO}_x$  chain cycle expressed by reactions (7.6, 7.7, 7.8, 7.9 and 7.10) can be represented more simply as,



Incidentally, the typical mixing ratios of  $\text{CH}_4$  and CO in the northern hemisphere mid-latitude clean atmosphere are ca. 1.8 ppmv and 120 ppbv, respectively, (Brasseur et al. 1999; Finlayson-Pitts and Pitts 2000). Using these values, the ratios of OH radicals to react with  $\text{CH}_4$  and CO can be estimated as ca. 30 and 70 %, respectively.

respectively. Therefore, through a series of these reactions, CH<sub>4</sub> is oxidized finally to CO<sub>2</sub> and H<sub>2</sub>O via HCHO and CO.

In any chain cycle, there exist chain termination reactions other than the chain propagation reactions presented above. In the case of the HO<sub>x</sub> chain cycle in the natural atmosphere,



are the main termination reactions to form peroxides such as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and methyl hydroperoxide (CH<sub>3</sub>OOH) (see Sects. 5.3.5 and 5.3.6). Therefore, assuming the trace amount of NO and NO<sub>2</sub>, the existence of HCHO, CO, H<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>OOH in the natural troposphere can be explained by the reactions of O<sub>3</sub> and CH<sub>4</sub> in the troposphere as presented by Levy (1971). As for the termination reaction of the HO<sub>x</sub> chain cycle other than reactions (7.17) and (7.18),



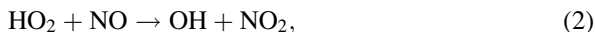
can also be conceived. Although the atmospheric concentration of OH is in general lower than HO<sub>2</sub> by two orders of magnitude (see Sect. 7.3.1), this reaction (7.19) is also important as chain termination reaction, since the rate constant of this reaction (Table 5.2) is two orders of magnitude larger than that of reaction (7.17) (Table 5.4) at room temperature.

## 7.2 Column 1 “Discovery” of the OH Radical Chain Reaction

The chain reaction mechanism with OH radical as a carrier, which is now accepted as the most fundamental reaction process in tropospheric chemistry, was proposed at the beginning of 1970s. The proposals were made in two research communities independently. One is out of the scientists who were interested in the mechanism of formation and dissipation of CO and HCHO in the natural atmosphere. In 1971 Levy (1971) presented the OH chain reaction scheme shown in Fig. 7.1 in Science for the purpose of explaining the formation of HCHO in the clean atmosphere. The chain reaction mechanism initiated by the reaction of OH and methane CH<sub>4</sub>,



and propagated by the regeneration of OH in the presence of NO,



was the essence of the proposed scheme. One of the point of this proposal was the assumption that the chain mechanism will be completed if then unknown rate

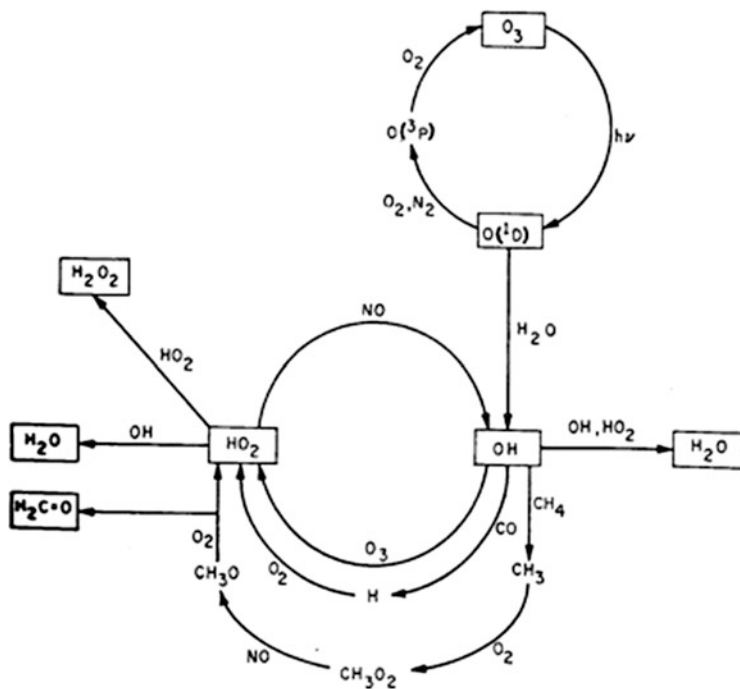


Fig. 7.1 Photochemical reaction scheme in the clean troposphere (Levy 1971)

constant of the reaction,  $\text{HO}_2 + \text{NO}$ , is larger than  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Later the rate constant of this reaction was found to be as large as  $8.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (298 K) as given in Table 5.4, and the Levy's hypothesis was verified to hold. Another point of this proposal is the initial supply of OH by the reaction of  $\text{O}(^1\text{D})$  and  $\text{H}_2\text{O}$  in which  $\text{O}(^1\text{D})$  is formed in the photolysis of  $\text{O}_3$ . By combining the OH generation by the photolysis of  $\text{O}_3$  in the clean atmosphere and the above chain reaction, the Levy's hypothesis realized the breakthrough to tropospheric chemistry, and now describe in all textbooks.

On the other hand, smog chamber experiments (see Column 2 on page 317) irradiating the mixtures of  $\text{NO}_x$  and NMHC in ppm-range with simulated sunlight ( $\lambda \geq 300 \text{ nm}$ ) were then conducted for studying the chemistry of the polluted atmosphere. In those experiments, the evidence of NO to  $\text{NO}_2$  conversion and  $\text{O}_3$  formation accompanying the decay of NMHC had been confirmed, and what chemical species react with NMHC and convert NO to  $\text{NO}_2$  was a big puzzle. For example, in the case of propylene  $\text{C}_3\text{H}_6$ , the reaction with then known O atoms and  $\text{O}_3$  could not explain even a half of the decay rate as shown in Fig. 7.2, strongly suggesting some other reactive species was necessary. In this research community, Weinstock (1971) and Hecklen (1971) discussed the possibility of OH radicals to



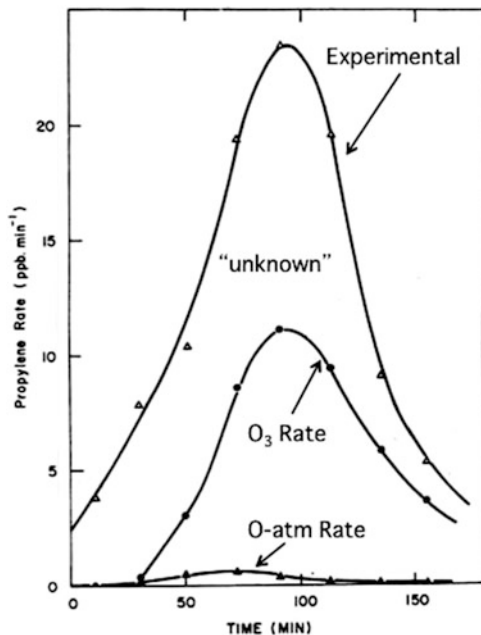
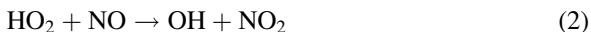
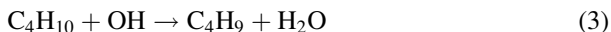


Fig. 7.2 Comparison of experimental loss rate of  $C_3H_6$  in the irradiation of a mixture of  $C_3H_6$  and  $NO_x$  in air in a smog chamber with the calculated loss rate by the reaction with O atom and  $O_3$  (Niki et al. 1972)

act a reactive species, and Heicklen (1971) proposed the OH chain reaction mechanism for reactive hydrocarbons, for example i-butene,



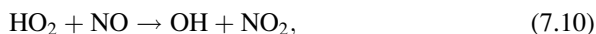
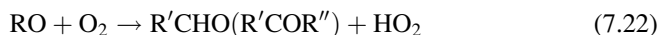
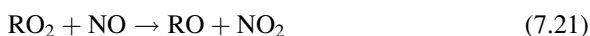
This mechanism is equivalent to the chain reaction for  $CH_4$  proposed by Levy, and was proposed independently. This reaction mechanism was originally presented in 1969 in the bulletin of Pennsylvania University (Heicklen et al. 1969). However, it was never published as a peer-reviewed journal paper, and followed the unhappy history that it is not referred in most of the present textbooks on atmospheric chemistry.

### 7.3 Oxidation Reaction Mechanisms of VOCs in Polluted Atmosphere

As the influence of human activities to the atmosphere is enhanced, the atmospheric concentrations of anthropogenic species such as nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ), volatile organic compounds (VOCs), etc. increase over a certain level. Tropospheric chemistry then exceeds the range of perturbation to the natural atmosphere, a chemical reaction system characteristic to the polluted atmosphere, sometimes called “smog reactions,” is brought about. Oxidation reaction mechanisms for the  $\text{NO}_x$ -VOC mixtures directly related to the OH chain reaction are described in this section.

In contrast to the  $\text{NO}_x$  mixing ratios 10–100 pptv in the clean lower atmosphere, those of  $\text{NO}_x$  in the urban polluted air are typically one to tens of ppbv, more than 100 times higher than the former (Finlayson-Pitts and Pitts 2000). Similarly, the mixing ratios of components of non-methane volatile organic compounds (NMVOCs) or non-methane hydrocarbons (NMHCs) in the polluted atmosphere, are also 0.1–100 ppbv, typically 100 times higher than 1–1000 pptv in the clean atmosphere (Finlayson-Pitts and Pitts 2000). In such a polluted atmosphere, most of the OH radicals formed by reactions (7.1) and (7.2) react with anthropogenic NMVOCs rather than  $\text{CH}_4$  and CO.

The oxidation reaction processes of VOC in the presence of  $\text{NO}_x$  are different for alkanes (saturated hydrocarbons), alkenes (unsaturated hydrocarbons with a double bond, also called olefins), alkynes (unsaturated hydrocarbons with a triple bond), and aromatic hydrocarbons (unsaturated hydrocarbons with a benzene ring). However, all NMVOCs react with OH, and the  $\text{HO}_x$  chain cycle can formally be expressed as,



in common to most NMVOCs in a similar way as  $\text{CH}_4$ . As for aldehydes, nearly the same form of the chain reaction mechanism can also be applied. The oxidation reactions with  $\text{O}_3$  and  $\text{NO}_3$  for alkenes and the reaction with  $\text{NO}_3$  for aldehydes are also important. In this section, the oxidation reaction mechanisms of hydrocarbons and aldehydes with OH,  $\text{O}_3$  and  $\text{NO}_3$  are summarized.

The oxidation reactions of alkanes, alkenes and aromatic hydrocarbons treated in this section are described in detail in monographs by Calvert et al. (2000, 2002, 2008), and reaction mechanisms for air quality models are summarized by Stockwell et al. (2012). Also, Calvert et al. (2011) and Mellouki et al. (2003) reviewed the oxidation reactions of oxygenated volatile organic compounds (OVOCs) which are not treated in this book. Detailed models for the photolysis

and the OH, O<sub>3</sub> and NO<sub>3</sub> reactions called MCM (Master Chemical Mechanism) have been reported in v3 (Part B) for aromatic hydrocarbons (Jenkin et al. 2003), and in v3 (Part A) for other than aromatic hydrocarbons (Saunders et al. 2003). Bloss et al. (2005) further reported the improved version v3.1 for aromatic VOCs.










### 7.3.1 *Reaction Rate Constants of OH, O<sub>3</sub>, NO<sub>3</sub> with Hydrocarbons and Aldehydes*

The rate constants for the elementary reactions of C<sub>1</sub>-C<sub>3</sub> hydrocarbons and aldehyde with OH, O<sub>3</sub> and NO<sub>3</sub> have been cited in Table 5.2 in Chap. 5, Table 7.1 summarizes the OH rate constants at 298 K for the alkanes, alkynes, and aromatic hydrocarbons with higher carbon numbers that are observed in polluted atmospheres. Table 7.2 shows rate constants at 298 K for C<sub>2</sub>-C<sub>6</sub> alkenes, and isoprene and α-, β-pinene, the most important biogenic hydrocarbons, with OH, O<sub>3</sub> and NO<sub>3</sub>. Although the rate constants for the C<sub>1</sub>-C<sub>3</sub> compounds have already been given in Table 5.2, they are cited again in Table 7.1 and 7.2 for the purpose of comparing with other > C<sub>3</sub> NMVOCs. The temperature parameters of the rate constants given in Table 7.1 and 7.2 are referenced to Atkinson (1989), Atkinson and Arey (2003), and the IUPAC subcommittee data sheet (Wallington et al. 2012).

The rate constants of OH at 298 K for the ≥ C<sub>3</sub> hydrocarbons given in Table 7.1 and 7.2 are several dozen times as large even for the most slowly reacting species, ethane, and a factor of three orders of magnitude is large for most hydrocarbons as compared to methane (Table 5.2). Assuming the daytime peak concentration of OH radical in urban atmosphere in summer as 4 × 10<sup>6</sup> molecules cm<sup>-3</sup> (see Sect. 7.4), the atmospheric lifetime of the species with the OH rate constants larger than 1 × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> is estimated to be within a few hours, and is understood to play an important role in the urban photochemical air pollution. Although the OH rate constants for the small molecules such as propane, n-butane, acetylene, benzene, ethylene, etc. are one order of magnitude smaller than this, these species are also important as other VOCs since their concentrations are generally relatively high in the urban atmosphere. From these reasons, in the discussion of the urban atmosphere, methane and other hydrocarbons are separated, and NMVOCs or NMHCs are more focused on discussion. Incidentally, the rate constants of ethane and OH, 2.4 × 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K is nearly the same as for CO (2.4 × 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K, 1 atm) (Table 5.2), and corresponds to the atmospheric lifetime of more than 1 month. Therefore, ethane does not directly contribute to urban photochemical air pollution, but can be a good tracer of anthropogenic pollution on the hemispherical scale.

As seen in Table 7.2, O<sub>3</sub> and NO<sub>3</sub> have large rate constants for alkenes, and they increase with the number of carbons. It is characteristic that the difference in rate constants are largely dependent on molecular structure, even though the carbon number is the same. As discussed in Sects. 5.4.3 and 5.5.3 in Chap. 5, these

**Table 7.1** Rate constants of reactions of alkanes, alkynes and aromatic hydrocarbons with OH at 298 K

Compounds	Chemical formula	Rate constants (298 K)	Ref.
		( $10^{-11}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	
<b>Alkanes</b>			
Methane	CH <sub>4</sub>	0.00064	(a)
Ethane	CH <sub>3</sub> CH <sub>3</sub>	0.024	(a)
Propane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	0.11	(a)
<i>n</i> -Butane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	0.24	(b)
2-methyl propane	CH <sub>3</sub> CH(CH <sub>3</sub> )CH <sub>3</sub>	2.1	(b)
<i>n</i> -Pentane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	3.8	(b)
2-Methylbutane	CH <sub>3</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub>	3.6	(b)
2,2-Dimethylpropane	CH <sub>3</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>3</sub>	0.83	(b)
Cyclopentane		5.0	(b)
<i>n</i> -Hexane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	5.2	(b)
2-Methylpentane	CH <sub>3</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	5.2	(b)
3-Methylpentane	CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub>	5.2	(b)
2,2-Dimethylbutane	CH <sub>3</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	2.2	(b)
2,3-Dimethylbutane	CH <sub>3</sub> CH(CH <sub>3</sub> )CH(CH <sub>3</sub> )CH <sub>3</sub>	5.8	(b)
Cyclohexane		7.0	(b)
<b>Alkynes</b>			
Acetylene	CH ≡ CH	0.078 <sup>a</sup>	(a)
Propyne	CH ≡ CCH <sub>3</sub>	0.59	(c)
1-butyne	CH ≡ CCH <sub>2</sub> CH <sub>3</sub>	0.80	(c)
2-butyne	CH <sub>3</sub> C ≡ CCH <sub>3</sub>	2.7	(c)
<b>Aromatic hydrocarbons</b>			
Benzene		0.12	(b)
Toluene		0.56	(b)
Ethylbenzene		0.70	(b)
<i>o</i> -Xylene		1.4	(b)
<i>m</i> -Xylene		2.3	(b)
<i>p</i> -Xylene		1.4	(b)
1,2,3-Trimethylbenzene		5.8	(b)





<sup>a</sup> 1 atm

(a) IUPAC Subcommittee Report Vol. II (Atkinson et al. 2006), (b) Atkinson and Arey (2003), (c) Atkinson (1989)

reactions are electrophilic addition reactions so that the rate constants for alkenes with a double bond adjacent to multiple methyl groups that pushes out electrons are very fast. Such alkenes are also called internal olefins. Although not shown in Table 7.2, it is known that NO<sub>3</sub> reacts with ≥ C<sub>4</sub> alkanes, and ≥ C<sub>8</sub> aromatic hydrocarbons with the rate constants with the order of ~10<sup>-16</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Atkinson and Arey 2003).

Aldehydes do not react with O<sub>3</sub>, but they have relatively large rate constants with OH and NO<sub>3</sub>, and their rate constants are in between the C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub>, as seen in

**Table 7.2** Rate constants for the reactions of alkenes, biogenic VOCs, and aldehydes with OH, O<sub>3</sub>, and NO<sub>3</sub> at 298 K

Compounds	Chemical formula	Rate constants (298 K) (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )		
		OH (Ref.) × 10 <sup>-11</sup>	O <sub>3</sub> (Ref.) × 10 <sup>-17</sup>	NO <sub>3</sub> (Ref.) × 10 <sup>-14</sup>
Ethylene	CH <sub>2</sub> =CH <sub>2</sub>	0.79 <sup>a</sup> (a)	0.16 (a)	0.0021 (a)
Propylene	CH <sub>2</sub> =CHCH <sub>3</sub>	2.9 <sup>a</sup> (a)	1.0 (a)	0.095 (a)
1-Butene	CH <sub>2</sub> =CHCH <sub>2</sub> CH <sub>3</sub>	3.1 (b)	0.96 (b)	0.13 (b)
<i>cis</i> -2-Butene	CH <sub>3</sub> CH=CHCH <sub>3</sub>	5.6 (b)	12.5 (b)	3.5 (b)
<i>trans</i> -2-Butene	CH <sub>3</sub> CH=CHCH <sub>3</sub>	6.4 (b)	19.0 (b)	3.9 (b)
2-Methylpropane	CH <sub>2</sub> =C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>3</sub>	5.1 (b)	1.1 (b)	3.4 (b)
1-Pentene	CH <sub>3</sub> CH=CHCH <sub>2</sub> CH <sub>3</sub>	3.1 (b)	1.1 (b)	0.15 (b)
<i>cis</i> -2-Pentene	CH <sub>3</sub> CH=CHCH <sub>2</sub> CH <sub>3</sub>	6.5 (b)	13 (b)	n/a <sup>b</sup>
<i>trans</i> -2-Pentene	CH <sub>3</sub> CH=CHCH <sub>2</sub> CH <sub>3</sub>	6.7 (b)	16 (b)	n/a
Cyclopentene		6.7 (b)	57 (b)	4.2 (b)
2-Methyl-1-butene	CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub>	6.1 (b)	1.4 (b)	n/a
3-Methyl-1-butene	CH <sub>2</sub> =CHCH(CH <sub>3</sub> )CH <sub>3</sub>	3.2 (b)	0.95 <sup>c</sup> (b)	n/a
2-Methyl-2-butene	CH <sub>3</sub> C(CH <sub>3</sub> )=CHCH <sub>3</sub>	8.7 (b)	40 (b)	94 (b)
1-Hexene	CH <sub>3</sub> CH=CHCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	3.7 (b)	1.1 (b)	0.18 (b)
2-Methyl-1-pentene	CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	6.3 (b)	1.6 (b)	n/a
2-Methyl-2-pentene	CH <sub>3</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> CH <sub>3</sub>	8.9 (b)	n/a	n/a
Cyclohexene		6.8 (b)	8.1 (b)	5.1 (b)
1,3-Butadiene	CH <sub>2</sub> =CH=CH=CH <sub>2</sub>	6.7 (b)	0.63 (b)	1.0 (b)
Isoprene	CH <sub>2</sub> =C(CH <sub>3</sub> )=CH=CH <sub>2</sub>	10 (a)	1.3 (a)	7.0 (a)
<i>α</i> -Pinene		5.3 (a)	9.0 (a)	62 (a)
<i>β</i> -Pinene		7.4 (b)	1.5 (b)	25 (b)
Formaldehyde	HCHO	0.85 (a)	n/r <sup>d</sup>	0.0056 (a)
Acetaldehyde	CH <sub>3</sub> CHO	1.5 (a)	n/r	0.027 (a)
Propanal	CH <sub>3</sub> CH <sub>2</sub> CHO	2.0 (a)	n/r	0.064 (a)
Butanal	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CHO	2.4 (a)	-n/r	0.11 (a)
2-Methylpropanal	CH <sub>3</sub> CH(CH <sub>3</sub> )CHO	2.6 (b)	-n/r	0.11 (b)

<sup>a</sup> High pressure limit, <sup>b</sup> Not available, <sup>c</sup> 293 K, <sup>d</sup> Not reactive

(a) IUPAC Subcommittee Report II (Atkinson et al. 2006, (b) Atkinson and Arey (2003)

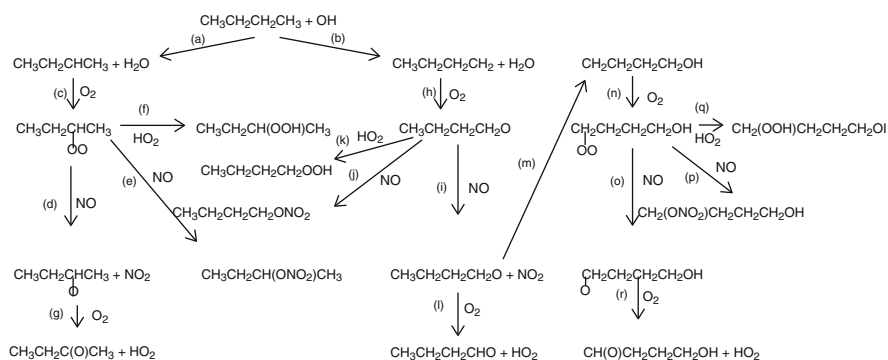
Table 7.2. The reactions of aldehydes with NO<sub>3</sub> are the main OH and HO<sub>2</sub> radical source in the nighttime polluted atmosphere together with the reactions of O<sub>3</sub> and NO<sub>3</sub> with alkenes (see Sect. 7.4.1).

As for the correlation between the rate constants of VOCs with OH, O<sub>3</sub> and NO<sub>3</sub> and molecular parameters, it has been reported that the rate constants of OH and alkene reactions have good correlation with highest occupied molecular orbitals (HOMO) of the reacting molecules as mentioned in Sect. 5.2.8 (King et al. 1999). Pfrang et al. (2006) gives the correlation formulas between the reaction rate constants for each of OH, O<sub>3</sub> and NO<sub>3</sub> and HOMO energy based on recently obtained quantum chemical calculations.

### 7.3.2 Oxidation Reaction Mechanism of Alkanes by OH

The initial process of the alkane reaction with OH is the hydrogen abstraction, the same as for CH<sub>4</sub>, and the abstraction of hydrogen from either the primary, secondary and tertiary carbon atom is possible for alkane with the carbon number  $\geq C_3$  (see Sect. 5.2.7). As an example of alkanes, the oxidation reaction mechanism of n-butane (*n*-C<sub>4</sub>H<sub>10</sub>) by OH in the presence of NO<sub>x</sub> is shown in Reaction Scheme 7.1. In the case of n-butane, 2-butyl and 1-butyl radical is formed by the abstraction process (a) from the secondary carbon and (b) from the primary carbon, respectively. In general, the reaction probability gets larger for primary < secondary < tertiary carbon reflecting the decrease of bond energy as  $\sim 420$ ,  $\sim 410$ ,  $\sim 400$  kJ mole<sup>-1</sup> for the primary, secondary and tertiary C-H, respectively (Haynes 2012–2013) as described in Sect. 5.2.7. The ratio of the process (a) and (b) is ca. 85 and 15 % in the case of n-butane at 298 K (Atkinson et al. 2006).

The alkyl radicals formed by the abstraction reaction react exclusively with O<sub>2</sub> in the atmosphere to form alkylperoxy radicals (pathways (c) (h)), and most of them are then transformed to alkoxy radicals by oxidizing NO to NO<sub>2</sub> in the presence of NO<sub>x</sub> (pathways (d) and (i)). However, some alkylperoxy radicals react with NO by the recombination isomerization reactions (e) and (j), to form alkyl nitrate (see Sect. 5.3.3). Although the yields of 2-butyl and 1-butyl nitrate are not large in the case of 2-butyl and 1-butyl radicals, 0.083 and  $\leq 0.04$ , respectively, the production yields of alkyl nitrates increase with the increase of carbon number of alkyl radicals as described in Sect. 5.3.3, and it is as large as  $>0.2$  for the C<sub>6</sub>, and C<sub>7</sub> secondary n-alkyl radicals (2-hexyl, 3-hexyl, 2-heptyl, and 3-heptyl radicals) (Lightfoot et al. 1992; Arey et al. 2001). Since these reactions act as termination reactions for the OH chain reaction, they are important as parameters in determining the ozone formation efficiency in model calculations. The production yields of RONO<sub>2</sub>

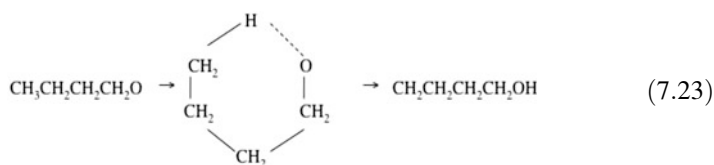


**Reaction Scheme 7.1** Oxidation reaction mechanism of n-butane with OH in the presence of NO<sub>x</sub>

in various alkylperoxy radicals ( $\text{RO}_2$ ) with  $\text{NO}$  are summarized by Arey et al. (2001).

The 2-butoxy, and 1-butoxy radicals formed in the reactions of 2-butyl and 1-butyl peroxy radicals with  $\text{NO}$  (path (d) and (j)), react with  $\text{O}_2$  to produce  $\text{HO}_2$  together with carbonyl compounds such as methyl ethyl ketone and butanal (path (g) and (l)), and complete the  $\text{HO}_x$  cycle. Under the typical  $\text{NO}_x$  concentrations in the polluted atmosphere, the formation rate of alkyl nitrates by the reactions of alkoxy radicals with  $\text{NO}_2$  is negligible, the recombination isomerization reaction by the alkylperoxy radicals with  $\text{NO}$  is the major pathway as the formation process of alkyl nitrate.

It is known that for straight-chain alkoxy radicals with a carbon number  $\geq 4$ , such as 1-butoxy radicals, isomerization forms alkoxy radicals to alcohol radicals though six-members rings can occur (Atkinson 1997a, b) as follows.



In the above Reaction Scheme 7.1, pathway (m) corresponds this process, and the formed n-butanol radicals produce hydroxyl butanal and 1-hydroxy butyl nitrate following the similar process as butyl radicals mentioned above (pathways (r) and (p), respectively). The rate constant for the isomerization reaction of alkoxy to alcohol radicals is in general  $10^5 \text{ s}^{-1}$  while the rate constants for the production of aldehydes or ketones by hydrogen abstraction by  $\text{O}_2$ ,



is  $\sim 1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson and Arey 2003), so that the isomerization and the abstraction reactions occur with nearly the same rates in the atmosphere.

Furthermore, as for alkoxy radicals with a carbon number  $\geq \text{C}_4$ , it is known that the following type of unimolecular decomposition to rupture C-C bond between the carbon attached to carboxyl group and the adjacent carbon atom occurs.



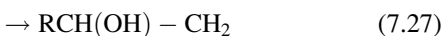
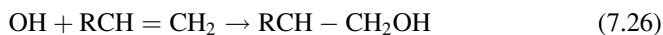
Since the unimolecular decomposition rate constants for the secondary alkoxy radicals with  $\geq \text{C}_4$  carbons, are  $\sim 10^4 \text{ s}^{-1}$  (Atkinson and Arey 2003), the reactions of the types (7.23), (7.24) and (7.25) can occur in parallel to give hydroxyl aldehyde, aldehyde with the same carbon number as the reactant alkanes, and aldehydes with one carbon less than the original alkane, respectively. The rate constants of for the isomerization reaction, reaction with  $\text{O}_2$ , and the unimolecular

decomposition reaction of typical alkoxy radicals are given by Finlayson-Pitts and Pitts (2000).

Under relatively low  $\text{NO}_x$  conditions in the atmosphere, a part of alkyl peroxy radicals, and hydroxyalkyl peroxy radicals react with  $\text{HO}_2$  to give hydroperoxy butane (pathways (f), (k)), and hydroxyhydroperoxy butane (pathway (q)). Thus, in oxidation reactions of alkane in the atmosphere, hydroperoxides, hydroxyhydroperoxides, and hydroxyalkyl nitrate, could also be produced in addition to the normal aldehydes, ketones and alkyl nitrates.

### 7.3.3 Oxidation Reaction Mechanism of Alkenes by OH

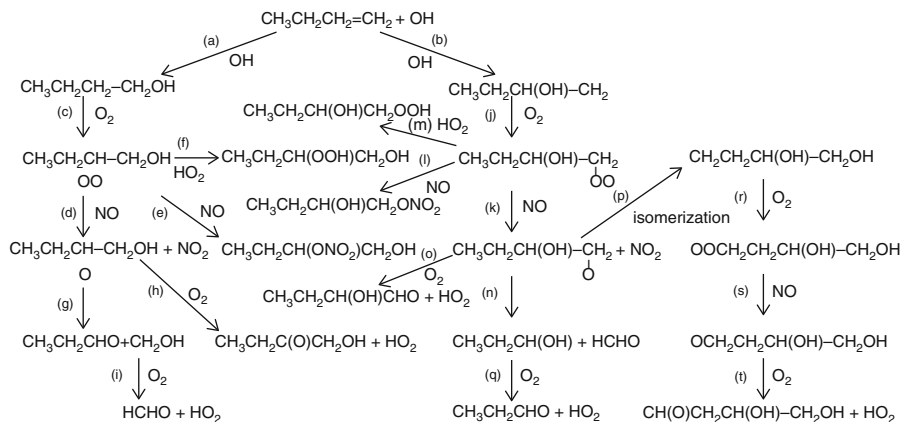
The initial reactions of alkenes and OH are the addition, and they are mostly in the high-pressure limit under atmospheric conditions including ethylene as seen in Chap. 5, Sect. 5.2.8. The addition reaction forms  $\beta$ -hydroxyalkyl radicals which have an OH group on the carbon adjacent to the carbon atom with an unpaired electron.



For asymmetric alkenes with carbon number  $\geq \text{C}_3$ , there is a possibility that the OH adds to either end of the double bond as shown above. It is known that the formation of a secondary radical by the addition of OH to the end carbon like reaction (7.26) predominates, and the ratios of the reaction type (7.26) and (7.27) is ca. 65 and 35 %, respectively in case of propylene (Finlayson-Pitts and Pitts 2000; Calvert et al. 2000).

Reaction Scheme 7.2 summarizes the reaction mechanism for 1-butene ( $1\text{-C}_4\text{H}_8$ ) as an example of alkenes. The hydroxyalkyl radicals formed by the pathways (a) and (b) is a kind of alkyl radicals mentioned in the previous Sect. (7.2.2), and exclusively forms hydroxyperoxy radicals by the reaction with  $\text{O}_2$  in the atmosphere. From the hydroxyperoxy radicals, oxyradicals (hydroxybutoxy radicals) and  $\text{NO}_2$  (pathways (d), (k)), and partially hydroxybutyl nitrate (pathways (e), (l)) are produced by the reaction with NO as in the case of alkylperoxy radicals described in the previous paragraph. The yields of hydroxyalkyl nitrates are 2–6 % for  $\text{C}_4\text{--C}_6$  alkenes (O'Brien et al. 1998), which is about half of those for alkyl nitrates from the alkoxy radicals. Hydroxyalkoxy radicals formed in pathways (d) and (k) are known to follow the three reaction pathways, unimolecular decomposition ((g), (n)), H-atom abstraction by  $\text{O}_2$  ((h), (o)), and dihydroxyl radical formation by isomerization (p), corresponding to reactions (7.25), (7.24) and





**Reaction Scheme 7.2** Oxidation reaction mechanism of the 1-butene by OH in the presence of  $\text{NO}_x$

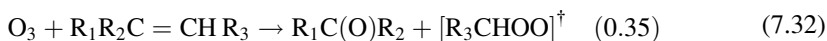
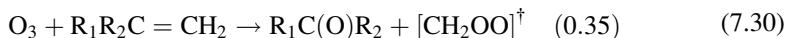
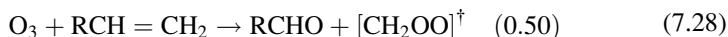
(7.23), in the case of oxyradicals, respectively (Atkinson 1997b). In the unimolecular decomposition pathway, carbonyl compounds ( $\text{CH}_3\text{CH}_2\text{CHO}$ ,  $\text{HCHO}$ ) with less carbon atoms than a reactant, and hydroxyl alkyl radicals ( $\text{CH}_2\text{OH}$ ,  $\text{CH}_3\text{CHOH}$ ) are formed. From the hydroxyl alkyl radicals,  $\text{HO}_2$  is produced by the reaction of  $\text{O}_2$ . From the H-atom abstraction reaction by  $\text{O}_2$ , hydroxyketone, hydroxyaldehyde, and  $\text{HO}_2$  radicals are formed. From the  $\text{HO}_2$  radicals, OH is reproduced by the reaction of  $\text{HO}_2$  and NO (reaction (7.2)) so that  $\text{HO}_x$  cycle is completed.

The hydroxyalkoxy radicals formed in pathway (k) can take place isomerization by intramolecular shift of H-atom via a six-membered ring as in the case of the alkoxy radical in the previous paragraph. Dihydroxyl aldehyde is then formed in pathways (q), (r), (s) though dihydroxyl radicals which has two OH groups in a molecule. The formation of dihydroxyl aldehyde has been confirmed in the laboratory experiment, and the yield of dihydroxyl aldehyde (3,4-dihydroxyl butanal) is 0.04 for 1-butene but it is as high as 0.6 for 1-octene (Kwok et al. 1996b). Under the low  $\text{NO}_x$  concentrations, a part of hydroxyperoxy radicals react with  $\text{HO}_2$ , and is known to produce hydroxyhydroperoxy butane (pathways (f), (m)) (Hatakeyama et al. 1995; Tuazon et al. 1998).

Thus, oxidation reactions of alkenes with OH in the polluted atmosphere are thought to result in various organic nitrates and hydroperoxides such as hydroxy nitrate, dihydroxyl nitrate, hydroxyhydroperoxide, and dihydroxyl hydroperoxyide. This suggests that there are many undetected and unidentified organic peroxides, and organic nitrates in the polluted atmosphere together with the OH oxidation products of alkenes discussed in the previous paragraph.

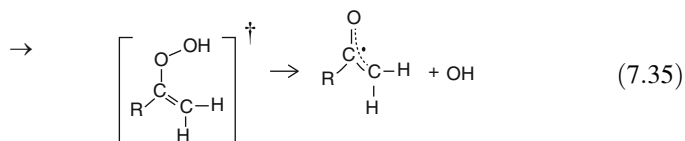
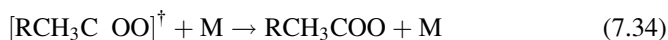
### 7.3.4 Oxidation Reaction Mechanism of Alkenes by O<sub>3</sub>

As for the pathways of O<sub>3</sub> and alkene reactions, detailed explanation has been made for C<sub>2</sub>H<sub>4</sub> in Chap. 5, Sect. 5.4.3, and the similar reaction mechanisms are basically considered for other alkenes. In the case of asymmetric chain alkenes, two reaction pathways can be considered depending on either end of double bond forms carbonyl oxide (Criegee intermediate) when the primary ozonides rupture corresponding to reaction (5.56).



As for the ratios of the two alternative pathways, carbonyl oxides containing more alkyl groups are attached are known to be formed preferentially, and the ratios are obtained experimentally to be 0.50, 0.65 and 0.65 for reactions (7.29), (7.31) and (7.33), respectively (Atkinson et al. 1997, 2006).

As for the reactions of vibrationally excited carbonyl oxides formed above, the formation of OH radicals by unimolecular decomposition and stabilized carbonyl oxides by collisional deactivation can be conceived.



The formation of OH radicals by the reaction of alkenes and O<sub>3</sub> in the polluted atmosphere is very important in atmospheric chemistry of ozone formation described in the next section. The yields of OH radicals under the atmospheric pressure are compiled by the IUPAC subcommittee (Atkinson et al. 2006) and summarized in Table 7.3. These values are those obtained by the batch type experiments with OH scavengers, while Kroll et al. (2001a) investigated pressure dependence (1–400 torr) of the initial OH yields in the reaction of O<sub>3</sub> and alkene using a high-pressure flow system coupled with the direct detection of OH by LIF. From this experiment, strong pressure dependence was found for the OH formation yields from alkenes other than ethylene with the OH yields higher than unity at low

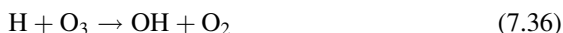
**Table 7.3** The yields of OH in the O<sub>3</sub>-alkene reactions under the atmospheric pressure

Alkenes	OH yields	Ref.
Ethene	0.14–0.20	(a)
Propene	0.32–0.35	(a)
1-Butene	0.41	(b)
1-Pentene	0.37	(b)
1-Hexene	0.32	(b)
cis-2-Butene	0.33	(a)
trans-2-Butene	0.54–0.75	(a)
2-Methylpropene	0.60–0.72	(a)
2-Methy-1-butene	0.83	(b)
2-Methyl-2-butene	0.80–0.98	(a)
2,3-Dimethyl-2-butene	0.80–1.00	(a)
Cyclopentene	0.61	(b)
Cyclohexene	0.68	(b)
Isoprene	0.25	(a)
α-Pinene	0.70–1.00	(a)
β-Pinene	0.35	(b)

(a) IUPAC Subcommittee Report Vol. II (Atkinson et al. 2006)

(b) Finlayson-Pitts and Pitts (2000)

pressure. This implies that other than reaction (7.35) the OH formation by the process,



due to H atoms formed in the reaction (5.60c) in the case of C<sub>2</sub>H<sub>4</sub> is important at low pressure. Meanwhile, the OH yields at around 1 atm is much smaller than pervious values shown in Table 7.3 except for C<sub>2</sub>H<sub>4</sub>. In order to solve the problem, Kroll et al. (2001b) obtained unimolecular decomposition rate of carbonyl oxides formed in the O<sub>3</sub>-alkene reactions by the RRKM calculation. As a result, it was confirmed that OH radicals are produced, other than those from the vibrationally excited carbonyl oxides, also from the stabilized carbonyl oxides formed by collisional stabilization in reaction (7.34) in a much longer time scale. Thus, it is thought that the total OH yields including this slow process has been obtained by the previous experiments with OH scavengers, and the values in Table 7.3 would be appropriate for use in atmospheric chemistry models. In the case of C<sub>2</sub>H<sub>4</sub>, the pressure dependence was not observed in the above experiment with the flow system, and the obtained value, 0.14 agreed well with the batch type experiments, suggesting a different reaction mechanism from other alkenes (Kroll et al. 2001c).

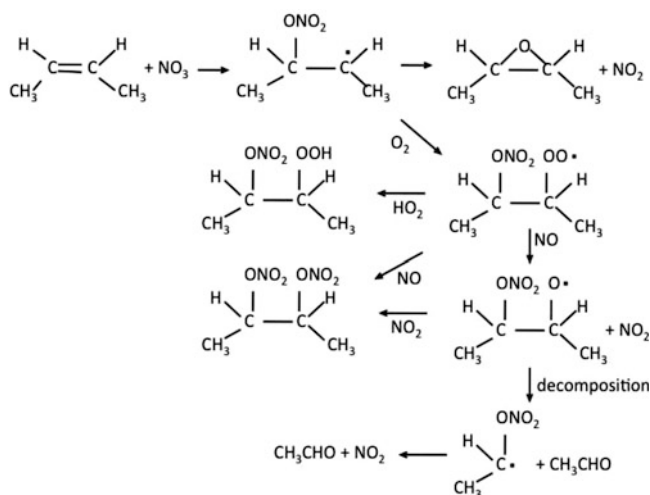
Johnson and Marston (2008) reviewed on the reactions of unsaturated VOC with O<sub>3</sub> in the troposphere, and Donahue et al. (2011) introduced new data and interpretation on the pressure dependence of the OH yields.

### 7.3.5 Oxidation Reaction Mechanism of Alkenes by $\text{NO}_3$

The initial reactions of  $\text{NO}_3$  and alkenes are the addition to double bonds as seen in Chap. 5, Sect. (5.5.3). As shown in Table 7.2, the reaction rate constants increase with carbon number, but for the same carbon number species those for the internal alkenes are much larger. The reaction mechanisms of the  $\text{NO}_3$ -alkene reactions are similar to those with OH and alkenes and an example for cis-2-butene can be illustrated as below.

As seen in Reaction Scheme 7.3, in the  $\text{NO}_3$  and alkene reactions epoxy alkanes (also called epoxides or oxiranes), hydroperoxy nitrates, carbonyl nitrates and dinitrates are produced characteristically (Bandow et al. 1980; Kwok et al. 1996a; Calvert et al. 2000), and some of them have been detected in the polluted atmosphere (Schneider et al. 1998). Recently, reactions of  $\text{NO}_3$  with alkenes are interesting from the view point of organic aerosol formation (Gong et al. 2005; Ng et al. 2008).

As for the initial pathways of the  $\text{NO}_3$ -alkene reactions, it has been shown that ring-opening addition reaction as seen in Reaction Scheme 7.3 occurs for  $\text{C}_2\text{H}_4$  and  $\text{C}_3\text{H}_6$  by quantum chemical calculations (Pérez-Casany et al. 2000; Nguyen et al. 2011), and the possibility of cycloaddition is also suggested for some alkenes (Cartas-Rosado et al. 2004).

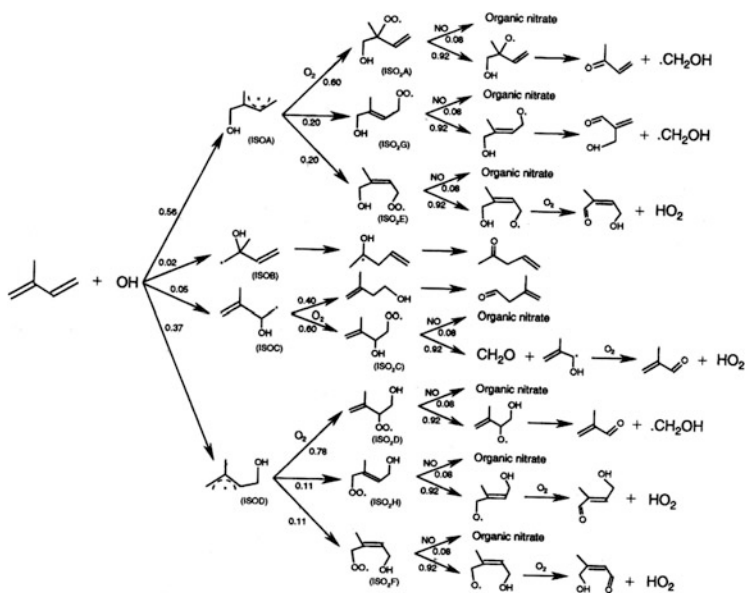


**Reaction Scheme 7.3** Oxidation reaction mechanism of cis-2-butene by  $\text{NO}_3$

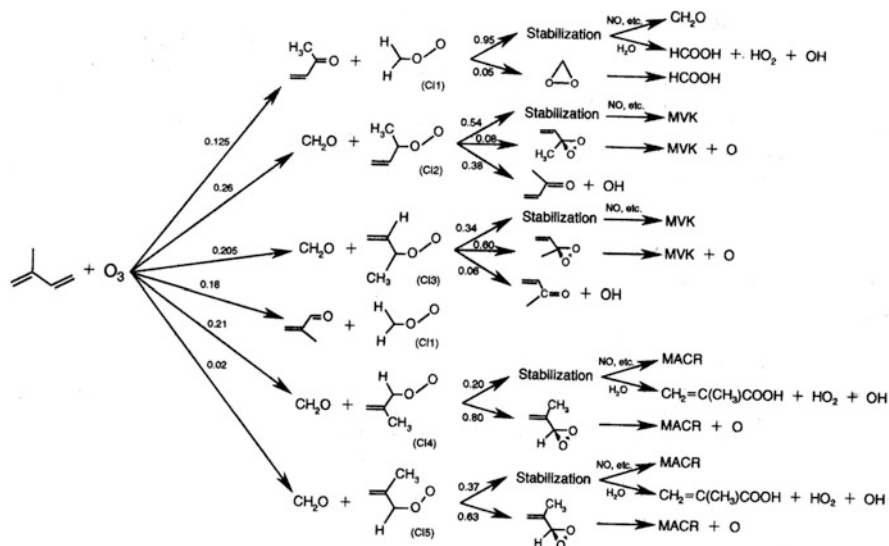
### 7.3.6 Oxidation Reaction Mechanism of Isoprene by OH, O<sub>3</sub>, and NO<sub>3</sub>

Isoprene (CH<sub>2</sub>=C(CH<sub>3</sub>)-CH=CH<sub>2</sub>) is called 2-methyl-1,3-butadiene by the nomenclature of IUPAC, a compound with two double bonds in a molecule, and is the most important biogenic hydrocarbons, which account for 50 % of the global emissions (Guenther et al. 2006). The rate constants of isoprene are large,  $1.0 \times 10^{-11}$ ,  $1.3 \times 10^{-17}$  and  $6.8 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K for OH, O<sub>3</sub> and NO<sub>3</sub>, respectively, as shown in Table 7.2. The reactions of either of these species are important in the atmosphere, particularly those with OH and O<sub>3</sub> in daytime and with NO<sub>3</sub> in nighttime (Calvert et al. 2000).

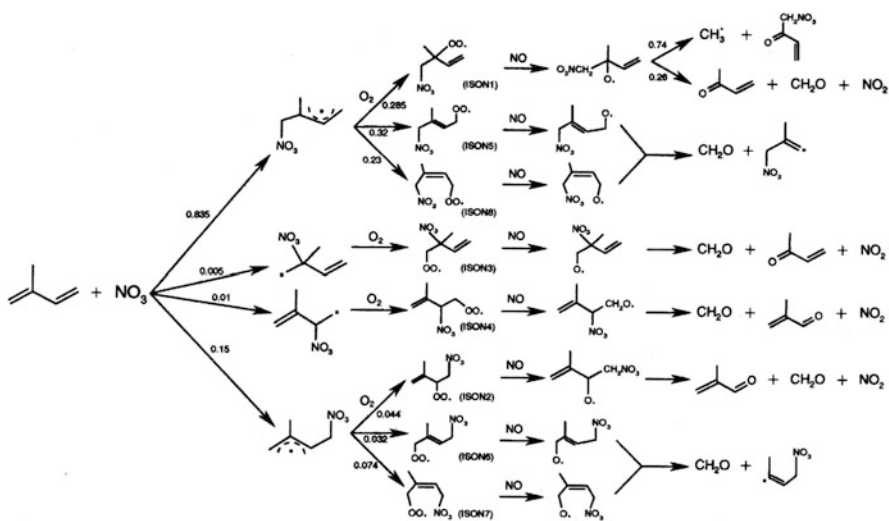
The oxidation mechanisms of isoprene with OH, O<sub>3</sub>, and NO<sub>3</sub> are addition reaction similar to alkenes and can be thought as an application of reactions described in Sects. 7.2.3, 7.2.4, and 7.2.5. However, since isoprene has asymmetric two double bonds, four reaction pathways have to be considered depending on the addition of active species to either of double bonds and either side of carbons. Many experimental and theoretical studies have been conducted as for the oxidation mechanism of isoprene (Finlayson-Pitts and Pitts 2000; Seinfeld and Pandis 2006), and Fan and Zhang (2004) presented the reaction scheme for each of OH, O<sub>3</sub> and NO<sub>3</sub> by summarizing those studies. Reaction Schemes 7.4, 7.5 and 7.6 illustrate the oxidation reaction mechanism of isoprene initiated by OH, O<sub>3</sub> and NO<sub>3</sub>, respectively, adapted from Fan and Zhang (2004).



**Reaction Scheme 7.4** Oxidation reaction mechanism of isoprene by OH in the presence of NO<sub>x</sub> (Adapted from Fan and Zhang 2004)



**Reaction Scheme 7.5** Oxidation reaction mechanism of isoprene by  $O_3$  in the presence of  $NO_x$  (Adapted from Fan and Zhang 2004)



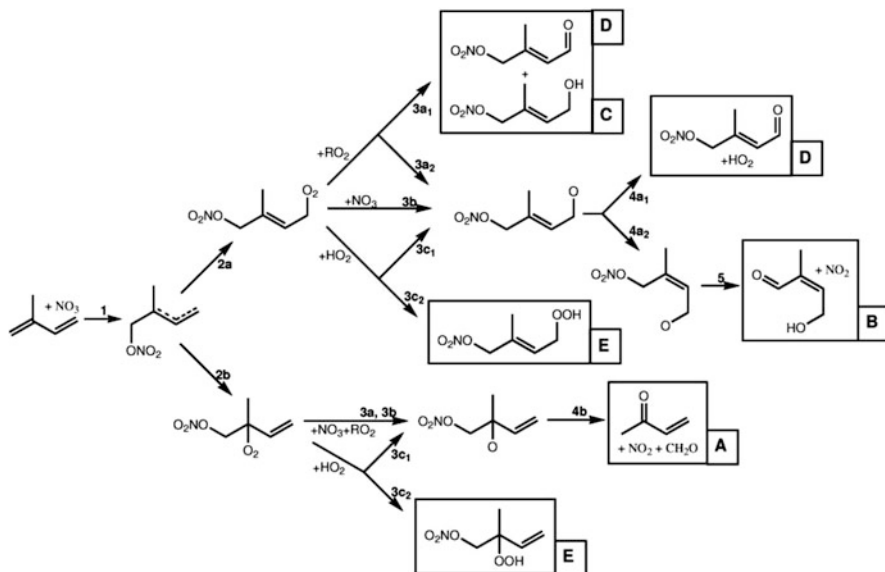
**Reaction Scheme 7.6** Oxidation reaction mechanism of isoprene by  $NO_3$  (Adapted from Fan and Zhang 2004)

As can be seen in Reaction Scheme 7.4, the main products of the oxidation reaction of isoprene by OH are methacrolein ( $\text{CH}_2 = \text{CH}(\text{CH}_3)\text{CHO}$ , MACR) and methyl vinyl ketone ( $\text{CH}_3\text{C}(\text{O})\text{CH} = \text{CH}_2$ , MVK) (Karl et al. 2006). Besides them unsaturated hydroxycarbonyl compounds and hydroxy nitrate are formed as characteristic products.

In the reaction of isoprene and  $\text{O}_3$ , via five kinds of carbonyl oxides (Criegee intermediates), MACR and MVK are formed as main products as in the case of oxidation reaction by OH, as well as HCHO, HCOOH and unsaturated carboxylic acids. In this reaction similar to the reaction of alkene and  $\text{O}_3$ , OH radicals are formed, which is important as a nighttime OH source. Zhang and Zhang (2002) showed by the quantum chemical calculation that the formation of cyclic primary ozonides occur to either of double bonds in the same ratio, and OH is formed by unimolecular decomposition of carbonyl oxides formed by the decomposition of primary ozonides. There are two kinds of OH formed by the unimolecular decomposition of carbonyl oxides, one generated from the vibrationally excited carbonyl oxides in a short timescale, and the another generated from collisionally stabilized carbonyl oxides with a time delay as described in the above Sect. 7.2.4 (Kroll et al. 2001b). The summed OH yields of these processes are important in atmospheric reaction chemistry. Malkin et al. (2010) reported the average OH yield as  $0.26 \pm 0.02$  obtained by the product analysis with scavenger and the direct measurement with FAGE/LIF (see Sect. 7.4.1), and the yield of  $\text{HO}_2$  by the FAGE method as  $0.26 \pm 0.03$  at 298 K and 1 atm. Meanwhile, the summed OH formation yield obtained by theoretical calculation is 0.24, agreeing well with the experiments (Zhang and Zhang 2002; Zhang et al. 2002). Although not taken up in this book, the reaction mechanisms of  $\text{O}_3$  with  $\alpha$ -pinene and  $\beta$ -pinene, which are important biogenic hydrocarbons next to isoprene, are summarized by Zhang and Zhang (2005).

In the reaction of isoprene with  $\text{NO}_3$  (Reaction Scheme 7.6), the reactions proceed through eight kinds of nitrooxyalkyl peroxy radicals (ISON1-ISON8) and 8 kinds of nitrooxyalkoxy radicals (ISN1-ISN8) formed from the formers by the reaction with NO. The main final products are formaldehyde, unsaturated aldehydes, ketones and organic nitrates, and the yields of MACR, MVK are small different from the reactions with OH and  $\text{O}_3$  (Barnes et al. 1990; Skov et al. 1992; Kwok et al. 1996a). From recent chamber experiments using proton-transfer mass spectrometer (PTR-MS) and thermal decomposition laser induced fluorescence (TD-LIF) as analytical methods, the yields of each of MACR and MVK are  $\sim 10\%$ , and those of organic nitrates are  $0.65 \pm 0.12$  (Perring et al. 2009). Furthermore, hydroxy nitrate (C), nitoxaldehyde (D), nitroxyhydroperoxide (E), etc. are observed among the products. Their reaction pathways, which are not included in Reaction Scheme 7.6, are shown in Reaction Scheme 7.7.

In recent field observations in the foothills of Sierra Nevada, United States, using a chemical ionization mass spectrometer (CIMS) and TD-LIF method, many organic nitrates, including hydroxy nitrates from isoprene and other BVOCs, are detected, and their ratio is reported amounting to two thirds of total organic nitrates (Beaver et al. 2012). Oxidation reactions of isoprene and other BVOCs in the



**Reaction Scheme 7.7** Pathways of the products found in the reaction of isoprene and  $\text{NO}_3$  for (A)  $\text{C}_4$ -carbonyl, (B)  $\text{C}_5$ -hydroxy carbonyl, (C) hydroxy nitrate, (D) nitroxy aldehyde, and (E) nitroxy hydroperoxide (Perring et al. 2009)

atmosphere are also interested from the viewpoint of organic aerosols formation (Claeys et al. 2004; Kroll et al. 2006; Zhang et al. 2007; Ng et al. 2008; Rollins et al. 2009).

### 7.3.7 Oxidation Reaction Mechanism of Alkynes by OH

As for the atmospheric dissipation of alkynes, the reaction with OH is the sole process. In addition, the initial reaction of OH with alkynes is similar to alkenes, and the reaction is in the high-pressure limit at 1 atm for alkynes with carbon number more than 3, although several atm is necessary to reach the high-pressure limit for acetylene ( $\text{C}_2\text{H}_2$ ) (see Sect. 5.2.9) (see Table 7.1). The main alkyne in the polluted atmosphere is  $\text{C}_2\text{H}_2$ , and its oxidation mechanism by OH is shown in Reaction Scheme 7.8.

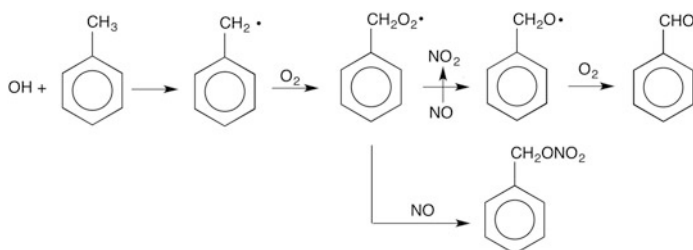
As seen in Reaction Scheme 7.8, glyoxal ( $\text{CHO-CHO}$ ) is the main product from the OH-added radical in the reaction of OH and  $\text{C}_2\text{H}_2$  through peroxy and oxy radicals (Hatakeyama et al. 1986; Galano et al. 2008). The main reaction pathway yields  $\text{HO}_2$  in the last step (e), and forms  $\text{HO}_x$  chain cycle. Similarly, methyl glyoxal ( $\text{CH}_3\text{COCHO}$ ) and biacetyl  $\text{CH}_3\text{COCH}_2\text{CO}$  are formed as main products from propyne ( $\text{C}_3\text{H}_4$ ), and 2-butyne ( $2\text{-C}_4\text{H}_6$ ), respectively (Hatakeyama et al. 1986).



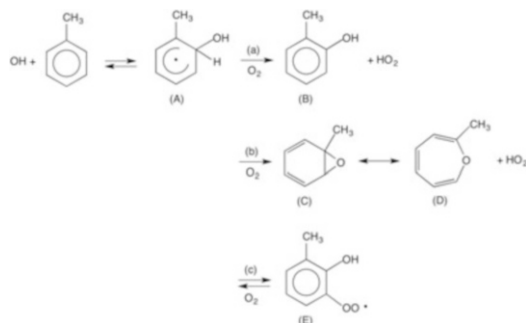


The direct measurements of the rate constants of the reaction of hydroxymethyl cyclohexadienyl radical with  $O_2$  has been made using the UV absorption method (Sect. 5.2.10), and the values of  $2.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for benzene (Bohn and Zetzsch 1999; Grebenkin and Krasnoperov 2004; Raoult et al. 2004; Nehr et al. 2011),  $6.0 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for toluene (Knispel et al. 1990; Bohn 2001) are reported. Therefore, most hydroxymethyl cyclohexadienyl radicals are thought to react solely with  $O_2$ . Also, the unimolecular decomposition rate of cyclohexadienyl radical from benzene back to  $C_6H_6 + OH$  has been reported as  $(3.9 \pm 1.3) \text{ s}^{-1}$  at 298 K (Nehr et al. 2011).

In the case of toluene, as shown in Reaction Scheme 7.10, three reaction pathways of hydroxymethyl cyclohexadienyl radical with  $O_2$  are conceived; the formation of (1) cresol (B) by the H-atom abstraction from the OH-added carbon (pathway a), (2) toluene 1,2-epoxide (C) and the 2-methyl oxepin (D) equilibrated with it, and (3) hydroxymethyl cyclohexadienyl peroxy radical (E) formed by the  $O_2$  addition to the benzene ring (Suh et al. 2003; Cartas-Rosado and Castro 2007; Baltaretu et al. 2009). The formation of cresol by pathway (a) is well known, and o-cresol is produced predominantly followed by p- and m-cresol reflecting the ortho- and para-orientation of the OH addition to benzene ring (see Sect. 5.2.10). However, the ratio of the H-atom abstraction from the benzene ring of hydroxy



**Reaction Scheme 7.9** Oxidation reaction mechanism of toluene by OH through H-atom abstraction process in the presence of  $NO_x$



**Reaction Scheme 7.10** Formation of hydroxymethyl cyclohexadienyl radical in the addition reaction of OH to toluene and its pathway for the reaction with  $O_2$

methyl cyclohexadienyl radical by  $O_2$  is c.a. 20 % for the reactions of OH with toluene, xylene and trimethyl benzene, and the pathways (b) and (c) are known to occur preferentially based on the product analysis (Klotz et al. 1998; Calvert et al. 2002; Atkinson and Arey 2003).

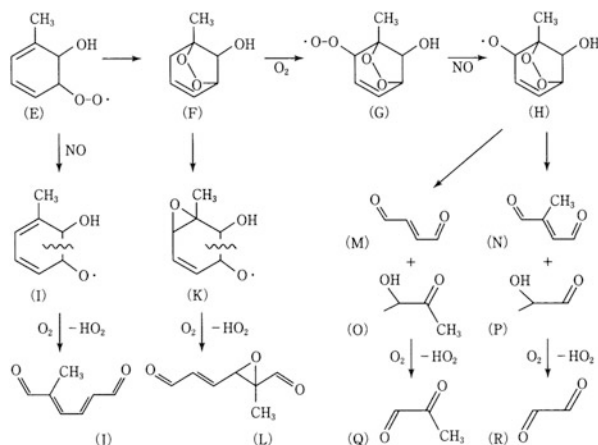
The production of toluene 1,2-epoxide (C) and 2-methyl oxepin (D) by the pathway (b) was proposed by Klotz et al. (2000). Their reaction rates with OH was found to be fast experimentally and theoretically, and they are thought to be one of the formation pathways to the open-ring compounds described below (Cartas-Rosado and Castro 2007). In the case of benzene, it has been reported that phenol is formed from the photolysis of benzene oxide and oxepin (Klotz et al. 1997), but the cresols are not formed from toluene 1,2-epoxide or 2-methyl oxepin (Klotz et al. 2000).

The formation of hydroxymethyl cyclohexadienyl peroxy radical (E) by pathway (c) in Reaction Scheme 7.10 is thought to be the most important as a process to produce ring-opened compounds, which are well known reaction products of OH and aromatic hydrocarbons. The  $O_2$  addition reaction to the OH-added benzene ring radical is reversible, and in the case of benzene, the equilibrium constant and the enthalpy change is given as  $K(298\text{ K}) = (8.0 \pm 0.6) \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1}$  (Johnson et al. 2002), and  $= (-44 \pm 2) \text{ kJ mol}^{-1}$  (Grebekina and Krasnoperov 2004) for the hydroxycyclohexadienyl radical. Therefore, hydroxycyclohexadienyl radicals formed in pathway (c) are in general stable in the atmosphere, and play an important role as intermediates in the oxidation reaction of aromatic compounds.

A peculiar feature of oxidation reaction of aromatic hydrocarbons is the production of dicarbonyl compounds by opening of the benzene ring. For example, glyoxal (CHOCHO) are known to be formed from benzene, glyoxal and methyl glyoxal (CHOC(CH<sub>3</sub>)O) from toluene, glyoxal, methyl glyoxal and biacetyl (C(CH<sub>3</sub>)OC(CH<sub>3</sub>)O) from o-xylene (Calvert et al. 2002; Atkinson and Arey 2003). Also, in the case of toluene C<sub>5</sub>, C<sub>6</sub> and C<sub>7</sub> dialdehyde, and hydroxy dicarbonyl compounds are formed. Further, formation of epoxide such as 2,3-epoxy-2-methyl hexenedial, has been confirmed (Yu and Jeffries 1997; Baltaretu et al. 2009) as mentioned below. The production yields and formation mechanism of these ring-opened compounds are not well established yet and the many studies are still going on.

Two reaction pathways to form ring-opened compounds in the oxidation reaction of toluene and OH are thought to occur, one through hydroxymethyl cyclohexadienyl peroxy radical (E) and the other through toluene-1,2-epoxide (C) or 2-methyl oxepin (D) in Reaction Scheme 7.10. Reaction Scheme 7.11 summarizes former pathways for peroxy radical (E) shown in Reaction Scheme in 7.10 based on recent findings.

From hydroxymethyl cyclohexadienyl peroxy radical (E), formation of an intermediate in which O-O bridges to a benzene ring, bicyclooxy radical (F) is predicted theoretically (Andino et al. 1996; García-Cruz et al. 2000; Suh et al. 2003, 2006). Most of ring-opened products are thought to be formed through this bicyclo radical, and in the case of toluene it is assumed that C<sub>7</sub> epoxide, epoxyethyl hexenedial (L), is thought to be formed by the isomerization of bicyclo-peroxy radical to



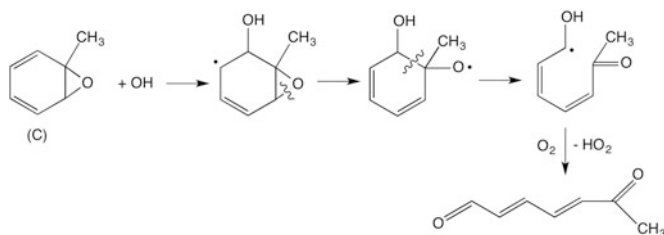
**Reaction Scheme 7.11** Formation pathways of ring-opened compounds through hydroxymethyl cyclohexadienyl peroxy radical (E) in the oxidation reaction of toluene with OH

hydroxy methyl epoxyoxy radical (K) (Bartolotti and Edney 1995; Baltaretu et al. 2009). Furthermore, Baltaretu et al. (2009) found methyl hexadienedial (J) containing all the carbon atoms of toluene is formed in high yields in the oxidation reaction of toluene with OH using a flow system chemical ionization mass spectrometer (Birdsall et al., 2010), and proposed a pathway through a oxy radical (I) formed from the reaction of cyclohexadienyl peroxy radical with NO without passing through the bicyclo intermediate (F).

Bicycloperoxy peroxy radical (G) formed by the further  $O_2$  addition to bicycloperoxy radicals has been detected experimentally by use of a chemical ionization mass spectrometer, and the production pathway of butanedial (M) and methyl glyoxal (Q), and 2-methyl butanedial (N) and glyoxal (R) are proposed through the unimolecular decomposition of bicyclo peroxy oxy radical (H) which is formed by the peroxyradical and NO reaction as shown in Reaction Scheme 7.11 (Volkamer et al. 2001; Suh et al. 2003; Baltaretu et al. 2009).

Meanwhile, reactions of toluene 1,2-epoxide (C) and 2-methyl oxepin (D) have not been studied well. According to quantum chemical calculations, the reaction rate constants of the former epoxide with OH largely at  $\approx 1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Cartas-Rosado and Castro 2007) reproducing well the experimental value of  $\approx 2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Klotz et al. 2000), the theoretical value of the rate constant of OH with the oxepin is very small as  $\approx 1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The formation of the reaction product 6-oxohepta-2,4-dienal obtained experimentally by Klotz et al. (2000) is also predicted by theoretical calculation, and the reaction pathways is proposed by Cartas-Rosado and Castro (2007), as shown in Reaction Scheme 7.12.

The oxidation reaction mechanism of aromatic hydrocarbons in the atmosphere has not been established yet. Although the validation for the reaction model MCM



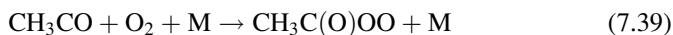
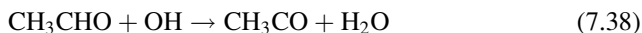
**Reaction Scheme 7.12** The formation pathway of 6-oxohepta-2,4-dial from the OH oxidation reaction of toluene 1,2-epoxide (C)

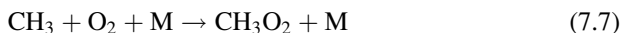
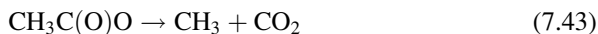
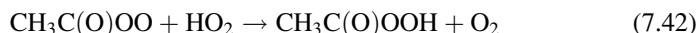
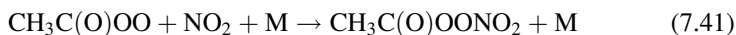
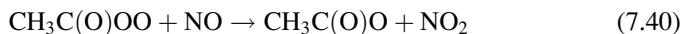
(master chemical reaction) based on the reaction schemes mentioned here, has been made by the experimental data using the outdoor smog chamber of European Union (EURPHORE) (see Column 2 on p. 317), still large discrepancies are reported regarding the concentrations of formed ozone, OH and HO<sub>2</sub>, etc. (Wagner et al. 2003; Bloss et al. 2005). In particular, experimental evidence on the NO<sub>x</sub> dependence of the products and the identification of nitrogen containing products are still poor.

As for the reaction products, many compounds not mentioned above are also reported and their production pathways are not known well. Furthermore, many of the products mentioned above such as dienes containing two double bonds and dials containing two aldehyde groups in a molecule, have large reaction rate constants with OH, and there is a possibility that the compounds formed secondarily from them may play an important role in the polluted atmosphere. It is easily anticipated that they would share the large fraction of unidentified VOCs in the atmosphere (see Sect. 7.4.2) and constitutes a large uncertainty factor in the predictive models for photochemical ozone and oxidants. Also, there are many carcinogenic and mutagenic substances among them, such as dials and epoxides, which are concerning from the aspect of health impact of photochemical air pollution.

### 7.3.9 Oxidation Reaction Mechanism of Aldehydes by OH and NO<sub>3</sub>

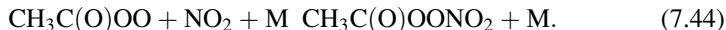
The oxidation reactions of aldehydes with OH in the presence of NO<sub>x</sub> are very important from the point of forming peculiar compounds with strong biological toxicity called peroxy acyl nitrates (PANs, RC(O)OONO<sub>2</sub>). The initial reaction of OH and aldehydes are H-atom abstraction forming the aldehyde group to form acyl radicals as seen in Chap. 5, Sect. 5.2.11. For example, in the case of acetaldehyde, the reaction mechanism is,





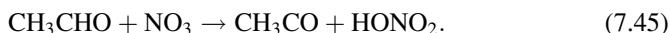
These reaction pathways are in parallel with those for alkanes mentioned in Sect. 7.2.2, and the reactions (7.7, 7.8 and 7.9) after  $\text{CH}_3$  radicals are formed in reaction (7.43) are the same as those in the oxidation processes of methane described in Sect. 7.1. The specific feature of oxidation reactions of aldehydes is the formation of a metastable peroxy acyl nitrates from the reaction of peroxy acyl radicals with  $\text{NO}_2$  by reaction (7.41). In the case of acetaldehyde, peroxy acetyl nitrate,  $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ , is formed. This compound is called PAN (Peroxy Acetyl Nitrate), and is known to have much stronger toxicity to plants than ozone. A group of peroxy acyl nitrates are collectively called PANs.

Since the bond energy  $D^\circ(\text{O}-\text{NO}_2)$  in  $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$  is as small as  $92 \text{ kJ mol}^{-1}$ , this molecule is easily thermal decomposed, and it is in thermal equilibrium in the troposphere,



The thermal decomposition rate constants of PAN is given by the IUPAC Subcommittee Report Vol. II as  $k_{\infty,7.44}(298 \text{ K}) = 3.8 \times 10^{-4} \text{ s}^{-1}$  (Atkinson et al. 2006), and the atmospheric lifetime of PAN is calculated as 43 min at 298 K. Thus, PAN is lost by the thermal decomposition and is not transported in a long range in the lower troposphere. However, the lifetime is much longer in the upper troposphere where the temperature is low, and it is transported in a long range as a  $\text{NO}_x$  reservoir, and serves as a slow regeneration source of  $\text{NO}_x$  subject to the reaction with OH or photolysis.

The reaction of aldehyde with  $\text{NO}_3$  is the H-atom abstraction (Mora-Diez and Boyd, 2002), the same as with OH, and for example, in the case of  $\text{CH}_3\text{CHO}$ ,



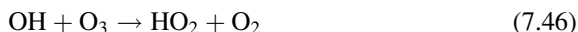
Therefore, the succeeding reactions are the same as reaction (7.39) and the following described above, and  $\text{HO}_2$  is formed by reaction (7.9). Thus the reaction of aldehyde and  $\text{NO}_3$  is important as a nighttime source of  $\text{HO}_x$  radicals.

## 7.4 Formation and Loss of O<sub>3</sub> by OH Radical Chain Reaction

The OH radical chain reaction described in Sect. 7.1 plays an essential role in tropospheric chemistry relating to the removal of almost all atmospheric organic compounds, the formation of secondary pollutants including organic aerosols, and the formation and destruction of ozone. Under the low NO<sub>x</sub> concentrations where the anthropogenic influence is small, OH radicals generated from the reaction of water vapor and the excited oxygen atom O(<sup>1</sup>D) formed in the photolysis of O<sub>3</sub> causes the loss of O<sub>3</sub> by reacting O<sub>3</sub> itself competing with the reactions with CH<sub>4</sub> and CO. On the other hand, under the condition of NO<sub>x</sub> level higher than a certain level, the OH radical chain reaction coupled with the photolysis of NO<sub>2</sub> causes the net formation of O<sub>3</sub>. Particularly in the polluted atmosphere with high concentrations of NO<sub>x</sub> and VOC, it produces a high concentration of O<sub>3</sub> causing photochemical air pollution. Therefore, the distribution of NO<sub>x</sub> and the resultant formation and destruction of O<sub>3</sub> is fundamentally important in determining the spatial distribution of O<sub>3</sub>. Further, quantitative elucidation of the relationships between the O<sub>3</sub> formation and the concentrations of NO<sub>x</sub> and VOC in the polluted atmosphere is important from the control strategy of photochemical air pollution. This section describes the HO<sub>x</sub> chain reaction mechanism which is the basis of such relationships between the NO<sub>x</sub> and VOC with O<sub>3</sub> formation.

### 7.4.1 Formation and Loss of O<sub>3</sub> in the Clean Atmosphere

When the atmospheric concentration of NO<sub>x</sub> is very low, the OH radicals formed in the reactions (7.1) and (7.2) triggered by the photolysis of O<sub>3</sub>, and the HO<sub>2</sub> radicals formed in the reactions of OH with CO and CH<sub>4</sub>, react with O<sub>3</sub> in addition to the radical-radical reactions (7.17) and (7.19) (Sects. 5.2.1 and 5.3.1),



which constitute a chain reaction to destruct O<sub>3</sub>. Also among the O(<sup>1</sup>D) formed in the photolysis of O<sub>3</sub>, the reactions with H<sub>2</sub>O to form OH itself,



causes the loss of O<sub>3</sub>. From these reactions, the in situ loss rate of O<sub>3</sub> can be expressed as,

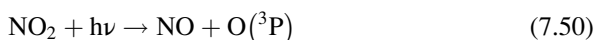
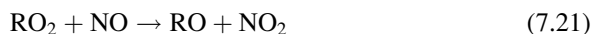
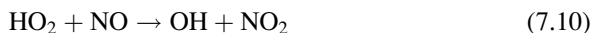
$$L(\text{O}_3) = (j_{7.1}f_{7.2} + k_{7.46}[\text{OH}] + k_{7.47}[\text{HO}_2])[\text{O}_3], \quad (7.48)$$

where  $j_{7.1}$  is the photolysis rate by reaction (7.1),  $f_{7.2}$  is the yield of OH formation from O(<sup>1</sup>D) produced in this reaction,  $k_{7.46}$  and  $k_{7.47}$  are the rate constants of reactions (7.46) and (7.47), respectively. The value of  $j_{7.1}$  can be calculated from the absorption cross sections of O<sub>3</sub> (Table 4.1) and the actinic flux given in Table 3.5, for example, for the earth surface,

$$f_{7.2} = \frac{k_{7.2}[\text{H}_2\text{O}]}{k_{7.2}[\text{H}_2\text{O}] + k_{7.3}[\text{N}_2] + k_{7.4}[\text{O}_2]}. \quad (7.49)$$

Here,  $k_{7.2}$ ,  $k_{7.3}$  and  $k_{7.4}$  are the rate constants of reaction (7.2), (7.3) and (7.4).

On the other hand, when the atmospheric NO<sub>x</sub> concentration increases, the HO<sub>x</sub> chain reaction of OH with CH<sub>4</sub> and CO operating under the low NO<sub>x</sub> conditions described in Sect. (7.1), is coupled to the O<sub>3</sub> formation reactions O(<sup>3</sup>P) from the photolysis of NO<sub>2</sub> (Sect. 4.2.2) and O<sub>2</sub>, to bring O<sub>3</sub> production.



From these equations, in situ O<sub>3</sub> production rate can be expressed as,

$$P(\text{O}_3) = (k_{7.10}[\text{HO}_2] + k_{7.21}[\text{RO}_2])[\text{NO}], \quad (7.52)$$

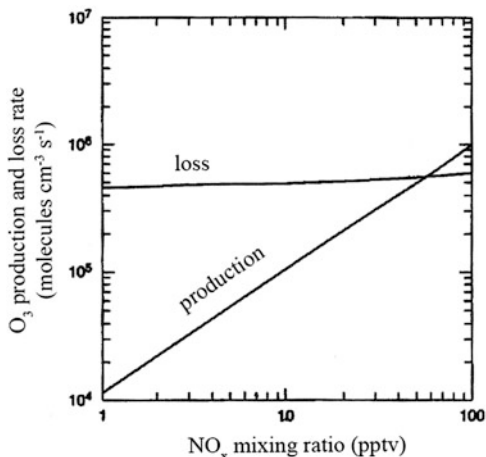
where  $k_{7.10}$  and  $k_{7.21}$  are the rate constants of reactions (7.10) and (7.21), and RO<sub>2</sub> stands for organic peroxy radicals. In the remote clean atmosphere over the open ocean, it is enough to consider only CH<sub>3</sub>O<sub>2</sub>, many other organic peroxide radicals seen in Sect. 7.2 has to be taken into account as natural and anthropogenic VOCs are added. From Eqs. (7.52) and (7.48), net in situ production rate of O<sub>3</sub>,  $N(\text{O}_3)$  can be expressed as,

$$N(\text{O}_3) = P(\text{O}_3) - L(\text{O}_3). \quad (7.53)$$

Figure 7.3 is an example of plot of the calculated formation and loss rate of O<sub>3</sub> as function of NO<sub>x</sub> in the clean atmosphere (Liu et al. 1992). The calculations are made for the diurnal averaged values for the atmospheric condition of Mauna Loa with the 1–100 pptv of NO<sub>x</sub>. As shown in Fig. 7.3, the loss rate of O<sub>3</sub> is almost constant independent of NO<sub>x</sub> concentration whereas the formation rate is nearly proportional to NO<sub>x</sub> concentration. This means that the daytime and nighttime averaged concentrations [OH], [HO<sub>2</sub>] and [RO<sub>2</sub>] in Eqs. (7.48) and (7.52) are almost constant being independent of NO<sub>x</sub> concentration.



**Fig. 7.3** Production and loss rate of  $O_3$  as a function of  $NO_x$  mixing ratio in the clean troposphere calculated by a model simulation (Adapted from Liu et al. 1992)



From Fig. 7.3, it can be seen that there is a threshold of  $NO_x$  concentration under which net  $O_3$  destruction and above which net  $O_3$  production occurs in the clean troposphere. Putting  $P(O_3) = L(O_3)$  in Eq. (7.53), the threshold value of  $NO$  concentration,  $[NO]_{th}$ , is calculated as,

$$[NO]_{th} = \frac{(j_{7.1}f_{7.2} + k_{7.46}[OH] + k_{7.47}[HO_2])[O_3]}{k_{7.10}[HO_2] + k_{7.21}[RO_2]}. \quad (7.54)$$

Here, substituting the typical values,  $j_{7.1} = 4 \times 10^{-5} \text{ s}^{-1}$ ,  $f_{7.2} = 0.1$ ;  $[HO_2] = 6 \times 10^8$ ,  $[OH] = 4 \times 10^6$ ,  $[CH_3O_2] = 3 \times 10^8 \text{ molecules cm}^{-3}$ ;  $k_{7.46} = 1.9 \times 10^{-15}$ ,  $k_{7.47} = 7.3 \times 10^{-14}$ ,  $k_{7.10} = 8.0 \times 10^{-12}$ ,  $k_{7.21}(CH_3O_2) = 7.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and  $[O_3] = 40 \text{ ppb}$ , the value of  $[NO]_{th} = \sim 25 \text{ ppt}$  is obtained.

Under the solar irradiation in daytime, the concentration ratio of  $NO$  and  $NO_2$  can be determined by the ratio of  $NO$  production rate by the photolysis of  $NO_2$  in reaction (7.50) and the conversion rate of  $NO$  to  $NO_2$  by  $O_3$  (Sect. 5.4.1),



so that,

$$\frac{[NO]}{[NO_2]} = \frac{j_{7.50}}{k_{7.55}[O_3] + k_{7.10}[HO_2] + k_{7.21}[RO_2]}. \quad (7.56)$$

Typical  $O_3$  mixing ratios are  $\sim 10 \text{ ppbv}$  and  $30\text{--}50 \text{ ppbv}$  over the clean ocean and the clean terrestrial, respectively, while those of peroxy radicals are  $\sim 10 \text{ pptv}$ , three orders of magnitude lower than  $O_3$ . However, the rate constants of the reaction of  $NO$  with the peroxy radicals, e.g.  $HO_2$ ,  $CH_3O_2$ , are  $\sim 8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which is nearly three orders of magnitude larger than that of  $NO$  and  $O_3$ ,

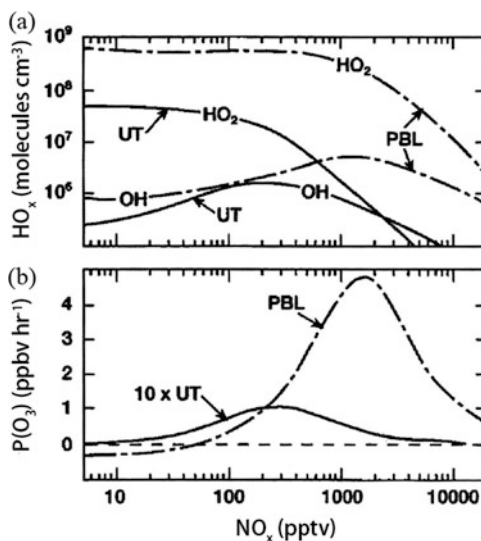
$1.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (see Table 5.4), the contributions of these peroxy radicals and O<sub>3</sub> are comparable to determine the equilibrium concentration ratio of NO and NO<sub>2</sub> in the daytime. The calculated ratio from Eq. (7.56) is  $[\text{NO}]/[\text{NO}_2] \approx 0.3$ . Using this value, the threshold value of NO<sub>x</sub> calculated from Eq. (7.53) is  $[\text{NO}_x]_{\text{th}} \approx 80 \text{ pptv}$ . From Fig. 7.3, the threshold value of NO<sub>x</sub> can be read as  $\sim 60 \text{ pptv}$ , and thus the threshold mixing ratio of NO<sub>x</sub> to determine whether production or destruction of net O<sub>3</sub> occurs in the clean atmosphere is in general thought to be a few 10 s to 100 pptv.

In the actual remote atmosphere, O<sub>3</sub> concentrations are determined mostly by long-range transport, and do not necessarily reflect the in situ production and destruction directly. However, the production and loss of O<sub>3</sub> described above are reflected in the regional scale distribution of O<sub>3</sub>, and are important for the consideration of the global budget of tropospheric ozone.

### 7.4.2 Formation of O<sub>3</sub> in the Polluted Atmosphere

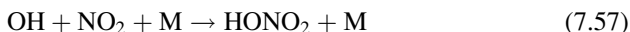
The dependence of production and loss of O<sub>3</sub> on NO<sub>x</sub> mixing ratio shows totally different features in the polluted atmosphere where the NO<sub>x</sub> mixing ratio exceeds 1 ppbv. Fig. 7.4 shows the plot of the OH and HO<sub>2</sub> concentrations, and net O<sub>3</sub> production rate against NO<sub>x</sub> mixing ratio from the clean regime of 1–100 pptv to the polluted regime of over 10 ppbv by a model calculation (Brune 2000). The calculated results for the two cases of planetary boundary layer (PBL) and upper troposphere (UP) are shown in the figure. As seen in Fig. 7.4a for the boundary layer, the OH concentrations are almost constant up to the NO<sub>x</sub> mixing ratio of a

**Fig. 7.4** Model-calculated dependence on NO<sub>x</sub> mixing ratio of (a) OH and HO<sub>2</sub> concentrations, (b) net ozone production rate. *PBL* planetary boundary layer, *UT* upper troposphere (Adapted from Brune 2000)



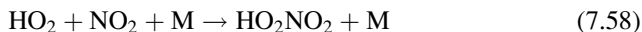
few 10s of pptv, and it increases when the  $\text{NO}_x$  mixing ratio exceeds this value, while the concentrations of OH and  $\text{HO}_2$  decreases rapidly when the  $\text{NO}_x$  mixing ratio exceeds ca. 1 ppbv. In the upper troposphere, these changes occur nearly one order of magnitude lower mixing ratios of  $\text{NO}_x$ , and the increase of OH is seen over ca. 10 pptv of  $\text{NO}_x$  and the decrease of OH and  $\text{HO}_2$  is seen over ca. 200 pptv of  $\text{NO}_x$ . On the other hand, as seen in Fig. 7.4b, the net production rate of  $\text{O}_3$ ,  $N(\text{O}_3)$ , in the boundary layer turns to positive over a few 10s of pptv being consistent with Fig. 7.3, rapidly increases over 100 pptv, and maximizes at 1–2 ppbv of  $\text{NO}_x$  and then rapidly decreases over the higher mixing ratios of  $\text{NO}_x$ .

These  $\text{NO}_x$  dependence of  $\text{HO}_x$  concentrations and  $N(\text{O}_3)$  can be explained as follows. In the low  $\text{NO}_x$  region of less than 100 pptv (lower than the threshold value of net  $\text{O}_3$  production) in the planetary boundary layer, OH formed in the photolysis of  $\text{O}_3$  and the succeeding  $\text{HO}_2$  are controlled by loss processes by the reaction with  $\text{O}_3$ , reactions (7.46) and (7.47), and radical-radical reactions, reactions (7.17, 7.18 and 7.19). Since the  $\text{HO}_2 + \text{NO}$ , reaction (7.10), cannot compete with them, the concentrations of OH and  $\text{HO}_2$  are nearly constant being independent on  $\text{NO}_x$  mixing ratio. As the increase of  $\text{NO}_x$ , the contribution of the reaction,  $\text{HO}_2 + \text{NO}$ , increases to control the  $\text{O}_3$  production, and simultaneously facilitate the conversion of  $\text{HO}_2$  to OH resulting the increase of OH concentrations. When the  $\text{NO}_x$  mixing ratio further increases over 1 ppbv, the reaction of OH and  $\text{NO}_2$  (see Sect. 5.2.4),

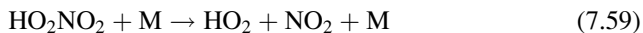


becomes effective to reduce OH and  $\text{HO}_2$  concentration as the  $\text{NO}_x$  mixing ratio increases. Thus, in the regime where  $\text{NO}_x$  exceeds 1–2 ppbv,  $\text{HO}_2$  concentration and net  $\text{O}_3$  production rate  $N(\text{O}_3)$  starts to decrease with  $\text{NO}_x$ . The  $\text{NO}_x$  mixing ratio of 10–100 ppbv can causes photochemical air pollution with high  $\text{O}_3$  pollution over 100 ppbv. The production rate and concentration of  $\text{O}_3$  shows strong non-linearity toward  $\text{NO}_x$  mixing ratios in this range as described in the next paragraph.

In the upper troposphere, the formation rate of OH by the reaction of  $\text{O}(^1\text{D})$  and  $\text{H}_2\text{O}$  is small due to the low humidity, so that the contribution of the photolysis of  $\text{H}_2\text{O}_2$  (Sect. 4.2.8), HCHO (Sect. 4.2.5) and  $\text{CH}_3\text{C}(\text{O})\text{CH}_3$  (Sect. 4.2.7) as a source of  $\text{HO}_x$  gets larger compared to the PBL. As seen in Fig. 7.4, the concentrations of OH and  $\text{HO}_2$  in the low  $\text{NO}_x$  range in the upper troposphere are small, and about one third for OH and about one tenth for  $\text{HO}_2$  as compared to the boundary layer. Therefore, the self-reactions of  $\text{HO}_x$  as a loss process of  $\text{HO}_x$  are not efficient there. On the other hand, the reaction of  $\text{HO}_2$  and  $\text{NO}_2$  to form  $\text{HO}_2\text{NO}_2$  (see Sect. 5.3.4),



becomes important with the increase of  $\text{NO}_x$  in the upper troposphere. This is because the thermal decomposition reaction rate of

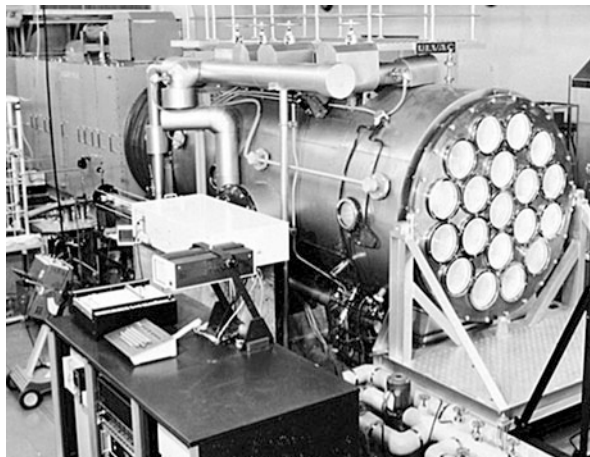


gets small at the low temperatures in the upper troposphere, and reaction (7.58) becomes an in situ substantial loss process of NO<sub>x</sub>. From the reason that the reaction with NO<sub>x</sub> is more effective compared to self-reactions of HO<sub>x</sub>, the OH and HO<sub>2</sub> concentrations and the net O<sub>3</sub> production rate starts to decrease at much lower NO<sub>x</sub> mixing ratio than in PBL as shown in Fig. 7.4. Thus, the maximum of OH concentration and *N*(O<sub>3</sub>) appears around 200 pptv of NO<sub>x</sub>, and the HO<sub>2</sub> concentration starts to decrease rapidly over 200 pptv, both happens for one order of magnitude lower NO<sub>x</sub> mixing ratios as compared to the PBL. The mixing ratio of NO<sub>x</sub> more than 100 pptv has been observed in the upper troposphere (Brasseur et al. 1999), and it should be noted that the production of O<sub>3</sub> is in the non-linear for NO<sub>x</sub> in this range.

### 7.4.3 Column 2 Photochemical Smog Chamber

The large reactive vessel designed to study the photochemical reactions in the polluted atmosphere is called “photochemical smog chamber” or simply “smog chamber” (also called photochemical chamber or environmental chamber). The prototype of the smog chamber is those fabricated in 1960s, which was a metal-framed plastic film box of a few m<sup>3</sup> volume with fluorescent lights (called black lights) outside for irradiating light of longer wavelength than 300 nm (for example, Rose and Brandt 1960). The large volume was required for smog chambers from the reasons of analysis and reaction. For the analysis of reactants and products in the chamber, air pollution monitoring instruments were conventionally used, which required to suck substantial amount of air, so that large volume was necessary for the reaction vessel. From the point of reaction involving low concentration gases, adsorption and desorption of sample and product gases to and from the vessel wall cannot be neglected, and a large reaction vessel was required in order to reduce surface/volume ratio.

In order to fulfill these two requirement, the smog chamber has been developed to two directions. One is the construction of evacuable smog chamber, which enabled to remove the adsorbed species by heating the wall under high vacuum and erase the memory of previous reactions to improve experimental accuracy. The idea is the extension of physical chemistry experiments on photochemistry using classical glass cells. The first evacuable smog chamber was built at University of California at Riverside (UCR) (Winer, et al. 1980), and the second one was built at National Institute for Environment (NIES) in Japan (Akimoto et al. 1979a). Figure 7.5 illustrates the picture of the NIES chamber. The volume of the chamber is 6.3 m<sup>3</sup> and heating oil is circulated through the aperture of the double wall realizing the baking at 200 °C and temperature control during experiments. Irradiation is made co-axially by the solar simulator consisting of xenon arc lamps. The chamber is



**Fig. 7.5** Evacuatable photochemical smog chamber at National Institute for Environmental Studies, Tsukuba, Japan

equipped with the long-path (133.5 m) Fourier transform infrared spectrometer in the short-axial direction, and the multi-reflection mirrors are supported on the base of concrete optical benches mechanically separated from the chamber wall which suffers the thermal strain of heating. This chamber was successful to give reproducible experimental data, and provided many useful results from the end of 1970s–1980s (see Sect. 7.3.3). Recent evacuatable chamber has been built at Universit es Paris-Est-Cr eteil et Paris Diderot in France (Wang et al. 2011).

Another direction of the smog chamber is the development of outdoor chambers. The advantage of the outdoor chamber is the usage of the natural sunlight as a light source, which enables much larger volume for the chamber. The first outdoor chamber with 156 m<sup>3</sup> was constructed at University of North Carolina (Fox et al. 1975). Later many outdoor chambers have been built. Among them European Commission (EC) built an outdoor chamber (photoreactor) with the volume of ca. 200 m<sup>3</sup> (EUPHORE) in Valencia, Spain (Becker 1996) as shown in Fig. 7.6, and it has been utilized for the validation of model simulation and the studies on atmospheric reaction mechanisms. A more recent one with the volume of 270 m<sup>3</sup> (SAPHIR) was built in J ulich, Germany, which is equipped with the long-path absorption cell for the measurement of OH radicals (Karl et al. 2004).

Thus, the smog chamber whose prototype was born in 1960s is the rare experimental equipment continuing to be constructed and utilized for more than 50 years. Recalling of early days when the smog chamber experiments were criticized that the scientific merit is low due to their low reproducibility, these seem to belong to another age.

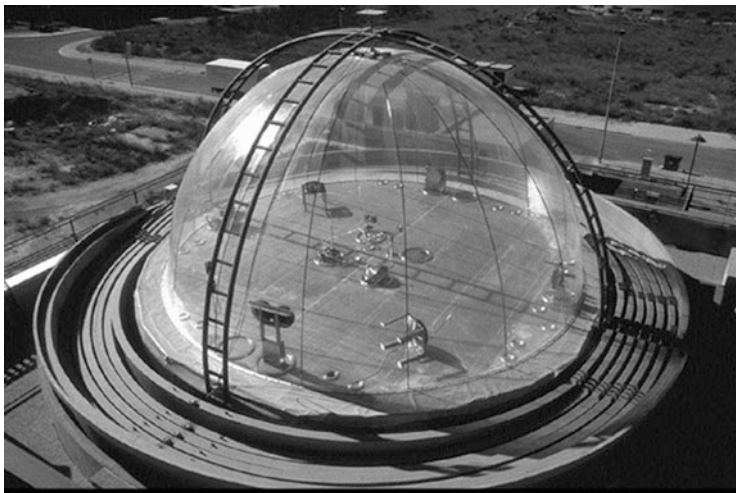
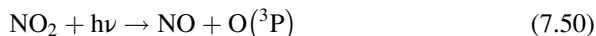


Fig. 7.6 Outdoor photoreactor (EUPHORE) in Valencia, Spain

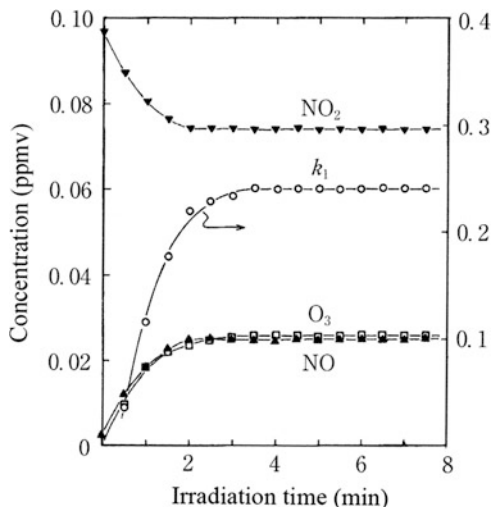
#### 7.4.4 Dependence of O<sub>3</sub> Formation on NO<sub>x</sub> and VOC, and Ozone Isopleths

In this paragraph, dependence of O<sub>3</sub> production on NO<sub>x</sub> and VOC concentrations under the conditions of polluted urban atmosphere is summarized referring to the photochemical smog chamber experiments (see Column 2 p. 317). The almost sole reaction of direct O<sub>3</sub> formation in the troposphere is the reaction of O<sub>2</sub> with the ground state oxygen atom O(<sup>3</sup>P) from the photolysis of NO<sub>2</sub>,

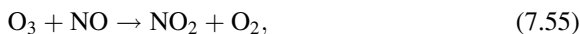


If only these reactions proceed, all NO<sub>2</sub> molecules in the atmosphere are photolyzed, and the same amount of O<sub>3</sub> as the initial concentration of NO<sub>2</sub> will be formed. Thus, for example, if the NO<sub>2</sub> mixing ratio in the polluted atmosphere is 100 ppb, the formed O<sub>3</sub> should also be 100 ppb. Figure 7.7 depicts the experimental plot of the mixing ratios of NO<sub>2</sub>, NO and O<sub>3</sub> when about 100 ppb of NO<sub>2</sub> is irradiated by the solar simulator in the smog chamber (Akimoto et al. 1979a). As seen in the figure, NO<sub>2</sub>, NO and O<sub>3</sub> reach photo-equilibrium within a couple of minutes so that only about 30 % of the initial concentration of NO<sub>2</sub> converts to the equivalent amounts of NO and O<sub>3</sub>, and no further conversion of NO<sub>2</sub> to O<sub>3</sub> can be seen. The  $k_1$  value shown in Fig. 7.7 is the experimental value of photolysis rate constant of NO<sub>2</sub> calculated from the concentrations of NO, NO<sub>2</sub> and O<sub>3</sub> by putting HO<sub>2</sub> and RO<sub>2</sub> is equal to zero in the photo-equilibrium Eq. (7.56). The  $k_1$  value, 0.24 min<sup>-1</sup>, after reaching to the photo-equilibrium corresponds to  $j_{7.50}$  in the text.

**Fig. 7.7** Time profiles of NO, NO<sub>2</sub> and O<sub>3</sub> mixing ratios under the irradiation of NO<sub>2</sub> in the smog chamber. The values of  $k_1$  in the figure is an experimentally obtained photolysis rate constant of NO<sub>2</sub> from the stationary state equation (see text) (Adapted from Akimoto et al. 1979a)



The reason of establishment of the photo-equilibrium is due to the reverse reaction between O<sub>3</sub> and NO (Sect. 5.4.1),

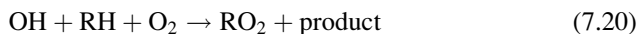


which brings back NO to NO<sub>2</sub>. From reactions (7.50), (7.51) and (7.50), the concentration of O<sub>3</sub> produced in the photostationary state when only NO<sub>x</sub> is present in the atmosphere can be approximated by,

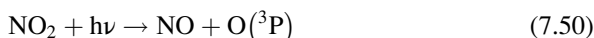
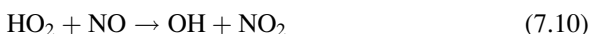
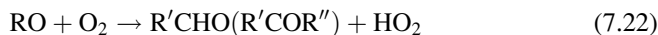
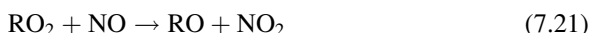
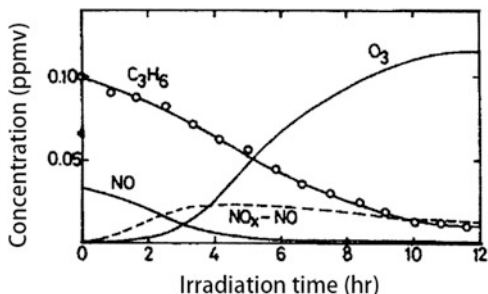
$$[\text{O}_3]_{ps} = [\text{NO}]_{ps} = \frac{-j_{7.50} + \sqrt{j_{7.50}^2 + j_{7.50}k_{7.55}[\text{NO}_2]_0}}{2k_{7.55}} \approx \sqrt{\frac{j_{7.50}}{k_{7.55}}} [\text{NO}_2]_0 \quad (7.60)$$

(Akimoto et al. 1979a). Here, [NO<sub>2</sub>]<sub>0</sub> is the initial concentration of NO<sub>2</sub>, and [O<sub>3</sub>]<sub>ps</sub> and [NO]<sub>ps</sub> are the photostationary concentrations of O<sub>3</sub> and NO, respectively, and  $j_{7.50}$  and  $k_{7.55}$  are NO<sub>2</sub> photolysis rate ( $4 \times 10^{-3} \text{ s}^{-1}$  in the experiment of Fig. 7.7) and the rate constant of reaction (7.50) ( $1.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , see Table 5.5), respectively. Incidentally, reaction (7.50) is important as causing in situ dissipation of O<sub>3</sub> by NO emitted from sources in urban atmosphere, and is called “NO titration reaction” since it decreases O<sub>3</sub> concentration stoichiometrically equal to the amount of NO concentration.

When VOC is added to the NO<sub>2</sub>-air mixture, the HO<sub>x</sub> chain reaction (7.20), (7.21), (7.22) and (7.10) mentioned in Sect. 7.2 are combined to the above reactions (7.50), (7.51) and (7.55) to constitute the following chain reaction system.



**Fig. 7.8** Time profiles of the mixing ratios of C<sub>3</sub>H<sub>6</sub>, NO, NO<sub>x</sub> - NO and O<sub>3</sub> in the irradiation of the mixture of C<sub>3</sub>H<sub>6</sub>, and NO<sub>x</sub> in air in the smog chamber (Adapted from Akimoto et al. 1979b)

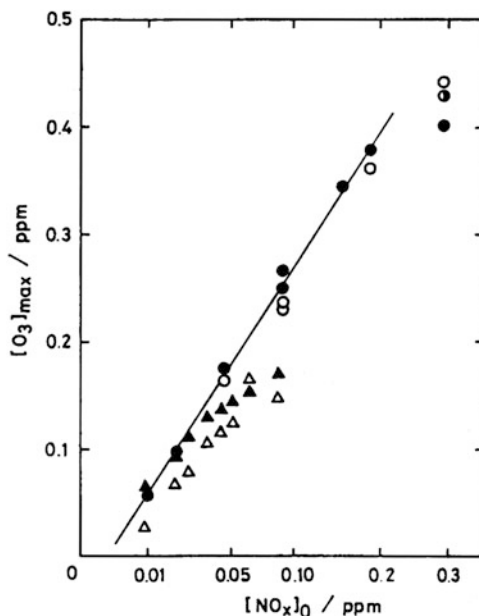


In this reaction system, NO formed in the photolytic reaction (7.50) returns to NO<sub>2</sub> preferentially reacting with HO<sub>2</sub> and RO<sub>2</sub> by reactions (7.10) and (7.21) without consuming O<sub>3</sub> by reaction (7.55). From the reproduced NO<sub>2</sub>, O<sub>3</sub> is produced again together with oxidation of NO to NO<sub>2</sub>, so that O<sub>3</sub> is accumulated to result in high concentration as the cycle proceeds in many times.

This feature is demonstrated by the chamber experiment in Fig. 7.8. This figure shows the change of concentrations of each compound when 34 ppbv of NO<sub>x</sub> (NO 33 ppbv, NO<sub>2</sub> 1 ppbv) and 100 ppbv of propylene (C<sub>3</sub>H<sub>6</sub>) are irradiated by the solar simulator (Akimoto et al. 1979b). From the figure, the features of NO to NO<sub>2</sub> oxidation, formation of O<sub>3</sub> in much higher concentration than the initial concentration of NO<sub>x</sub> and the decay of C<sub>3</sub>H<sub>6</sub> can be seen. The [NO<sub>x</sub>-NO] in the figure stands for the concentration of nitrogenous compounds other than NO, which is almost identical to the concentration of NO<sub>2</sub> until reaching the peak of [NO<sub>x</sub>-NO], but reflects the sum of nitrogenous compounds including PAN and partially nitric acid as the irradiation time gets longer. This is because the commercial chemiluminescent instrument with a molybdenum convertor used in the experiment reduces many of the secondary nitrogenous compounds other than NO<sub>2</sub> to NO, and their sum is represented as NO<sub>x</sub>. As shown in Fig. 7.8, O<sub>3</sub> formation rate decreases in the latter half of the experiment, and reaches the maximum because the reactant NO<sub>x</sub> is removed from the reaction system by the formation of nitric acid (reaction (7.57)), PAN (reaction (7.44)), and hydroxy alkyl nitrate (reaction scheme 7.2), etc. Meanwhile, the decay of C<sub>3</sub>H<sub>6</sub> shown in Fig. 7.8 is due to the reaction of OH and O<sub>3</sub> as seen in Sect. 7.2.



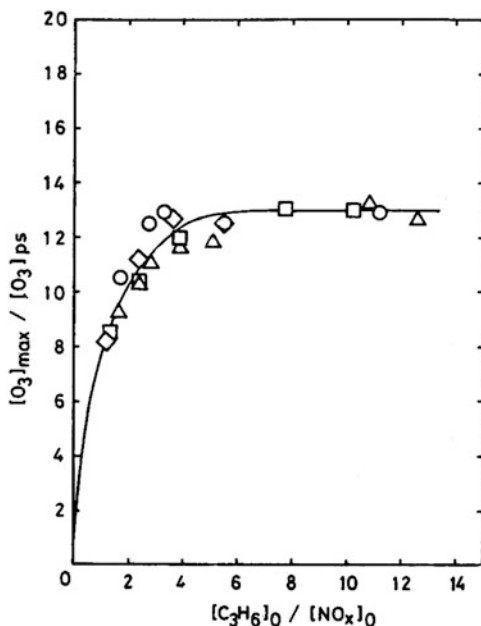
**Fig. 7.9** The dependence of the maximum ozone mixing ratio  $[O_3]_{\max}$  as a function of the square root of initial mixing ratio of  $NO_x$ ,  $[NO_x]_0$ , in the irradiation of the mixture of  $C_3H_6$  and  $NO_x$  in air in the smog chamber. The abscissa axis is in a square root scale. The initial concentration of  $C_3H_6$  is 500 ppbv ( $\circ$ ,  $\bullet$ ) and 100 ppbv ( $\triangle$ ,  $\blacktriangle$ ). Experimental (*open symbols*) and model-calculated (*filled symbols*) values are compared (Sakamaki et al. 1982)



In Fig. 7.8, it took nearly 10 hours for  $O_3$  to reach its maximum, but it is generally known that the  $O_3$  formation rate is roughly proportional to VOC concentration (Akimoto and Sakamaki 1983). According to Eq. (7.52), the  $O_3$  formation rate  $P(O_3)$  is proportional to the concentration of  $HO_2$  and  $RO_2$ , and the reaction of  $OH$  with  $RH$ , reaction (7.20), is the rate-determining step for the formation rate of the peroxy radicals. As deduced by the chamber experiment,  $OH$  concentration is nearly constant when the  $VOC/NO_x$  ratio is higher than a certain value ( $VOC$ -excess or  $NO_x$ -limited), so that the reaction rate of  $OH$  and  $VOC$  is nearly proportional to the  $VOC$  concentration (Akimoto et al. 1980).

Figure 7.9 shows a comparison between experiment and reaction model calculation for the relationship between the initial concentrations of  $NO_x$  and  $VOC$  and maximum  $O_3$  concentration  $[O_3]_{\max}$  obtained by the chamber experiment under the  $VOC$ -excess condition. In this experiment,  $C_3H_6$  is used as  $VOC$ , and prolonged irradiation was made for the  $C_3H_6$  initial concentration of 100 and 500 ppbv by changing the initial concentrations of  $NO_x$  in the range of 10–300 ppbv. As shown in Fig. 7.9, the  $O_3$  concentrations finally reached are almost independent of  $C_3H_6$  and is approximately proportional to the square root of the initial concentration of  $NO_x$  (Akimoto et al. 1979b), which is well reproduced by the model calculation (Sakamaki et al. 1982). Similarly, it was confirmed that  $[O_3]_{\max}$  is proportional to square root of photolysis rate constant of  $NO_2$ ,  $j_{7.44}$ , by the experiments and the model calculations (Sakamaki et al. 1982). From these results, they defined  $[O_3]_{ps}$  as,

**Fig. 7.10** Dependence of  $[O_3]_{\max}/[O_3]_{ps}$  on  $[C_3H_6]_0/[NO_x]_0$  in the irradiation of  $C_3H_6$ - $NO_x$  mixtures in air in the smog chamber (Sakamaki et al. 1982)

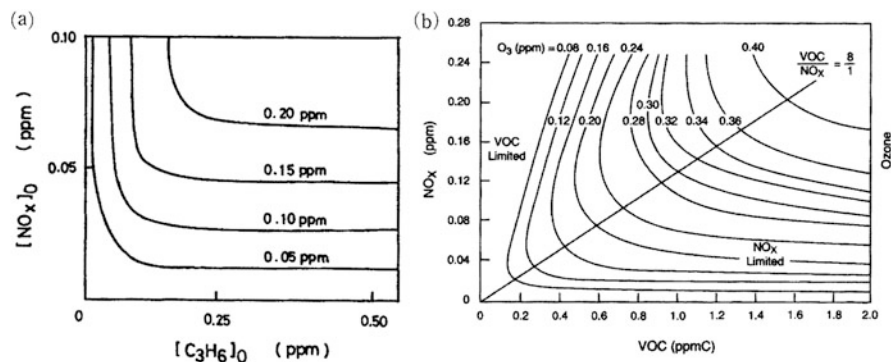


$$[O_3]_{\max} \propto [O_3]_{ps} \equiv \sqrt{\frac{j_{7.44}}{k_{7.50}} [NO_x]_0} \quad (7.61)$$

by modifying Eq. (7.60), and showed that  $[O_3]_{\max}$  is proportional to  $[O_3]_{ps}$  for the long-enough irradiation under the VOC-excess conditions. (Sakamaki et al. 1982).

It is seen in Fig. 7.9, both experimental and calculated  $[O_3]_{\max}$  values for  $[C_3H_6]_0 = 100, 500$  ppbv are deviated downward from the linear line against  $[NO_x]_0$  of higher than a certain value for each  $[C_3H_6]_0$ . This means that the maximum concentration of  $O_3$  gets dependent more strongly on the initial concentration of  $[VOC]_0$  rather than  $[NO_x]_0$  as  $[VOC]_0/[NO_x]_0$  decreases. In such  $NO_x$ -excess it has been shown that  $[O_3]_{\max}$  is proportional approximately to the square root of the initial concentration of VOC (Sakamaki et al. 1982). Figure 7.10 shows their plot of the calculated values of  $[O_3]_{\max}/[O_3]_{ps}$  by the reaction model against various combinations of  $[C_3H_6]_0/[NO_x]_0$  (Sakamaki et al. 1982). It is shown in the figure that the maximum concentrations of  $O_3$  are primarily determined by the ratios of  $[VOC]_0/[NO_x]_0$  under the concentration range met usually in the polluted urban atmosphere.

The two-dimensional plot showing the dependence of maximum ozone concentration on the initial concentrations of  $NO_x$  and VOC is called “ozone isopleths”. Usually, VOC concentration is taken as abscissa and  $NO_x$  concentration as ordinate as in Fig. 7.11a, b. Figure 7.10a is the plot of the data of Fig. 7.9 obtained in the



**Fig. 7.11** Ozone isopleths for the maximum concentration of  $O_3$  obtained by (a) a smog chamber experiment after long-time irradiation to reach ultimate maximum (Sakamaki et al. 1982), and (b) EKMA model with limited-time irradiation to simulate daily ozone (Dodge 1977)

chamber experiment in the form of isopleths, while Fig. 7.10b shows the isopleths calculated for the mixture of VOC obtained by the EKMA (Empirical Kinetic Modeling Approach) model calculation (Dodge 1977; Finlayson-Pitts and Pitts 2000). It is apparent that the shapes of the both curves look different, but the cause of difference is due to the difference in irradiation time. In Fig. 7.11b maximum ozone concentrations reached after a fixed few hours irradiation are plotted, while in Fig. 7.11a ultimate maximum ozone concentrations reached after the irradiation of more than 10 h. In general, when the irradiation is terminated in a few hours, ozone has not yet reached the ultimate maximum, which tends to give a larger positive slope of the isopleths in the high  $NO_x$  side and to give a plot showing that ozone increases with the decrease of  $NO_x$ . In Fig. 7.11b, the straight line drawn at  $VOC/NO_x = 8$  represents the ridge of the isopleths, and the right lower and the left upper region are usually called the  $NO_x$ -limited and VOC-limited, respectively. Such plots are often discussed as a basis of ozone (oxidant) control strategy, claiming that an emission control of VOC is more effective when the  $VOC/NO_x$  ratio is in the VOC-limited, and  $NO_x$  control is more effective if the ratio is in the  $NO_x$ -limited in a particular city. However, the following caution is necessary for the application of ozone isopleths to the policy proposal.

The first issue is the problem of uncertainty of the model, which arises from the situation that the chemical accuracy of the model is not fully validated in the actual ambient atmosphere. The second problem is the temporal and spatial expanse of photochemical air pollution, i.e. the relationship between the  $O_3$  and the initial concentrations of  $NO_x$  and VOC in the source area and down-wind area where  $O_3$  is reached after a few hours of transport is quite different. As for the chemical accuracy of the model, in the case of chamber experiments where the reactant VOC is well defined, the isopleths based on the model which can reproduce the experiment are recognized as accurate within the limit of validation, and they are useful for understanding the relationships between  $O_3$  and initial concentrations of  $NO_x$  and VOC conceptually and quantitatively. However, in the actual ambient

atmosphere, VOCs are not captured fully well in the conventional chemical analysis in the most cases as will be discussed in the next section (Sect. 7.4.2). In such a case, the calculation that considers only the captured VOC tends to lead to the VOC-limited than the reality. Furthermore, although the accuracy of the reaction model has to be validated by the field observation of the concentrations of chain carriers, OH and HO<sub>2</sub>, previous measurements tend to underestimate of HO<sub>2</sub> in the higher NO<sub>x</sub> region. This means there is a missing process which facilitates O<sub>3</sub> production under the higher NO<sub>x</sub> concentrations, and the O<sub>3</sub> forming potential based on a such model calculation also leads to VOC-limited tendency.

In the air pollutant emission area of the central part of a city, the results of model calculation tend to give VOC-limited since the concentration of NO<sub>x</sub> is high relative to VOC. Since the O<sub>3</sub> formation rate is proportional to VOC concentration in the morning, it is generally shown that the reduction of VOC is more effective for the O<sub>3</sub> control. However, under the geographical and meteorological conditions where the polluted plume is transported to downwind areas in the afternoon, the O<sub>3</sub> concentration tends to depend more on NO<sub>x</sub> as the reaction proceeds, and it tends to switch to the NO<sub>x</sub>-limited regime. Then, the concentration of O<sub>3</sub> gets more sensitive to the further addition of NO<sub>x</sub>. Such a situation has been analyzed by three-dimensional models, and the conclusion of the preference of either NO<sub>x</sub> or VOC control is largely different depending on which area affected by the transport is targeted for the control. Such an example has been clearly shown in the Los Angeles basin. According to the ozone isopleths, VOC control is more effective in the central part of Los Angeles city, but the 100 km downwind area NO<sub>x</sub> control is more effective (Milford et al. 1989; Finlayson-Pitts and Pitts 2000). Also in the calculation targeting still wider area in the eastern part of United States, it has been shown that the VOC control is more effective within cities, but NO<sub>x</sub> control is more effective in rural areas (Sillman et al. 1990).

## 7.5 Atmospheric Measurements of OH and HO<sub>2</sub> Radicals, and Model Validation

It is a prerequisite for proving the validity of the chemical transport model to compare the reproducibility of calculated results with the observational values of the concentrations of O<sub>3</sub> and its precursors, NO<sub>x</sub>, VOC, CO etc. at various sites. However, since the concentrations of chemical species in the atmosphere are determined by the combination of in situ production and loss, and inflow and outflow by transport, the agreement between the calculated and observational values does not necessarily assure the accuracy of chemical reaction mechanism included in the model. Particularly, in the case of using the chemical transport model for ozone control policy to discuss how NO<sub>x</sub> and VOC should be controlled for the reduction of O<sub>3</sub> in future, the conclusion can largely be dependent on if the

model accurately describes important reaction pathways as well as on if the emissions of  $\text{NO}_x$  and VOCs are accurately input.

In order to validate the reaction mechanism related to the formation and loss of  $\text{O}_3$ , comparisons between the direct measurements of the chain carriers, OH and  $\text{HO}_2$  radicals in the ambient atmosphere and the model calculations have been made. Since the atmospheric lifetime of OH and  $\text{HO}_2$  is as short as less than 1 s and a few tens of seconds, respectively, their concentrations are determined in situ and the effect of transport can be excluded. Therefore, the comparison of the calculated OH and  $\text{HO}_2$  concentrations by a box model (zero-dimensional model without including transport) with constraints of using simultaneously measured concentrations of many chemical species and photolysis rate with observed values, can be one-level higher method of validation of the chemistry model than the comparison of the concentrations of  $\text{O}_3$  and its precursors. The measurements of OH,  $\text{HO}_2$  and  $\text{RO}_2$  radicals in the ambient atmosphere are themselves challenging scientific subjects and have become possible through many technical developments. In this section, OH measured by the direct measurements by optical and mass spectroscopic methods, and  $\text{HO}_2$  measured by converting to OH are addressed. However, it has recently been noted that in the measurement of  $\text{HO}_2$  by adding NO to convert to OH, OH is also produced by the reaction of  $\text{RO}_2$  and interfere the measurement of  $\text{HO}_2$  (Fuchs et al. 2011). This interference is known to be large when the isoprene, alkene and aromatic hydrocarbons are present in high concentrations, and  $\text{RO}_2$  from alkanes with small number of carbon atoms does not produce OH. Thus, previous measurements in the free troposphere and remote sites may not be affected, but the previously reported  $\text{HO}_2$  values in the urban and particularly in the forest atmosphere where the concentrations of BVOC is high would have been overestimated. Although the qualitative conclusion of the comparison with the model would not be affected, caution should be used for quantitative discussions, and the values may be revised in future.

The agreement between the measured and calculated values of these radicals is, however, still a necessary but not a sufficient condition of the accuracy of the chemical reaction mechanism. As for these radicals, their concentrations are determined by the ratio of formation and loss rate, and the possibility cannot be excluded that if the error of formation and loss rates are in the similar magnitude, agreement is obtained when these factors are compensated. For further validation of the  $\text{HO}_x$  chemical reaction processes in the atmosphere, a method of checking of the unknown loss processes of OH has been developed, which produces OH in pulse in the air and measures its time decay to compare with the decay rate calculated from the simultaneously measured VOCs and  $\text{NO}_x$  concentrations. This method is called the measurement of OH reactivity and it is an effective method for checking the OH loss process relating to the OH budget directly.

In this section, validation of the  $\text{HO}_x$  chain reaction mechanism by the comparison of OH and  $\text{HO}_2$  concentrations obtained by recent field measurements and box model calculations, and the grasp of unknown OH-removing species by the field measurements of the OH reactivity are described. Meanwhile, although the comparison between the output of three-dimensional models with aircraft

measurements of OH and HO<sub>2</sub> concentrations is important for the validation of quantitative estimate of O<sub>3</sub> formation and loss in the free troposphere. It is mentioned rather briefly in the next paragraph since it is difficult to incorporate detailed chemical species and reaction mechanism in 3-D models. As for the comparison between the field observations and models of OH and HO<sub>2</sub> radicals, a recent review has been made by Stone et al. (2012).

### 7.5.1 *Measurements of Concentrations of OH and HO<sub>2</sub>, and Comparison with Models*

The typical atmospheric concentrations of OH and HO<sub>2</sub> radicals in the daytime are ~10<sup>6</sup> and ~10<sup>8</sup> molecules cm<sup>-3</sup> (~0.1 pptv and a few pptv), respectively. The detection techniques whose accuracy is thought to be satisfactory for their measurements are laser-induced fluorescence (LIF) at low pressure which is called Fluorescence Assay by Gas Expansion (FAGE), and chemical ionization mass spectrometry (CIMS), and they have recently been used widely. In either of the methods, directly measured is OH, and HO<sub>2</sub> is measured by converting to OH utilizing the reaction of HO<sub>2</sub> + NO → OH + NO<sub>2</sub> (reaction (7.10)) adding NO to the atmospheric samples just before the introduction to the detector. Other than these methods, differential optical absorption spectroscopy (DOAS) is also used for the measurements of OH in fields and smog chambers.

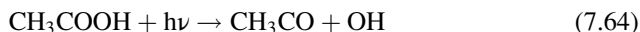
Measurements of OH and HO<sub>2</sub> have been made in the upper troposphere using aircrafts, and in the marine, forest and urban boundary layers. From the point of validation of HO<sub>x</sub> reaction mechanism, it implies verification for more complex systems with more variety of chemical species in this order.

**Upper Troposphere** The measurements of HO<sub>x</sub> in the upper troposphere over the ocean correspond to the simplest reaction system with the lowest VOCs concentrations. The measurements of this atmospheric domain have been made by many missions of the United States NASA during the latter half of 1990s–2000s, and comparisons with models have been made (Stone et al. 2012). From these investigations, the primary source of HO<sub>x</sub> in the upper troposphere under less than 100 ppmv of H<sub>2</sub>O at the altitude of higher than 8 km, it has been analyzed that in addition to the process,

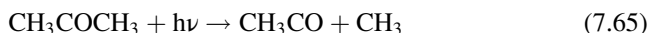


the processes (Sects. 4.2.5 and 4.2.7),



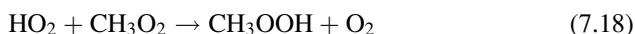
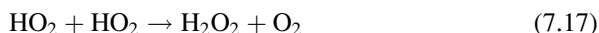


contribute substantially (Tan et al. 2001b; Ren et al. 2008). Photolysis of acetone (Sect. 4.2.6),

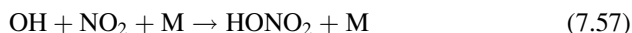


was once thought to be a major source of  $\text{HO}_x$  in the upper troposphere, its contribution is now estimated to be lower since it has been found that the photolysis quantum yield has temperature dependence and it is much lowered at low temperature (Arnold et al. 2004; Blitz et al. 2004). Meanwhile, it is estimated that the reaction of  $\text{O}(^1\text{D}) + \text{H}_2\text{O}$  is dominant at lower than 7 km (Tan et al. 2001b).

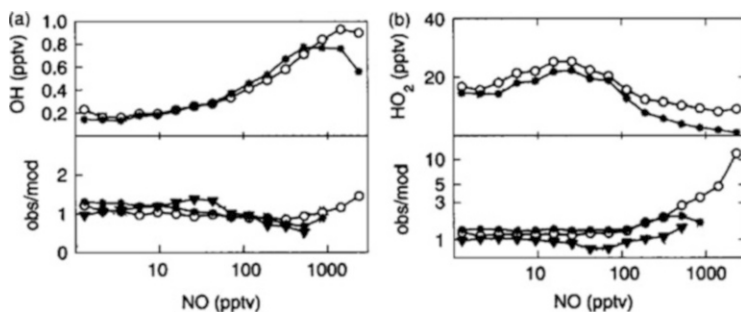
The main loss processes of  $\text{HO}_x$  in the upper troposphere are,



Further, the reaction,



gains importance as a sink of  $\text{HO}_x$  at the altitude of higher than 8 km as the concentration of  $\text{NO}_x$  increases with the altitude due to the influence of stratospheric  $\text{NO}_x$ . Ren et al. (2008) obtained the plot of the comparison of the measured values obtained in INTEX, TRACE-P, and PEM-Tropics-B with the box-model calculations as shown in Fig. 7.12. The results show a good agreement of the calculated and the observed values for OH within observational errors over the whole domain in the upper troposphere. As for  $\text{HO}_2$ , the ratios of the observed and

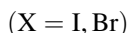
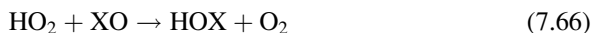


**Fig. 7.12** Comparisons of the NO dependence of (a) OH and (b)  $\text{HO}_2$  in the upper troposphere by aircraft campaigns. *Top*: measured ( $\circ$ ), modeled ( $\star$ ), *Bottom*: measured to modeled ratios in INTEX-A ( $\circ$ ), TRACE-P ( $\star$ ), PEM-Tropics B ( $\blacktriangledown$ ) (Adapted from Ren et al. 2008)

calculated values agree within 1.2 at the altitude of lower than 8 km where NO mixing ratios are less than 100 pptv, the ratio exceeds 3 at higher than 11 km where the NO mixing ratio is over 1000 pptv. From these analysis it is generally thought that the calculated values of the concentrations of OH and HO<sub>2</sub> agrees well with the observed one at the upper troposphere where the NO<sub>x</sub> mixing ratio is low and the HO<sub>x</sub> chain cycle can be well explained by the known reaction processes. On the other hand, the underestimate of the calculated concentrations of HO<sub>2</sub> is the same situation as in the polluted atmosphere, and suggests the presence of unknown reaction pathways from OH to HO<sub>2</sub> as will be discussed later.

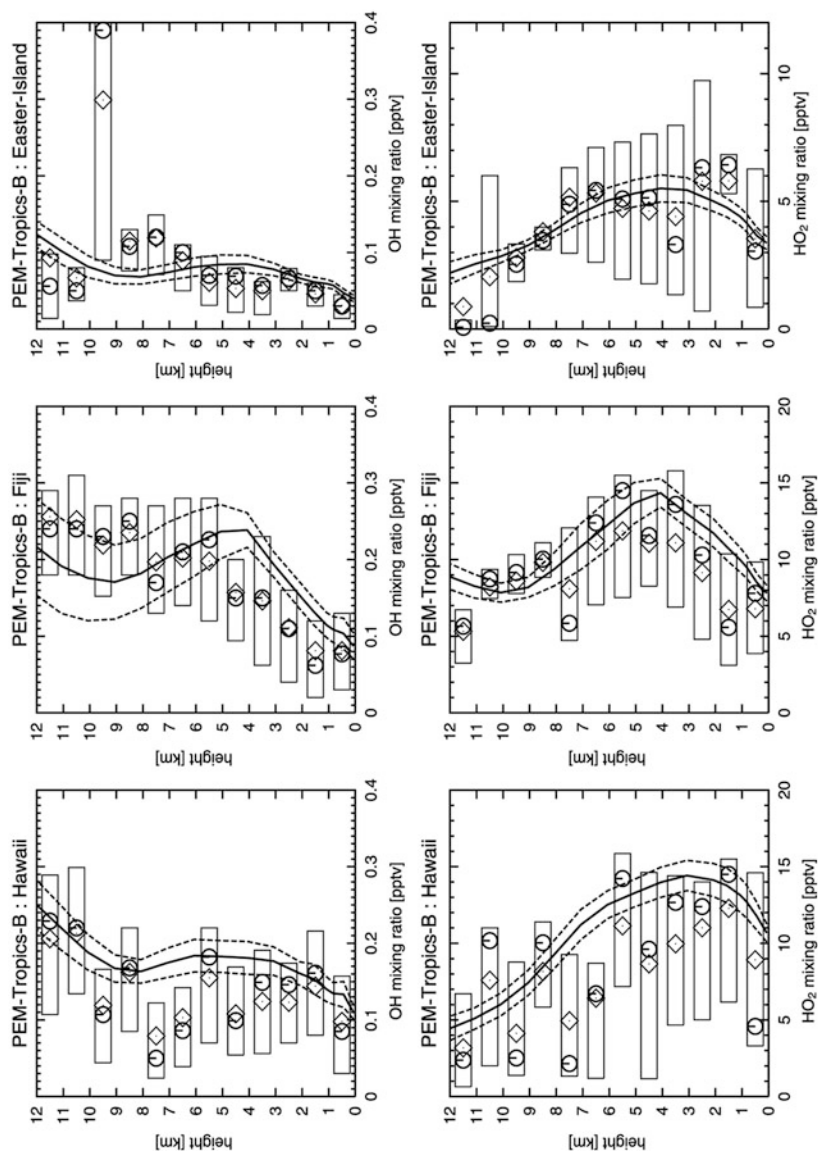
The three-dimensional simulations are also performed for such aircraft measurements of OH and HO<sub>2</sub>, to make comparison in the free troposphere (Sudo et al. 2002; Zhang et al. 2008; Regelin et al. 2012). Figure 7.13 is an example by Sudo et al. (2002). In the figure, the comparisons are made for the observation over Hawaii, Fiji, and Easter islands by the CHASER model showing reasonably good agreement in general.

**Marine Boundary Layer** The measurements of OH and HO<sub>2</sub> in the remote marine boundary layer are useful for the validation of the model of the atmospheric reaction mechanism under the condition without the influence of anthropogenic activities, and many measurements have been performed (Stone et al. 2012). From these measurements, diurnal maximum concentrations of OH and HO<sub>2</sub> have been obtained typically as  $(3-10) \times 10^6$  molecules cm<sup>-3</sup> and  $(1-6) \times 10^8$  molecules cm<sup>-3</sup> (4-25 pptv), respectively. In the comparison between the observational and calculated values, it has been reported that the calculated concentrations of HO<sub>2</sub> often overestimate the observed one by a factor of up to 3 in the field campaigns, OKIPEX 1998 in Oki Island, and RISOTTO 2000 and 2003 in Rishiri Island in Japan (Kanaya et al. 2000, 2002, 2007a). On the other hand, the differences between the calculated and observed values for OH concentrations are within 10-30 %, much smaller than for HO<sub>2</sub>. Figure 7.14 shows the comparison between the box-model calculation using the RACM reaction model (Stockwell et al. 1997) for HO<sub>2</sub> and OH with the observation in the RISOTTO campaign (Kanaya and Akimoto 2002). Halogen chemistry is not included in this model, and Kanaya et al. (2002), and Kanaya and Akimoto (2002) suggested the possibility that the chain reaction involving halogens such as IO which have been detected in the marine boundary layer (Alicke et al. 1999),



may convert more HO<sub>2</sub> to OH. Other suggested possibilities include the heterogeneous loss of HO<sub>2</sub> on aerosols, net loss of HO<sub>x</sub> radicals by the heterogeneous





**Fig. 7.13** Comparison of the vertical profiles of OH and HO<sub>2</sub> mixing ratios between aircraft observation (PEM-Tropics-B) and three-dimensional model (CHASER). *Solid and dotted lines* are the average values and the values of  $\pm 1\sigma$ , respectively, by the model calculation.  $\diamond$  and  $\circ$  are the average and median values of the observation, respectively, and the *boxes* represent the data within  $\pm 50\%$  (Adapted from Sudo et al. 2002)

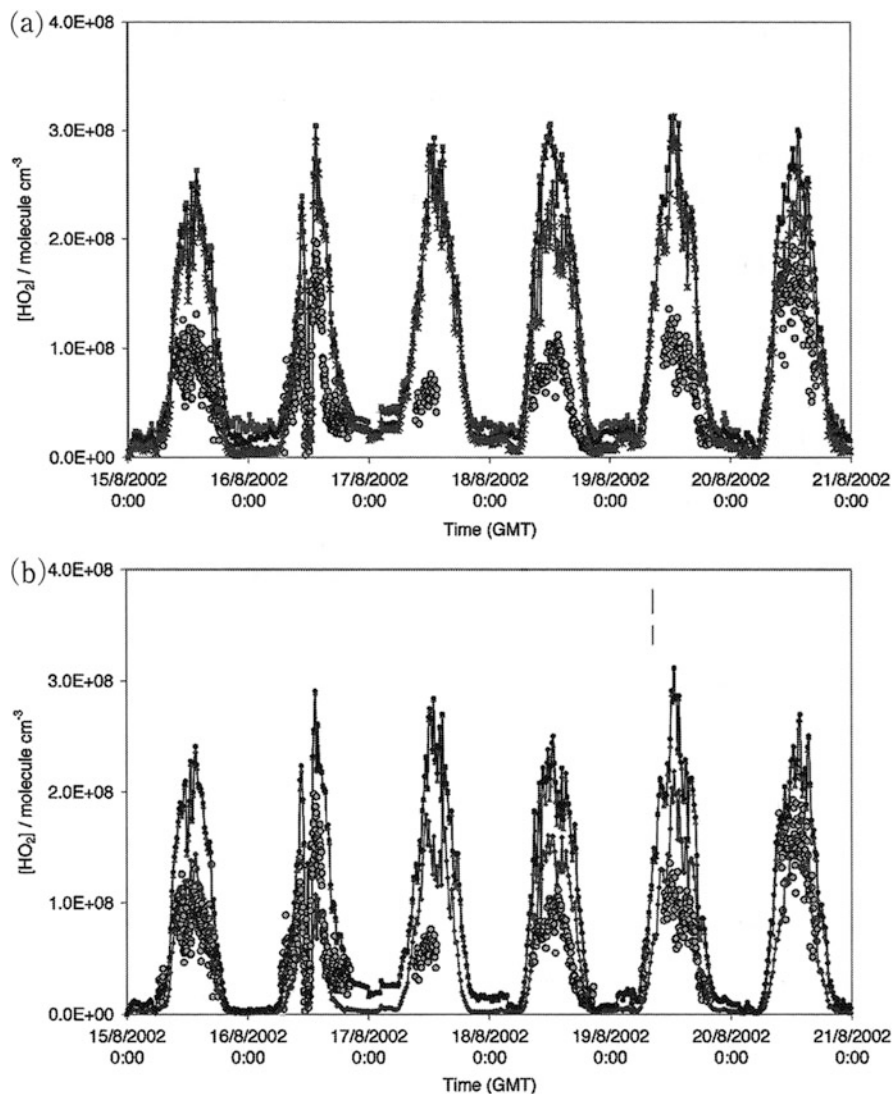


**Fig. 7.14** Comparison of HO<sub>2</sub> and OH in the RISOTTO campaign at Rishiri, Japan, between the box-model calculation and observation (Adapted from Kanaya and Akimoto 2002)

reactions of HOX (HOI, etc.), and underestimates of some of the unknown rate constants of the HO<sub>2</sub> + RO<sub>2</sub> reactions.

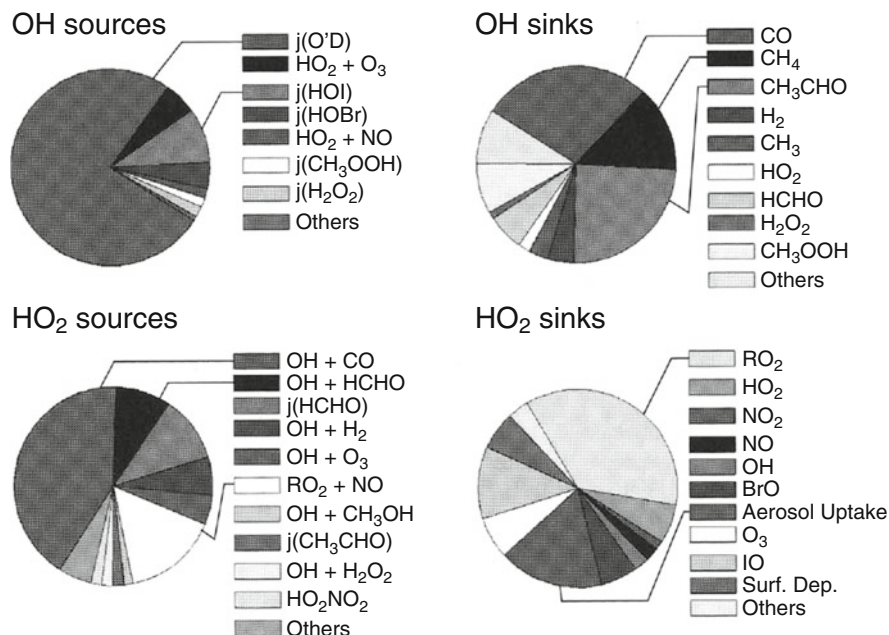
Simultaneous measurements of OH and HO<sub>2</sub> with BrO, IO, OIO and I<sub>2</sub> were made in the NAMBLEX campaign at Mace Head, Island in 2002 (Saiz-Lopez et al. 2006). Observed maximum mixing ratios of IO and BrO are 4 and 6.5 pptv, respectively, and the comparison between the measurement and calculation by the MCM reaction model (Bloss et al. 2005) based on these observed values are shown in Fig. 7.15 for HO<sub>2</sub> (Sommariva et al. 2006). In this model calculation, a wide range of VOC reactions the calculations are included, and the comparisons between with and without including IO reactions, is shown in Fig. 7.15a, and the those between with and without uptake of HO<sub>2</sub> and HOI on aerosols are shown in Fig. 7.15b. As shown in Fig. 7.15a, the overestimate of HO<sub>2</sub> is improved as much as maximum 30 % when the IO reactions are included, but the improvement is not enough. When the uptake of HO<sub>2</sub> on aerosols with the maximum coefficient of  $\gamma = 1$ , overestimation of the calculation improves by as much as 40 %, for example on August 15 and 20, and the calculated values are reversed to underestimate on August 16. The uptake coefficient of HO<sub>2</sub> for the actual aerosols sampled at Mt. Tai and Mt. Mang in China has been given to be as large as  $\gamma = 0.1 - 0.4$  by Taketani et al. (2012) (Sect. 6.2.3), which implies that the heterogeneous uptake of HO<sub>2</sub> is important, as well as IO, in the marine boundary layer.

Furthermore, in the RHaMBLe campaign in 2007 at Cape Verde in the tropical Atlantic Ocean, IO and BrO has been measured by DOAS together with HO<sub>2</sub>. The calculation by MCM model based on these observed values agrees well with observed values within the measurement error of 20 % when halogen chemistry and heterogeneous loss process of HO<sub>2</sub> with  $\gamma(\text{HO}_2) = 0.1$  are taken into account



**Fig. 7.15** Comparison of observed  $\text{HO}_2$  concentration in the NAMBLEX campaign at Mace Head and the model calculation considering IO. (a) comparison of calculation without IO (■), with IO (●) and observation (○), (b) comparison of calculation with IO and uptake of  $\text{HOI}$  (●), with IO and uptake of  $\text{HO}_2$  (◆) and observation (○) (Adapted from Sommariva et al. 2006)

(Whalley et al. 2010). Figure 7.16 depicts the contribution ratios of each chemical process for the formation and loss of OH and  $\text{HO}_2$  obtained by the model calculation (Whalley et al. 2010). As shown in the figure, the contribution of halogens combining the photolysis of  $\text{HOI}$  and  $\text{HOBr}$  is 13 % whereas the  $\text{O}(^1\text{D})$  reaction by the photolysis of  $\text{O}_3$  is 76 % for the formation of OH. As for the loss processes of



**Fig. 7.16** The contribution of each chemical process for the production and loss of OH & HO<sub>2</sub> obtained by the simulation for the RHAMBLE campaign at Cape Verde (Adapted from Whalley et al. 2010)

OH, the contribution of the reactions with CO and CH<sub>3</sub>CHO is the largest, 28 % and 25 %, respectively. Meanwhile, the contributions of OH + CO reaction is 41 %, and those of the OH + HCHO and the photolysis of HCHO are ca. 10 % each for the formation of HO<sub>2</sub>. As the loss processes of HO<sub>2</sub>, contribution of RO<sub>2</sub> + HO<sub>2</sub> is the largest, ca. 40 %, uptake on aerosol surface is 23 %, and the reaction with IO and BrO is 19 % total.

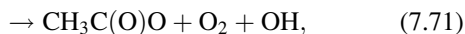
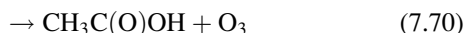
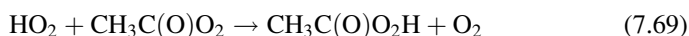
In the marine boundary layer, it is known that HO<sub>2</sub> exists in a few ppbv even at nighttime. They are thought to be due to the O<sub>3</sub> reaction with isoprene, monoterpenes, internal alkenes, etc. influenced by the emissions from surrounding lands (Kanaya et al. 2007a; Smith et al. 2006; Whalley et al. 2010). In general, the nighttime OH in the marine boundary layer is under the detection limit.

**Forest Air** The measurements of HO and HO<sub>2</sub> in the forest air influenced by biogenic hydrocarbons such as isoprene and monoterpenes and comparison with model calculations have also been made on many occasions (Stone et al. 2012). These studies have implications for the validation how well the reaction mechanism of for example isoprene described in Sect. 7.2.6 reflects the role of HO<sub>x</sub> radical chain mechanism. In general, it has been known that the model calculation underestimates the observed values of OH to a large extent for the sites where the isoprene, etc. have significant impact. For example, the calculation by the RACM

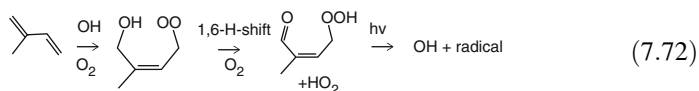
model for the PROPHET-98 campaign conducted in Michigan state, United States, where isoprene concentration is high, underestimates the observation of OH by a factor of 2.7, and the disagreement reached a factor of 6 when the NO concentration is low (Tan et al. 2001a). On the other hand, the calculated values for HO<sub>2</sub> agree well with the observation within 15 %. This means that unknown reactions converting HO<sub>2</sub> to OH exist in the HO<sub>x</sub> chain reaction system when the concentration of NO is low. In the succeeding campaign, PROPHET-2000, the measurement of the OH reactivity was also made, and it was revealed that there are many unknown BVOCs are present (Di Carlo et al. 2004).

Substantial underestimate of calculated OH and HO<sub>2</sub> has also been reported for the measurements in GABRIEL in Amazonian tropical forest in 2005 (Sander et al. 2005), and in Borneo Sabah in 2008 (Whalley et al. 2011). However, observational values of HO<sub>2</sub> are thought to suffer the large positive interference by RO<sub>2</sub> originated from BVOC as described above so that the quantitative discussions would have to be revised in future.

Particularly under the low concentration of NO, several reactions of peroxy radicals that may produce excessive OH has been proposed. Dillon and Crowley (2008) reported that in the reaction of HO<sub>2</sub> and peroxy radicals with carbonyl group, e.g. acetyl peroxy radical,



the yield of OH-forming pathway (7.71) is  $\alpha(298 \text{ K}) = 0.5 \pm 0.2$ . It is also suggested that in the case of peroxy radicals with carbonyl group formed in the reaction of OH and isoprene, the reactions with HO<sub>2</sub> produce OH radicals, which could contribute excess OH in the forest air under low NO concentrations. Meanwhile, Peeters and Müller (2010) suggested that the photolysis of hydroperoxy methyl butanal formed by the intramolecular hydrogen transfer in hydroperoxy radical in the reaction of OH with isoprene, gives OH with quantum yield of unity, and may contribute to the excess OH in forest air.



Therefore, the oxidation reaction mechanism of isoprene and monoterpenes under low NO concentration is still shown to have many uncertainties from the direct measurement of HO<sub>x</sub>.

On the other hand, in the PRIDE-PRD campaign in the suburbs of Guangzhou, China in 2006, very high daytime concentrations of OH and HO<sub>2</sub>,  $(15\text{--}26) \times 10^6$  and  $(3\text{--}25) \times 10^8$  molecules cm<sup>-3</sup> (80 pptv), respectively, has been reported under the conditions of high VOC containing 20 % of isoprene and low NO (200 ppt in the daytime) (Hofzumahaus et al. 2009; Lu et al. 2012). The model calculations

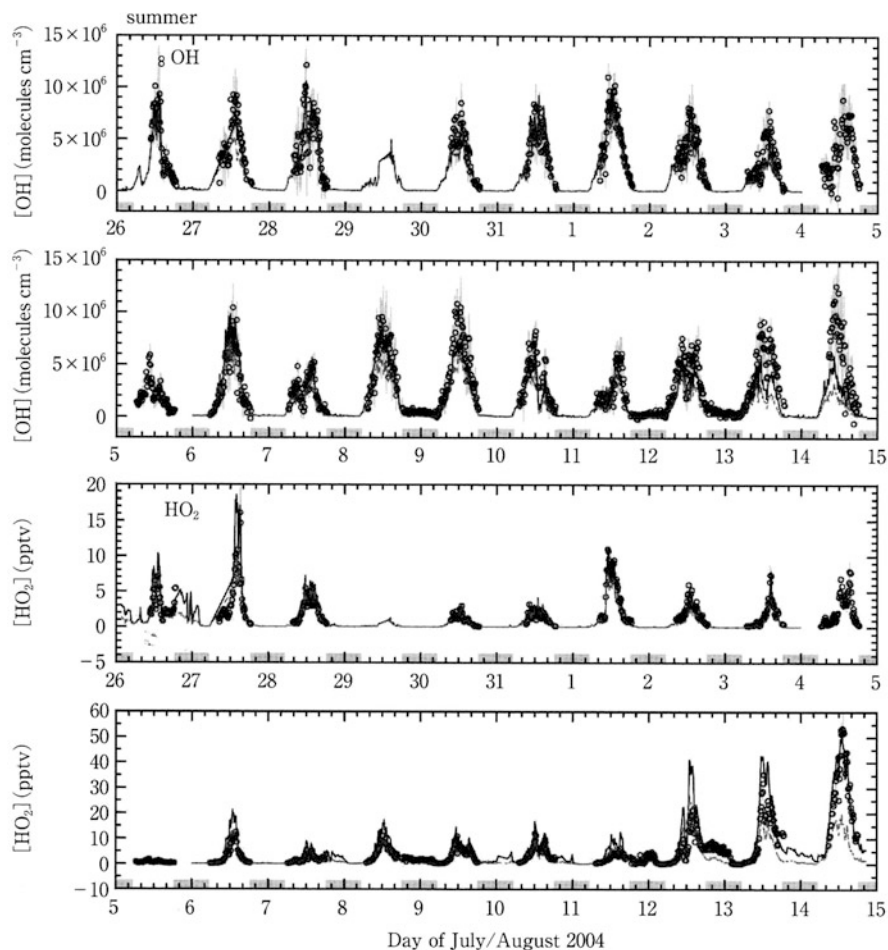
reproduce reasonably well for HO<sub>2</sub> concentrations, whereas those for the OH concentrations are underestimated by a factor of 3–5. These results imply that OH sources are in shortage in the known reaction mechanism. The difference cannot be explained by the OH forming reaction from HO<sub>2</sub>+RO<sub>2</sub> with taking  $\alpha=1$ , and the presence of an unknown reaction cycle to form OH from HO<sub>2</sub> other than the reaction with NO has been suggested (Hofzumahaus et al. 2009; Lu et al. 2012).

The nighttime concentrations of OH and HO<sub>2</sub> in the PROPHET-98 in Michigan, United States are  $1 \times 10^6$  molecules cm<sup>-3</sup> and 2 pptv, respectively, showing very high OH but relatively low HO<sub>2</sub> concentrations. The model calculation using the observed monoterpenes and O<sub>3</sub> underpredicts the OH concentration by a factor of 2 (Faloona et al. 2001).

**Urban Polluted Air** Urban polluted air contains a few hundred species of hydrocarbons and oxygen containing volatile organic compounds (OVOCs) (Lewis et al. 2000), and the observation of OH and HO<sub>2</sub> concentrations there validates the reaction model with the whole set of these VOCs. Comparisons between the model calculation and observation of OH and HO<sub>2</sub> concentrations in urban air are also interesting from the point of checking the dependence of O<sub>3</sub> formation rate on NO<sub>x</sub> and VOC in the polluted atmosphere, and are important as validation of a reaction model for the discussion of the oxidant control strategy as described in the previous section. From these viewpoints, many measurements of and the comparison with model calculations have been made in urban air, and the values of  $(3-20) \times 10^6$  molecules cm<sup>-3</sup> for OH, and  $(1-12) \times 10^8$  molecules cm<sup>-3</sup> (4–50 pptv) for HO<sub>2</sub> concentration, which are similar or higher than in the marine boundary layer, have been reported (Stone et al. 2012).

As an example of the comparison between the measurements and calculations by the RACM model for OH and HO<sub>2</sub> in urban air, Fig. 7.17 shows the results for the IMPACT campaign in Tokyo, Japan in the summer of 2004 by Kanaya et al. (2007b). In this measurement, the maximum concentration of OH  $13 \times 10^6$  molecules cm<sup>-3</sup> and the daytime median concentration  $6.3 \times 10^6$  molecules cm<sup>-3</sup> with relatively small day-to-day variation, and the maximum mixing ratio of HO<sub>2</sub> 50 pptv and the daytime median value 5.7 pptv with large day-by-day variation have been obtained. The observational maximum and median values of OH and HO<sub>2</sub> at the same site in 2004 winter are  $1.5 \times 10^6$  molecules cm<sup>-3</sup> and 1.1 pptv, respectively, both are about one fifth of the summer values. As seen in the figure, the calculated and measured median values of OH and HO<sub>2</sub> are in reasonably good agreement within the error range for summer, and the ratios of the calculated to the measured values of OH and HO<sub>2</sub> are 0.81 and 1.21, i.e. about 20 % under- and over-estimation, respectively. Meanwhile, the calculated/measured ratios of the median value are 0.93 for OH showing good agreement, but 0.48 for HO<sub>2</sub> resulting in underestimation about a factor of 2.

The comparisons of measurements and calculations for OH and HO<sub>2</sub> in urban air have been made in various cities, Los Angeles, Nashville, Birmingham, Houston, New York, Essex, Mexico City, etc. Although in most cases, the ratios of measured



**Fig. 7.17** Comparison of the observed and calculated OH and HO<sub>2</sub> concentrations in IMPACT campaign in Tokyo (Kanaya et al. 2007b). ○ observation, — base-case calculation, --- calculation including the heterogeneous loss process of HO<sub>2</sub>

and calculated values agree within 50 %, the models tend to overestimate OH in general, and to underestimate HO<sub>2</sub> when the NO<sub>x</sub> concentration is high (Stone et al. 2012). However, for example in Mexico City, the calculated values of HO<sub>2</sub> underestimated the observation by a factor of 5 (around at 10 am), and those of OH overestimated by a factor of 1.7 (around at noon), which are ascribed to the reason that many hydrocarbons e.g. aromatics are not captured in the VOC measurement (Dusanter et al. 2009). Furthermore, in the PMTACS campaign in New York City in winter, it has been reported that the calculated daytime HO<sub>2</sub> concentration gives underestimation by a factor of 6, and particularly the disagreement is large when NO concentration is high (Ren et al. 2006).

From these many measurements, it has been revealed in general that the photolysis of HONO, alkene-ozone reaction, and photolysis of aldehyde contribute to a large extent as a source of total HO<sub>x</sub> in the urban air, and the contribution of the O(<sup>1</sup>D)+H<sub>2</sub>O reaction due to the photolysis of O<sub>3</sub> is only a few %. The major photolytic species for the HO<sub>x</sub> source is understandably dependent on cities, and for example, it is reported that the contribution of photolysis of dialdehyde (glyoxal and methyl glyoxal) in addition to formaldehyde, is large in Mexico City (Dusanter et al. 2009). Incidentally, HONO observed in high concentration in the daytime urban air is thought to be formed by the photocatalytic reaction of NO<sub>2</sub> near the ground surface as described in Chap. 6, Sect. 6.4.2. From the study of the model inter-comparison for the RACM, MCM, etc., the differences between the reaction models are relatively small for urban air, which suggests that the effect of differences in the VOC reaction mechanism is not large, and the effect of NO<sub>x</sub> chemistry is more important as an uncertainty factor for the urban air as described below (Chen et al. 2010).

Figure 7.18 depicts the dependence of the concentrations of OH, HO<sub>2</sub>, and the ratio of HO<sub>2</sub>/OH on NO concentration obtained in winter and summer in Tokyo (Kanaya et al. 2007b). As seen in the figure, the concentrations of OH and HO<sub>2</sub>, and the ratio of HO<sub>2</sub>/OH decreases with the increase of NO concentration in the range of 1–100 ppbv, and this tendency is well reproduced by the model calculation. However, both of the calculated values OH and HO<sub>2</sub> tend to overestimate in the lower concentration range of NO, and underestimate in the higher concentration range of NO. This tendency is more apparent for HO<sub>2</sub> in winter, and also for the HO<sub>2</sub>/OH ratio. The expanded underestimation of HO<sub>2</sub> concentration in the high concentration range of NO is also seen apparently in the observation in Mexico City in April (Sheehy et al. 2010; Volkamer et al. 2010), and in New York in winter, and this tendency is a commonality in many observations (Stone et al. 2012). A similar trend is also seen in the upper troposphere by the aircraft campaign (Ren et al. 2008), which suggests strongly that unknown process exists in the reaction mechanism related to NO<sub>x</sub> used in the chemistry model.

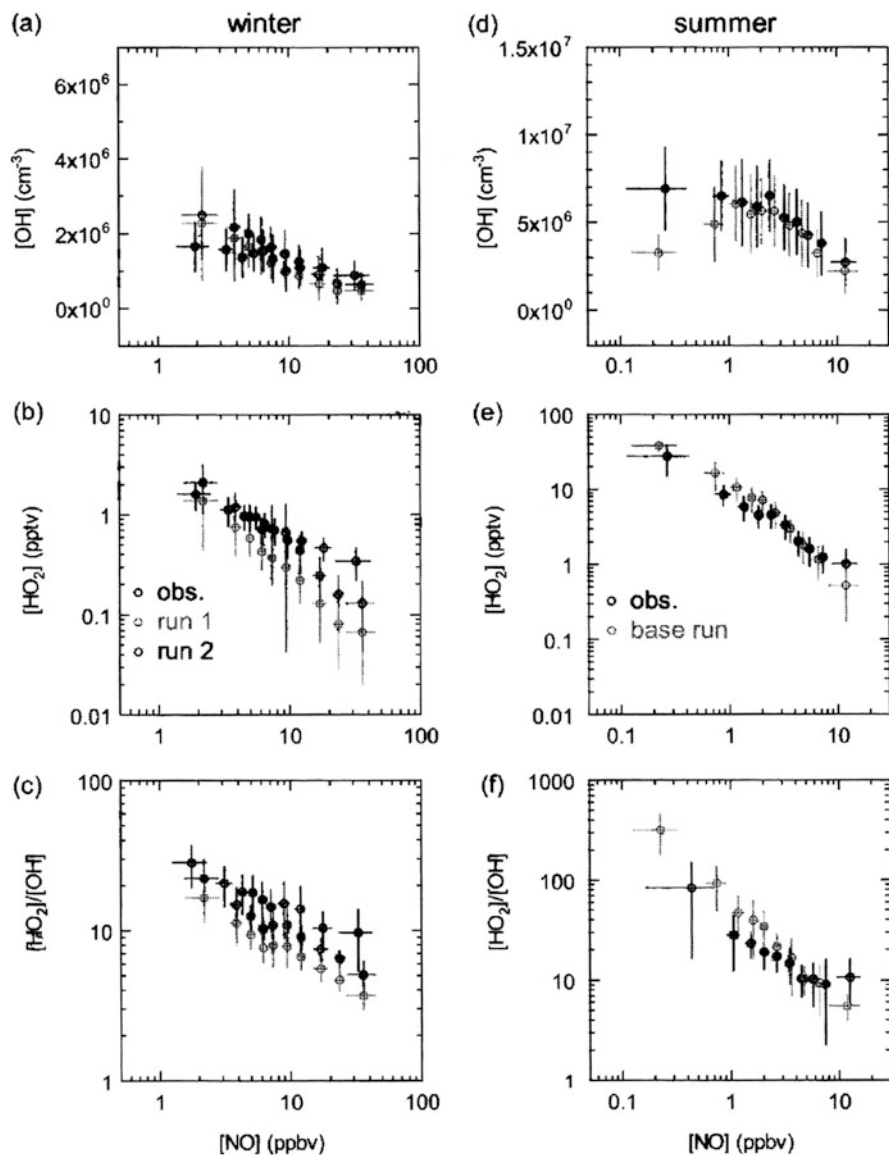
As seen in Sect. 7.3.2, the net formation rate of O<sub>3</sub> in the atmosphere is expressed as  $P(O_3)$ - $L(O_3)$  where

$$P(O_3) = (k_{7.10}[HO_2] + k_{7.21}[RO_2])[NO] \quad (7.52)$$

$$L(O_3) = (j_{7.1f}f_{7.2} + k_{7.47}[HO_2] + k_{7.46}[OH])[O_3], \quad (7.48)$$

so that it is found that the concentrations of OH, HO<sub>2</sub> and RO<sub>2</sub> are the key parameters of net O<sub>3</sub> formation. Therefore, the proper reproduction of the observed NO<sub>x</sub> and VOC dependence of OH and HO<sub>2</sub> by the reaction mechanism used in the model should be prerequisite for the discussion of the NO<sub>x</sub>-limited and VOC-limited using the isopleths described in Sect. 7.3.2. Kanaya et al. (2008) plotted the  $P(O_3)$ - $L(O_3)$  based on the measurement of OH and HO<sub>2</sub> in Tokyo on the isopleths calculated by the model as a function of NO<sub>x</sub> and VOC concentrations,





**Fig. 7.18** Observed NO-dependence of the OH and HO<sub>2</sub> concentrations, and the HO<sub>2</sub>/OH ratio obtained by the measurement in Tokyo in winter and summer (Adapted from (Kanaya et al. 2007b). Run 2 is the calculation when the internal olefin (OL1) and reactive alkene (HC8) in RACM was increased by a factor of 3.5

and showed that the behavior of the observed and calculated tendency does not necessarily agree, particularly in winter.

Nighttime OH and HO<sub>2</sub> are in general observed in the urban and suburban polluted atmosphere. For example,  $1.9 \times 10^5$  molecules cm<sup>-3</sup> of OH and 4 ppt of HO<sub>2</sub> are observed in the BERLIOZ campaign in Germany in summer 1998, and the analyses are made to show the contribution of 36 % of NO<sub>3</sub> reaction and 64 % of O<sub>3</sub> reaction for OH, and 53 and 47 % for HO<sub>2</sub>, respectively (Geyer et al. 2003). The average concentrations of  $2.6 \times 10^5$  molecules cm<sup>-3</sup> of OH, and  $2.9 \times 10^7$  molecules cm<sup>-3</sup> (1.2 pptv) of HO<sub>2</sub> are observed in the TORCH campaign in Essex, UK in summer 2003. The contribution of 66 % of O<sub>3</sub> reaction, and 33 % of NO<sub>3</sub> reaction are estimated as radical sources, but the calculated values are 41, and 16 % underestimate for OH and HO<sub>2</sub>, respectively (Emmerson and Carslaw 2009).

### 7.5.2 Measurements of OH Reactivity and Missing Reactivity

As described in the previous paragraph, since the atmospheric concentrations of OH and HO<sub>2</sub> are determined by the balance of formation and loss of these radicals, the reproduction of measured values by the calculated value by the model does not necessarily guarantee the accuracy of the terms of source and sink of these radicals. Among the formation and loss rates that determine the atmospheric concentration of OH, the measurement technique for the loss rate called “OH reactivity” has been developed by producing pulsed OH artificially in the ambient air to observe its time decay directly (Sadanaga et al. 2004; Sinha et al. 2008; Ingham et al. 2009).

The loss rate of atmospheric OH can be expressed by,

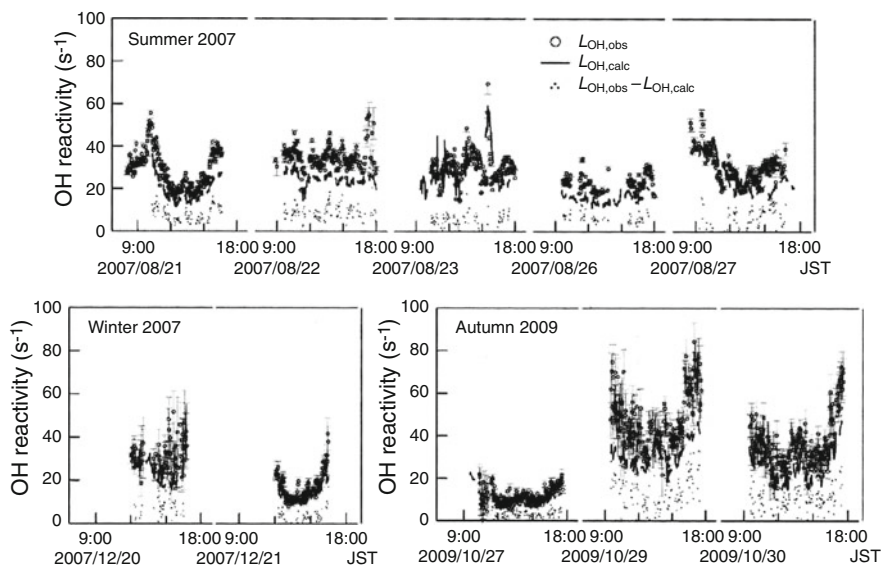
$$L(\text{OH}) = \sum_i k_{\text{VOC}_i}[\text{VOC}_i] + k_{\text{CO}}[\text{CO}] + k_{\text{NO}_2}[\text{NO}_2] + k_{\text{NO}}[\text{NO}] + k_{\text{SO}_2}[\text{SO}_2] + k_{\text{O}_3}[\text{O}_3] + k_{\text{CH}_4}[\text{CH}_4] + \dots \quad (7.73)$$

as the sum of the products of each reactant concentration and corresponding OH rate constant. In the measurement of OH reactivity, the loss rate  $L(\text{OH})$  is observed directly by,

$$[\text{OH}]_t = [\text{OH}]_0 \exp\{-L(\text{OH})t\} \quad (7.74)$$

$$\ln([\text{OH}]_t/[\text{OH}]_0) = -L(\text{OH})t. \quad (7.75)$$

From such a measurement, the missing loss rate can be estimated quantitatively by comparing the observed with the computed value based on the simultaneously observed individual VOCs, NO<sub>x</sub> and other species and their OH reaction rate constants. In the urban atmosphere few hundreds of VOCs are estimated to exist (Lewis et al. 2000), and furthermore if the biogenic VOCs are included, the numbers are enormous (Goldstein and Galbally, 2007) and the bottom-up description in the model is in general unrealistic. Since the OH reactivity measurements

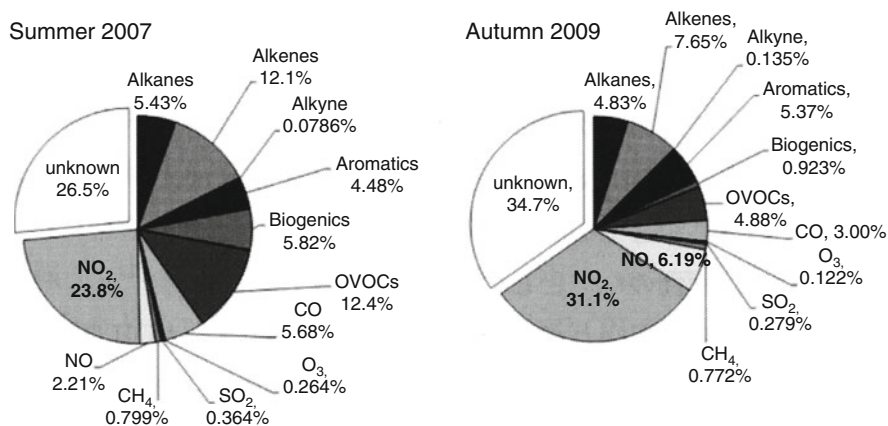


**Fig. 7.19** Comparison of the observed ( $L_{\text{OH, obs}}$ ) and calculated ( $L_{\text{OH, calc}}$ ) values of the OH reactivity in urban air (Adapted from Yoshino et al. 2012)

can make their overall evaluation, it is very useful for providing the boundary condition to the model.

Measurements of the OH reactivity in forest air have been made in the temperate forest in Michigan United States, tropical forest in Amazon, and boreal forest in Finland. In Michigan, the missing reactivity that is not explained by the measured VOC is considerably high. Since its magnitude has the same temperature dependence as other terpenes, it is deduced that BVOCs and OVOCs formed from them are thought to be the unknowns (Di Carlo et al. 2004). Furthermore, in the tropical forest, the missing reactivity reached ten times of the calculated reactivity based on the measured VOCs (Lelieveld et al. 2008). In the forest in Finland, 30 species of BVOCs were quantified by using a proton transfer mass spectrometer (PTR-MS), but the calculated OH reactivity captured only 50 % of the measured one (Sinha et al. 2010).

Meanwhile the OH reactivity in urban air, has been measured in Tokyo in August, and December in 2007, and in October, 2009 by Yoshino et al. (2012). In these observations, more than 60 species of VOCs by GC-MS and several OVOCs e.g. HCHO, CH<sub>3</sub>CHO, CH<sub>3</sub>COCH<sub>3</sub>, CH<sub>3</sub>OH, etc. by PTR-MS have been measured simultaneously, and the comparison between the measured and calculated OH reactivity was made, as shown in Fig. 7.19. As seen in the figure, the measured OH reactivity was 17–70 s<sup>-1</sup> in August, and 10–80 s<sup>-1</sup> in October, which is substantially higher than the calculated one, suggesting that there are still many unanalyzed VOCs and OVOCs. The missing reactivity amounted to 27 % in August and 35 % in October. The contributions of the each category of measured species to



**Fig. 7.20** The contribution percentage of each observed species to the OH reactivity observed in Tokyo in summer 2007, and autumn 2009 (Yoshino et al. 2012)

the OH reactivity are shown in Fig. 7.20. Thus, in summer, NO<sub>x</sub> (NO + NO<sub>2</sub>) is 26.0 %, anthropogenic VOC, 22.1 %, OVOC, 12.4 %, and biogenic VOC, 5.8 %, and in autumn, NO<sub>x</sub> is 37.3 %, anthropogenic VOC, 18.0 %, OVOC, 4.9 %, and biogenic VOC, 0.9 %.

It should be noted that by adding unknown VOCs and OVOCs deduced from the measurements of OH reactivity in the model calculation, the calculated results of ozone formation tends to shift from the VOC-limited to NO<sub>x</sub>-limited regime.

## 7.6 Tropospheric Halogen Chemistry

The important roles of halogens, Cl, Br, and I, in the chemical reaction system in the troposphere was recognized rather recently in 1980s. The trigger was the findings of the phenomenon that the mixing ratio of surface ozone in the Arctic Circle in spring decreases from a normal value of ca. 30 ppbv to nearly zero within a few hours depending on the day, which was then discovered to be due to the O<sub>3</sub> destruction by BrO by Barrie et al. (1988). Later the similar phenomenon was also found in the Antarctica. Furthermore, active halogen species containing Cl, Br and I, have been widely observed in the marine boundary layers in the mid- and high-latitudes and are found to affect the concentrations of OH and HO<sub>2</sub> as mentioned in the previous section to cause the decrease of O<sub>3</sub> in situ. The chemical reactions in which halogens are related have also been found out around salt lakes and in volcanic plumes (Saiz-Lopez and von Glasow 2012). Although volcanic halogens are not mentioned in this chapter, they are found not only in intermittent eruption but also in stationary plumes, and it tends to be treated in general within tropospheric

chemistry (Bobrowski, et al. 2003, 2007; Lee et al. 2005; Aiuppa et al. 2009; Vance et al. 2010).

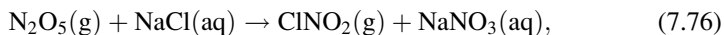
The overall tropospheric halogen chemistry has recently been reviewed by Saiz-Lopez and von Glasow (2012). Also, reviews on heterogeneous reactions on sea salt (Finlayson-Pitts 2003; Rossi 2003) and other specific topics of tropospheric halogen chemistry (Carpenter 2003; Sander et al. 2003; Simpson et al. 2007; von Glasow 2010; Abbatt et al. 2012; Saiz-Lopez et al. 2012) are available.

## 7.6.1 Initial Source of Halogens

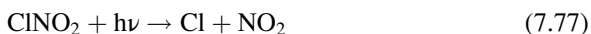
One of the big issues on tropospheric halogen chemistry is that the initial process of releasing halogens to the atmosphere has not been well established in spite that the succeeding chain reactions relevant to Cl, Br and I are relatively well known. So far, heterogeneous reactions on sea salt and biogenic emissions have been identified as the main initial source of inorganic halogens. However, their detailed processes and the contributing ratios are very much different by region and halogen species, and in many cases, the parameters relevant to the release have not been quantified well. In this section, present knowledge on these processes are described for each of Cl, Br and I.

### 7.6.1.1 Chlorine

In spite of the large molar ratio of 660:1 of Cl over Br, the ratio of Cl released to the atmosphere by heterogeneous reactions of gaseous oxidizing species on sea salt is much smaller than Br. Among the Cl releasing processes from sea salt as photochemically active species, the formation of nitryl chloride  $\text{ClNO}_2$  by the reaction of  $\text{N}_2\text{O}_5$  and sea-salt particles in polluted urban plumes has been well established (see Sect. 6.2.4) (Rossi 2003; Finlayson-Pitts 2003). The overall reaction combining reactions (6.5), (6.16) in Sect. 6.2.4 can be expressed as,



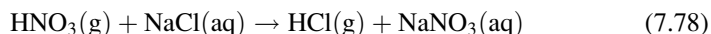
and the product  $\text{ClNO}_2$  is easily photolyzed in the troposphere to release Cl atoms (see Sect. 4.4.8).



Although the release of Cl by this reaction is limited to the areas under direct influence of polluted air, such as coastal zone of large cities and harbors where ship emissions prevail, the contribution of this reaction is thought to be large even globally since the condition applies to many coastlines worldwide. Recently,  $\text{ClNO}_2$  has been observed not only in the coastal zone (Osthoff et al. 2008), but

also in inland cities where sea salt does not exist (Thornton et al. 2010; Mielke et al. 2011). In this case, ClNO<sub>2</sub> is thought to be formed from the reaction of N<sub>2</sub>O<sub>5</sub> on the aerosol surface containing anthropogenic chlorine compounds. The reaction of N<sub>2</sub>O<sub>5</sub> on sea-salt particles also release Br<sub>2</sub> other than ClNO<sub>2</sub>, and the ratio has been found to depend on temperature (Lopez-Hilfiker et al. 2012).

On the other hand, the reaction of HNO<sub>3</sub> and sea salt (Sect. 6.2.5)



is important over the ocean apart from coastal lines since the atmospheric lifetime of HNO<sub>3</sub> is much longer than N<sub>2</sub>O<sub>5</sub>. However, the product, HCl is not photolyzed in the troposphere (see Sect. 4.4.3), and the rate constants of the reaction with OH is not large,  $7.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (see Table 5.2), so that reaction (7.70) is not important as a source of Cl atoms in the troposphere.

As mentioned in Sect. 7.5.4, Cl<sub>2</sub> has been observed sporadically in the marine boundary layer. As for the process of the release of Cl<sub>2</sub>, the surface reaction of OH on deliquescent sea salt has been confirmed experimentally (Oum et al. 1998a; Knipping et al. 2000). While the reaction of O<sub>3</sub> with sea salt (see Sect. 6.2.1) is known to be the most important process of the release of Br<sub>2</sub> as will be described later, it has been reported that the reaction of O<sub>3</sub> with Fe<sup>3+</sup>-doped NaCl releases Cl<sub>2</sub> (Sadanaga et al. 2001), and the possibility of Cl<sub>2</sub> release after the depletion of Br<sub>2</sub> has been suggested. Since rather ubiquitous distribution of Cl<sub>2</sub> in the marine boundary layer has been known recently, further studies are necessary for the processes of the Cl<sub>2</sub> release into the atmosphere. Since the absorption spectrum of Cl<sub>2</sub> extends to visible region (Fig. 4.36) and it is easily photolyzed to release Cl atoms (see Sect. 4.4.1), it is an important active species in the troposphere.

### 7.6.1.2 Bromine

Among the tropospheric halogen species, active bromine species such as BrO are best known and widely measured not only in the polar region but also in the low- and mid-latitude marine boundary layers. As a source of active bromine to the atmosphere, the reaction of O<sub>3</sub> on sea salt surface has been studied well and thought to be the most important (Hirokawa et al. 1998; Mochida et al. 2000; Anastasio and Mozurkewich 2002) (see Sect. 6.2.1). Furthermore, the reactions of O<sub>3</sub> with snow surface on which sea ice and sea salt are co-deposited, are also known as Br<sub>2</sub> source in the polar region (Tang and McConnell 1996; Oum et al. 1998b). Br<sub>2</sub> has absorption spectrum extending to still longer wavelength in the visible region than Cl<sub>2</sub>, and thus is photolyzed in shorter periods of time to release Br atoms, and thus play the most important role in the tropospheric halogen chemistry.

On the other hand, since the absorption cross section of tribromomethane (bromoform, CHBr<sub>3</sub>) released from seaweed is small in the spectrum region of actinic flux (Gillotay et al. 1989), it is not a very important source of photoactive bromine species in the troposphere.

### 7.6.1.3 Iodine

Since the ratio of contents of iodine in sea salt is very small,  $5 \times 10^{-8}$ , the release of I from sea salt is negligible, and the source of IO widely observed in the marine boundary layer is thought to be the photolysis of organoiodine compounds e.g. iodomethane (methyl iodide,  $\text{CH}_3\text{I}$ ), iodoethane (ethyl iodide,  $\text{C}_2\text{H}_5\text{I}$ ), 1-iodopropane (1-propyl iodide,  $1\text{-C}_3\text{H}_7\text{I}$ ), chloriodomethane ( $\text{CH}_2\text{ICl}$ ), bromiodomethane ( $\text{CH}_2\text{IBr}$ ) and diiodo methane ( $\text{CH}_2\text{I}_2$ ) etc., and inorganic iodine,  $\text{I}_2$ , from marine organisms (Saiz-Lopez et al. 2012). These organoiodine compounds are emitted from seaweeds in the coastal zone and from microalgae in the ocean. Recently, non-biological emissions from sea surface reactions between ozone and organic compounds in sea surface water are also considered (Martino et al. 2009). Among the organoiodine compounds, the emissions of  $\text{CH}_3\text{I}$  and  $\text{CH}_2\text{I}_2$  are estimated to be the largest globally (Saiz-Lopez et al. 2012). Meanwhile,  $\text{I}_2$  is known to be emitted from seaweed in coastal zones, but the sources over the ocean are not well known yet.

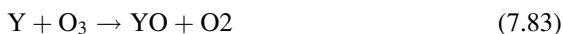
The absorption spectrum of iodomethane is shown in Fig. 4.32 in Chap. 4. Organoiodine compounds including iodomethane have strong absorption in the tropospheric actinic flux region so that they are easily photolyzed to release I atoms (see Sect. 4.3.8 for  $\text{CH}_3\text{I}$ ).

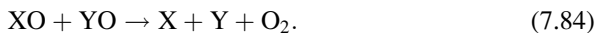


The calculated photolytic lifetimes are few days, a few hours, and a few minutes for  $\text{CH}_3\text{I}$ ,  $\text{CH}_2\text{ICl}$ ,  $\text{CH}_2\text{I}_2$ , respectively (Saiz-Lopez et al. 2012). As seen in Sect. 4.4.1 and Fig. 4.36,  $\text{I}_2$  is easily photolyzed by the visible light and forms I atoms.

## 7.6.2 Gas Phase Halogen Chain Reaction

The halogen atoms formed in the atmosphere by the photolysis of  $\text{Cl}_2$ ,  $\text{ClNO}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ , and organoiodine compounds reacts with  $\text{O}_3$  to produce ClO, BrO, and IO radicals, which play a role in reducing the concentration of tropospheric  $\text{O}_3$  by the chain reactions described below. Representing these halogen atoms by X and Y (= Cl, Br, I), the main chain cycle in e.g. in the polar region where the concentrations of active halogen are high, can be expressed as,





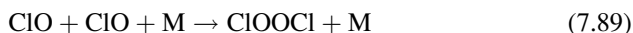
These reactions constitute chain cycle to cause net  $\text{O}_3$  dissipation,



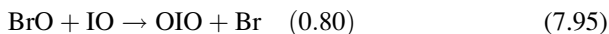
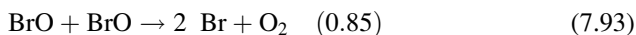
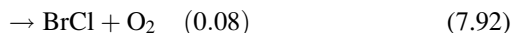
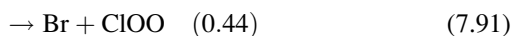
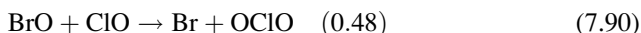
However, the actual reaction of  $\text{XO} + \text{YO}$  follow the pathways other than reaction (7.84) depending on different kinds of halogens, and they have to be considered for the detailed analysis of reaction mechanism.



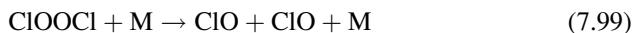
For example, the reaction of  $\text{ClO} + \text{ClO}$  under the atmospheric pressure proceeds almost solely as,



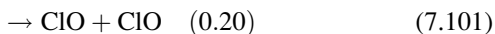
(see Sect. 5.6.6), while  $\text{BrO}$  and  $\text{IO}$ , the following reaction pathways and branching ratios are given at 298 K (Sander et al. 2011; Atkinson et al. 2007; Saiz-Lopez et al. 2012).



The  $\text{ClOOC}$  (Sects. 4.4.6, 5.6.6),  $\text{BrCl}$  (Sect. 4.4.1),  $\text{Br}_2$  (Sect. 4.4.1),  $\text{IBr}$ , and  $\text{O}$  formed by these reactions will be susceptible to thermal decomposition or photolysis (see Sects. 4.4.1 and 4.4.6).

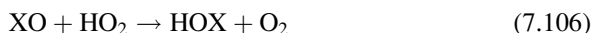






As for the photolysis of OIO in reaction (7.105), the quantum yield of unity is reported in the experiment (Gómez Martín et al. 2009). The absorption spectrum and photolytic processes of the chain carriers, ClO, BrO, IO, which result in the depletion of O<sub>3</sub> by the reactions (7.82), (7.83) and (7.84), have been described in Chap. 4, Sect. 4.4.5.

For such a gas phase chain reaction, radical-radical reactions (7.84, 7.86–7.88) predominate when the mixing ratios of halogen radicals (XO) exceed e.g. 3 pptv. However, as their mixing ratios decrease, the formation of HOX by the reaction of XO with HO<sub>2</sub>,

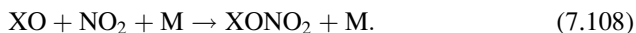


becomes more important. As for the successive reaction of HOX, other than the photolysis (see Chap. 4, Sect. 4.4.4),

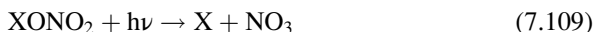


the multiphase reaction described in the following Sect. 7.5.3 is important particularly for HOBr.

In the environment affected by polluted air with high NO<sub>x</sub> concentration, XONO<sub>2</sub> forming reaction by XO and NO<sub>2</sub> gets important as the chain termination reaction (see Sect. 5.6.5 for ClONO<sub>2</sub>),



The produced XONO<sub>2</sub> will be photolyzed as,

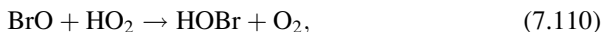


to form X and NO<sub>3</sub> (see Sect. 4.4.2), although the photolysis rate of ClONO<sub>2</sub> in the troposphere is relatively small.

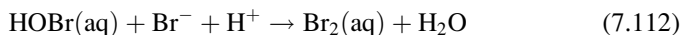
### 7.6.3 Multiphase Halogen Chain Reaction

As for a chain reaction involving halogens in the troposphere, other than the gas phase reactions, multiphase reactions through the surface of sea salt solution is

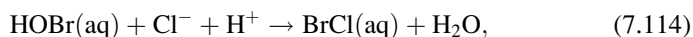
known particularly for bromine. From HOBr formed by the type of reaction (7.106) in the previous paragraph,



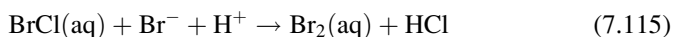
Mozukewich (1995) suggested that Br<sub>2</sub> is released to the gas phase on the acidic sea salt surface in the polar region, and Sander and Crutzen (1996) proposed that a similar processes occurs in the polluted marine boundary layer in the mid-latitude.



In such a heterogeneous reactions on sea salt particles, Cl<sup>-</sup> also participate in the reaction to form BrCl,



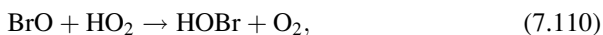
but BrCl is transformed to Br<sub>2</sub> in solution,



as far as Br<sup>-</sup> remains in the sea salt surface solution. Thus, Br<sub>2</sub> is released preferentially, and BrCl could be released into the atmosphere only after Br<sup>-</sup> is depleted (Vogt et al. 1996),

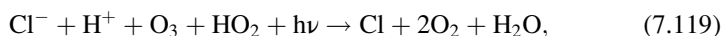
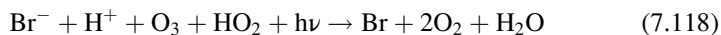


Br<sub>2</sub> and BrCl thus emitted to the gas phase, returns to HOBr by the reactions,



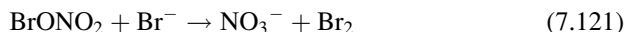
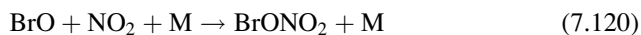
and a multiphase chain reaction are constituted as far as the sea salt particle surface is available. The chain cycle composed of a series of above reactions are also called autocatalytic reactions. The rate determining step of this multiphase chain reaction is the heterogeneous reaction of HOBr(g) with NaBr/NaCl. The uptake coefficient of this reaction is  $\gamma > 10^{-2}$  at 253 K (-20 °C), and increases as the temperature goes down (Adams et al. 2002).

The net reactions of this multiphase chain cycle can be expressed as,



showing the loss of  $\text{O}_3$  occurs by a series of this reactions. As seen in the next paragraph, it has been known that a sudden decrease of near surface  $\text{O}_3$  occurs in the polar zone in springtime by high concentration of Br. Since the phenomenon cannot be explained by the gas phase chain reaction mentioned in the previous paragraph, it is thought that multiphase chain reaction occurs on the sea salt on ice, and the abrupt increase of Br in the polar region is called “bromine explosion” (Wennberg 1999).

In polluted marine boundary layer, a multiphase chain reaction involving the reactions of  $\text{BrONO}_2$ ,



has been analyzed by Sander et al. (1999).

## 7.6.4 Atmospheric Measurements of Active Halogens and Comparison with Models

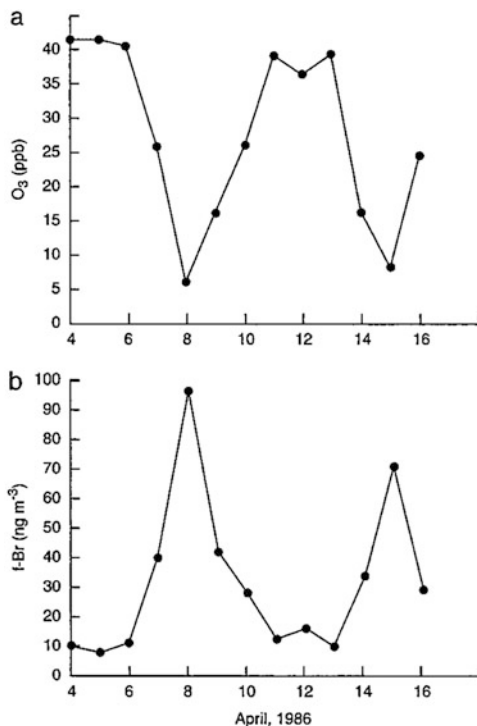
The observed mixing ratios of active halogen species in the troposphere is in general 1–100 ppt, and the direct measurements of these species are usually made by using the methods, Long-Path Differential Absorption Spectroscopy (LP-DOAS), Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS), Chemical Ionization Mass Spectrometer (CIMS) and Laser Induced Fluorescence (LIF). As for BrO and IO, satellite observation gives spatial distribution of its tropospheric column.

In this paragraph, in situ measurements of active halogen species and their impact on ozone in the marine boundary layer and around salt lakes, and the satellite observation of BrO and IO are described comparing with the model calculation.

### 7.6.4.1 Polar Region

It has been known from the long-term monitoring data from Barrow, Alaska, that surface ozone concentration often decreases regularly in springtime (Oltmans and Komhyr 1986). Barrie et al. (1988) found that surface ozone rapidly drops in spring, from around 40 ppbv to a few ppb also at Alert in the polar zone of Canada, and

**Fig. 7.21** Correlation between the (a) surface ozone and (b) filterable bromine ion (f-Br) concentration at Alert (Barrie et al. 1988)

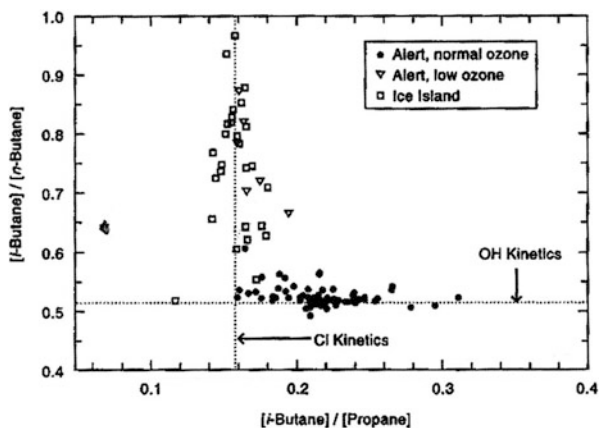


reported a clear anti-correlation between the concentrations of O<sub>3</sub> and bromine in the aerosols sampled on filters as shown in Fig. 7.21. This finding brought the recognition of the importance of halogen chain reaction in the troposphere. Later, measurements of BrO in the polar sunrise at Alert were made by LP-DOAS, and the 24-h averaged mixing ratio, 4–17 pptv, was reported (Hausmann and Platt 1994). This concentration level of BrO has been shown to be enough for O<sub>3</sub> to decrease to near zero within a day by the reactions,



Later, real-time measurement of Br<sub>2</sub> and BrCl were made by CIMS in ALERT2000 campaign, and their maximum mixing ratios were obtained to be 27 and 35 pptv, respectively, while Cl<sub>2</sub> could not be observed over the detection limit of 2 pptv (Foster et al. 2001; Spicer et al. 2002). On the other hand, the evidence of the major role of Cl atoms instead of OH radicals in the consumption of hydrocarbons in the period of low O<sub>3</sub> was found by Jobson et al. (1994), and the presence of Cl atoms in the low O<sub>3</sub> plume has been proved. Figure 7.22 is the plot of *i*-butane/*n*-butane against *i*-butane/propane ratio for the low ozone and normal ozone period (Jobson et al. 1994). The rate constants of *i*-butane and propane for

**Fig. 7.22** Plot of the ratios of  $i\text{-C}_4\text{H}_{10}/n\text{-C}_4\text{H}_{10}$  vs.  $i\text{-C}_4\text{H}_{10}/\text{C}_3\text{H}_8$  at Alert when surface ozone is depleted (*open symbols*) and ozone is in normal (*filled symbols*) (Jobson et al. 1994)

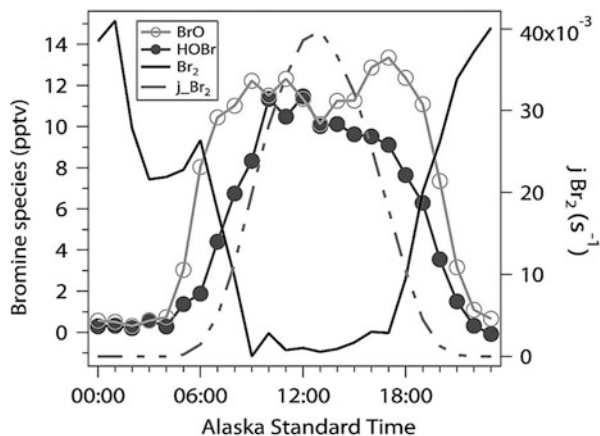


Cl atoms are nearly the same and those for OH are different whereas the rate constants of *i*-butane and *n*-butane for OH are nearly the same and those for Cl atoms are different. Based on this, nearly constant ratio of *i*-butane/propane ratio for the low  $\text{O}_3$  period and nearly constant ratio of *i*-butane/*n*-butane for the normal  $\text{O}_3$  period as shown in Fig. 7.22, implies that hydrocarbons are consumed by Cl and OH, respectively, for each period.

Regarding Arctic Cycle sites other than Alert, at Ny Ålesund in Spitsbergen Island, maximum BrO, 30 pptv, ClO, 1–2 pptv, and filterable aerosols Br, 120 ng  $\text{m}^{-3}$  have been measured in a low ozone period by using DOAS in 1995–1996 (Tuckermann et al. 1997; Lehrer et al. 1997). On this occasion,  $\text{NO}_2$  and  $\text{SO}_2$  were less than 50 pptv indicating that the surface ozone depletion in the polar region is a natural phenomenon which has no relation with anthropogenic pollution. Furthermore, in the recent observation at Barrow using CIMS, the average daytime HOBr mixing ratio was measured at 10 pptv with a maximum value of 26 pptv, and the average nighttime  $\text{Br}_2$  was at 13 pptv with a maximum of 46 pptv which is strongly anti-correlated with ozone as shown in Fig. 7.23 (Liao et al. 2012). It has been reported that the box model calculation including the heterogeneous reactions reproduces well the diurnal variation of the BrO, HOBr, and  $\text{Br}_2$  (Liao et al. 2012).

The surface ozone depletion by halogens in the polar region is also observed in Antarctica (Kreher et al. 1997). The daytime maximum mixing ratio of BrO was 13 pptv, and nighttime  $\text{Br}_2$  and BrCl were 46 and 6 pptv, respectively, by the CIMS measurement at Hallay (Buys et al. 2013). Meanwhile, the maximum mixing ratio of IO at 10 pptv was measured at Neumayer, which is very different from Antarctica where IO is low (Frieß et al. 2001). In observations around Antarctica, these active halogens have good correlations with the contact time with sea ice by trajectory analysis, which supports the presumption that the phenomena is caused by the increase of the concentrations of active halogens due to the heterogeneous chain reaction on sea salt surface as described in the previous Sect. (Wagner et al. 2007). The high concentration of iodine over Antarctica as compared to the Arctic Circle may be ascribed to the difference in the emission strength of biogenic

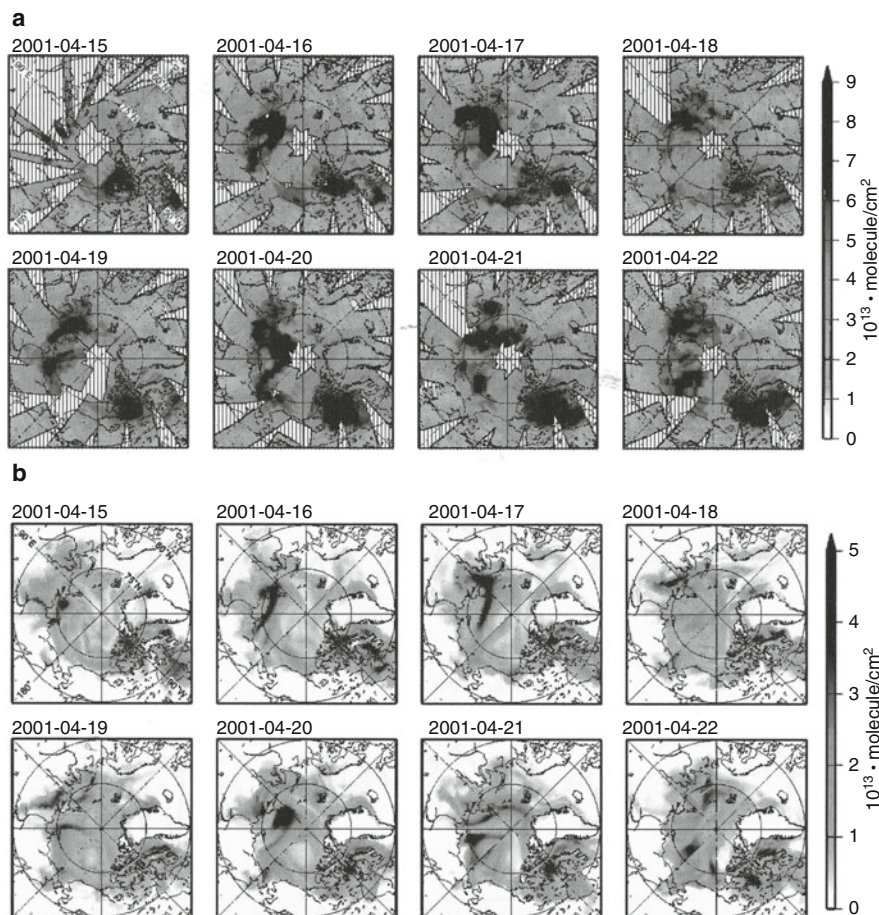
**Fig. 7.23** Observed mixing ratios of BrO, HOBr and Br<sub>2</sub>, and photolysis rate of Br<sub>2</sub> ( $j_{Br_2}$ ) at Barrow, Alaska (Adapted from Liao et al. 2012)



photoactive organoiodine compounds from the sea surface around the ice bound sea (Frieß et al. 2001). The satellite observation of IO in the Antarctica has been made by the SCIAMACHY, which shows the maximum column density in Spring (October) and relatively high in summer and autumn, but the increase of IO is not observed in winter (Schönhardt et al. 2008). It has been confirmed that such an increase of IO column density is not observed in the Arctic Circle, and the reason is thought to be the difference in the distribution of marine biota emitting iodine compounds.

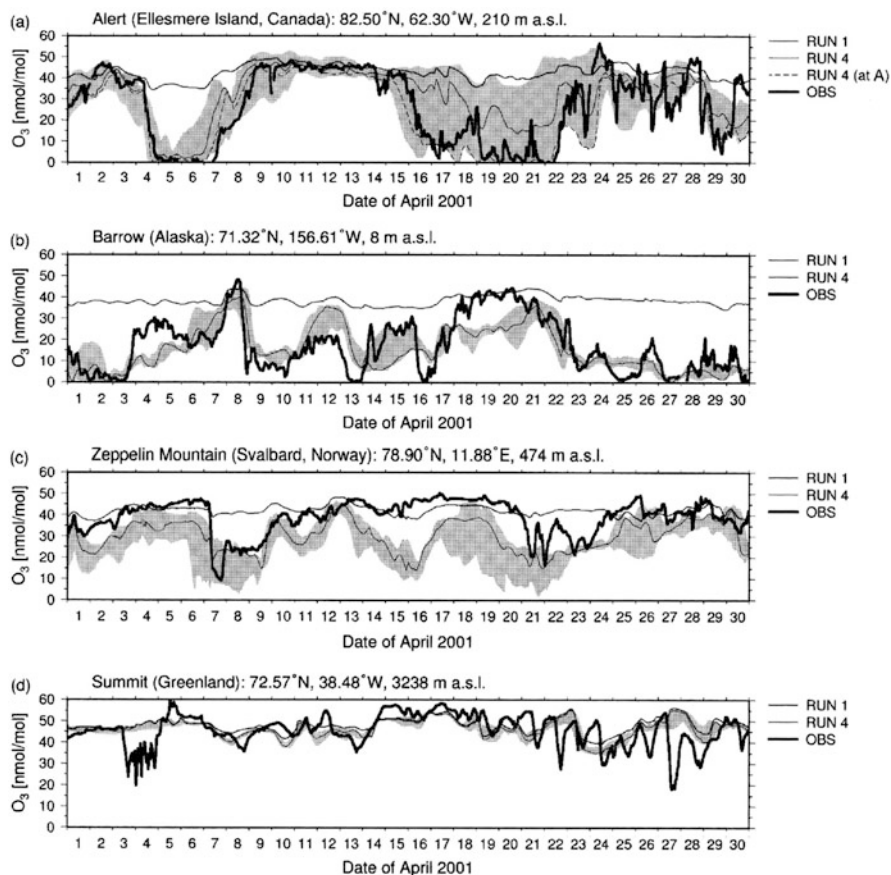
The polar ozone depletion is confirmed to occur within the boundary layer, about 1 km from the ground surface by the slant column measurements of MAX-DOAS, and also by ozone sondes, while the active halogens are known to spread to the free troposphere as observed by aircrafts (Hönninger and Platt 2002; Choi et al. 2012). Furthermore, the BrO column density has been widely observed by satellite sensors, GOME, etc., and it is concluded that the high density in the polar region is due to the tropospheric column, and those of other regions are due to the stratospheric column (Platt and Wagner 1998). According to the satellite data, tropospheric BrO in the polar region in spring spreads in the timescale of 2–4 days and the spatial scale of 2000 km as “bromine clouds”, which proves that tropospheric halogen chemistry is not limited to the local phenomena only around the sites where the surface ozone depletion is observed.

The three dimensional modelling studies on the BrO formation and boundary layer ozone depletion in the polar region have been conducted recently (Zhao et al. 2008; Toyota et al. 2011). Toyota et al. (2011) assumed the reaction of sea salt contained in the snow on the sea ice with O<sub>3</sub> is the sole initial process of Br<sub>2</sub> release into the atmosphere, and calculated the BrO formation and O<sub>3</sub> depletion for the Arctic Circle using the three dimensional model based on the autocatalytic chain reaction described in the previous paragraph. Figure 7.24 compares the GOME satellite data and model calculation of tropospheric column of BrO in the Arctic region in April 2001. On April 16–17, and 20–22, large bromine clouds are



**Fig. 7.24** Comparison of tropospheric BrO column density in “bromine explosion” events in Arctic Circle. (a) satellite observation and (b) model calculation (Adapted from Toyota et al. 2011)

seen over 1000 km over the Siberian fringe and Canadian Arctic region, respectively. Shown in Fig. 7.24b is the result of RUN 3 model in which critical temperature for the Br<sub>2</sub> from the reactions of O<sub>3</sub>, HOBr and BrONO<sub>2</sub> with sea salt on snow cover was set as  $T_c = -10$  °C. The RUN 3 model reproduced reasonably well the temporal variation and spatial distribution of BrO. In this model study, it is reported that the emerging timing and place of the bromine clouds do not match with the satellite data if  $T_c$  is set as  $-15$  °C, and the bromine clouds do not appear at all when they set  $T_c = -20$  °C. Meanwhile, the experimentally obtained uptake coefficient of HOBr on NaCl-covered ice is  $\gamma \approx 1 \times 10^{-2}$  at  $-15$  °C, and increase with decrease of temperature but the temperature dependence is not very strong (Adams et al. 2002). Figure 7.25 depicts the comparison between the observation and model calculation for surface ozone at Alert, Barrow, Zeppelin



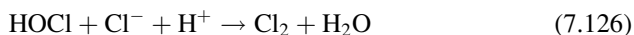
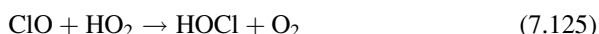
**Fig. 7.25** Comparison of surface  $O_3$  mixing ratios between the observation and model calculation at (a) Alert, Canada, (b) Barrows, Alaska (c) Zeppelin Mountain, Svalbard, Norway, and (d) Summit, Greenland (Adapted from Toyota et al. 2011)

Mountain (Spitsbergen Island, Norway), and Greenland Summit in April 2001 (Toyota et al. 2011). As shown in the figure, the  $O_3$  depletion does not appear in RUN 1 in which the release of Br is not considered, the episodic  $O_3$  depletions are reproduced well by RUN 4 in which  $T_c$  is set at  $-15^\circ\text{C}$ . From this model investigation, as for the cause for the sporadic bromine explosion, meteorological conditions is suggested to influence the contact time of  $O_3$  with sea salt on snow cover by transport and turbulent diffusion. As for the bromine release, the first year fresh snow is thought to be important and it is sensitive to the critical temperature mentioned above.



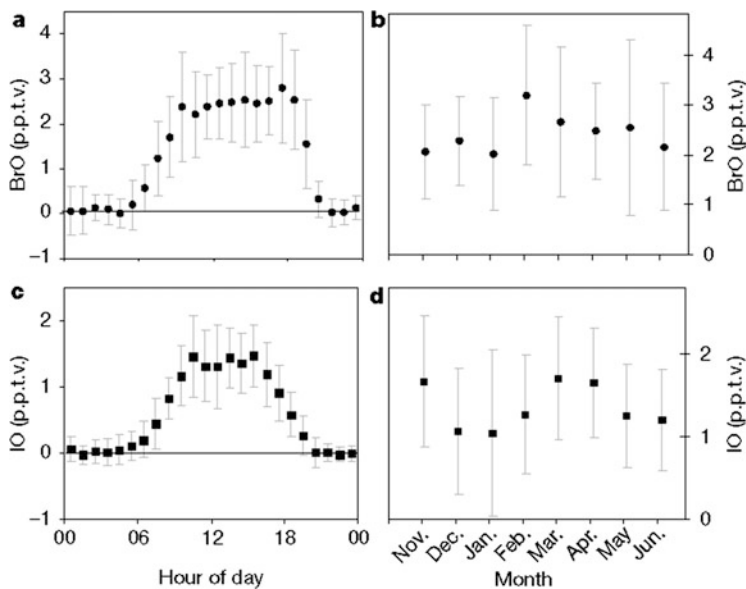
### 7.6.4.2 Low- and Mid-Latitude Marine Boundary Layer

Inorganic halogens have been observed, not only in the polar region, but widely in the marine boundary layer. The concentrations of halogens in the marine boundary layer are apparently different in the polluted and clean air, and in general the concentration is much higher in the air influenced by pollution. The difference is marked for Cl, and for example at Cape Verde Island in the tropical eastern Atlantic Ocean in summer in 2009, mixing ratios of HOCl and Cl<sub>2</sub> in the air mass from the open ocean are maximum 60 pptv in the daytime, and 10 pptv in the nighttime, whereas those in the air mass from European continent are over 100 ppt and 35 pptv in maximum, respectively (Lawler et al. 2011). Lawler et al. (2011) analyzed the data by using a box model including the multiphase photochemical chain reaction,

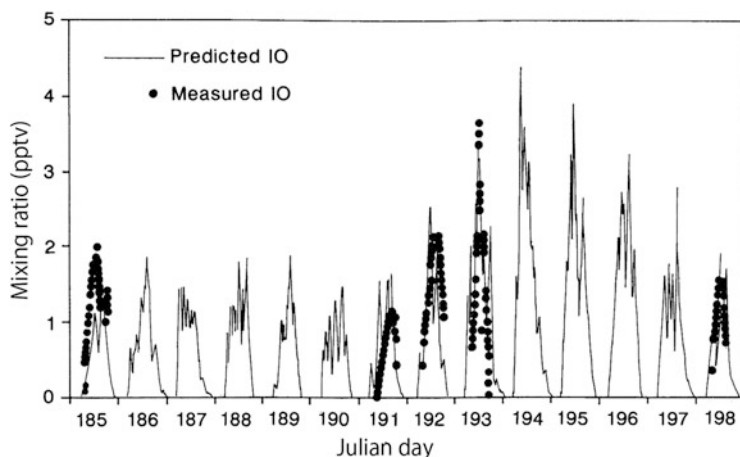


considering the presence of observed 0.6 pptv of HCl. The model reproduced 10 pptv of the nighttime Cl<sub>2</sub> well, but could not reproduce a few tens of pptv of the daytime HOCl, suggesting the existence of a missing source of HOCl. From the analysis for this observational data by a one-dimensional model including Br, Sommariva and von Glasow (2012) concluded that 5–11 % of CH<sub>4</sub> loss is due to Cl atoms, and 35–40 % of O<sub>3</sub> loss is due to halogens (mainly Br).

At Cape Verde, year-around observation of BrO and IO has been conducted, and the averaged mixing ratios of BrO  $2.5 \pm 1.1$  (1 $\sigma$ ) pptv and IO  $1.4 \pm 0.8$  pptv are reported for November 2006–June 2007. Figure 7.26 shows the observed diurnal and seasonal variation of BrO and IO. The measured value of NO at this site is very low,  $3.0 \pm 1.0$  pptv, and photochemical loss of O<sub>3</sub> occurs in the daytime, as mentioned in Sect. 7.3.1, and it is deduced that 30–50 % of the O<sub>3</sub> loss is due to the halogens (Read et al. 2008). Also, Dickerson et al. (1999) estimated by a model calculation for the observation in the tropical Indian Ocean that against the observed 32 % loss of the daytime O<sub>3</sub>, only 12 % is explained by the HO<sub>x</sub> chain reaction and loss by the multiphase chain reaction including BrO/HOBr/HBr amounts to 22 %. The sources of iodine at the sites where seaweed is not present, such as at Cape Verde and over the mid-latitude open ocean, are thought to be CH<sub>2</sub>I<sub>2</sub>, CHClI<sub>2</sub>, and CH<sub>3</sub>I formed by the sea surface reaction of organic compounds with iodine under the sunlight (Martino et al. 2009; Mahajan et al. 2010). As shown in Fig. 7.27, McFiggans et al. (2000) obtained a good agreement for the diurnal variation of IO with a box model calculation using the mixing ratios of CH<sub>2</sub>I<sub>2</sub>, CH<sub>2</sub>BrI and CH<sub>3</sub>I (0.03, 0.3, 3 pptv, respectively) measured in the remote Atlantic Ocean as a boundary condition. From this calculation, the ratios of initial I atom



**Fig. 7.26** (a) Diurnal variation of BrO, (b) seasonal variation of BrO, (c) diurnal variation of IO, and (d) seasonal variation of IO at Cape Verde. Designated error is  $1\sigma$ . (Adapted from Read et al. 2008)



**Fig. 7.27** Comparison between the observed mixing ratio of IO and the estimated values from the observed concentrations of  $\text{CH}_2\text{I}_2$ ,  $\text{CH}_2\text{BrI}$  and  $\text{CH}_3\text{I}$  over Atlantic Ocean (Adapted from McFiggans et al. 2000)

release are calculated as  $\text{CH}_2\text{I}_2$  64 %,  $\text{CH}_2\text{BrI}$  34 % and  $\text{CH}_3\text{I}$  4 %, and the observed maximum IO mixing ratio of 3 pptv is well reproduced.

In the relatively clean marine boundary layer at Mace Head, Ireland, maximum mixing ratios of BrO at 6.5 pptv, the daytime averaged value of 2.3 pptv, and the maximum values of I<sub>2</sub>, IO, OIO at 93, 2.5 and 10.8 pptv, respectively, were observed by LP-DOAS (Saiz-Lopez et al. 2004, 2006). The source of high concentration of iodine at Mace Head is thought to be due to seaweed, based on the correlation with low tide.

On the other hand, in marine boundary layers under the strong influence of polluted air, very high concentrations of ClNO<sub>2</sub> and Cl<sub>2</sub> have been observed. For example, the maximum mixing ratios of ClNO<sub>2</sub> and Cl<sub>2</sub> at 2100 and 200 ppt (Riedel et al. 2012) in the harbor near Los Angeles, and nighttime maximum Cl<sub>2</sub> at 150 pptv in Long Island, United States (Spicer et al. 1998). These high concentration of halogens are thought to be ClNO<sub>2</sub>, formed by reaction (7.76) between N<sub>2</sub>O<sub>5</sub> with sea salt in the polluted air from cities and harbor ships, and Cl<sub>2</sub> formed by the self-catalytic reaction described in Sect. 7.5.3. However, as for Cl<sub>2</sub> in the suburbs of Los Angeles, either of the cases where it has high correlation or no correlation with ClNO<sub>2</sub> has been reported, and the direct emission of Cl<sub>2</sub> from urban pollution sources are suggested in the latter case (Riedel et al. 2012).

#### 7.6.4.3 Salt Lakes

Reactive halogens in the troposphere have been known to exist not only over the marine boundary layer, but also in the surroundings of terrestrial salt lakes. As for the halogen species at the inland salt lakes, the Dead Sea in Israel is best investigated, and maximum mixing ratio of 100–200 pptv of BrO has been observed regardless of season (Matveev et al. 2001; Tas et al. 2005). Other than BrO, maximum 10 pptv of IO has also been measured (Zingler and Platt 2005). As for the sources of halogens at Dead Sea, discussions have been made that iodine source is not biogenic, but heterogeneous photochemical reactions between the halogen ions in water with gas-phase O<sub>3</sub> at the surface of water has been discussed (Zingler and Platt 2005; Tas et al. 2006; Smoydzin and von Glasow 2009). Furthermore, ClO and BrO have been observed at Great Salt Lake, United States and BrO at Salar de Uyuni, Bolivia (Stutz et al., 2002; Hönninger et al., 2004), and it has been established that the presence of active halogen species in the atmosphere around the inland salt lakes is a general phenomenon.

## 7.7 Tropospheric Sulfur Chemistry

Historically, sulfur compounds in the troposphere have been the cause of concern from the viewpoint of air pollution since the industrial revolution; sulfur dioxide directly emitted from fossil fuel combustion and sulfuric acid aerosols formed by its oxidation in the atmosphere have been studied as the most important air pollutants, and the acid rain caused by their uptake into clouds and fog followed by liquid

phase reactions have also been studied intensively (Finlayson-Pitts and Pitts 2000). On the other hand, sulfur compounds of natural biogenic origin such as dimethyl sulfide (DMS) are oxidized in the atmosphere to form sulfuric acid aerosols over the open ocean. They have been attracting much attention from the viewpoint that they act as cloud condensation nuclei (CCN) to form clouds, which influences radiation budget of the earth and has a possibility to generate negative feedback to control the emission of DMS (Charlson et al. 1987). Sulfuric acid aerosols formed from the sulfur dioxide of anthropogenic sources also affect the radiation budget, and are important from the point of climate change caused by human activities (IPCC 2013).

Sulfur compounds in the atmosphere include hydrogen sulfide ( $\text{H}_2\text{S}$ ), methanethiol ( $\text{CH}_3\text{SH}$ ), dimethyl sulfide (DMS,  $\text{CH}_3\text{SCH}_3$ ), dimethyl disulfide ( $\text{CH}_3\text{SSCH}_3$ ), and carbonyl sulfide (COS) which are mainly marine biogenic origin, carbon disulfide ( $\text{CS}_2$ ) which is both marine and anthropogenic origin, and sulfur dioxide ( $\text{SO}_2$ ) which is mainly anthropogenic but partly volcanic origin. Among the natural origin sulfur compounds, DMS is the most important (Bates et al. 1992), and its gas phase oxidation mechanism is described in this section. The rate constant of COS with OH is small and its tropospheric lifetime is more than 10 years, so that most of them reach to stratosphere causing the stratospheric aerosols as described in Chap. 8, Sect. 8.5.

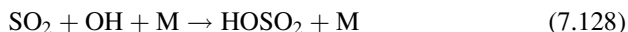
As for  $\text{SO}_2$ , after the gas phase oxidation reactions are described in Sect. 7.6.1, multiphase heterogeneous reactions (see Sect. 2.4) in fog water and rain droplet are covered in Sect. 7.6.2.

### ***7.7.1 Gas Phase Homogeneous Oxidation Reaction Mechanism***

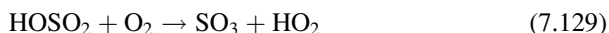
Most of oxidation reactions of sulfur compounds in the troposphere are initiated by OH radicals, but the reactions with NO, and active halogen species such as BrO and IO has to be considered in the polluted air and in the marine boundary layer, respectively. As for  $\text{SO}_2$ , other than the gas phase reaction with OH, oxidation reaction in cloud and fog droplet is important which will be described later.

#### **7.7.1.1 $\text{SO}_2$**

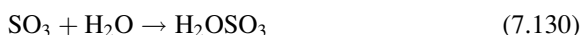
The main emission source of sulfur dioxide  $\text{SO}_2$  is anthropogenic fossil fuel combustion, and the emissions from volcanoes and biomass burning are added to it (Bates et al. 1992). Atmospheric  $\text{SO}_2$  reacts with OH,



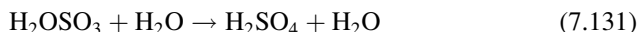
to form HOSO<sub>2</sub> radicals (see Sect. 5.2.6). The formation of sulfur trioxide (SO<sub>3</sub>) and HO<sub>2</sub> from HOSO<sub>2</sub>,



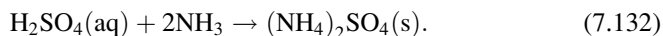
was first proposed by Stockwell and Calvert (1983), and an important consequence of this process is that it produces HO<sub>2</sub> so that the reaction of SO<sub>2</sub> and OH does not serve as the termination reaction of OH chain reaction (see Sect. 7.3). The reaction of SO<sub>3</sub> to form sulfuric acid is second order to H<sub>2</sub>O, and it is known that the adduct of SO<sub>3</sub> and H<sub>2</sub>O formed by



reacts with another H<sub>2</sub>O molecule to form H<sub>2</sub>SO<sub>4</sub> (Lovejoy et al. 1996).



The generated H<sub>2</sub>SO<sub>4</sub> is a gaseous molecule but since the vapor pressure is low, it condense with water vapor in the atmosphere to yield H<sub>2</sub>SO<sub>4</sub>(aq) and forms sulfuric acid aerosols. They further react with ammonia molecules to yield solid ammonium sulfate,



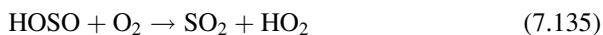
From the rate constant of gaseous reaction of OH and SO<sub>2</sub> at 298 K and 1 atm given in Table 5.2, average atmospheric lifetime of SO<sub>2</sub> is more than 1 week when the average concentration of OH is assumed to be  $8 \times 10^5$  molecules cm<sup>-3</sup>, but it is generally much shorter when the multiphase reaction is considered.

### 7.7.1.2 CS<sub>2</sub>

Carbon disulfide CS<sub>2</sub> is known to be mainly emitted from industries and partially from natural biota in the ocean (Chin and Davis 1993). The reaction of CS<sub>2</sub> and OH is the addition reaction,



The CS<sub>2</sub>OH radical reacts with O<sub>2</sub> to generate OCS and SO<sub>2</sub> with the yield of ca. 0.83–0.84 (Stickel et al. 1993), and the reaction pathways,



have been proposed by quantum chemical calculation (Zhang and Qin 2000; McKee and Wine 2001). Carbonyl sulfide, COS formed in the atmospheric reaction of CS<sub>2</sub> has a long lifetime in the troposphere as mentioned below, and it is mostly transported to the stratosphere. Although other products, CO and SO<sub>2</sub> are formed in this reaction with the yields of ca. 0.16 and 0.30, respectively, their detailed production pathways are not well known.

The reaction rate constant of CS<sub>2</sub> and OH under the atmospheric conditions is about the same as of SO<sub>2</sub> (see Table 5.2), and its atmospheric lifetime is 1–2 weeks.

### 7.7.1.3 COS

Carbonyl sulfide COS is a sulfur compound present in the troposphere at ca. 0.5 ppbv. It is emitted from volcanic activities and also formed in the atmospheric reaction of CS<sub>2</sub> and OH as mentioned above. Among the global emission of COS, the ratio of the secondary formation from CS<sub>2</sub> is estimated to be ca. 30 % (Chin and Davis 1993). The rate constant of the reaction of COS and OH is very small as seen in Table 5.2 ( $2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K), and the atmospheric lifetime calculated from the average concentration of OH assumed to be  $8 \times 10^5 \text{ molecules cm}^{-3}$  is about 20 years. Therefore, most of COS emitted and formed in the troposphere is transported to the stratosphere, where it is photolyzed to yield H<sub>2</sub>SO<sub>4</sub>, which causes the stratospheric aerosols (see Chap. 8, Sect. 8.5).

### 7.7.1.4 H<sub>2</sub>S

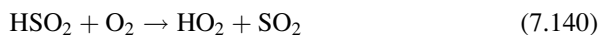
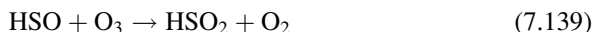
Hydrogen sulfide H<sub>2</sub>S is emitted to the atmosphere either from natural sources, e.g. volcanos, soils, biomass burning, and marine biology, or from anthropogenic sources, mainly industries. The reaction of H<sub>2</sub>S with OH yields HS (sulfanyl radical) by abstraction reaction,



The formed HS radicals react with O<sub>3</sub> or NO<sub>2</sub> in the atmosphere,



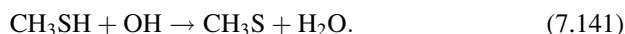
to yield HSO (sulfhydryl) radicals, from which SO<sub>2</sub> is produced.



The rate constant of the OH and H<sub>2</sub>S reaction is  $4.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K as given in Table 5.2, and the tropospheric lifetime is calculated to be ca. 70 h assuming the OH concentration of  $8 \times 10^5 \text{ molecules cm}^{-3}$ .

### 7.7.1.5 CH<sub>3</sub>SH

Methanethiol, CH<sub>3</sub>SH is also called methyl mercaptan, and its sources are mainly marine biology. The reaction with OH radicals is thought to be the hydrogen abstraction (Atkinson et al. 2004; Sander et al. 2011),



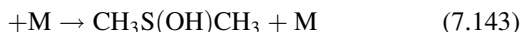
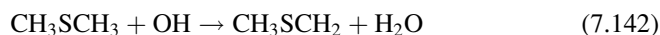
The product, CH<sub>3</sub>S (methylthiyl) radicals are very important as the intermediate of the atmospheric oxidation reaction of DMS (CH<sub>3</sub>SCH<sub>3</sub>), and will be described later in detail in this paragraph.

The rate constant of the reaction, CH<sub>3</sub>SH and OH (see Table 5.2) is 7 times higher than H<sub>2</sub>S, and the tropospheric lifetime of CH<sub>3</sub>SH is calculated to be a few hours.

### 7.7.1.6 CH<sub>3</sub>SCH<sub>3</sub>

Dimethyl sulfide (DMS), CH<sub>3</sub>SCH<sub>3</sub>, has the highest emission rate among the natural origin sulfur compounds (Bates et al. 1992), and is concerned as the precursor of the natural origin SO<sub>2</sub>, particulate methane sulfonic acid (MSA), CH<sub>3</sub>SO<sub>3</sub>H, and dimethyl sulfoxide (DMSO), CH<sub>3</sub>SOCH<sub>3</sub>. Other than OH, the rate constant of DMS with NO<sub>3</sub> is also large, and the reaction is important in the coastal area with strong influence of anthropogenic activities. DMS is known also to react with active halogen species such as ClO and BrO. Many studies have been reported on the atmospheric oxidation processes of DMS, and a review is given by Barnes et al. (2006).

It has been known that the initial reaction of DMS and OH is both hydrogen abstraction and addition to S atom (Albu et al. 2006).



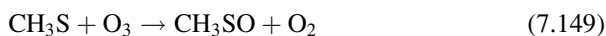
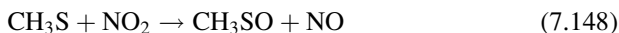
As seen in Table 5.2, the abstraction reaction has positive activation energy and the reaction rate constant increases with temperature, while the addition reaction has negative temperature dependence and the rate constant increases with the decrease

of temperature. The pressure dependence is also seen for the addition reaction as a three-body reaction, so that the branching ratio of reaction (7.142) and (7.143) changes depending on temperature and pressure. For example, about 80 % of the reaction is abstraction at 298 K and 1 atm, the ratio of the addition reaction increases with the decrease of temperature (Albu et al. 2006). The rate constant for the abstraction reaction at 298 K is  $4.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (see Table 5.2), which is nearly the same as  $\text{H}_2\text{S}$  and the atmospheric lifetime is several tens of hours.

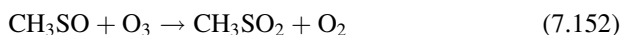
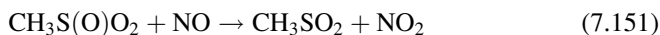
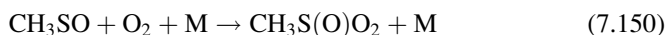
The  $\text{CH}_3\text{SCH}_2$  radical formed in reaction (7.142) react with  $\text{O}_2$ , and is thought to follow the same pathways as alkyl radicals in the presence of  $\text{NO}$  (Barnes et al. 2006).



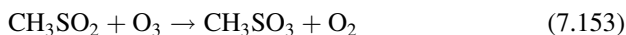
Many studies have been conducted as for the reaction pathways of  $\text{CH}_3\text{S}$  radicals formed in the above reaction (7.146), and reaction (7.141) of  $\text{CH}_3\text{SH}$  and  $\text{OH}$ , most of them are based on the analysis of final products, and the precise reaction mechanism has not been established yet. In the atmosphere,  $\text{CH}_3\text{S}$  is thought to react with  $\text{NO}_2$  and  $\text{O}_3$ ,



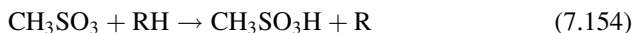
to form  $\text{CH}_3\text{SO}$ , which would further reacts as,



to produce  $\text{CH}_3\text{SO}_2$ . The reaction of  $\text{CH}_3\text{SO}_2$  with  $\text{O}_3$ ,



would form  $\text{CH}_3\text{SO}_3$ , and a mechanism to produce methane sulfonic acid (MSA,  $\text{CH}_3\text{SO}_3\text{H}$ ) as a final product,



has been considered (Barnes et al. 2006).

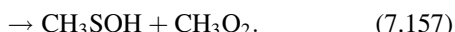


The production of  $\text{SO}_2$  as well as  $\text{CH}_3\text{SO}_3\text{H}$  in the OH oxidation reaction of DMS under the atmospheric conditions has been known experimentally (Hatakeyama et al. 1982). As for the pathways to form  $\text{SO}_2$ , a thermal decomposition of  $\text{CH}_3\text{SO}_2$  formed in the above reaction (7.152),



has been proposed, but the reaction pathway has not been established.

Meanwhile, from  $\text{CH}_3\text{S}(\text{OH})\text{CH}_3$  formed in the addition reaction (7.143) of DMS and OH, dimethyl sulfoxide (DMSO),  $\text{CH}_3\text{SOCH}_3$ , and methanesulfenic acid,  $\text{CH}_3\text{SOH}$ , are thought to be produced (Gross et al. 2004; Ramírez-Anguita et al. 2009) as,

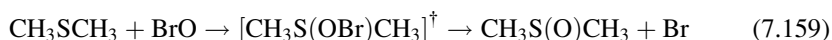


The reaction of DMS with  $\text{NO}_3$  is assumed to give initial adduction from the observed negative temperature dependence, but is considered to be basically an abstraction reaction based on the experimentally observed H/D isotope effect,



to give  $\text{CH}_3\text{SCH}_2$  radicals, the same as in the reaction with OH (Atkinson et al. 2004; Sander et al. 2011).

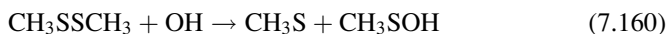
As for the atmospheric reactions of DMS, the reactions with the active halogen species, as seen in Sect. 7.5 are also known. For example, the reaction with BrO,

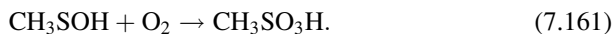


has a negative temperature effect, and gives DMSO with a reaction yield of unity. The reactions of ClO and IO are also known to produce DMSO directly (Atkinson et al. 2004; Sander et al. 2011).

### 7.7.1.7 $\text{CH}_3\text{SSCH}_3$

Dimethyl disulfide (DMDS),  $\text{CH}_3\text{SSCH}_3$ , is released mainly from marine biology and biomass burning. The rate constant of the OH reaction is very fast,  $2.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K, and the atmospheric lifetime is very short within a few hours. The reaction is thought to give methane sulfonic acid (MSA) directly (Barnes et al. 1994) as,





### 7.7.2 *Multiphase Reactions and Acidification of Clouds and Fog*

The studies on multiphase reactions in the troposphere have been developed through atmospheric environmental problem of acid rain/wet deposition. Most of oxidizing processes in rainwater relevant to sulfate, nitrate, and carbonate ions have been well established, as mentioned in this paragraph. However, multiphase reactions in the troposphere involving uptake and reaction on the surface of aerosol surface for many atmospheric species, and reactions in the aerosol aqueous solution relevant to organic aerosols are the research fields studied intensively at the present time, as they are relevant to secondary organic aerosol formation, and further development in future is expected. For the content of this paragraph, textbooks by Finlayson-Pitts and Pitts (2000), Seinfeld and Pandis (2006), and McElroy (2002) are of use as references. Since the actual field observations of acid rain are not covered in this book, the above textbooks should be referred for this aspect and also Cowling (1982) for the historical aspect.

Here, the uptake of  $\text{SO}_2$  to clouds and fog droplet, liquid phase oxidation processes to sulfuric acid, and the acidification of water droplets are considered. As seen in Chap. 2, Sect. 2.4.1, multiphase reaction processes of atmospheric molecules consist of (1) transport and diffusion of gaseous molecules to the gas-liquid surface, (2) uptake of gaseous molecules to liquid phase, (3) diffusion in the bulk liquid, and (4) chemical reactions in the bulk liquid phase (Schwartz and Freiberg 1981).

#### 7.7.2.1 Multiphase Processes in Water Droplets

First, assuming that the transport and diffusion of gaseous molecules occurs by molecular diffusion to spherical water particles, transport rate constant  $\beta_{gd}$  ( $\text{s}^{-1}$ ) is equal to the heterogeneous rate constant  $k_{het}$  in Chap. 2 Sect. 2.4.1, it can be expressed as,

$$\beta_{gd} = k_{het} = \frac{1}{\tau_g} = \frac{1}{4} \Gamma_g u_{av} A \quad (7.162)$$

by putting  $\gamma = \Gamma_g$  in Eq. (2.81). Here,  $\tau_g$  is the characteristic time for the gas phase diffusion to the liquid droplets,  $u_{av}$  is the average thermal kinetic velocity,  $A$  is the surface area density of droplets contained in the unit volume of gas. Considering here water droplets with radius  $r$ ,  $A$  can be expressed as,

$$A = 4\pi r^2 N_p \quad (7.163)$$

where  $N_p$  (particles  $\text{cm}^{-3}$ ) is the number of particles in a unit gas volume. Meanwhile, if we define liquid water content (LWC) as the weight of water contained in a unit volume of atmosphere (Wallace and Hobbs 2006; Seinfeld and Pandis 2006),

$$L = \frac{4}{3}\pi r^3 N_p \quad (7.164)$$

from the definition, and

$$A = \frac{3L}{r} \quad (7.165)$$

By substituting this equation and Eq. (2.84) in Sect. 2.4.1 for  $\Gamma_g$  into Eq. (7.143),

$$\beta_{gd} = \frac{3D_g L}{r^2} \quad (7.166)$$

is obtained. When typical values of diffusion constant,  $D_g = 0.1 \text{ cm}^2 \text{ s}^{-1}$ , clouds and fog radius,  $r = 7 \times 10^{-4} \text{ cm}$ , and liquid water content,  $L = 5 \times 10^{-7} \text{ (l(aq)/l(air))}$  ( $0.5 \text{ g m}^{-3}$ ) are assumed,  $\beta_{gd}$  is calculated to be  $\approx 0.3 \text{ s}^{-1}$ , and the characteristic time for diffusion is the order of  $\sim 1 \text{ s}$  by taking the reciprocal.

On the other hand, transport rate constant for the accommodation process at the gas-liquid surface,  $\beta_i$  ( $\text{s}^{-1}$ ), can be expressed similarly by  $\gamma = \alpha$  putting in Eq. (2.81),

$$\beta_i = k_{het} = \frac{1}{4}\alpha u_{av} A = \frac{3u_{av}\alpha L}{4r} \quad (7.167)$$

If we use the accommodation coefficient of  $\text{SO}_2$  molecule to the water particle surface given in Table 6.1,  $\alpha \geq 0.12$ ,  $u_{av} = 4.7 \times 10^4 \text{ cm s}^{-1}$ , and liquid water content,  $L = 5 \times 10^{-7} \text{ (l(aq)/l(air))}$ , and particle radius,  $r = 7 \times 10^{-4} \text{ cm}$ ,  $\beta_i$  is calculated to be  $3.0 \text{ s}^{-1}$ , and the characteristic time necessary for the uptake from the gas phase to the liquid surface is the order of  $\sim 0.1 \text{ s}$  by taking the reciprocal. Furthermore,  $\text{SO}_2$  molecules taken into water droplets react with  $\text{H}_2\text{O}$  molecules at the liquid surface, and reach to chemical equilibrium with three sulfur species,  $\text{SO}_2 \cdot \text{H}_2\text{O}$ ,  $\text{HSO}_3$  and  $\text{SO}_3^{2-}$  as mentioned later. The time for reaching to the chemical equilibrium is as short as  $10^{-3} \text{ s}$ .

Next, the diffusion of the taken-up molecule in the water droplets can be treated by converting the one-dimensional diffusion Eq. (2.93) in Chap. 2, Sect. 2.4.3, to the three-dimensional polar coordinate considering diffusion in a spherical liquid droplet,

$$\frac{\partial N_{aq}}{\partial t} = D_{aq} \left( \frac{\partial^2 N_{aq}}{\partial r^2} + \frac{2}{r} \frac{\partial N_{aq}}{\partial r} \right) \quad (7.168)$$

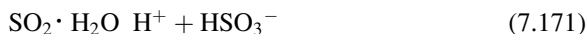
Here,  $r$  is the position coordinate in radial direction,  $N_{aq}$  is the molecular density (molecules  $\text{cm}^{-3}$ ) of molecule contained in the unit volume of aqueous solution, and  $D_{aq}$  is the diffusion constant of molecules in the aqueous solution. After solving this equation by assuming the initial and boundary conditions, the diffusion rate constant,  $\beta_{ad}$  ( $\text{s}^{-1}$ ) of the molecules inside of the liquid phase can be obtained as,

$$\beta_{ad} = \frac{\pi^2 D_{aq}}{r^2} \quad (7.169)$$

The characteristic diffusion time of molecules in water droplets is smaller than the gas phase diffusion by four orders of magnitude if liquid phase molecular diffusion is assumed. Finally, reactions in the liquid layer is considered. For the particles with radius smaller than  $10 \mu\text{m}$  such as clouds and fog droplets, the time for the gas phase diffusion to the liquid surface, transfer from the gas to the liquid phase, and diffusion within the liquid droplet is less than 1 s, and they cannot be a rate-limiting step for the multiphase oxidation reaction process. Thus, the liquid phase reaction within the water droplet as described below is the rate-limiting step.

### 7.7.2.2 Dissolution of $\text{SO}_2$ Into Water

The  $\text{SO}_2$  molecule dissolved in water forms a molecular complex  $\text{SO}_2 \cdot \text{H}_2\text{O}$ , and then generates bisulfate ion  $\text{HSO}_3^-$  and sulfite ion  $\text{SO}_3^{2-}$  though the following two step ionic dissociation,



Then,

$$K_{H,\text{SO}_2} = \frac{[\text{SO}_2 \cdot \text{H}_2\text{O}]}{p_{\text{SO}_2}} \quad (7.173)$$

$$K_{S1} = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{SO}_2 \cdot \text{H}_2\text{O}]} \quad (7.174)$$

$$K_{S2} = \frac{[\text{H}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]}, \quad (7.175)$$

where  $K_{H,\text{SO}_2}$  is the Henry's law constant of  $\text{SO}_2$  for water,  $K_{S1}$ ,  $K_{S2}$  are the dissociation constants for reactions (152) and (153), is the partial pressure of  $\text{SO}_2$

in the atmosphere. Each values at 298 K are given as  $K_{H,SO_2} = 1.4 \text{ M atm}^{-1}$  (Table 2.6),  $K_{S1} = 1.3 \times 10^{-2} \text{ M}$ ,  $K_{S2} = 6.6 \times 10^{-8} \text{ M}$  (Seinfeld and Pandis 2006). As shown in Table 2.6, Henry's law constant of  $SO_2$  is in the medium level, much smaller than those for nitric acid, aldehydes and organic acids, but much larger than for  $CO_2$ ,  $NO$  and  $NO_2$ . Meanwhile, the dissociation constant  $K_{S1}$  for  $SO_2 \cdot H_2O$  to  $H^+ + HSO_3^-$  is considerably large but  $K_{S2}$  for  $HSO_3^-$  to  $H^+ + SO_3^{2-}$  is very small. Using these values of the constants, concentrations of  $SO_2 \cdot H_2O$ ,  $HSO_3^-$ , and  $SO_3^{2-}$  are given by,

$$[SO_2 \cdot H_2O] = K_{H,SO_2} p_{SO_2} \quad (7.176)$$

$$[HSO_3^-] = \frac{K_{S1}[SO_2 \cdot H_2O]}{[H^+]} = \frac{K_{H,SO_2} K_{S1} p_{SO_2}}{[H^+]} \quad (7.177)$$

$$[SO_3^{2-}] = \frac{K_{S2}[HSO_3^-]}{[H^+]} = \frac{K_{H,SO_2} K_{S1} K_{S2} p_{SO_2}}{[H^+]^2}, \quad (7.178)$$

respectively.

Thus,  $SO_2$  molecules taken up to aqueous solution exists in the form of three chemical species,  $SO_2 \cdot H_2O$ ,  $HSO_3^-$  and  $SO_3^{2-}$ . Since they are all sulfur compounds with the oxidation number (valence) of 4, they are expressed as S(IV) in total,

$$S(IV) = SO_2 \cdot H_2O + HSO_3^- + SO_3^{2-}. \quad (7.179)$$

By using Eqs. (7.176), (7.177) and (7.178), the concentration of total sulfur S(IV) can be expressed as,

$$[S(IV)] = K_{H,SO_2} p_{SO_2} \left[ 1 + \frac{K_{S1}}{[H^+]} + \frac{K_{S1} K_{S2}}{[H^+]^2} \right]. \quad (7.180)$$

Here, if we define an effective Henry's law constant for S(IV), as,

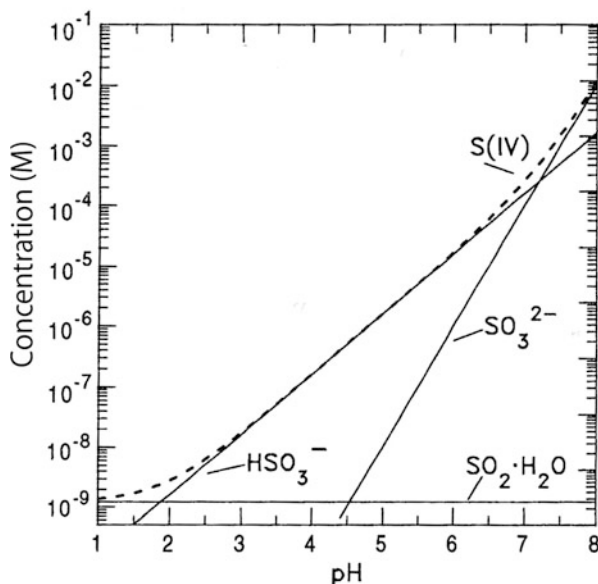
$$K_{H,S(IV)}^* = K_{H,SO_2} \left[ 1 + \frac{K_{S1}}{[H^+]} + \frac{K_{S1} K_{S2}}{[H^+]^2} \right], \quad (7.181)$$

the Henry equilibrium equation for the total amount of dissolving sulfur dioxide can be expressed as,

$$[S(IV)] = K_{H,S(IV)}^* p_{SO_2}. \quad (7.182)$$

From these equations, mole concentrations (M) for  $SO_2 \cdot H_2O$ ,  $HSO_3^-$ ,  $SO_3^{2-}$  and S(IV) in the aqueous solution for 1 ppbv of  $SO_2$  are shown in Fig. 7.28 as a

**Fig. 7.28** Concentrations of  $\text{SO}_2 \cdot \text{H}_2\text{O}$ ,  $\text{HSO}_3^-$ ,  $\text{SO}_3^{2-}$  and S(IV) as a function of solution pH for gas phase  $\text{SO}_2$  mixing ratio of 1 ppbv at 298 K (Seinfeld and Pandis 2006)

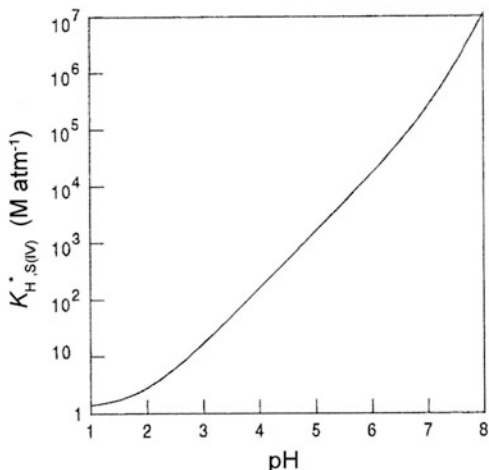


function of hydrogen ion exponent, pH (Seinfeld and Pandis 2006). As is well known, pH is defined by,

$$\text{pH} = -\log_{10}[\text{H}^+] \quad (7.183)$$

As seen in Fig. 7.28, the concentration of S(IV) in the aqueous solution increases rapidly with the increase of pH. In the aqueous solution of  $\text{pH} = 2-7$ , most of S(IV) is present as  $\text{HSO}_3^-$ . The concentrations of  $\text{SO}_3^{2-}$  and  $\text{SO}_2 \cdot \text{H}_2\text{O}$  are dominant for  $\text{pH} > 7$  and  $\text{pH} < 2$ , respectively, but the concentration of  $\text{SO}_2 \cdot \text{H}_2\text{O}$  is kept constant by the Henry's equilibrium being independent on pH. The reason for the concentrations of  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$  increase with pH is that  $\text{H}^+$  is included in the right side of reactions (7.171), (7.172), and the equilibrium proceeds to the right side as the concentration of  $\text{H}^+$  decreases with pH. This follows the Le Chatelier's principle, which states that in general when either of the concentration, temperature or pressure relevant to reactions is changed, the equilibrium shift to the direction to compensate the change. In Fig. 7.29, the pH dependence of the effective Henry's law constant for water defined by Eq. (7.181) is shown (Seinfeld and Pandis 2006). Reflecting the pH dependence of S(IV) concentration on pH as shown in Fig. 7.28, also increases rapidly with pH. For  $\text{pH} \approx 1$  where only  $\text{SO}_2 \cdot \text{H}_2\text{O}$  exists in the aqueous solution, the value of effective Henry's law constant is almost the same as given in Table 2.6,  $1.36 \text{ M atm}^{-1}$ , while it is as large as  $\sim 10^3 \text{ M atm}^{-1}$  at  $\text{pH} = 5$ , and  $\sim 10^5 \text{ M atm}^{-1}$  at  $\text{pH} = 7$ .

**Fig. 7.29** Effective Henry's law constant  $K_{H, s}^{*}$  (IV) of  $\text{SO}_2$  to water as a function of solution pH at 298 K (Seinfeld and Pandis 2006)



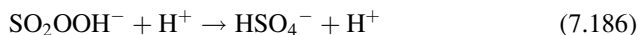
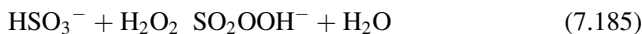
### 7.7.2.3 Oxidation Reaction of S(IV) in Aqueous Solution

The S(IV) taken up to water droplet is oxidized to form sulfate ion  $\text{SO}_4^{2-}$ , and the most important reactions for this oxidation process are the liquid phase reactions with  $\text{H}_2\text{O}_2$  and  $\text{O}_3$ . The typical mixing ratio of  $\text{H}_2\text{O}_2$  in the atmosphere is the order of  $\sim 1$  ppbv which is much lower than  $\text{O}_3$ , but the Henry's law constant of  $\text{H}_2\text{O}_2$  is  $8.44 \times 10^4 \text{ M atm}^{-1}$  at 298 K, which is nearly 7 orders of magnitude larger than the value,  $1.03 \times 10^{-2} \text{ M atm}^{-1}$ , for  $\text{O}_3$  (see 2.6). Therefore, the  $\text{H}_2\text{O}_2$  concentration in the aqueous solution is  $\sim 1 \times 10^{-4} \text{ M}$ , which is 5 orders of magnitude larger than  $\text{O}_3$ .

The dissociation constant for the ionic dissociation reaction of  $\text{H}_2\text{O}_2$  dissolved in water,

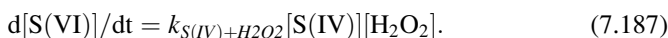
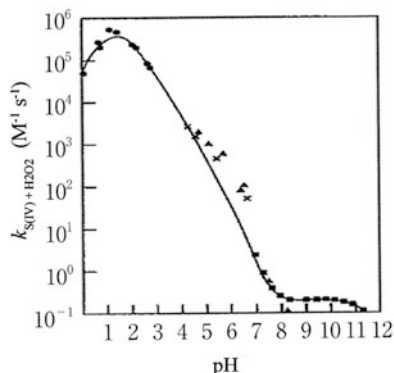


is extremely small,  $2.2 \times 10^{-12} \text{ M atm}^{-1}$  at 298 K (Pandis and Seinfeld 1989), so that  $\text{H}_2\text{O}_2$  exists mainly as a molecule in the aqueous solution. It reacts with the main component of S(IV) in the solution,  $\text{HSO}_3^-$ ,



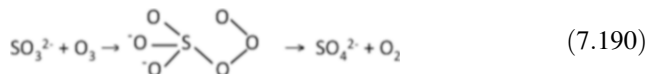
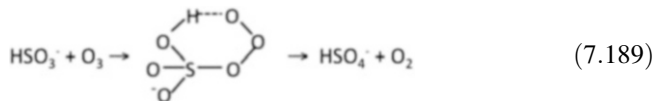
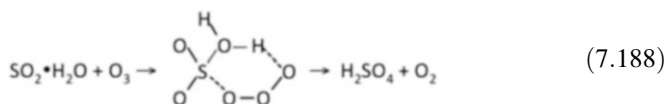
to form hydrogen sulfate ion  $\text{HSO}_4^-$  through peroxy sulfite ion,  $\text{SO}_2\text{OOH}^-$  (McArdle and Hoffmann 1983). Expressing  $\text{HSO}_4^-$  as S(VI) since the valence of sulfur in  $\text{HSO}_4^-$  is 6, the rate constant of the overall reaction of S(IV) and  $\text{H}_2\text{O}_2$  can be defined as,

**Fig. 7.30** Second order rate constant of the reaction of S(IV) and  $\text{H}_2\text{O}_2$  in aqueous solution as a function of pH at 298 K:  $d[\text{S(IV)}]/dt = k_{S(IV)+\text{H}_2\text{O}_2} [\text{S(IV)}][\text{H}_2\text{O}_2(\text{aq})]$  (Martin and Damschen 1981) (Refer to the source for the literature of individual data in the figure)



Here, the value of  $k_{S(IV)+\text{H}_2\text{O}_2}$  has been confirmed to be strongly dependent on pH, and the pH dependence of the experimental value of  $k_{S(IV)+\text{H}_2\text{O}_2}$  is illustrated in Fig. 7.30 (Martin and Damschen 1981). As seen in Fig. 7.30, the rate constant of this reaction has a maximum value of  $\sim 5 \times 10^5 \text{ M s}^{-1}$  at around  $\text{pH} = 1.5$ , and decreases with the increase of pH. As seen in Fig. 7.28, the concentration of  $\text{HSO}_3^-$  increases with pH, which is in contrast to the pH dependence of  $k_{S(IV)+\text{H}_2\text{O}_2}$  shown in Fig. 7.30. For this reason the oxidation rate of S(IV) by  $\text{H}_2\text{O}_2$ , a product of these two values, have a characteristic of almost constant being independent on pH.

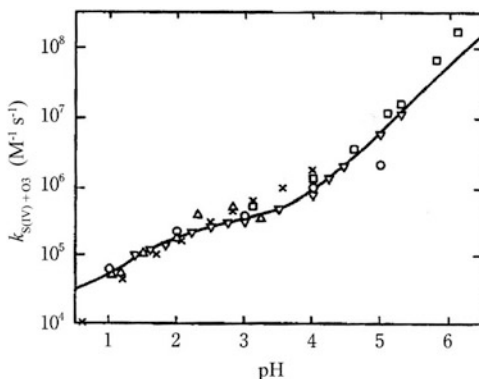
The reaction of S(IV) and  $\text{O}_3$  in aqueous solution is known to occur for either of the species,  $\text{SO}_2 \cdot \text{H}_2\text{O}$ ,  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$ ,



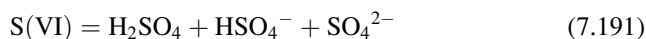
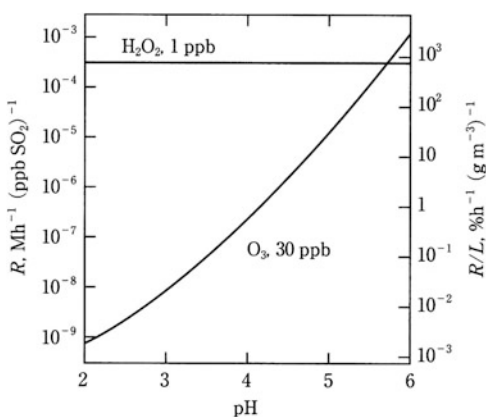
and forms sulfuric acid  $\text{H}_2\text{SO}_4$ , bisulfate ion  $\text{HSO}_4^-$ , and sulfate ion  $\text{SO}_4^{2-}$ , respectively, through each reaction complex (Hoffmann 1986). When we put each reaction rate constant as  $k_0$ ,  $k_1$ ,  $k_2$ , they have been obtained as  $k_0 = (2.4 \pm 1.1) \times 10^4$ ,  $k_1 = (3.7 \pm 0.7) \times 10^5$  and  $k_2 = (1.5 \pm 0.6) \times 10^9 \text{ M s}^{-1}$  (Hoffmann 1986). Since the reaction products,  $\text{H}_2\text{SO}_4$ ,  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$  are all in the oxidation state of 6, they are expressed as S(VI) in total,



**Fig. 7.31** Second order rate constant for the reaction of S(IV) and O<sub>3</sub> reaction as a function of solution pH at 298 K:  $d[S(IV)]/dt = k_{S(IV)+O_3} + O_3 [S(IV)][O_3(aq)]$  (Seinfeld and Pandis 2006) (Refer to the source for the literature of individual data in the figure)



**Fig. 7.32** Rate of aqueous phase oxidation of S(IV) by 1 ppb of H<sub>2</sub>O<sub>2</sub> and 30 ppbv of O<sub>3</sub> as a function of solution pH at 298 K. R represents the aqueous phase reaction rate per ppb of gas phase SO<sub>2</sub>. The R/L on the right axis represents reaction rate referred to gas phase SO<sub>2</sub> per unit cloud liquid water content (g m<sup>-3</sup>) (Adapted from Seinfeld and Pandis 2006)



and the reaction rate constant of overall reaction of S(IV) and O<sub>3</sub> can be defined by,

$$d[S(VI)]/dt = k_{S(IV)+O_3}[S(IV)][O_3] \quad (7.192)$$

Figure 7.31 shows the pH dependence of  $k_{S(IV)+O_3}$  thus defined (Seinfeld and Pandis 2006). As shown in the figure, the rate constant of the reaction of S(IV) and O<sub>3</sub> increases with pH. Referring to the pH dependence of  $k_0$ ,  $k_1$  and  $k_2$ , the individual rate constant for reactions (7.188), (7.189) and (7.190), respectively, given by Hoffmann (1986),  $k_0$  is independent on pH whereas  $k_1$  and  $k_2$  increases with pH so that the dependence of  $k_{S(IV)+O_3}$  shown in Fig. 7.30 reflects this feature. As seen in Fig. 7.28, since the concentrations of HSO<sub>3</sub><sup>-</sup> and SO<sub>3</sub><sup>-</sup> increase rapidly with pH, the oxidation reaction rate of O<sub>3</sub> by S(IV) multiplying them with the rate constants is thought to increase rapidly with pH.

Figure 7.32 depicts the pH dependence of the oxidation rate of SO<sub>2</sub> in aqueous solution per 1 ppbv of gaseous SO<sub>2</sub> using the values of above  $k_{S(IV)+H_2O_2}$  and  $k_{S(IV)}$

+O<sub>3</sub>, taking the mixing ratios of H<sub>2</sub>O<sub>2</sub> 1 ppbv and O<sub>3</sub> 30 ppbv in the atmosphere. As shown in the figure, the oxidation of SO<sub>2</sub> is mainly due to H<sub>2</sub>O<sub>2</sub> for pH < 5, and the oxidation by O<sub>3</sub> predominates only for pH > 6.

#### 7.7.2.4 pH of Clouds and Fog

The clouds and fog droplets are acidified by the uptake of SO<sub>2</sub> and other acidic species. Before discussing this, let us discuss the pH of water droplets by CO<sub>2</sub> in the atmosphere. The CO<sub>2</sub> molecule dissolved into water dissociates to bicarbonate ion, HCO<sub>3</sub><sup>-</sup>, and carbonate ion, CO<sub>3</sub><sup>2-</sup>, after forming a molecular complex between H<sub>2</sub>O molecule, CO<sub>2</sub>•H<sub>2</sub>O, by two step dissociation,



These processes are in parallel with the dissociation of SO<sub>2</sub> in the aqueous solution. Similar to the case of SO<sub>2</sub>, the concentrations of CO<sub>2</sub>•H<sub>2</sub>O, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup> can be written as,

$$[\text{CO}_2 \cdot \text{H}_2\text{O}] = K_{H,\text{CO}_2} p_{\text{CO}_2} \quad (7.196)$$

$$[\text{HCO}_3^-] = \frac{K_{C1} [\text{CO}_2 \cdot \text{H}_2\text{O}]}{[\text{H}^+]} = \frac{K_{H,\text{CO}_2} K_{C1} p_{\text{CO}_2}}{[\text{H}^+]} \quad (7.197)$$

$$[\text{CO}_3^{2-}] = \frac{K_{C2} [\text{HCO}_3^-]}{[\text{H}^+]} = \frac{K_{H,\text{CO}_2} K_{C1} K_{C2} p_{\text{CO}_2}}{[\text{H}^+]^2} \quad (7.198)$$

by using Henry's law constants and dissociation constants. Here,  $K_{H,\text{CO}_2}$  is the Henry's law constant of CO<sub>2</sub> for water,  $K_{C1}$  and  $K_{C2}$  are the dissociation constants for reactions (7.194) and (7.195), respectively, and is the partial pressure (atm) of CO<sub>2</sub> in the atmosphere. Each value are given as  $K_{H,\text{CO}_2} = 3.4 \times 10^{-2} \text{ M atm}^{-1}$  (Table 2.6),  $K_{C1} = 4.3 \times 10^{-7} \text{ M}$ , and  $K_{C2} = 4.7 \times 10^{-11} \text{ M}$  at 298 K (Seinfeld and Pandis 2006). The Henry's law constant of CO<sub>2</sub> is about one fourth of SO<sub>2</sub> and twice of NO<sub>2</sub>. Meanwhile,  $K_{C1}$  and  $K_{C2}$  are 4 and 3 orders of magnitude smaller than  $K_{S1}$  and  $K_{S2}$ , respectively, showing that carboxylic acid is much weaker acid than sulfurous acid.

Assuming the partial pressure of CO<sub>2</sub> in the present day atmosphere is  $4.0 \times 10^{-4} \text{ atm}$  (400 ppmv),  $[\text{H}^+] = 2.42 \times 10^{-6} \text{ M}$  is obtained from Eqs. (7.196) and (7.197) by putting  $[\text{CO}_2 \cdot \text{H}_2\text{O}] = 1.36 \times 10^{-5} \text{ M}$  and  $[\text{H}^+] = [\text{HCO}_3^-]$ , which implies pH = 5.62. Thus, the pH of water droplet equilibrated with atmospheric CO<sub>2</sub> is about 5.6. However, the pH of actual natural clouds, fog and rain droplet, is as low as pH = 4 over the open ocean due to the influence of H<sub>2</sub>SO<sub>4</sub> due to DMS, and as high as pH = 7 when influenced by yellow sand or Saharan dust.

Assuming that the partial pressure of atmospheric  $\text{SO}_2$  is  $1.0 \times 10^{-9}$  atm (1 ppbv), and only sulfurous acid is present in a water droplet,  $[\text{H}^+] = 4.3 \times 10^{-6}$  M and  $\text{pH} = 5.4$  is obtained by putting  $[\text{SO}_2 \cdot \text{H}_2\text{O}] = 1.4 \times 10^{-9}$  M and  $[\text{H}^+] = [\text{HSO}_3^-]$  similarly to the case of  $\text{CO}_2$ . As seen in Fig. 7.29, under this condition, the concentration of  $\text{SO}_3^{2-}$  is two orders of magnitude lower than  $\text{HSO}_3^-$ , and can be neglected. Incidentally,  $\text{pH} = 4.9$  is obtained for the  $\text{SO}_2$  partial pressure is  $1.0 \times 10^{-8}$  atm (10 ppbv). On the other hand, if all of S(IV) in the droplet is converted to  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4$  is strong acid and thus,



Since the dissociation constants of reactions (7.199) and (7.200) at 298 K are very large, 1000 M, and  $1.0 \times 10^{-2}$  M, respectively (Pandis and Seinfeld 1989), one molecule of S(IV) gives two  $\text{H}^+$  ions. If we assume the partial pressure of  $\text{SO}_2$  is  $10^{-9}$  atm (1 ppbv), the molar concentration of  $\text{SO}_2$  in the atmosphere is,

$$[\text{SO}_2(\text{g})] = p_{\text{SO}_2}/RT = 4.1 \times 10^{-11} \text{ moles } l^{-1},$$

where  $R = 0.082$  atm l  $\text{K}^{-1}$  mol $^{-1}$  and  $T = 298$  K. Assuming the cloud water content to be  $L = 0.5 \times 10^{-6}$  l(aq)/l(gas), the concentration of  $\text{H}_2\text{SO}_4$  in the water droplets when all of  $\text{SO}_2$  is oxidized to  $\text{H}_2\text{SO}_4$  is,

$$[\text{H}_2\text{SO}_4(\text{aq})] = [\text{SO}_2(\text{g})]/(0.5 \times 10^{-6}) = 0.82 \times 10^{-4} \text{ mole } l^{-1},$$

which gives  $[\text{H}^+] = 1.6 \times 10^{-4}$  mole  $l^{-1}$  and  $\text{pH} = 3.8$ . If the atmospheric mixing ratio of  $\text{SO}_2$  is 10 ppbv, cloud water pH decreases to 2.8. In the actual field, clouds with average pH of 3.4–3.9 have been observed (Aneja and Kim 1993). As for fog droplets, taking  $L = 0.05 \times 10^{-6}$  l(aq)/l(gas) ( $0.05 \text{ g m}^{-3}$ ), pH can be as low as 2.8 and 1.8 for 1 and 10 ppbv of  $\text{SO}_2$ , which is even lower than in the cloud droplets. Actually, fog with pH 2.2 has been observed in the field (Munger et al. 1983), and they are called “acid fog”. In the case of rainwater, the water content is larger than clouds but has wide ranges. In general rainwater with pH 4–5 is often observed in the polluted atmosphere and they are called “acid rain”. In the actual rainwater the process of uptake of sulfuric acid aerosols formed by the gas phase oxidation reaction of  $\text{SO}_2$  also occurs in parallel.

Here, acidity of clouds, fog and rainwater have been discussed only from the viewpoint of sulfur chemistry. In actual clouds, fog, and rainwater further acidification by  $\text{HNO}_3$  formed from  $\text{NO}_x$ , neutralization by  $\text{NH}_4^+$  by the uptake of gaseous  $\text{NH}_3$  and  $\text{Ca}^{2+}$  from soil dust occurs simultaneously, their pH is determined by the overall ion balance of these species.

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## Chapter 8

# Stratospheric Reaction Chemistry

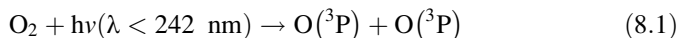
One of the most peculiar chemical characteristics of the earth's atmosphere is the formation of  $O_3$  through the photolysis of  $O_2$ , one of the major constituents of the atmosphere, by the ultraviolet radiation in the stratosphere. Photochemically produced  $O_3$  in the stratosphere forms the ozone layer, which absorbs nearly 100 % of the ultraviolet radiation with wavelength shorter than 300 nm preventing it to reach to the earth's surface. Since the DNA molecules constituting the cells of creatures on the earth are destructed photochemically, when they absorb the light with wavelengths shorter than 300 nm, organisms cannot survive under such ultraviolet radiation. From the point of view of the earth's history, a story is told that the ozone layer formed due to the increase of  $O_2$  in the atmosphere by photosynthesis of primitive organisms in the ocean, and it prevents harmful ultraviolet radiation from reaching the earth's surface, therefore enabling the migration of the earth's creatures to the land and bringing about the biosphere as seen in the present day (Berkner and Marshall 1965). This implies inversely that the decrease of stratospheric ozone for any reason would jeopardize the existence of terrestrial organisms, and the depletion of the ozone layer by human activities has been a big issue since the 1970s (Dotto et al. 1978; Middleton and Tolbert 2000; Finlayson-Pitts and Pitts 2000). Among them, the depletion of ozone layer by chlorofluorocarbons (CFCs) has been actualized, and atmospheric chemists have played a central role in raising the issue, understanding the phenomena, and bringing about a solution.

Almost all species related to the chemical reactions in the stratosphere except  $O_3$  have their origin on the earth's surface, and are brought to the stratosphere from the troposphere. Since it takes about 1–2 years for the transport and mixing between the troposphere and stratosphere, compounds with sufficiently long lifetimes to reach to the stratosphere are rather limited among the numerous chemical species present in the troposphere, as seen in the previous chapter. For this reason, reaction chemistry in the stratosphere is far more simple compared to that in the troposphere, and is expected to be described more precisely by a chemical reaction model than for the troposphere.

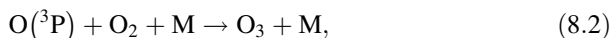
Stratospheric chemistry is described in detail by Brasseur and Solomon (2005), including the mesosphere, and is also given in the textbooks by Warneck (1988), Brasseur et al. (1999), Finlayson-Pitts and Pitts (2000), Wayne (2000), McElroy (2002), Seinfeld and Pandis (2006). A review on the reactions of halogen radicals in the stratosphere has been given by Bedjanian and Pullet (2003), and an updated review on stratospheric ozone depletion has been provided periodically by WMO (2011). In the present chapter, chemical reaction system is described exclusively among the stratospheric chemistry in which transport and reaction are coupled together.

## 8.1 Pure Oxygen Atmosphere and Ozone Layer

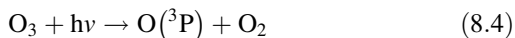
Chapman (1930a, b) showed successfully that the characteristics of the height of the ozone layer and ozone density in the earth's atmosphere can be described by assuming only oxygen is present as a reactive species in the atmosphere, and this reaction scheme is called pure oxygen theory or Chapman mechanism. Photolysis of  $O_2$  occurs by the solar radiation of wavelength shorter than 242 nm (see Sect. 4.3.1). Only the photolytic process,



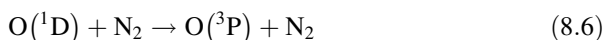
is energetically possible in the stratosphere where the solar radiation of wavelength longer than 180 nm reaches. From the ground state oxygen atoms  $O(^3P)$ ,  $O_3$  is formed by the reaction,

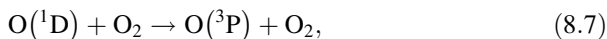


and this is the sole reaction in the atmosphere to directly produce  $O_3$ . The  $O_3$  molecule produced returns to  $O_2$  by the reaction of  $O(^3P)$  atoms (Sect. 5.1.2) or by photolytic reactions (Sect. 4.3.2) such as,



Although most of the excited oxygen atoms  $O(^1D)$  thus formed are quenched (see Sect. 7.1 and Table 5.1) in the atmosphere,





a part of them react with trace gases in the stratosphere, and give a large impact on stratospheric  $\text{O}_3$  concentration as described in the next section. Thus, the mixing ratios of O and  $\text{O}_3$  in the stratosphere are determined by the photo-equilibrium by reactions (8.1), (8.2), (8.3), (8.4), and (8.5), and photochemical reactions with trace species which will be described later.

Since the concentration of  $\text{O}({}^1\text{D})$  is much smaller than  $\text{O}({}^3\text{P})$ , by simply expressing  $\text{O}({}^3\text{P})$  as O neglecting  $\text{O}({}^1\text{D})$ , the rate equations for O and  $\text{O}_3$  can be expressed,

$$\frac{d[\text{O}]}{dt} = 2j_{8.1} - k_{8.2}[\text{O}][\text{O}_2][\text{M}] - k_{8.3}[\text{O}][\text{O}_3] - j_{8.4+8.5}[\text{O}_3] \quad (8.8)$$

$$\frac{d[\text{O}_3]}{dt} = k_{8.2}[\text{O}][\text{O}_2][\text{M}] - k_{8.3}[\text{O}][\text{O}_3] - j_{8.4+8.5}[\text{O}_3] \quad (8.9)$$

Summing these equations and defining the sum of O and  $\text{O}_3$  as odd oxygen  $\text{O}_x$ ,

$$[\text{O}_x] = [\text{O}] + [\text{O}_3],$$

then,

$$\frac{d[\text{O}_x]}{dt} = \frac{d[\text{O}]}{dt} + \frac{d[\text{O}_3]}{dt} = 2j_{8.1}[\text{O}_2] - 2k_{8.3}[\text{O}][\text{O}_3], \quad (8.10)$$

which shows simply  $\text{O}_x$  is produced by the photolysis of  $\text{O}_2$  and dissipated by the reaction of O and  $\text{O}_3$  (reaction 8.3). Here, assuming the steady state,  $d[\text{O}_3]/dt = 0$  and  $d[\text{O}_x]/dt = 0$ , Eqs. (8.9) and (8.10) give,

$$k_{8.2}[\text{O}][\text{O}_2][\text{M}] = k_{8.3}[\text{O}][\text{O}_3] + j_{8.4+8.5}[\text{O}_3] \quad (8.11)$$

and

$$j_{8.1}[\text{O}_2] = k_{8.3}[\text{O}][\text{O}_3], \quad (8.12)$$

respectively. From Eqs. (8.11) and (8.12), the quadratic equation with stationary concentration of  $\text{O}_3$ ,

$$j_{8.4+8.5}k_{8.3}[\text{O}_3]^2 + j_{8.1}k_{8.3}[\text{O}_2][\text{O}_3] - j_{8.1}k_{8.2}[\text{O}_2]^2[\text{M}] = 0 \quad (8.13)$$

is obtained, and the solution is

$$[O_3]_{ss} = \frac{-j_{8.1} + \sqrt{j_{8.1}^2 + 4j_{8.1}j_{8.4+8.5}k_{8.2}[M]/k_{8.3}}}{2j_{8.4}} [O_2]. \quad (8.14)$$

The vertical profile of the stationary state concentration of  $O_3$  in the stratosphere can be obtained by using the values of  $j_{8.1}$ ,  $j_{8.4}$ ,  $[O_2]$ , and  $M(=[O_2] + [N_2])$  at each altitude. In approximation, assuming  $2j_{8.1}[O_2] \ll j_{8.4}[O_3]$  and  $k_{8.2}[O_2][M] \gg k_{8.3}[O_3]$  in the stratosphere, Eq. (8.8) under the steady state of  $d[O]/dt = 0$  gives,

$$[O]_{ss} = \frac{2j_{8.1}[O_2] + j_{8.4+8.5}[O_3]}{k_{8.2}[O_2][M] + k_{8.3}[O_3]} \approx \frac{j_{8.4+8.5}[O_3]}{k_{8.2}[O_2][M]}. \quad (8.15)$$

Substituting this to Eq. (8.10),

$$\frac{d[O_x]}{dt} = 2j_{8.1}[O_2] - \frac{2k_{8.3}j_{8.4+8.5}[O_3]^2}{k_{8.2}[O_2][M]}. \quad (8.16)$$

Here, since most of  $O_x$  is  $O_3$  in the stratosphere, putting  $d[O_x]/dt = d[O_3]/dt = 0$  in the steady state, from Eq. (8.16),

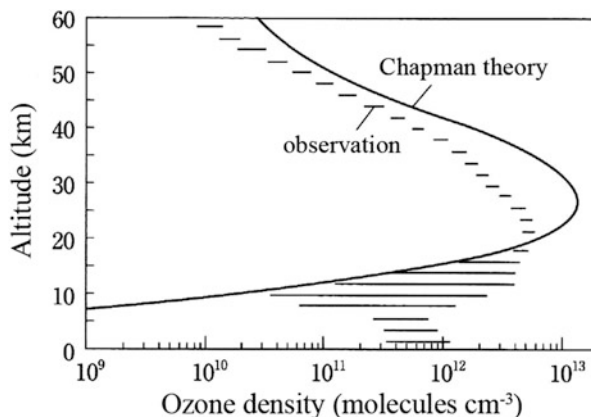
$$[O_3]_{ss} \approx \sqrt{\frac{j_{8.1}k_{8.2}[M]}{j_{8.4+8.5}}} [O_2] \quad (8.17)$$

is obtained. Equation (8.17) is the approximation of Eq. (8.14). Since the altitude dependence of  $j_4$  is relatively small among the parameters,  $[O_3]_{ss}$  is mainly determined by the dependence of  $j_{8.1}$ ,  $[O_2]$  and  $[M]$  on altitude. Since  $j_{8.1}$  is proportional to the actinic flux,  $j_{8.1}$  increases with altitude, while  $[O_2]$  and  $[M]$  decrease with altitude. Therefore,  $[O_3]_{ss}$  has maximum at a certain altitude, which is the ozone layer deduced from the Chapman mechanism.

Figure 8.1 shows the comparison of ozone density profile in the mid-latitude between the calculated and observed values. The horizontal lines with the observation curve represent the observed range of ozone density. It can be seen that the Chapman mechanism predicts the maximum of the ozone layer at around 25 km and its ozone density almost properly. However, there are two points of deviation of the theoretical curve from the observation. One is the overestimation of the density by a factor of two above the altitude of ozone maximum and the theoretical value of the altitude of the maximum is higher than observation by a few km. Another is that in the lower stratosphere to the troposphere, the theoretical value of ozone decreases rapidly whereas the observed value keeps nearly a constant value.

The first point is due to the incomplete treatment of the pure oxygen theory, ignoring trace constituents other than  $O$ ,  $O_2$  and  $O_3$ , which will be described in detail below. The second point is due to the transport of ozone within the stratosphere and into the troposphere. Photochemical lifetime of stratospheric  $O_3$  is the order of 10 min at the altitude of 45 km and the diurnal cycle is observed. On the

**Fig. 8.1** Comparison of vertical ozone profiles calculated by the pure oxygen atmosphere theory (Chapman mechanism) and by observation (Adapted from Shimazaki et al. 1987)



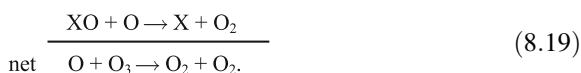
other hand, the lifetime is more than a few days at the altitude of 20 km, so that it is necessary to consider the effect of transport in order to reproduce the  $O_3$  distribution at the lower altitude than this. In the lower stratosphere, the decrease rate of  $O_3$  density with the decrease of altitude is much smaller than calculated by the photo-equilibrium due to the descending  $O_3$  from the ozone layer at the higher altitude. The deviation of  $O_3$  density at lower altitude than the lower stratosphere in Fig. 8.1 is due to this reason.

## 8.2 Ozone Loss Cycles by Trace Constituents

Although the vertical profile of stratospheric ozone given by the pure oxygen theory had been thought to be correct for nearly 30 years since advocated by Chapman in 1930, a more accurate rate constant of the reaction (8.3) was obtained in 1960s, and by using the updated value, it was revealed that the profile by the pure oxygen theory over-predicted by about a factor of two as seen in Fig. 8.1. Since the other rate constants related to the pure oxygen theory,  $j_{8.1}$ ,  $k_{8.2}$ ,  $j_{8.4}$  were thought to be accurate, it implied that there is a chemical reaction other than reaction (8.3) to destruct  $O_3$ . As described in sect. 7.1, a chain reaction is a prerequisite process for the trace species to affect the higher concentration of  $O_3$ . The possibility of such a chain reaction was first suggested regarding the effect of water vapor on the upper atmosphere by Bates and Nicolet (1950), but it was at the end of 1960s to the beginning of 1970s when it were investigated more in detail. The importance of nitrogen oxides for stratospheric ozone was then proposed by Crutzen (1970), and further the relevance of chlorine was pointed by Stolarski and Cicerone (1974) and Wofsy and McElroy (1974). The stratospheric ozone chemistry research in those days was reviewed by Nicolet (1975). Among the research on ozone dissipation by trace gases in those days, the advocate based on atmospheric chemistry by Johnston (1971) on the possibility of ozone destruction by oxides of nitrogen emitted from

supersonic stratospheric transport (SST) is particularly important, since it opened human's eyes to the impact of anthropogenic activity on the stratosphere for the first time. Although the flight of SST was not realized, the followed advocacy of the possibility of ozone destruction by chlorofluorocarbons (CFCs) by Molina and Rowland (1974) was actually realized, as will be seen in sects. 8.3 and 8.4, which has had a large impact on the real world by resulting the prohibition of manufacturing of CFCs by an international agreement called the Montreal Protocol.

As for the chain reactions contributing the dissipation of ozone in the stratosphere, there are three processes called  $\text{HO}_x$ ,  $\text{NO}_x$ , and  $\text{ClO}_x$  cycles, which can be written formally as,



In the  $\text{HO}_x$ ,  $\text{NO}_x$ , and  $\text{ClO}_x$  cycles, OH, NO, and Cl mainly act as X, respectively, and play a role in causing  $\text{O}_3$  dissipation as a net reaction, the same as reaction (8.3).

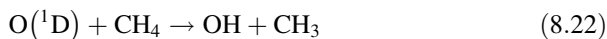
### 8.2.1 Hydrogen Containing Species and $\text{HO}_x$ Cycle

The sources of active species containing H atom like OH,  $\text{HO}_2$ , etc. in the stratosphere are  $\text{H}_2\text{O}$ ,  $\text{H}_2$ , and  $\text{CH}_4$ . Although water vapor ( $\text{H}_2\text{O}$ ) exists at 0.1–1 % in the troposphere, the vapor pressure drops when it passes through the cold tropopause (at 195 K, above tropics), and the mixing ratio of water vapor in the stratosphere is typically 5–6 ppmv. It should be noted, however, the half of  $\text{H}_2\text{O}$  present in the stratosphere is that produced in situ by the oxidation of  $\text{CH}_4$ . Stratospheric  $\text{H}_2\text{O}$  is a source of OH by the reaction with  $\text{O}(^1\text{D})$  formed in the photolysis of  $\text{O}_3$  just the same as in the troposphere (Sect. 5.1.4).

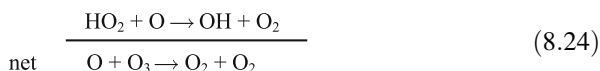


Meanwhile, the mixing ratio of troposphere-origin  $\text{H}_2$ , is about the same as in the troposphere, ca. 0.55 ppmv in the lower stratosphere, and it decreases to ca. 0.4 ppmv above 30 km in the upper stratosphere (Brasseur and Solomon 2005). Similarly, the mixing ratio of troposphere-origin  $\text{CH}_4$  is ca. 1.8 ppmv at the tropopause, nearly the same as in the troposphere, and it decreases rapidly within the stratosphere to ca. 0.3 ppmv in the upper stratosphere (Brasseur and Solomon 2005). Neither of  $\text{H}_2$  nor  $\text{CH}_4$  is photolyzed in the stratosphere but they reacts to form OH by the reaction with  $\text{O}(^1\text{D})$  similar to  $\text{H}_2\text{O}$  (see Sect. 5.1.6 for  $\text{CH}_4$ ).

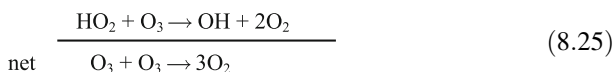
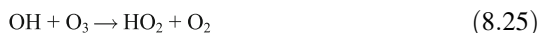




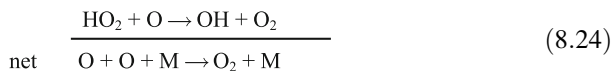
From  $\text{CH}_3$  formed in reaction (8.22), H, HCO,  $\text{H}_2$  and CO are produced via HCHO in the similar reaction process as in the troposphere mentioned in Chap. 7, sect. 7.1. The H and HCO are then transformed to  $\text{HO}_2$  by the reaction with  $\text{O}_2$ , and they constitute ozone dissipation cycle in the stratosphere.



In the lower stratosphere (<30 km) where the O atom concentration is low, the chain reaction,



is more important, while in the upper stratosphere (>40 km) where the O atom concentration is high, the chain reaction,

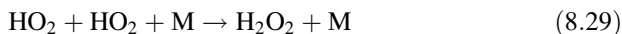


also operates for dissipating the odd oxygen  $\text{O}_x$ . The sum of H, OH and  $\text{HO}_2$  is called odd hydrogen family,  $\text{HO}_x$ , and the above chain cycles are collectively called  $\text{HO}_x$  cycle.

The main termination reaction of the  $\text{HO}_x$  cycle (Sect. 5.3.5) is,



while the reaction,

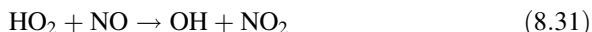


is not effective since the formed  $\text{H}_2\text{O}_2$  is photolyzed (Sect. 4.2.8) rapidly in the stratosphere,

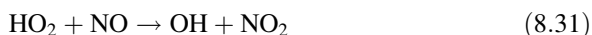


In the lower stratosphere, the reaction of  $\text{HO}_2$  with NO (Sect. 5.3.2),



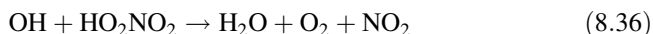
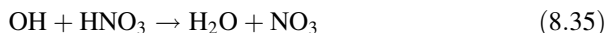
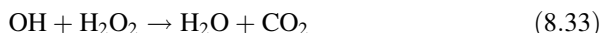


is also important competing with the above reaction (8.25) with  $\text{O}_3$ . While this reaction is the most important reaction to produce  $\text{O}_3$  in the troposphere (Sects. 7.3.1 and 7.3.2), it forms a chain cycle combining with the  $\text{HO}_x$  cycle in the stratosphere as,



When the both sides of the equations are summed up, they are cleared to leave nothing, which means nothing happens. This kind of chain reaction is called “null cycle”, where null means zero in German. In the null cycle neither net production nor destruction of ozone occurs.

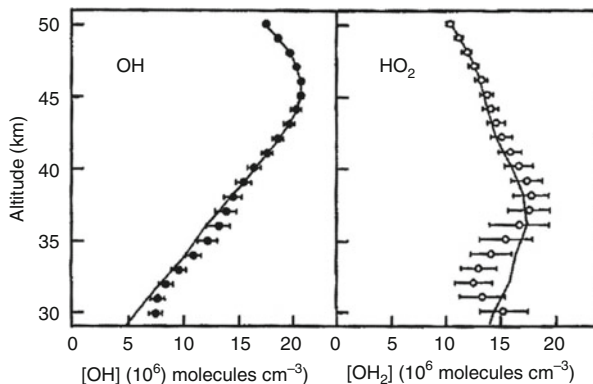
Furthermore in the lower stratosphere, the reactions,



are also important as loss processes of OH in addition to reactions with O,  $\text{O}_3$  and  $\text{HO}_2$ .

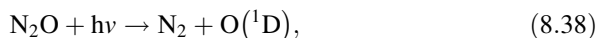
Figure 8.2 shows a comparison of satellite observation and model calculation for the vertical profiles of OH and  $\text{HO}_2$  above Fairbanks, Alaska ( $65^\circ\text{N}$ ) in 1997 (Jucks et al. 1998). As shown in the figure, the maximum densities of [OH] and [ $\text{HO}_2$ ] are  $2 \times 10^7$  and  $1.8 \times 10^7$  molecules  $\text{cm}^{-3}$  at the altitude of 45 km and 35–40 km, respectively, and [ $\text{HO}_x$ ] as their sum has maximum value of  $3.4 \times 10^7$  molecules  $\text{cm}^{-3}$  in the upper stratosphere at 40–45 km. The model calculation using the rate constants given by the NASA/JPL evaluation No. 12 (DeMore et al. 1997) agrees well with the vertical profile of OH density in the whole stratosphere, while that for  $\text{HO}_2$  agrees well in the upper stratosphere, but overestimate its density about 30 % in the lower stratosphere. The observed ratio of [ $\text{HO}_2$ ]/[OH] is  $<1$  in the upper stratosphere, and  $\sim 2$  at the altitude of 30 km.

**Fig. 8.2** Comparison of satellite observation in 1977 (symbols) and model calculation (solid lines) for the vertical profiles of the OH and HO<sub>2</sub> mixing ratios in the stratosphere over Fairbanks, Alaska (Adapted from Jucks et al. 1998)

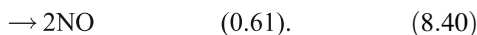
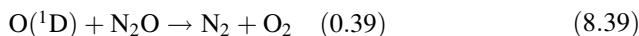


### 8.2.2 Nitrogen Containing Species and NO<sub>x</sub> Cycle

The source of active nitrogen, NO, NO<sub>2</sub>, etc. in the stratosphere is N<sub>2</sub>O of tropospheric origin. The mixing ratio of N<sub>2</sub>O in the stratosphere is kept as about 320 ppbv of the tropospheric value up to the altitude of 20 km, and it decreases rapidly to about 20 ppbv at 40 km (Brasseur and Solomon 2005; Seinfeld and Pandis 2006). The 90 % of this rapid decrease is due to the photolysis (Sect. 4.3.4),

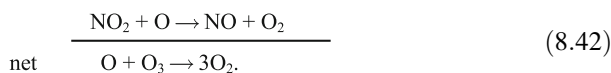


and the rest is mainly due to the reaction with O(<sup>1</sup>D) (Sect. 5.1.5) formed in the photolysis of O<sub>3</sub>,



The NO formed in reaction (8.40) is the main source of NO<sub>x</sub> in the stratosphere. The recommended value for the branching ratio of reaction (8.40) is 0.61 by the NASA/JPL panel evaluation No. 17 (Sander et al. 2011) (see Sect. 5.1.5).

The NO formed in the stratosphere reacts with O<sub>3</sub> to be converted to NO<sub>2</sub>, and NO<sub>2</sub> returns to NO by reacting with O atoms, which results in net O<sub>3</sub> loss as,



Typical conversion time for the NO to NO<sub>2</sub> by reaction (8.41) in the stratosphere is about 1 min, and that of NO<sub>2</sub> to NO by reaction (8.42) is about 10 min. In stratospheric chemistry the nitrogenous species including N<sub>2</sub>O<sub>5</sub>, HNO<sub>3</sub>, ClONO<sub>2</sub>, etc. in addition to NO and NO<sub>2</sub>, are called odd nitrogen family, NO<sub>x</sub>,

and chain reaction including these species is called  $\text{NO}_x$  cycle. It should be noted the definition of  $\text{NO}_x$  here is different from in tropospheric chemistry where  $\text{NO}_x$  is defined as  $\text{NO} + \text{NO}_2$ . The chain reaction consisting of reaction (8.41) and (8.42) occurs in high efficiency in the upper stratosphere where the concentration of O atoms are high. When the photolysis of  $\text{NO}_2$  competes reaction (8.42),



a series of the processes,

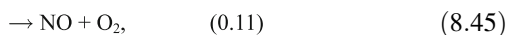
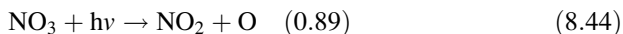


forms null cycle, and net loss of  $\text{O}_3$  does not occur.

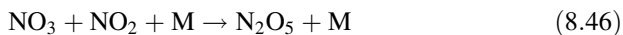
Another reaction between  $\text{NO}_x$  and  $\text{O}_x$ ,



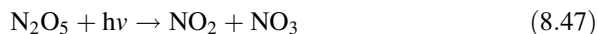
produces  $\text{NO}_3$ , but  $\text{NO}_3$  is photolyzed very rapidly during the daytime (Sect. 4.2.4),



and dissipates within a few seconds. The branching ratio of photolytic reaction (8.44) and (8.45) is known to depend on wavelength and temperature, it is deduced to be about 9:1 under the stratospheric conditions (Sander et al. 2011). The net sequence of reaction (8.41) and (8.44) corresponds to the photolysis of  $\text{O}_3$ . In the nighttime,  $\text{NO}_3$  is stable, and further react with  $\text{NO}_2$  to form  $\text{N}_2\text{O}_5$  (Sect. 5.5.2).



The produced  $\text{N}_2\text{O}_5$  is dissipated by the photolysis in the daytime (Sect. 4.2.4),



As for the photolytic process, reaction (8.47) is known to be the main route but reaction (8.48) also proceeds partly under the stratospheric conditions (Atkinson et al. 2004; Sander et al. 2011). The heterogeneous reactions of  $\text{N}_2\text{O}_5$  on ice particle of polar stratospheric clouds (PSC) (Sects. 6.1.5 and 6.5.1),

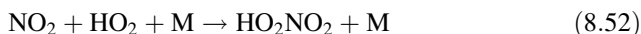
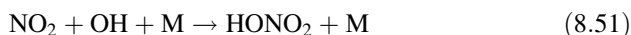


will be discussed in the next section. In contrast the thermal decomposition reaction of  $\text{N}_2\text{O}_5$  (Sect. 5.5.2),

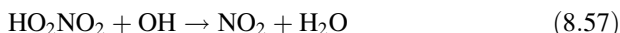
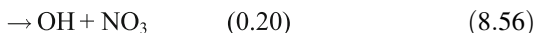
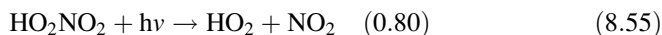
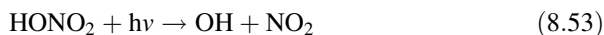


is not important in general in the stratosphere since the temperature low.

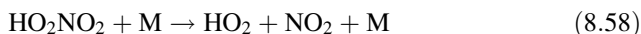
As for the loss process of  $\text{NO}_2$  in the stratosphere, cross reactions with  $\text{HO}_x$  cycle mentioned in the previous section,



are the most important (Sects. 5.2.4 and 5.3.4). Particularly,  $\text{HONO}_2$  ( $=\text{HNO}_3$ ) is an important reservoir of  $\text{NO}_x$  in the lower stratosphere, and reaction (8.51) is important as a termination reaction of the  $\text{HO}_x$  and  $\text{NO}_x$  cycles. Also,  $\text{HO}_2\text{NO}_2$  formed in reaction (8.52) exists as an important reservoir of  $\text{NO}_x$  since it is thermally stable in the lower and middle stratosphere where the temperature is low. The chemical loss processes of  $\text{HONO}_2$  and  $\text{HO}_2\text{NO}_2$  are the photolysis and reaction with OH (Sect. 5.2.5 for  $\text{HONO}_2$ ).

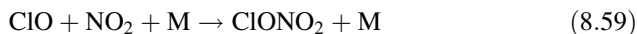


The thermal decomposition of  $\text{HO}_2\text{NO}_2$  (Sect. 5.3.4),



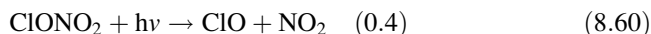
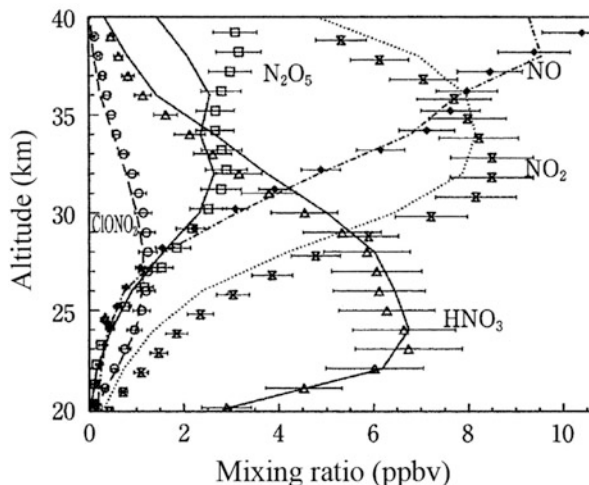
is not important in general due to the low temperature.

Other than these processes, the production of  $\text{ClONO}_2$  by the cross reaction of  $\text{NO}_2$  with the main carrier ClO (Sect. 5.3.4) of  $\text{ClO}_x$  cycle mentioned later, is important as the reservoir of  $\text{NO}_x$ .



The dissipating reaction of  $\text{ClONO}_2$  is mainly photolysis (Sect. 4.4.2),

**Fig. 8.3** Comparison of balloon observation (*symbols*) and model calculation (*lines*) for the vertical profiles of odd nitrogen ( $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_3$ ,  $\text{ClONO}_2$ ) mixing ratio in the stratosphere at dawn over New Mexico, US (Adapted from Seinfeld and Pandis 2006 based on Sen et al. 1998)



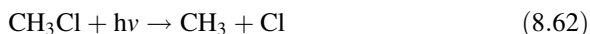
The heterogeneous reaction of  $\text{ClONO}_2$  in the polar region will be described in sect. 8.4.

Figure 8.3 depicts the comparison between the observed vertical profiles of odd nitrogen compounds ( $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_3$ ,  $\text{ClONO}_2$ ) in the stratosphere obtained by an FTIR (Fourier transform infrared spectrometer) loaded on a balloon in New Mexico, United States, in autumn 1993, and 24 h-averaged calculated values assuming photochemical equilibrium (Sen et al. 1998). As shown in the figure, the mixing ratio of  $\text{NO}$  in the mid-latitude increases from ca. 0.1 ppbv at 20 km to ca. 10 ppbv at 40 km by a factor of 100. On the other hand, the mixing ratio of  $\text{NO}_2$  increases from ca. 1 ppbv at 20 km to the maximum of ca. 8 ppbv at 30–35 km, and then decreases at the higher altitude to ca. 5 ppbv at 40 km. In the lower and mid-latitude, the most part of  $\text{NO}_x$  exists as  $\text{HNO}_3$  and its mixing ratio is ca. 3 ppbv at 20 km, maximizes to ca. 6 ppbv at around 23 km, and then decreases rapidly at the higher altitude than 30 km. The mixing ratio of  $\text{N}_2\text{O}_5$  is the highest at higher than 30 km, but shows a large diurnal cycle, high in the nighttime and low in the daytime (Brasseur and Solomon 2005). The largest mixing ratio at dawn shown in Fig. 8.3 is ca. 3 ppbv over 30 km, which is about 20 % of  $\text{NO}_x$  and decrease to 5–10 % in the daytime average. The mixing ratio of  $\text{ClONO}_2$  shows the maximum of ca. 1 ppbv at 25–30 km. The total amount of odd nitrogen is almost constant at ca. 18 ppbv at higher altitude than 30 km, and decreases to ca. 10 and 3 ppbv at 25 and 20 km, respectively (Sen et al. 1998). As shown in Fig. 8.3, the calculation assuming the photo-equilibrium reproduces the absolute values and vertical profiles of mixing ratios of  $\text{NO}_x$  well, suggesting that the reaction system of  $\text{NO}_x$  chemistry in the stratosphere is understood fully. Within the ozone hole where PSC develops,  $\text{N}_2\text{O}_5$  and  $\text{HNO}_3$  are removed almost completely from the gas phase by

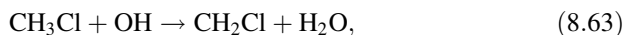
heterogeneous reactions, and it should be noted that the profile of  $\text{NO}_x$  is largely different from Fig. 8.3. The stratospheric reaction chemistry relevant to PSC within the ozone hole is described in sect. 8.4.

### 8.2.3 Chlorine Containing Species and $\text{ClO}_x$ Cycle

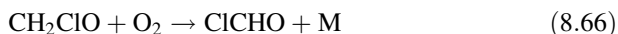
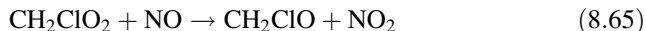
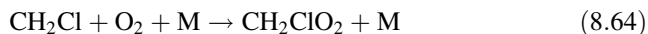
Among the halogen compounds emitted in the troposphere, marine origin  $\text{CH}_3\text{Cl}$  has the relatively long atmospheric lifetime of 1.5 years (Brasseur and Solomon 2005), and partly reaches to the stratosphere to become a Cl atom source in the natural stratosphere. The mixing ratio of  $\text{CH}_3\text{Cl}$  in the clean troposphere is ca. 550 ppbv, and it is thought to intrude into the stratosphere with this mixing ratio. From  $\text{CH}_3\text{Cl}$  molecules reached to the stratosphere, Cl atoms and chloromethyl radical are formed by photolysis (Sect. 4.3.8),



and reaction with OH,



respectively. The  $\text{CH}_2\text{Cl}$  formed in reaction (8.63) is the alkyl-type radical, and it proceeds through the following reaction processes,



to produce formyl chloride (ClCHO). From formyl chloride, Cl atoms are released by the similar type of photolysis as formaldehyde,



The Cl atoms released by reactions (8.62) and (8.67) react mainly with  $\text{O}_3$ ,

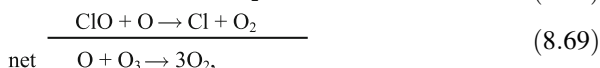


to form ClO radicals (Sect. 5.6.1). As for the reaction of ClO, the reactions with O atoms (Sect. 5.1.3) and NO in the upper and lower stratosphere are important, respectively.

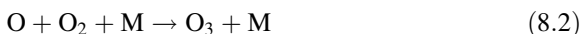




Reactions (8.68) and (8.69) forms an O<sub>3</sub> dissipation cycle,

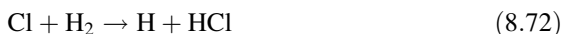


and reactions (8.68) and (8.70) forms a null cycle,



Here, the active chlorine family, Cl, ClO, HOCl and ClONO<sub>2</sub>, is called ClO<sub>x</sub>, and the chain reaction consisting of them is called the ClO<sub>x</sub> cycle. The rate determining steps of the above two ClO<sub>x</sub> cycles are ClO + O and ClO + NO, respectively, and the contributions of these two ClO<sub>x</sub> cycles at the altitude of 40 km in the upper stratosphere are calculated to be nearly equal, based on the mixing ratios of [O] and [NO], and their rate constants (Seinfeld and Pandis 2006).

The Cl atoms, a chain carrier of ClO<sub>x</sub> cycles, react with species other than O<sub>3</sub> to form HCl,

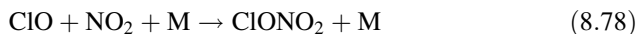


The main loss processes of HCl are photolysis (Sect. 4.4.3) and reaction with OH and O(<sup>1</sup>D),

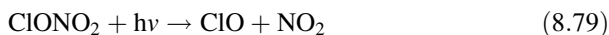


However, since the rate constants of these reactions are not very large, reactions (8.71), (8.72) and (8.73) act as the effective chain termination reactions, and HCl becomes the most important reservoir of ClO<sub>x</sub> in the stratosphere.

As for the reaction of ClO, another chain carrier of the ClO<sub>x</sub> cycle, the reaction with NO<sub>2</sub> (Sect. 5.6.5) is the most important, except the reactions with O and NO mentioned above.

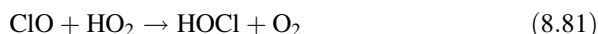


Although a major loss process of  $\text{ClONO}_2$  is the photolysis (Sect. 4.4.2),



the photolytic rate is not very large, so that  $\text{ClONO}_2$  becomes an important reservoir in the mid-stratosphere. As shown later, the amount of  $\text{ClONO}_2$  is about 50 % of  $\text{HCl}$  at 25–30 km as a reservoir of  $\text{ClO}_x$ , and  $\text{ClO}_x$  exists almost exclusively as  $\text{HCl}$  at  $\geq 30$  km.

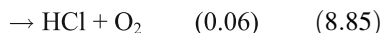
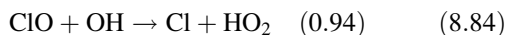
Other than these reactions, the reaction of  $\text{ClO}$  with  $\text{HO}_2$  (Sect. 5.6.4),



is important as an  $\text{HOCl}$  forming reaction. Since  $\text{HOCl}$  is easily photolyzed by visible light (Sect. 4.4.4),



it cannot be an effective reservoir. However, the mixing ratio of  $\text{HOCl}$  gets higher in the stratosphere of polar night, and its heterogeneous reactions are important together with those of  $\text{ClONO}_2$ . Other than these reactions, photolysis of  $\text{ClO}$  itself (Sect. 4.4.5) and reaction with  $\text{OH}$  (Sect. 5.6.3) have to be considered.



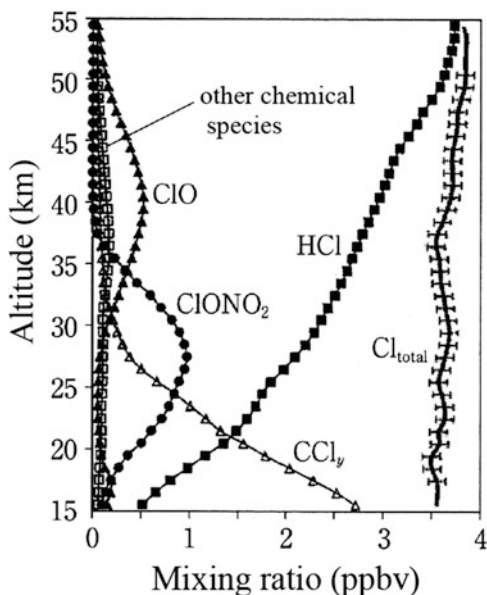
Although the ratio of reaction (8.85) is small, it affects to decrease the  $[\text{ClO}]/[\text{HCl}]$  ratio in the upper stratosphere.

Figure 8.4 depicts the observed vertical profiles of chlorine species in the mid-latitude (30–60°N) stratosphere obtained by satellite observation in 2004 (WMO 2007). As shown in the figure, the mixing ratio of total  $\text{Cl}$  is ca. 3.6 ppbv. Since the mixing ratio of the natural source  $\text{Cl}$  is ca. 550 pptv, the rest can be ascribed to the anthropogenic chlorine compounds described in sect. 8.3, which amounts to a few times the natural emission. Among the chlorine compounds,  $\text{HCl}$  is the most abundant, and the mixing ratio increases from ca. 1.5 ppbv at 20 km to ca. 3 ppbv at 40 km. Next abundant species is  $\text{ClONO}_2$  which amounts to the maximum mixing ratio of ca. 1 ppbv at 20–30 km. The mixing ratio of  $\text{ClO}$  maximizes at ca. 0.5 ppbv at 35–40 km, and other chlorine species such as  $\text{HOCl}$ , etc. are less than 0.2 ppbv at all altitude.

Accompanying to the increase of the mixing ratio of  $\text{ClO}_x$  due to the increase of anthropogenic chlorine containing compounds, self-reaction between  $\text{ClO}_x$  is getting important, which will be described in sect. 8.3.



**Fig. 8.4** Vertical profiles of active chlorine compounds by the satellite observation in 2004 in the stratosphere at northern hemisphere mid-latitude (30–60°N).  $\text{CCl}_y$  is the total organic chlorine compounds (Adapted from WMO 2007)

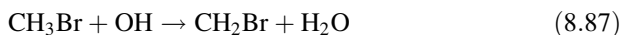
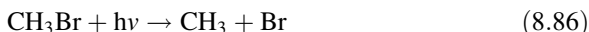


### 8.2.4 Reactions of Other Halogen (Bromine, Iodine, Fluorine) Compounds

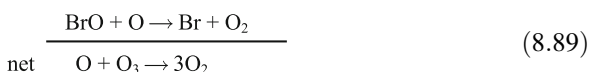
Other than chlorine, halogen compounds containing bromine, iodine and fluorine are present in the stratosphere. Among these, the most important from the point of ozone depletion is bromine. Although iodine also forms an ozone-destroying chain cycle, its impact is limited since its mixing ratio is low. In contrast, fluorine does not constitute such a chain cycle due to its reactivity, and does not contribute to ozone destruction.

**Bromine** The most important bromine compound of natural origin is  $\text{CH}_3\text{Br}$  from marine organisms as with  $\text{CH}_3\text{Cl}$ . The mixing ratio of  $\text{CH}_3\text{Br}$  in the clean troposphere is ca. 10 pptv, and since the atmospheric lifetime is ca. 1.5 years, nearly the same as  $\text{CH}_3\text{Cl}$ , bromine is thought to be present in the natural stratosphere with this mixing ratio (Brasseur and Solomon 2005). In spite of the fact that the mixing ratio of Br is only one 50<sup>th</sup> of Cl in the natural stratosphere, the impact of Br on ozone dissipation is thought to be comparable to Cl. The reason is ascribed to the very efficient ozone destructing chain cycle of Br as compared to Cl.

After reaching to the stratosphere,  $\text{CH}_3\text{Br}$  releases Br atoms by photolysis (Sect. 4.3.8) and reaction with OH.



The rate constant of the OH reaction (8.87) is about the same as for CH<sub>3</sub>Cl (Table 5.2), but the absorption cross section of CH<sub>3</sub>Br at the solar ultraviolet region in the stratosphere (around 200 nm) is about a few tens of times larger than CH<sub>3</sub>Cl (Fig. 4.32), the release of Br by th0065 photolysis occurs at much faster rate than CH<sub>3</sub>Cl. This is one of the reasons that the chain cycle of Br is efficient for the ozone destruction. Since the Br atoms released into the stratosphere react with O<sub>3</sub> and the formed BrO reacts with O atoms to regenerate Br, the BrO<sub>x</sub> cycle is formed to dissipate O<sub>3</sub> just like the ClO<sub>x</sub> cycle.



Other than the reaction with O atoms, BrO reacts with NO and OH to regenerate Br,



However, the more important Br regenerating process is the photolysis of BrO itself,



Since BrO has a large absorption cross section in wavelength regions longer than 300 nm (Fig. 4.40), the conversion efficiency from BrO to Br by photolysis is much higher than in the case of ClO photolysis to give Cl.

On the other hand, the formation of HBr by the reaction of Br and HO<sub>2</sub>,

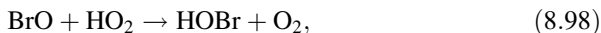
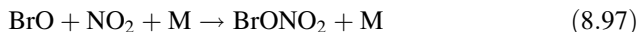


is important as the chain termination reaction of the BrO<sub>x</sub> cycle. Since Br does not react with CH<sub>4</sub> and H<sub>2</sub>, the above reaction is the major process to form HBr. The produced HBr returns to Br rather efficiently by the photolysis and reactions with OH and O(<sup>1</sup>D),



Therefore, HBr cannot be an important reservoir, and the efficiency of reaction (8.93) for the chain termination of the BrO<sub>x</sub> cycle is not very high.

Another chain termination reaction of BrO operates with NO<sub>2</sub> and HO<sub>2</sub> similar to the case of ClO,



to form BrONO<sub>2</sub> and HOBr. However, both of BrONO<sub>2</sub> and HOBr are photolyzed (Sects. 4.4.2 and 4.44.4) with high rates,



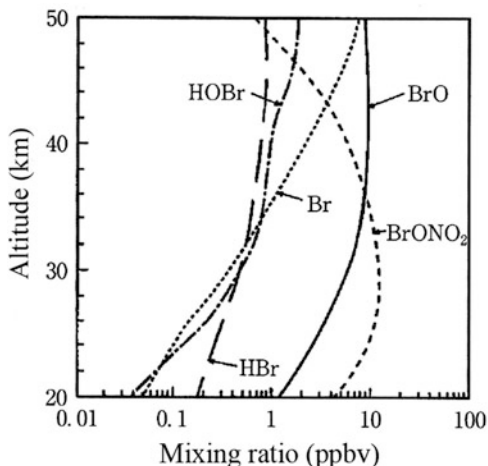
they cannot be effective reservoirs and the efficiency of reactions (8.88) and (8.89) as chain termination are also low. Thus, the low effectiveness of the chain termination reactions is another reason for the high efficiency of the BrO<sub>x</sub> cycle and enhances the importance of Br in the ozone destruction reaction even though the mixing ratio is relatively low. The BrONO<sub>2</sub> and HOBr are stable in the absence of solar radiation, and play an important role in the multiphase chain reaction system including heterogeneous reactions on PSC together with ClONO<sub>2</sub> and HOCl in the stratospheric polar night, which will be mentioned in the next section.

The mixing ratio of bromine compounds in the present day stratosphere is ca. 20 pptv, which is less than one 150th of chlorine compounds whose mixing ratio is ca. 3.5 ppbv. Since the mixing ratio of Br from natural origins is ca. 10 pptv, this means that anthropogenic Br compounds intrude into the stratosphere in about the same amount as CH<sub>3</sub>Br from the natural source. With the increase of the emissions of anthropogenic halocarbons, the cross reactions between ClO<sub>x</sub> and BrO<sub>x</sub> are getting important, and will be described in sect. 8.3.

Figure 8.5 shows the vertical distribution of active bromine compounds in 24-h average at 30°N obtained by the model calculation (McElroy 2002). Summing up all these compounds, the total mixing ratio of bromine in the stratosphere is ca. 20 pptv, as mentioned earlier. Among BrO<sub>x</sub>, BrO and BrONO<sub>2</sub> are the most abundant, at ca. 10 pptv each, at the altitudes higher and lower than 35 km, respectively. Meanwhile, the mixing ratio of Br atoms increases with the altitude monotonically, and reaches to ca. 10 pptv, nearly the same as BrO at the stratopause. The mixing ratio of HBr is very low, less than 1 pptv, implying that it does not act as an effective Br reservoir, being different from HCl in the case of Cl. The mixing ratio of HOBr is less than 1 pptv in the upper stratosphere, and even decreases further at altitudes of less than 30 km.

**Iodine** Although several biogenic iodine compounds are emitted from natural sources, their photolytic lifetime in the troposphere is short, e.g. only a few days even for the relatively long-life species like CH<sub>3</sub>I (Brasseur and Solomon 2005). Therefore, in general, it is thought that tropospheric CH<sub>3</sub>I does not intrude into the stratosphere. However, it has been suggested that strong updraft in the tropics could

**Fig. 8.5** Vertical profiles of active bromine compounds in the stratosphere by model calculation in 24-h average at 30°N (Adapted from McElroy 2002)



rapidly transport  $\text{CH}_3\text{I}$  near the sea-surface to the stratosphere, and may further cause dissipation of  $\text{O}_3$  (Solomon et al. 1994).

Iodine atoms are released from  $\text{CH}_3\text{I}$  and reach to the stratosphere by rapid photolysis (Sect. 4.3.8).



The reactions of I atoms are similar to Br, e.g. with  $\text{O}_3$ ,



However, the photolysis rate of formed IO (Sect. 4.3.4) is very large,



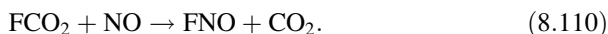
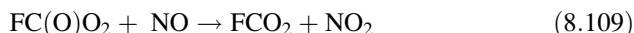
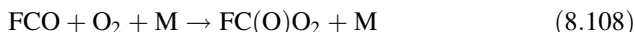
and together with reactions,



they compose the  $\text{IO}_x$  cycle resulting from  $\text{O}_3$  destruction. Since the intermediates such as  $\text{IONO}_2$  and  $\text{HOI}$  formed in the reactions of IO with  $\text{NO}_2$  and  $\text{HO}_2$  are photolyzed more rapidly than  $\text{BrONO}_2$  and  $\text{HOBr}$ , they do not work as termination reactions, and the chain reaction is characterized by very high efficiency.

**Fluorine:** Among halogens, fluorine is very different from Cl, Br and I in respect that it does not cause  $\text{O}_3$  dissipation. Fluorine is transported to the stratosphere in the form of anthropogenic CFCs and HCFCs as described in the following section, and also as  $\text{CF}_4$  and hydrofluorocarbons (HFCs). From the decomposition processes

of these compounds (see sect. 8.3),  $\text{COF}_2$ ,  $\text{COFCl}$ , etc. are formed, and their photolysis and the succeeding reactions give F atoms and other reactive species,



The rate constants of reactions (8.108), (8.109) and (8.110) at 296 K have been obtained by Wallington et al. (1994) as  $k_{8.108} = (1.2 \pm 0.2) \times 10^{-12}$ ,  $k_{8.109} = (2.5 \pm 0.8) \times 10^{-11}$ ,  $k_{8.110} = (1.3 \pm 0.7) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively, and they are all known to be fast reactions.

The rate constant of the reaction of F atoms and  $\text{O}_3$ ,



is  $k_{8.111}(298 \text{ K}) = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which is about the same as  $k_{8.68}(298 \text{ K}) = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reaction of  $\text{Cl} + \text{O}_3$ . However, in case of F, the reaction of F atom with the atmospheric major component,  $\text{O}_2$ ,



has the equilibrium constant  $K_{8.112}(298 \text{ K}) = 3.7 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1}$ , which is much larger than that for Cl,  $2.9 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1}$  (Sander et al. 2011), so that the equilibrium between F and  $\text{FO}_2$  inclines to  $\text{FO}_2$  to give  $[\text{FO}_2]/[\text{F}] \sim 10^4$ . Therefore, the reaction of  $\text{F} + \text{O}_3$  is much less important than the reaction with  $\text{O}_2$ . Meanwhile, F atoms react with  $\text{CH}_4$ ,  $\text{H}_2\text{O}$  and  $\text{H}_2$  with rate constants of the order of  $\sim 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Sander et al. 2011) to form HF.



Since the bond dissociation energy of H-F is very large ( $D_{298} = 568 \text{ kJ mol}^{-1}$ ), HF is photochemically stable and toward reactions becomes a very stable reservoir so it is eventually transported to the troposphere and washed away by precipitation.

The  $\text{FO}_2$  formed by reaction (8.112) does not react with  $\text{O}_3$ , and its main reactions are thought to be,





(Wallington et al. 1995; Burley et al. 1993).

Although FO formed by the reaction of F atoms and O<sub>3</sub> can react with NO and O to regenerate F (Sander et al. 2011),



F atoms are mostly removed as HF from the reaction system, and O<sub>3</sub> destruction cycle by F does not have an effect.

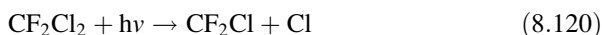
The abundance of F compounds in the stratosphere has been obtained as 1.2 ppbv by satellite observations as of 1985, and most compounds are present as HF at the altitude of higher than 30 km (Zander et al. 1992).

### 8.3 Gas Phase Chain Reactions and Ozone Depletion by CFCs

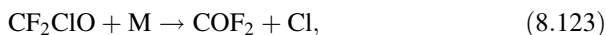
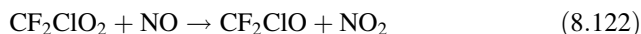
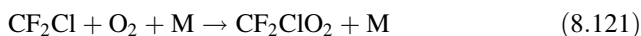
While the HO<sub>x</sub>, NO<sub>x</sub> and ClO<sub>x</sub> cycles, which tend to decrease O<sub>3</sub> mixing ratios in the stratosphere, are naturally occurring chemical reactions caused by trace species of natural origin, Molina and Rowland (1974) advocated the possibility of the depletion of the ozone layer by anthropogenic chlorofluorocarbons (CFCs) adding large amount of Cl to the stratosphere. The CFCs are the carbon compounds containing only chlorine and fluorine in a molecule and they are all anthropogenic. Since they undergo neither photolysis nor reactions with active species such as OH, etc., they have no sink in the troposphere, and all reached to the stratosphere where they are photolyzed to release Cl atoms. There are many other anthropogenic substances causing ozone destruction in the stratosphere, such as hydrochlorofluorocarbon (HCFCs) containing hydrogen in addition to chlorine and fluorine in a molecule, 1, 1, 1-trichloroethane (CH<sub>3</sub>CCl<sub>3</sub>), carbon tetrachloride (CCl<sub>4</sub>), and bromochlorofluorocarbons (halon) containing bromine, chlorine and fluorine in a molecule (WMO 2011; Brasseur and Solomon 2005). They are collectively called halocarbons. The atmospheric lifetime of the species that do not have a hydrogen atom in a molecule, such as CFCs, halons, CCl<sub>4</sub>, etc., are determined by the photolysis rate in the stratosphere and are in general very long, a few tens to more than 100 years. Since the hydrogen containing species like HCFCs and CH<sub>3</sub>CCl<sub>3</sub> are consumed by the reaction with OH in the troposphere, their atmospheric lifetimes are shorter, a few to ten-odd years comparable to CH<sub>4</sub>, but they also reach to the stratosphere and release Cl atoms to take part in the ozone depletion (Brasseur and Solomon 2005). Among CFCs, the mixing ratios of

$\text{CF}_2\text{Cl}_2$  (CFC-12) and  $\text{CFCl}_3$  (CFC-11) are the highest, ca. 540 and 240 ppbv in 2008, respectively, followed by 190 and 90 ppbv of other anthropogenic chlorine-containing compounds,  $\text{CHF}_2\text{Cl}$  (HCFC-22) and  $\text{CCl}_4$ , respectively. The total amount of chlorine in the stratosphere is ca. 3.5 ppbv, including 550 ppbv of natural origin  $\text{CH}_3\text{Cl}$  (WMO 2011). Similarly, as for anthropogenic bromine compounds,  $\text{CF}_2\text{ClBr}$  (halon-1211) and  $\text{CF}_3\text{Br}$  (halon-1301) have the highest mixing ratios, ca. 4.3 and 3.2 pptv, respectively. The total bromine mixing ratio is ca. 20 pptv by adding these halons, and  $\text{CH}_3\text{Br}$  at ca. 10 pptv which is from both natural and anthropogenic origins (WMO 2011).

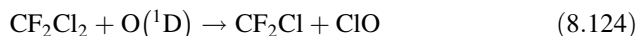
Ultraviolet radiation with 200–220 nm reaches to the altitude of 30–40 km in the middle stratosphere, which is called the “atmospheric window” of the stratosphere (see Chap. 4, sect. 4.1). The absorption spectra of CFCs, HCFCs and halons have large cross section around 200 nm (Figs. 4.33, 4.34, and 4.35) and match with the atmospheric window resulting efficient photolysis. For example, CFC-12 is photolyzed to give Cl atoms.



Simultaneously formed  $\text{CF}_2\text{Cl}$  is an alkyl type radical, and the succeeding processes release another Cl atom,

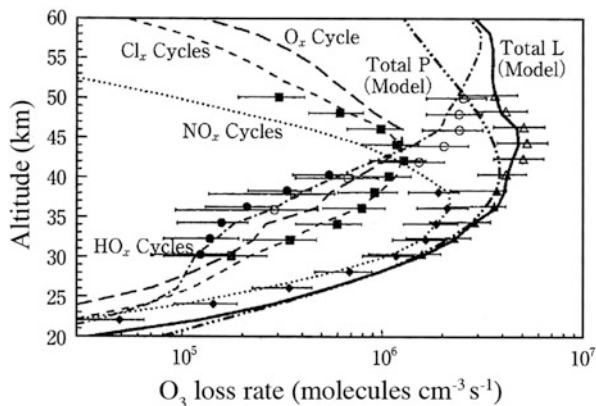


and carbonyl fluoride  $\text{COF}_2$  is produced. In the case of  $\text{CFCl}_3$ , including the photolysis of similarly formed carbonyl chlorofluoride ( $\text{COFCl}$ ), all three Cl atoms are ultimately released. Other than photolysis, CFCs react with  $\text{O}(^1\text{D})$ , and in the case of  $\text{CF}_2\text{Cl}_2$ , the main reaction is,

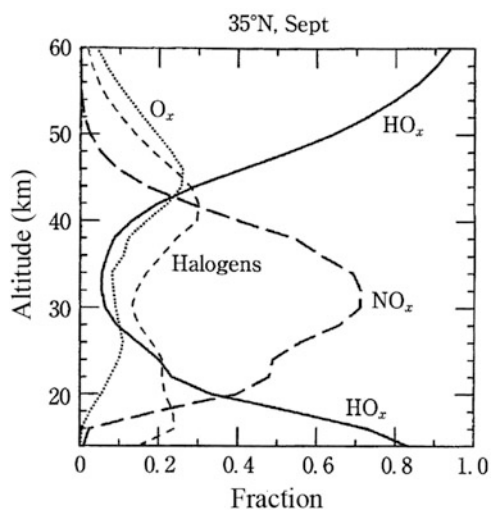


to form  $\text{CF}_2\text{Cl}$  and  $\text{ClO}$ . The release of Br and BrO from halons are similar due to photolysis and the reaction with  $\text{O}(^1\text{D})$ .

Figure 8.6 compares the vertical profiles of the  $\text{O}_3$  destruction rates by each of the  $\text{O}_x$ ,  $\text{HO}_x$ ,  $\text{NO}_x$ ,  $\text{ClO}_x$  and  $\text{BrO}_x$  cycles, calculated by a model considering all the reactions mentioned in Sects. 8.1, 8.2 and in this section, with those values calculated based on the observed values of radicals by a balloon (Osterman et al. 1997). As shown in the figure, these gas phase chain cycles cause large  $\text{O}_3$  destruction above 30 km in the upper stratosphere, and in the middle and lower stratosphere below 30 km the dissipation rate is less than  $2 \times 10^6$  molecules  $\text{cm}^{-3} \text{s}^{-1}$ . Figure 8.7 shows the relative contribution of each cycle to the  $\text{O}_3$  destruction (Osterman et al. 1997). As shown in Fig. 8.7, the contribution of  $\text{HO}_x$  is the most important in the upper stratosphere above 40 km and also in the lower stratosphere



**Fig. 8.6** Comparison of observed (*symbols*) and model calculated (*lines*) vertical profiles of ozone dissipation rate by each cycle of  $O_x$ ,  $ClO_x$ ,  $NO_x$  and  $HO_x$  (Adapted from Seinfeld and Pandis 2006 based on Osterman et al. 1997 updating the reaction rate constants). ●, ○ are the contribution of  $HO_x$  based on different observations, ■, ◆ are the contribution of  $ClO_x$  and  $NO_x$  based on observation, respectively, and ▲, △ are the total dissipation rate from observation and that partly using model calculation for unobserved  $NO_x$ , respectively. — and (2点鎖線) are total dissipation and formation rate of  $O_3$  by model calculation, respectively



**Fig. 8.7** Contributions of  $O_x$ ,  $HO_x$ ,  $NO_x$  and  $ClO_x$  cycles to the ozone depletion by altitude (Adapted from Seinfeld and Pandis 2006 based on Osterman et al. 1997 updating the reaction rate constants)

below 20 km, and  $NO_x$  cycle is the most important in between in the middle stratosphere. Meanwhile, the contribution of halogen cycles ( $ClO_x$ ,  $BrO_x$ ) maximizes at around 40 km.

From these considerations, it has been deduced theoretically that the ozone depletion due to the increase of anthropogenic CFCs and halons occurs in the



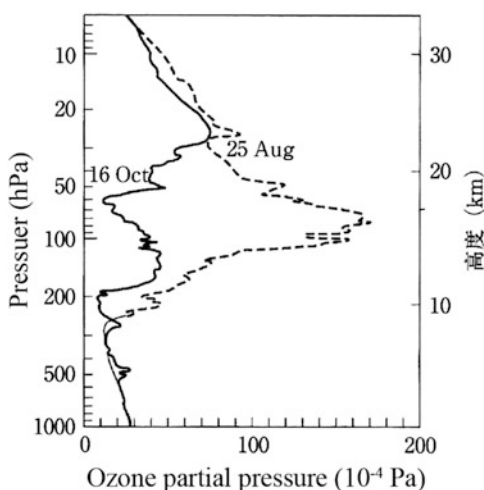
upper stratosphere at 30–35 km at the mid- and low latitude, and the decreased amount of ozone from 1980 to 2004 is 5–10 % (WMO 2007). This value agrees well the observed value of ca. 7 % decrease obtained by satellites and sondes (WMO 2007). In contrast, the more distinct ozone depletion in the lower stratosphere in the polar region, known as the “ozone hole,” is due to the multiphase chain reaction involving PSCs as discussed in the next section.

## 8.4 Heterogeneous Reactions on PSCs and Ozone Hole

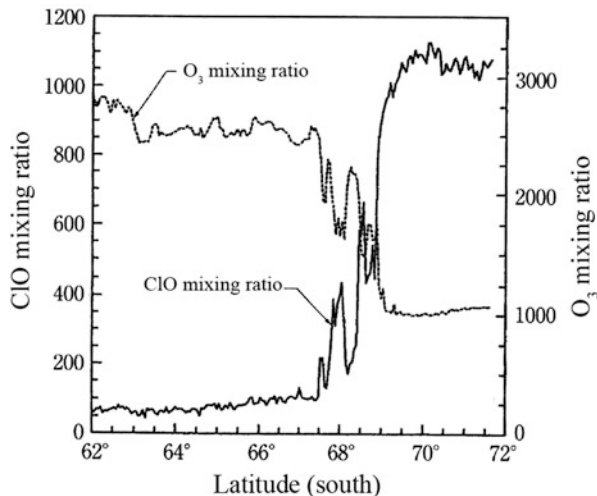
As mentioned in the previous section, ozone depletion by the increase of CFCs and halons had been anticipated to occur at 5–10 % in the 33–35 km altitude region. In contrast, it was discovered surprisingly that the ozone column density in the Antarctic Continent in spring (September–October) decreased to ca. 100 DU (Dobson Unit, 100 DU is equivalent to 1 mm thickness of  $O_3$  at 0 °C, 1 atm) from the normal value of ca. 300 DU (Farman et al. 1985; Chubachi 1985), and the ozone depletion was found to be happening in the lower stratosphere. This phenomenon was revealed by satellite observation to occur in the spatial scale to cover the whole of Antarctica, and is called Antarctic ozone hole. Figure 8.8 shows typical vertical profiles of the partial pressure of  $O_3$  before and after the development of ozone hole (Hofmann et al. 1987). Although there were various views for the cause of this phenomenon shortly after the discovery, Anderson et al. (1989) found by aircraft observation that ClO and  $O_3$  have distinct anti-correlation spatially and temporarily in the ozone hole as depicted in Fig. 8.9, and proved that the direct cause is due to the chemistry of the ClO<sub>x</sub> cycle.

However, the springtime is the dawn of Antarctica, and enough UV radiation does not reach it. Therefore, O atom mixing ratio is low, and the phenomenon cannot be explained by the ClO<sub>x</sub> cycle considering only the gas phase reactions

**Fig. 8.8** Comparison of the ozone vertical profiles in 1986 before ozone hole formation (August 25) and after its development (October 26) (Adapted from Hofmann et al. 1987)



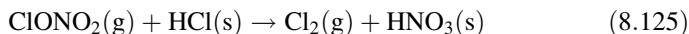
**Fig. 8.9** Anti-correlation between  $O_3$  and Cl mixing ratios in the ozone hole observed by an aircraft (Adapted from Anderson et al. 1989)



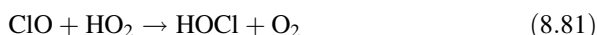
described in the previous section. Owing to the later studies, the ozone hole was found to be caused by the combination of a physical phenomenon called the polar vortex, due to the peculiar meteorology over Antarctica, and chemical phenomenon consisting of heterogeneous reactions on the surface of PSCs and succeeding gas phase chain reactions. A very stable polar vortex develops from winter to spring over Antarctica because of the cooling of the atmosphere by the cold continent, which provides the reaction field like a closed vessel blocking the outside air to mix with (Schoeberl et al. 1992; Brasseur and Solomon 2005). Since the stratospheric air is very dry, with only a few ppmv of water vapor, clouds are not formed in general. However, the temperature of the stratosphere in Antarctic winter is lower than 195 K, water vapor freezes to form clouds called nacreous clouds, or mother-of-pearl, and the clouds co-condensing HCl,  $HNO_3$  etc. are called PSCs (see Chap. 6, sect. 6.5). The altitude of the appearance of PSCs is 10–25 km, which roughly agrees with the regime where  $O_3$  is depleted extremely in the ozone hole.

Later, polar ozone depletion was found to occur not only over the Antarctica but also the Arctic circle (McElroy et al. 1986; Müller et al. 1997). However, in the Arctic, different from the Antarctic, a polar vortex does not sufficiently develop due to the larger inhomogeneity of the earth surface along the latitude, and higher temperatures than Antarctica, the size of ozone hole is smaller in general, but the similar ozone depletion due to CFCs etc. occurs by similar chemical reactions to those in the Antarctic. Particularly, ozone depletion comparable to the Antarctic ozone hole for density and spatial size was observed over the Arctic in 2011 (Manney et al. 2011).

The most important heterogeneous reaction with PSCs is the  $Cl_2$  release into the gas phase by the reaction of  $ClONO_2(g)$  in the gas phase and  $HCl(s)$  on the solid surface (Sect. 6.5.5).



By this reaction, photolytically active  $\text{Cl}_2$  is formed from  $\text{HCl}$  and  $\text{ClONO}_2$  reserved in the polar vortex during polar night. In spring, when the polar stratosphere starts to receive the solar radiation,  $\text{Cl}_2$  is rapidly photolyzed to release  $\text{Cl}$  atoms and ozone destruction proceeds. From  $\text{Cl}_2$  formed in reaction (8.125),  $\text{HOCl}$  is formed,



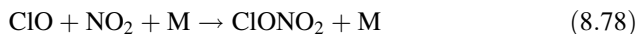
and  $\text{ClO}$  and  $\text{HO}_2$  are regenerated by the photolysis of  $\text{HOCl}$ ,



so that a chain reaction is constituted and  $\text{O}_3$  is dissipated by reactions (8.68) and (8.23). Since the ozone hole develops at altitudes lower than 20 km as seen in Fig. 8.8, the  $\text{O}$  atom mixing ratio is low, and it is a distinct feature that the reaction to regenerate  $\text{Cl}$  atoms mentioned in Sect. 8.2.3,

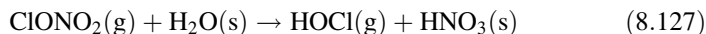


does not work effectively. Also in the polar vortex, the mixing ratio of  $\text{NO}_2$  in the gas phase is very low since  $\text{NO}_2$  is mostly taken into PSCs as  $\text{HNO}_3$ . Therefore, the chain termination reaction,



is not effective, so that the above  $\text{O}_3$  dissipation reactions are promoted effectively. Among the PSCs, NAT (nitric acid trihydrate) (sect. 6.5 Table 6.2) is particularly stable, grows to a large particle with the diameter of 1–20  $\mu\text{m}$ , and is removed from the stratosphere to the troposphere by gravitational sedimentation. This process brings about ultimate removal of  $\text{NO}_x$  from the stratosphere resulting in the very low mixing ratio of  $\text{NO}_2$  and acceleration of the  $\text{O}_3$  dissipation cycle under the solar radiation in springtime.

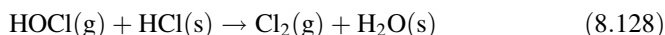
Next to reaction (8.116), the hydrolysis reaction of  $\text{ClONO}_2$  by  $\text{H}_2\text{O}(\text{s})$  on PSCs (Sect. 6.5.4),



is an important reaction to release photolytically active HOCl into the gas phase. While HOCl is photolyzed,

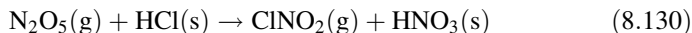
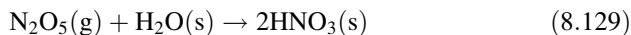


to give OH and Cl as seen above and facilitate the O<sub>3</sub> destruction by the gas phase homogeneous reaction, HOCl participates in a heterogeneous reaction with HCl (s) in PSCs (Sect. 6.5.3),

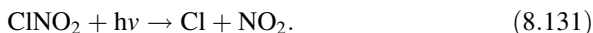


to release Cl<sub>2</sub> into the gas phase.

As other heterogeneous reactions on PSCs, the reactions of N<sub>2</sub>O<sub>5</sub>,

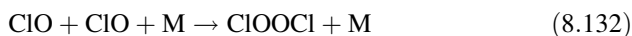


are also known (Sects. 6.5.1 and 6.5.2). Reaction (8.130) releases photochemically active ClONO<sub>2</sub> into the gas phase, and Cl atoms are formed by the photolysis of ClONO<sub>2</sub>,



Meanwhile, the active nitrogen is taken into PSCs as HNO<sub>3</sub> by reactions (8.129) and (8.130).

A characteristic of the gas phase reaction in the polar vortex is that the importance of radical-radical reactions of ClO with ClO, and ClO with BrO since the mixing ratios of ClO and BrO become very high in spring as compared to the normal stratosphere. The formation of ClO dimer, ClOOC1 (Sect. 5.6.6), and its photolysis can facilitate O<sub>3</sub> depletion as has been proposed by Molina and Molina (1987).



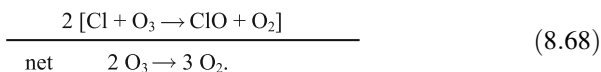
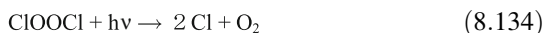
At present, ClOOC1 is the most abundant Cl species in the gas phase at polar night in the lower stratosphere over the polar region (Brasseur and Solomon 2005). The ClOOC1 is photolyzed (Sect. 4.4.6) in the polar vortex in spring,



to yield Cl and ClOO, and ClOO is further decomposed photolytically or thermally to Cl + O<sub>2</sub>,



The  $\text{O}_3$  destruction reactions through the ClO dimer can be expressed as,



Similarly, the  $\text{O}_3$  destruction via the cross reaction of ClO and BrO is important in the polar vortex in spring (McElroy et al. 1986).



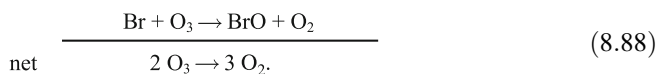
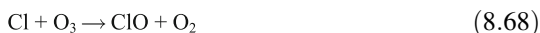
Here, formed OC is known to photolyse to give O atom and ClO (Sect. 4.4.7),



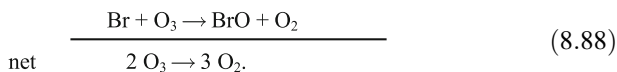
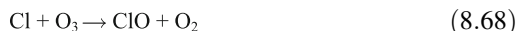
BrCl formed in the reaction (8.139) is also photolyzed easily to give Br and Cl atoms (Sect. 4.4.1),



Since the mutual reaction of ClO, and reaction of ClO with BrO regenerate Cl or Br except the O atom forming reaction (8.140), they all accelerate the  $\text{O}_3$  depleting chain reaction. The ozone destruction by these reactions are expressed either by,



or,



The relative contribution of ClO + ClO and BrO + ClO to the ozone depletion in the Antarctic ozone hole has been estimated as 60 and 40 %, respectively (Seinfeld and Pandis 2006).

## 8.5 Stratospheric Sulfur Chemistry

Most inorganic and organic sulfur compounds emitted from the earth's surface do not reach to the stratosphere since their atmospheric lifetime is shorter than 1 year. One exception, however, is the carbonyl sulfide COS emitted from marine organisms and volcanoes. COS is not photolyzed in the troposphere and the rate constant of the reaction with OH is as small as  $2.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (298 K) (Table 5.2), its tropospheric lifetime is as long as a few years and reaches to the stratosphere. The mixing ratio of COS is ca. 500 pptv in the troposphere and enters into the stratosphere with this value. In the stratosphere it is easily photolyzed, and the mixing ration decreases to ca. 15 pptv at the altitude of 35 km (Brasseur and Solomon 2005). By the photolysis of COS, sulfuric acid ( $\text{H}_2\text{SO}_4$ ) molecules are formed as gaseous molecules, and then they condense to form sulfuric acid aerosol since the vapor pressure of  $\text{H}_2\text{SO}_4$  is very low. The sulfuric acid aerosol layer in the stratosphere spreads around the altitude of 20 km, and called Junge layer after the name of the discoverer. The particle diameter of stratospheric aerosol is 0.01–1  $\mu\text{m}$ , and it affects the climate through changing the thermal budget of the earth by reflecting, absorbing and scattering the solar and terrestrial radiation (Brühl et al. 2012). Sulfur compounds in the stratosphere other than COS include  $\text{SO}_2$ , sporadically input by a large-scale volcano eruption, which increases the stratospheric aerosols temporarily, and tends to decreases the earth surface temperature for some years.

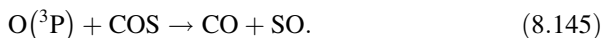
The COS reached to the stratosphere is photolyzed as described in Chap. 4, Sect. 4.3.6,



to release S atoms. The sulfur atoms in the atmosphere react with  $\text{O}_2$  immediately,



to form sulfur monoxide SO (Donovan and Little 1972). Also COS reacts with oxygen atom O(<sup>3</sup>P) to form SO,



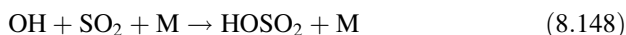
However, the rate constant of this reaction is relatively small,  $1.3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (298 K) (Table 5.1), so that the photolysis is the major pathway of the source of SO. The SO formed in reaction (8.144) reacts with O<sub>2</sub> to form SO<sub>2</sub> (Black et al. 1982; Atkinson et al. 2004),



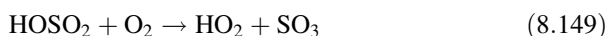
The SO<sub>2</sub> is subject to photolysis (Sect. 4.3.7) in the stratosphere,



and also reacts with OH (Sect. 5.2.6) and forms HOSO<sub>2</sub> radicals as seen in the troposphere.



The HOSO<sub>2</sub> reacts with O<sub>2</sub> in the atmosphere,



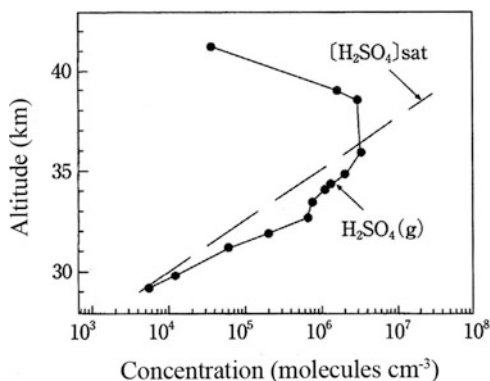
to form sulfur trioxide SO<sub>3</sub> (Stockwell and Calvert 1983). Sulfuric acid molecule H<sub>2</sub>SO<sub>4</sub> is formed from SO<sub>3</sub> by the homogeneous or heterogeneous reaction with H<sub>2</sub>O (Jayne et al. 1997; Atkinson et al. 2004),



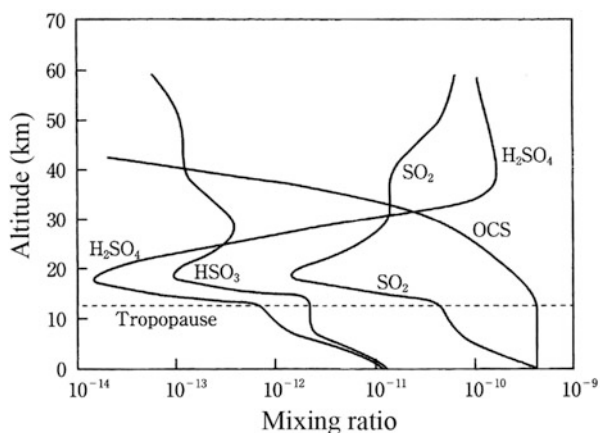
The formed H<sub>2</sub>SO<sub>4</sub> is a gaseous molecule but condenses to form sulfuric acid aerosol due to its low vapor pressure. Observation of gaseous H<sub>2</sub>SO<sub>4</sub> in the stratosphere has been made by a negative ion mass spectrometer board on a balloon (Krieger and Arnold 1994). Figures 8.10 and 8.11 depicts an example of the measurement (Reiner and Arnold 1997). Since the saturation vapor pressure of H<sub>2</sub>SO<sub>4</sub> increases with temperature, the mixing ratio of H<sub>2</sub>SO<sub>4</sub>(g) increases with the altitude, maximizes at 35–38 km, and decreases rapidly at the higher altitude. This is due to the depletion of COS, and the formation of H<sub>2</sub>SO<sub>4</sub> does not occur much in the upper stratosphere.

Figure 8.11 shows the vertical profiles of the mixing ratios of sulfur species by model calculation (Turco et al. 1979). As shown in the figure, COS is photolyzed within the lower stratosphere, and H<sub>2</sub>SO<sub>4</sub> exists as a major sulfur species with the

**Fig. 8.10** Vertical profile of  $\text{H}_2\text{SO}_4$  (g) in the stratosphere by observation (Adapted from Reiner and Arnold 1997). Dashed line is the equilibrium vapor pressure of  $\text{H}_2\text{SO}_4$  on liquid sulfuric acid aerosols



**Fig. 8.11** Vertical profiles of sulfur compounds in the stratosphere by model calculation (Adapted from Turco et al. 1979)



mixing ratio of 100–200 pptv above 35 km.  $\text{SO}_2$  exists at a few tens of pptv near the tropopause, decreases rapidly within a few km from the tropopause, and increases again in the upper stratosphere to 10–30 pptv.

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