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Chemical Kinetics and Atmospheric Chemistry: Role of Data Evaluation

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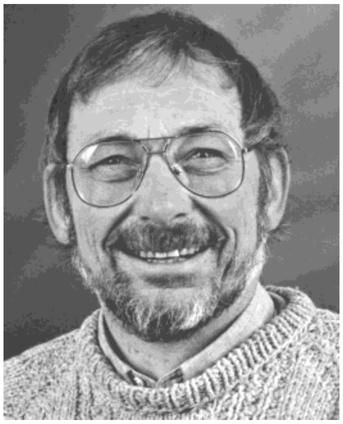

Dr. Cox graduated in 1966 from University of Manchester, UK, with a Ph.D. in physical chemistry. After postdoctoral work at NRC, Ottawa, Canada, with R. J. Cvetanovic, he joined the Environmental and Medical Sciences Division at the UKAEA Harwell laboratory in 1968. There he undertook research in many aspects of tropospheric and stratospheric chemistry, with an emphasis on laboratory studies of kinetics and photochemistry of gas-phase reactions. In later years he was instrumental in the development of several international programs in atmospheric chemistry. Since joining the Department of Chemistry at Cambridge University in 1995, he has established a research group studying kinetics of heterogeneous atmospheric reactions. He was a founding member of the IUPAC Subcommittee for Gas Kinetic Data Evaluation for Atmospheric Chemistry in 1977, and is now chairman of the subcommittee.

1. Introduction

This review deals with the development and application of chemical kinetics and photochemical databases for use in atmospheric modeling. Initiated by the suggestion that the release of nitric oxide into the stratosphere from the exhaust gases of supersonic aircraft could seriously deplete stratospheric ozone, the quest for such a database began in 1971. The first evaluations, coordinated by the U.S. National Bureau of Standards (now NIST), covering a limited number of reactions, appeared in the early 1970s. A comprehensive list of recommended rate coefficients for atmospheric modeling was published as part of NASA's Upper Atmosphere Research Program in 1977, and later by the CODATA Chemical Kinetics Task Group in 1980. Subsequently these evaluation activities have continued and expanded. The present article traces the historical background to kinetic data evaluation for atmospheric chemistry, as well as the advancement in knowledge of the detailed chemistry of the homogeneous gas-phase reactions which control the composition of the atmosphere, as reflected in the successive evaluations. It also includes coverage of heterogeneous chemistry, which is now known to be involved in the Antarctic "ozone hole". Current activities and future prospects for the on-going maintenance of a reaction rate database for atmospheric chemistry modeling, as applied to issues of atmospheric pollution and global climate change, are summarized.

1.1. Chemistry of Stratospheric Ozone

Although it had been realized in the 19th century that chemical reactions occurred in the atmosphere and that these led to oxidation of pollutants and the formation of acidity in rainwater, ideas on the role of photochemistry in the atmosphere, in particular for the formation of ozone, did not emerge until the advances in kinetics of elementary gas-phase reactions in the 1920s. The first photochemical theory of stratospheric ozone formation, involving four gas-phase reactions of oxygen species, was first proposed by Chapman in 1930:[1]

$$O_2 + h\nu \rightarrow O + O \qquad (1)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (2)$$

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$$O_3 + h\nu \rightarrow O + O_2 \quad (3)$$

$$O + O_3 \rightarrow 2\ O_2 \quad (4)$$

This was the foundation of the new interdisciplinary science of aeronomy, which is a combination of atmospheric physics and kinetics and mechanism of elementary chemical reactions, to describe the composition of the upper atmosphere. Rate constant measurements in the 1950s showed that reaction 4 was in fact much slower than was believed at the time of Chapman's theory, which resulted in ozone amounts calculated from this reaction sequence that were greater than those observed in the stratosphere. This led to the postulation by Hunt[2] in 1966 that catalytic cyclical reactions of OH radicals (H, OH, HO_2), originally expounded in 1950 by Bates and Nicolet,[3] were responsible for some of the "missing" ozone removal arising from the slow rate of reaction 4. For example, the following cycle has the same effect as reaction 4:

$$H + O_3 \rightarrow OH + O_2 \quad (5)$$

$$OH + O \rightarrow H + O_2 \quad (6)$$

$$\text{Net:} \quad O_3 + O \rightarrow 2O_2$$

The next developments in the photochemical theory of ozone took place in the early 1970s. Crutzen[4] proposed the catalytic cycle involving nitrogen oxides NO and NO_2,

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (7)$$

$$NO_2 + O \rightarrow NO + O_2 \quad (8)$$

$$\text{Net:} \quad O_3 + O \rightarrow 2\ O_2$$

and Johnston[5] suggested that nitrogen oxides from the exhaust of supersonic aircraft flying in the stratosphere would cause depletion of the ozone layer, with serious consequences for life due to the resulting increased transmittance of ultraviolet light.

More urgency was given to the problem of ozone depletion in 1974, by the suggestion of Molina and Rowland[6] that chlorine atoms, produced by photochemical degradation of chlorofluorocarbons (CFCs) in the upper stratosphere, may lead to large depletions of ozone via the catalytic cycle

$$Cl + O_3 \rightarrow ClO + O_2 \quad (9)$$

$$ClO + O \rightarrow Cl + O_2 \quad (10)$$

$$\text{Net:} \quad O_3 + O \rightarrow 2O_2$$

which had been first proposed by Stolarski and Cicerone[7] in 1974, in their consideration of the impact of HCl emissions from solid-fuelled rockets on stratospheric ozone. CFCs were rapidly building up in the atmosphere at that time, and it was recognized that, because of their long lifetime, any deleterious effects of these molecules would be impossible to reverse on reasonable time scales. Thus arose the need for predictive mathematical models which could predict the amounts of atmospheric ozone now and in the future, taking into account the impact of pollutants.

Efforts over the past 30 years have been devoted to development of these models, which are now used for a range of problems in atmospheric chemistry. The earlier one- and two-dimensional (latitude−altitude) models have now been to a considerable extent superseded by three-dimensional chemistry/transport models (CTMs) which use wind fields from numerical weather prediction models to describe atmospheric transport. The chemistry in these models may contain upward of 150 elementary gas-phase chemical and photochemical reactions. The performance of these models has been frequently intercompared, and the chemical kinetics database used in their formulation has been reviewed and evaluated periodically, so that predictions of future ozone change is as scientifically sound as possible.

A major surprise came in 1985, when large springtime depletions of ozone over Antarctica—the "ozone hole"—were reported by Farman et al.[8] The current models did not predict these changes, and subsequent intensive studies, both in the field and in the laboratory, revealed the occurrence of novel chemical processes in the lower stratosphere in polar regions. These include heterogeneous reactions occurring on the surface of polar stratospheric clouds (PSC) which form at the low temperatures characteristic of the polar winter, by condensation of sulfuric acid, nitric acid, and water. These reactions lead to conversion of much of the chlorine contained in its stable reservoir species, HCl and $ClONO_2$, to catalytically active forms. Also a novel catalytic cycle involving the dimer of ClO is now known to play a major role in ozone loss:

$$2Cl + 2O_3 \rightarrow 2ClO + 2O_2 \quad (9)$$

$$ClO + ClO \rightarrow Cl_2O_2 \quad (11)$$

$$Cl_2O_2 + h\nu \rightarrow 2Cl + O_2 \quad (12)$$

$$\text{Net:} \quad O_3 + O_3 \rightarrow 3\ O_2$$

These developments in the mid-1980s highlighted chlorine compounds as a serious threat to the ozone layer. This has resulted in international agreements to phase out production of the long-lived CFCs and replace them by molecules with similar properties, but which are more readily removed in the atmosphere, for example by oxidation in the troposphere by reaction with OH radicals.

Further research has aimed at a quantitative explanation of the polar ozone losses and the ozone losses in the lower stratosphere at mid-latitude inferred from the analysis of trends in the global ozone column changes since the 1970s. This research has also identified a role for bromine-containing compounds in ozone loss, first proposed by Wofsy et al. in 1975.[9] In polar regions, the BrO + ClO reaction leads to the following catalytic cycle,[10] leading to ozone loss:

$$BrO + ClO \rightarrow Br + Cl + O_2 \qquad (13)$$

$$Br + O_3 \rightarrow BrO + O_2 \qquad (14)$$

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (9)$$

and in mid-latitudes a more extended photochemical cycle involving the reaction:

$$BrO + HO_2 \rightarrow HOBr + O_2 \qquad (15)$$

followed by photolysis of HOBr to Br + OH, also leads to ozone loss. International agreements aimed at protecting the ozone layer also include the phase-out of production of long-lived man-made bromofluorocarbons (Halons).

1.2. Chemical Reactions in the Troposphere

Work carried out by Haagen-Smit and co-workers[11,12] in California in the 1950s on the problem of photochemical smog first identified the gas-phase reactions leading to the generation of ozone in the lower atmosphere. Nitrogen dioxide, a common pollutant formed from combustion emissions, can be photolyzed in sunlight, yielding atomic O, which recombines with O_2 to form ozone, and NO, which reacts with ozone, re-forming NO_2:

$$NO_2 + h\nu \rightarrow NO + O \qquad (16)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (17)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (7)$$

This reaction cycle leads to no net chemical change, but the photostationary state between NO, NO_2, and O_3 is established rapidly in the sunlit atmosphere on a time scale of ~100 s.[13] Perturbation of the photostationary state occurs when NO reacts with radicals such as HO_2:[14,15]

$$NO + HO_2 \rightarrow NO_2 + OH \qquad (18)$$

These reactions, where NO is converted to NO_2, result in ozone production due to reactions 16 and 17, and can account for photochemical smog formation from NO_x and volatile organic compounds in polluted air. This research pointed to the importance in tropospheric chemistry of free radicals of the HO_x family (H, OH, HO_2) and related radicals derived from organic species (e.g., CH_3O_2, CH_3O), which are formed from the degradation of volatile organic compounds (VOCs).

Until the 1970s, tropospheric photochemistry was thought to be a local phenomenon associated with air pollution. In 1971, Levy[16] outlined a new theory which predicted significant OH concentrations in the normal sunlit troposphere and pointed out its significance for the chemical removal of many minor constituents, both natural and man-made. This theory involves production of OH from the small amount of highly reactive excited atomic oxygen, $O(^1D)$, produced by photolysis of O_3 at wavelengths less than $\lambda \approx 320$ nm, which reacts with water vapor, present at high concentrations in the lower troposphere, in competition with quenching to the ground state:

$$O_3 + h\nu\ (\lambda < 310\ \text{nm}) \rightarrow O(^1D) + O_2 \qquad (19)$$

$$O(^1D) + M \rightarrow O + M \qquad (20)$$

$$O(^1D) + H_2O \rightarrow 2OH \qquad (21)$$

Tropospheric photochemistry has developed rapidly since Levy's (1971) proposal. In 1972, Weinstock and Niki[17] proposed that OH radicals led to the oxidation of CO in the global atmosphere:

$$OH + CO \rightarrow CO_2 + H \qquad (22)$$

Because of the high reactivity of the OH radical, it provides an important sink for many trace gases, and estimates of the mean steady-state concentration of OH allow the lifetime of trace gases to be determined. Further developments in modeling of tropospheric photochemistry followed the pioneering work of Demerjian et al.[18] in formulating the mechanisms for hydrocarbon oxidation in the presence of NO_x, leading to ozone production in polluted air. These mechanisms now form the basis of models that are used to develop regulatory policy for abatement of photochemical oxidant pollution worldwide.

Global chemical transport models are now used to describe the chemistry controlling the composition of the troposphere. These models play a key role in international assessments of the human impact on global climate and air pollution. The ozone depletion potentials of the CFC replacement compounds have been evaluated on the basis of their atmospheric lifetimes, calculated using models of global tropospheric chemistry. There is currently a major effort in assessment of the impact of aviation on the composition of the troposphere and resulting effects on global climate change.[19] Global atmospheric chemistry is strongly coupled to the biosphere through trace gas emissions, and prediction of future climate–chemistry interactions is likely to be carried out with global circulation models containing elements of the biogeochemical cycles.

To increase the accuracy and facilitate comparison of results from such models, it is essential that they contain up-to-date chemical mechanisms. The complexity of both tropospheric and stratospheric chemistry requires accurate kinetics data for a large number of elementary gas-phase reactions as well as photochemical and heterogeneous reactions. The development of techniques such as flash photolysis and low-pressure discharge–fast-flow systems for the investigation of the kinetics of fast reactions in the 1950s had led to the establishment of a body of kinetic data for the reactions of some simple atoms and free radicals of interest to atmospheric chemistry. The subsequent development of improved measurement techniques based on lasers, mass spectrometry, and other spectroscopic methods has led to a vast improvement in capability for measurement of the rate coefficients of elementary reactions. Data evaluation has played an important role in drawing together the extensive experimental and theoretical information obtained in the laboratory, which is pertinent to provision of these chemical mechanisms. The historical development of a reliable kinetic and mechanistic database is briefly outlined in the next section of this review.

2. Development of Kinetic Data Evaluation for Atmospheric Chemistry

2.1. Historical Background

The Chemical Kinetics Information Center at the National Bureau of Standards (NBS), Washington, DC, initiated the evaluation of kinetic data specifically for application in atmospheric modeling studies in 1971. The impetus for this effort came from the suggestion that a substantial reduction in the stratospheric ozone content might occur due to the direct injection of nitric oxide into the stratosphere from the exhaust gases of supersonic aircraft.[5] These data evaluation efforts at NBS were soon incorporated into the Climatic Impact Assessment Program (CIAP) of the U.S. Department of Transportation. This program was established in 1970−1971 to determine the potential ecological impact of propulsion effluents from fleets of supersonic transports flying in the stratosphere. The assessment of the photochemistry and the rate constants of stratospheric reactions formed an essential part of the CIAP.

The first output from work coordinated at the NBS consisted of two reports published in 1972, edited by R. Hampson,[20,21] covering a total of 27 elementary reactions. The reports were subsequently combined and published in the open literature.[22] The data evaluation work involved in the CIAP culminated in the publication of a further NBS report, edited by Hampson and Garvin (1975),[23] which subsequently became a "Citation Classic" in *Current Contents*.[24] The chemical kinetics community immediately recognized the utility of these evaluations in guiding experimental work.

In September 1974, the CODATA Panel on Chemical Kinetics, under the chairmanship of S. W. Benson, held an International Symposium entitled "Chemical Kinetics Data for the Upper and Lower Atmosphere". This meeting, and the proceedings which were subsequently published,[25] proved to be a cornerstone in establishing the importance of kinetic data in atmospheric chemistry. In 1977, Hampson and Garvin[26] published an article entitled "Evaluation and Compilation of Reaction Rate Data", which set out the rationale, *modus operandi*, and state-of-the-art of kinetic data evaluation at that time, including that contributing to the growing discipline of atmospheric chemistry.

With the culmination of CIAP in 1975, the National Aeronautics and Space Administration (NASA) was given lead agency status for stratospheric research, and under NASA's auspices the evaluation of kinetic and photochemical data for use in atmospheric studies has continued from 1995 until the present day. The next milestone in atmospheric data evaluation came with the publication, in 1977, of NASA Reference Publication 1010, "Chlorofluoromethanes and the Stratosphere", edited by R. D. Hudson.[27] This publication included recommendations covering 104 gas-phase chemical reactions and 48 photochemical processes. Soon afterward, there followed the last in the series of NBS reports specifically relating to atmospheric chemistry and emanating from the renamed Chemical Kinetics Data Center.[28] The above-mentioned NASA Reference Publication 1010 contained the first of what has become a regular series of kinetic and photochemical data evaluations for use in stratospheric modeling, prepared by the NASA Panel for Data Evaluation and published by the Jet Propulsion Laboratory, Pasadena, California. This series has been running since 1977 at the level of one report approximately every 18 months, the last publication in hard copy (Evaluation No. 12) appearing in 1997.[29]

At about the same time as the NASA Panel for Data Evaluation was initiated, it was appreciated that there was also a need for the establishment of an international panel to produce a set of critically evaluated rate parameters for reactions of interest for atmospheric chemistry. To this end, the CODATA Task Group on Chemical Kinetics, under the auspices of the International Council of Scientific Unions (ICSU), was reconstituted in 1977. The first evaluation by this international committee was published in the *Journal of Physical and Chemical Reference Data* in 1980,[30] followed by supplements in 1982 and 1984. In 1989, the IUPAC Subcommittee on Data Evaluation superseded the original CODATA Task Group for Atmospheric Chemistry, and the Subcommittee has continued its data evaluation program with supplements published in 1989, 1992, 1997, 1999, and 2000.[31−36]

There has been a close working relationship between the NASA panel and the CODATA task group/IUPAC subcommittee during these past 20 years of evaluating rate data for atmospheric chemistry. The NASA evaluations have appeared more frequently and until recently have been more focused toward stratospheric chemistry, whereas the CODATA/IUPAC evaluations have been somewhat broader in their approach and now take in a range of tropospheric as well as stratospheric reactions. At one stage the two panels, which have always included some members involved with both groups, together produced a combined evaluation of the then available data for publication in the WMO report entitled "The Stratosphere 1981".[37]

The discovery of the ozone hole and the identification of the role of heterogeneous reactions has also led to compilation and evaluation of the kinetics data relating to heterogeneous reactions on condensed-phase substrates of atmospheric relevance. These now form a component of the published evaluations of these two panels. The establishment of these two independent groups of evaluators, which complement each other, recognizes the need for evaluation of kinetic and photochemical data by a group of experienced workers to tackle the difficult problems of deciding the recommendations to be put forward on a collective basis. The U.S. based NASA data panel provides a national framework for the relatively rapid dissemination of data for ozone layer research, while the international IUPAC subcommittee provides a broader-based output, which has traditionally covered wider issues of atmospheric chemistry and the general requirements of the laboratory chemical kinetics community.

2.2. Dissemination on the World Wide Web

The utility of the evaluations depends on easy and prompt availability of the material to the atmospheric and kinetic communities. Up until Evaluation No. 12 published in 1997,[29] the NASA data panel had been able to publish and disseminate widely its periodic revisions in the form of a reference book, by making use of the NASA publication services at the Jet Propulsion Laboratory in Pasadena, California. Recent updates are accessible only from the World Wide Web. The NASA website allows Evaluations 12 and 13 (which updates and supplements Evaluation 12) and 14 to be downloaded as PDF files (http://jpldataeval.jpl.nasa.gov/, accessed Feb 24, 2003). The availability of the CODATA/IUPAC data evaluations has always been limited by the cost and publication schedules of the *Journal of Physical and Chemical Reference Data* volumes, which have generally been available only through institution subscriptions. Following the last of these publications in 2000 (Supplement VIII[36]), the evaluation has been updated and published on the World Wide Web. The IUPAC website (http://www.iupac-kinetic.ch.cam.ac.uk/, accessed December 2002) hosts an interactive database with a search facility and implemented hyperlinks between the summary table and the data sheets, both of which can be downloaded as individual PDF files.

3. Format for Data Evaluation

3.1. Kinetics of Gas-Phase Reactions

Prior to the establishment of the NASA and CODATA panels' kinetic data, presentations of evaluations were either extensive, discussing individual measurements in a detailed way, such as in the High-Temperature Evaluations of the Leeds Group,[38] or brief, as in the early tabulations from the National Bureau of Standards.[23] The NASA panel chose a format providing only the recommended kinetic and photochemical data in tabular form, with endnotes containing limited details about the experimental studies, information to explain the basis of the recommendation, and references to the individual data sources. The CODATA/IUPAC group adopted an intermediate degree of detail in which individual rate data were compiled together with experimental techniques and conditions. The discrepancies between various studies and their possible causes were fully discussed in reaching recommended values for the rate parameters, which were contained in a summary sheet.

The representation of the rate coefficients of bimolecular reactions is generally straightforward and involves the simple Arrhenius expression, $k = A\ \exp(-B/T)$, where B is either positive or negative. Representations of k as a function of temperature characterize simple "direct" bimolecular reactions. Sometimes it is found that k also depends on the pressure and the nature of the bath gas. This may be an indication of complex formation during the course of the bimolecular reaction, which is always the case in combination reactions.

The representation of the pressure and temperature dependences of the rate coefficients of thermal dissociation reactions and the reverse radical recombination reactions is more complicated. Instead of using elaborate versions of unimolecular reaction rate theory, both the NASA and the CODATA/IUPAC groups decided to follow the simplified procedure of Troe.[39−41] Here, the rate coefficient is treated in terms of the limiting low-pressure and high-pressure rate coefficients, k_0 and k_∞, respectively, together with a suitable interpolating expression. This interpolation is based on the Lindemann−Hinshelwood mechanism:

$$\mathrm{A} + \mathrm{B} \Leftrightarrow \mathrm{AB}^* \tag{1,−1}$$

$$\mathrm{AB}^* + \mathrm{M} \Leftrightarrow \mathrm{AB} + \mathrm{M} \tag{2,−2}$$

Assuming steady state for AB*, it can be shown that in the low-pressure limit ([M] → 0) the overall rate coefficient is proportional to [M]; in the high-pressure limit ([M] → ∞) it is independent of [M]. It is useful to express k in terms of the limiting low-pressure and high-pressure rate coefficients,

$$k_0 = \lim_{[\mathrm{M}] \to 0} k([\mathrm{M}])$$

and

$$k_\infty = \lim_{[\mathrm{M}] \to \infty} k([\mathrm{M}])$$

respectively. From this convention, the Lindemann−Hinshelwood equation is obtained:

$$k = \frac{k_0 k_\infty}{k_0 + k_\infty}$$

It follows that for combination reactions, $k_0 = k_1k_2[\mathrm{M}]/k_{-1}$ and $k_\infty = k_1$, while for dissociation reactions, $k_0 = k_{-2}[\mathrm{M}]$ and $k_\infty = k_{-1}k_{-2}/k_2$. Since detailed balancing applies, the ratio of the rate coefficients for combination and reverse dissociation at a fixed T and [M] is given by the equilibrium constant $K_c = k_1k_2/k_{-1}k_{-2}$.

Starting from the high-pressure limit, the rate coefficients fall off with decreasing third-body concentration [M], and the corresponding representation of k as a function of [M] is termed the "falloff curve" of the reaction. In practice, the above Lindemann−Hinshelwood expressions do not suffice to characterize the falloff curves completely. Because of the multistep character of the collisional deactivation (k_2[M]) and activation (k_{-2}[M]) processes, and energy and angular momentum dependencies of the association (k_1) and dissociation (k_{-1}) steps, as well as other phenomena, the falloff expressions have to be modified. This can be done by including a broadening factor F to the Lindemann−Hinshelwood expression:[29−31]

$$k = \frac{k_0 k_\infty}{k_0 + k_\infty} F$$

The broadening factor F depends on the ratio k_0/k_∞, which is proportional to [M], and can be used as a measure of "reduced pressure". The first factors on the right-hand side represent the Lindemann–Hinshelwood expression, and the additional broadening factor F, at not too high temperatures, is approximately given by

$$\log F \cong \frac{\log F_c}{1 + [\log(k_0/k_\infty)/N]^2}$$

where $\log = \log_{10}$ and $N = \{0.75 - 1.27 \log F_c\}$. In this way, the three quantities k_0, k_∞, and F_c characterize the falloff curve for the present application. Alternatively, the three quantities k_∞, $[M_c]$, and F_c (or k_0, $[M_c]$, and F_c) can be used.

A simpler policy of fitting falloff was chosen by the NASA/JPL panel in putting $F_c = 0.6$ and $N = 1$. This generally leads to different values of the fitted k_0 and k_∞ and their temperature dependencies than derived here, although experimental data over the range of atmospheric interest can be generally reproduced equally well. However, the derived k_0 and k_∞ differ from the true limiting rate coefficients and thus should not be interpreted by theory. The formulation of the complex pressure dependence of many atmospheric reactions in this simple way has been of immense benefit for accurate atmospheric chemistry modeling.

The dependence of k_0 and k_∞ on the temperature T for association reactions is represented in the form

$$k \propto T^{-n}$$

except for cases with an established energy barrier in the potential. This form of temperature dependence has been adopted because it usually gives a better fit to the data for association reactions over a wider range of temperature than does the Arrhenius expression. It should be emphasized that the chosen form of the temperature dependence is often only adequate over limited temperature ranges, such as 200–300 K. Obviously, the relevant values of n are different for k_0 and k_∞.

3.2. Kinetics of Heterogeneous Reactions

A heterogeneous reaction involves diffusion of a gas-phase species to the reactive surface, accommodation at the surface, followed by reaction on or beneath the surface. The rate of this process is usually expressed in terms of the uptake coefficient, γ, which is defined as the fraction of molecules colliding with the surface that are permanently lost from the gas phase. According to the kinetic theory of gases, the rate of collisions at the surface, per unit area, is $[A]c/4$, where [A] is the concentration (molecules cm^{-3}) of the gaseous species and c the mean molecular speed of the gas molecules. The rate of reaction of molecules at the surface can be expressed as a first-order reaction:

$$-\frac{d[A]}{dt} = k_{het}[A] \qquad k_{het} = \frac{\gamma c}{4} S$$

S is the surface area of the atmospheric particles per unit volume. Uptake may lead to chemical reaction on the surface or in the condensed phase, leading to products that either desorb or remain in the condensed phase. A gas may also be taken up into a liquid due to its solubility. This is expressed in terms of the Henry's law constant, H (M atm^{-1}), which relates the partial pressure of the trace gas and its molar concentration in the liquid phase at equilibrium. Uptake coefficient measurements can be used to deduce the mechanisms of the heterogeneous processes as well as providing a representation for rates in the atmosphere.

The NASA and IUPAC groups have both addressed the evaluation of heterogeneous reactions for use in atmospheric models. Only a few reactions are sufficiently well defined to make recommendations for uptake parameters. Part of the difficulty is the definitions of the surface characteristics of the atmospheric particles supporting the reactions. The most progress has been made in understanding of the reactions at low temperature on supercooled liquid sulfate aerosols. In its most recent evaluation, NASA has given recommendations for a full parametrization of the reactions of N_2O_5, $ClONO_2$, and HOCl on supercooled sulfuric acid aerosols for stratospheric conditions. This is based on a model in which the rate of uptake of trace gas onto a fluid is expressed by the overall uptake coefficient γ, which includes contributions from different processes such as gas diffusion, mass accommodation, re-evaporation, bulk reaction, and dissolution, elaborated by Kolb et al.[42] The total rate may be calculated according to a resistance model which is based on steady-state solutions to the decoupled differential equations describing each separate process by itself.[43] The formulation is based on approximations to the exact solutions, and the overall net uptake rate coefficient is expressed in terms of the sum of resistances, which are the inverse of the dimensionless uptake rate coefficients, Γ_i, of the separate processes involved:

$$1/\gamma = 1/\Gamma_g + 1/\alpha + 1/(\Gamma_{sol} + \Gamma_{rxn})$$

In the above expression, $1/\Gamma_g$, $1/\Gamma_{sol}$, and $1/\Gamma_{rxn}$ are the resistances corresponding to gas diffusion of the trace gas to the interface, the competing (nonreactive) dissolution following Henry's law, and chemical reaction in the condensed phase, respectively. The mass accommodation coefficient, α, is defined as the fraction of molecules colliding with the surface which adsorb or are trapped at the interface. To calculate the flux of trace gas across the interface, the calculated γ is used in the rate expression. The resistance model is a useful approximation which is usually sufficiently accurate.

The IUPAC group have assembled a large compilation of experimental data related to heterogeneous reactions on a range of substrates of atmospheric relevance, including some of tropospheric significance, such as sea salt aerosols, sulfates, dusts, and carbonaceous aerosol. Uptake on solids is, in principle, similar to uptake on liquids, except that the diffusion coefficient for the condensed phase is several orders of magnitude smaller than the corresponding value for a liquid. Consequently, uptake on solids is prone to saturation phenomena once the surface has been covered or has reacted, unless the interface is modified so as to generate new adsorption/reaction sites. The uptake kinetics are currently described in terms of a single value of the uptake coefficient γ, as given in the above rate equation. Very few atmospheric models give a detailed explicit representation of these heterogeneous rate processes.

3.3. Photochemical Reactions

Rates of atmospheric photochemical reactions require knowledge of the absorption cross sections and quantum yields for the relevant photochemical pathways over the range of wavelengths where significant dissociation occurs. Conventionally for calculation of atmospheric photolysis rates, cross sections are presented as “absorption cross sections per molecule, base e”, which are defined according to the equations

$$I/I_0 = \exp(-\sigma[\mathrm{N}]l)$$

$$\sigma = \{1/([\mathrm{N}]l)\}\ \ln(I_0/I)$$

where I_0 and I are the incident and transmitted light intensities, σ is the absorption cross section per molecule (expressed in this paper in units of cm^2), [N] is the number concentration of absorber (expressed in molecule cm^{-3}), and l is the path length (expressed in cm).

Both the NASA and the IUPAC evaluations provide recommended absorption cross sections and photolysis quantum yields, Φ. They are usually presented in tabulated form at 5 to 10 nm intervals, except where higher resolution data are appropriate, e.g., for structured spectra or where Φ varies rapidly with wavelength. The aim in presenting these preferred data is to provide a basis for calculating atmospheric photolysis rates. Any temperature dependence of the absorption cross sections is usually given as a simple empirical expression of the form $\log_{10}(\sigma_{T_1}/\sigma_{T_2}) = B(T_1 - T_2)$. For absorption continua, the temperature dependence is sometimes represented by Sulzer–Wieland-type expressions.[44]

3.4. Assignment of Uncertainties

All evaluations need to contain estimates of the absolute accuracies of the recommended values of the rate parameters over the quoted temperature range. In the IUPAC evaluation, the accuracy of the preferred rate coefficient, k, at 298 K is quoted as the term $\Delta \log k$, where $\Delta \log k = D$, and D is defined by the equation $\log_{10} k = C \pm D$. This is equivalent to the statement that k is uncertain to a factor of F, where $D = \log_{10} F$. The accuracy of the preferred value of E/R is quoted as the term $\Delta(E/R)$, where $\Delta(E/R) = G$, and G is defined by the equation $E/R = H \pm G$. The NASA evaluation simply cites an uncertainty factor $f(298)$ and $\Delta(E/R)$.

For second-order rate coefficients listed in the IUPAC evaluations, an estimate of the uncertainty at any given temperature within the recommended temperature range may be obtained from the equation

$$\Delta \log k(T) = \Delta \log k(298\ \mathrm{K}) + 0.4343 \exp\{\Delta E/R(1/T - 1/298)\}$$

In the NASA evaluations, upper and lower bounds for the rate constant at any temperature can be obtained by multiplying or dividing the rate coefficient at a given temperature by the uncertainty factor $f(T)$, given by the equation

$$f(T) = f(298) \exp|\Delta E/R(1/T - 1/298)|$$

In both evaluations, the assignment of these absolute uncertainties in k and E/R is a subjective assessment of the evaluators. They are not determined by a rigorous, statistical analysis of the database, which is generally too limited to permit such an analysis. Rather, the uncertainties are based on a knowledge of the techniques, the difficulties of the experimental measurements, the potential for systematic errors, and the number of studies conducted and their agreement or lack thereof. As a result, the probability distribution will not show the normal Gaussian form, and the true rate constant may lie farther away from the recommended value than would be expected from the standard deviation of a normal distribution. Experience shows that for rate measurements of atomic and free radical reactions in the gas phase, the precision of the measurement, i.e., the reproducibility, is usually good. Thus, for single studies of a particular reaction involving one technique, standard deviations, or even 95% confidence limits, of ±10% or less are frequently reported in the literature. Unfortunately, when evaluators come to compare data for the same reaction studied by more than one group of investigators and involving different techniques, the rate coefficients often differ by more than the combined cited uncertainties. This can only mean that one or more of the studies has involved large systematic uncertainties which are difficult to detect. This arises from the challenge in studying atomic and free radical reactions in isolation, and consequently mechanistic and other difficulties frequently arise. Thus, in the case where a rate coefficient has been measured by a single investigation using one particular technique and is unconfirmed by independent work, the IUPAC evaluators assign minimum uncertainty limits of a factor of 2. The scarcity of apparently reliable data for the photochemical reactions does not justify assignment of uncertainty limits to the parameters recommended.

4. Highlights of the Current Database for Atmospheric Reactions

4.1. Reactions of Oxygen Species

The most important issues in the evaluations of the O_x group of reactions have involved the absorption cross sections and quantum yields for photolysis of

O_2 and O_3. Absorption by these molecules determines to a large extent the penetration of actinic UV radiation through the atmosphere, and the atomic O photofragments play a fundamental role in atmospheric chemical change.

In the O_2 Schumann–Runge wavelength region (175–200 nm), a detailed analysis of the penetration of solar radiation requires absorption cross section measurements with very high spectral resolution. Absorption cross section values for the (0,0)–(12,0) Schumann–Runge bands measured in recent years by the Harvard–Smithsonian group[45] are the first set of values which are independent of instrumental resolution. Minschwaner et al.[46] have fitted O_2 cross sections for the frequency range 49 000–57 000 cm^{-1} (175–204 nm) with temperature-dependent polynomial expressions for the temperature range 130–500 K using the latest laboratory spectroscopic data. This model provides an efficient and accurate means of determining Schumann–Runge band absorption cross sections at 0.5 cm^{-1} resolution. These calculated values at high resolution differ from those in the earlier WMO[47] recommendations by up to 10–20% at some wavelengths.

There has been an extensive discussion concerning the branching ratio of ozone photolysis to produce excited atomic oxygen, $O(^1D)$. The two channels producing the excited atomic products are

$$O_3 + h\nu(\lambda < 411\ \text{nm}) = O(^1D) + O_2(^3\Sigma_g) \qquad (25)$$

$$O_3 + h\nu\ (\lambda < 310\ \text{nm}) = O(^1D) + O_2(^1\Delta_g) \qquad (19)$$

A wealth of data for the quantum yield for $O(^1D)$ production and its coproduct, $O_2(^1\Delta_g)$, in the spin-allowed dissociation channel (19), give clear evidence for substantially enhanced dissociation into electronically excited products beyond the thermodynamic threshold at 310 nm. This is attributed to the contribution of vibrational energy contained in ground-state O_3 molecules. Recent measurements also show that significant $O(^1D)$ production occurs at $\lambda = 320$–370 nm, which is attributed to the spin-forbidden channel (25). The most recent evaluations by NASA and IUPAC (post-1997) produced a complete revision in the recommended quantum yields for $O(^1D)$ production, which included the "tail" in $\phi[O(^1D)]$ at wavelengths beyond 312 nm which had previously been ignored. The attribution of part of the "tail" to the involvement of vibrationally excited ozone leads to a falloff in $\phi[O(^1D)]$ with temperature in the important region between 308 and 320 nm, which has now been confirmed in several studies. Evidence from photofragment time-of-flight experiments and the Doppler profiles of nascent $O(^1D)$ strongly points to a contribution from the spin-forbidden channel (25) at $\lambda > 320$ nm.

Recently, an independent group involving the principal investigators of these recent studies have conducted a rigorous evaluation of the data. The group had access to all experimental data and were able to harmonize and renormalize the quantum yield values to eliminate systematic errors. They have fitted the renormalized quantum yield data for $306 < \lambda(\text{nm}) < 328$ and $200 < T(\text{K}) < 320$ with an expression using three Gaussian terms and a constant term representing the spin-forbidden channel (4).[48] Figure 1 shows the quantum yields calculated with this expression at 203, 298, and 320 K, together with selected experimental data from Talukdar et al.[49] This expression is now recommended for use in the wavelength and temperature ranges given above.

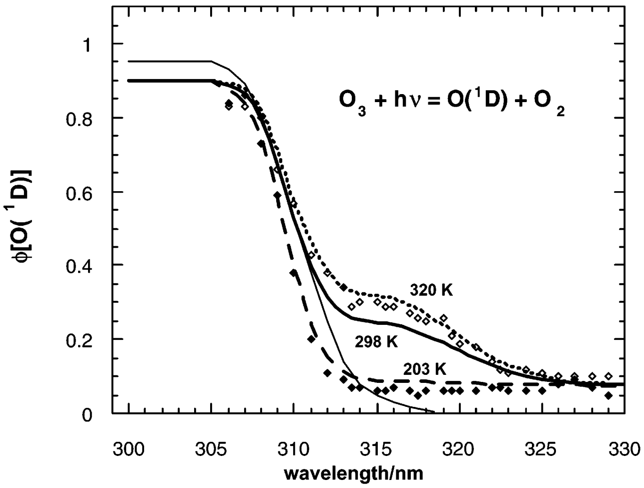

Figure 1. Temperature dependence of quantum yields for $O(^1D)$ production from O_3 photolysis. The curves show values at 202, 298, and 320 K, calculated using the expression derived by Matsumi et al.[48] using three Gaussian terms and a constant term representing the spin-forbidden channel (4). The 1997 IUPAC recommendation, which was based on the JPL 1994 evaluation and did not take account of the contribution from vibrationally excited O_3 and the spin-forbidden channels, is shown as a "thin" line. Selected experimental data from Talukdar et al.[49] at 203 and 320 K are also shown.

4.2. HO_x Reactions

Well before their involvement in stratospheric chemistry had been suggested, the kinetics of elementary reactions of OH species had been studied because of the central role which the H_2/O_2 system has played in the development of combustion chemistry. The atmospheric evaluation studies in the CIAP program[23] were able to draw upon earlier data evaluations[37] already in existence for combustion modeling. However, at that stage, a number of reactions vital to atmospheric chemistry, but of less importance to combustion, had received little study. Much of the existing data referred to higher temperatures, and little attention had been paid to the pressure dependence of reactions. Nevertheless, even in the early 1970s, the values of the rate coefficients for reactions of O with HO, the reaction of $O(^1D)$ with H_2O, and the reaction of OH with HO_2 were reasonably well established at room temperature. Subsequent direct experimental studies since then have shown that many of the OH rate coefficients with radicals and closed-shell molecules were known to within a factor of 2, although some exhibited unexpected pressure dependencies which led to significant revision for atmospheric conditions, e.g., the reaction of OH with CO.

The greatest uncertainty was associated with reactions involving the HO_2 radical. Progress was slow until the development during the 1970s of suitable methods for production, detection, and monitoring of the concentration of HO_2 in flash photolysis and discharge flow reaction systems used for direct kinetic studies. Since then, HO_2 reactions have been studied extensively, and their rate coefficients are now fairly well known. Such studies have been able to characterize the temperature dependence of the rate of the reaction of HO_2 with ozone,

$$HO_2 + O_3 \rightarrow 2OH + O_2 \qquad (26)$$

which is a key reaction in the cycle leading to ozone loss in the lowermost stratosphere and in the troposphere. The reaction is slow, is difficult to measure because of secondary chemistry of the OH radical produced, and exhibits a non-Arrhenius temperature dependence. As a result, the earlier recommended values at stratospheric temperatures, based on extrapolation assuming a simple Arrhenius expresssion, were significantly lower than values predicted with the currently recommended three-parameter temperature dependence, which is based on data from the most recent studies by Herndon et al.[50]

Extensive studies have revealed a number of unexpected influences of pressure, temperature, and gas composition on the rate coefficents of HO_2 reactions, which suggest that the reactions at low temperature proceed via weakly bound complexes. An example is the combination reaction of HO_2 radicals:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (27)$$

The reaction converts HO_2 radicals to hydrogen peroxide and is a key reaction controlling steady-state concentrations of HO_x radicals in the troposphere, as well as the main source of hydrogen peroxide. The kinetics of this reaction have been studied over a wide range of temperature, pressure, and diluent gas conditions, to define the reaction rate coefficient for atmospheric modeling. The main kinetic features are the following:

− The reaction is second order in $[HO_2]$ for all conditions.

− The rate coefficient is pressure dependent, increasing by a factor of ∼2 between 10 and 1000 mbar at 298 K.

− There is a negative temperature dependence (*k* decreases with temperature), which is larger at higher pressures.

− The rate coefficient at 1 bar increases with inert gas diluent, $He < Ar < N_2 < SF_6$.

− The rate coefficient increases with partial pressure of H_2O and other polar molecules, with no change in kinetic order.

Such complex kinetic behavior presents difficulties for data evaluation, as the detailed reaction mechanism needs to be known in order to have confidence in making recommendations for the rate coefficient. The observed behavior is interpreted in terms of a mechanism in which the reaction proceeds by two channels, one of them pressure dependent and the other involving a direct bimolecular interaction.[51,52] The pressure and temperature dependence is attributed to the involvement of a short-lived intermediate, H_2O_4, which can dissociate either into the stable products or back to form reactants.

The effect of polar molecules such as H_2O on the rate has been interpreted as being due to the participation of a weakly bound complex between HO_2 and H_2O,[53] which acts as a chaperone to achieve the high-pressure regime where the product formation from H_2O_4 is predominant. The detailed mechanism is not confirmed but is consistent with the kinetics under atmospheric conditions. An empirical expression is used to correct the overall rate coefficient for the effect of water vapor. In 1988, Andersson et al.[54] showed that methanol also acts as a chaperone for the $HO_2 + HO_2$ reaction, and recently Christensen et al.[55] made a detailed study of this effect over the temperature range 222−295 K. The results showed that previous studies using methanol as a source of HO_2 were strongly influenced by this chaperone effect and therefore led to an erroneously large temperature dependence of the rate coefficient for atmospheric modeling. Their new suggested expression for the pressure and temperature dependence is compared with that recommended previously in Figure 2, which also shows recommendations for the rate coefficients at 1 bar pressure and two water vapor pressures, to demonstrate the large effect of water vapor. The revised rate at stratospheric conditions largely accounts for a discrepancy between modeled and measured $[H_2O_2]$ in the lower to middle stratosphere.[55] This exemplifies the importance of new experimental studies needed to refine the kinetics data, and the dangers of categorizing a well-studied reaction as "well defined".

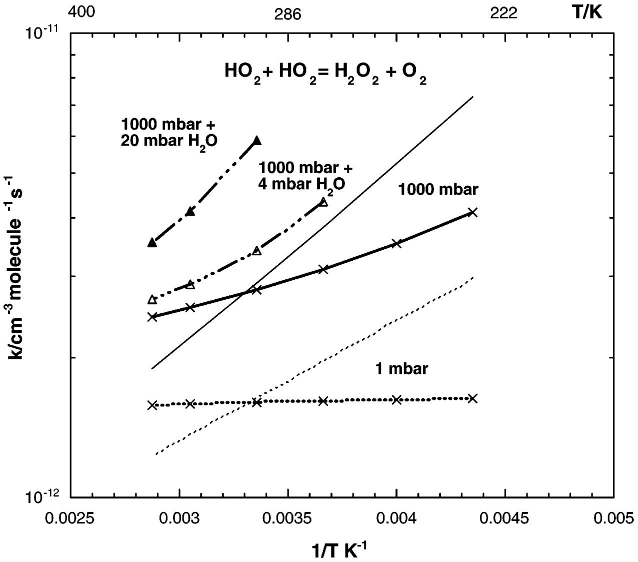

Figure 2. Temperature dependence of the rate coefficient for the HO_2 self reaction, at different pressures and water vapor amounts, illustrating the complex dependence on these factors. The "thin" lines are calculated using the IUPAC recommended expressions for the overall rate coefficient, and the "thick" lines are based on the results of very recent work reported by Christensen et al.[55]

4.3. NO_x Reactions

While the kinetics database for reactions of NO_x species is now relatively well established, there have been significant changes in the recommended values for several key reactions since the beginning of the Climatic Impact Assessment Program, which focused on the effects of nitrogen oxides on the ozone layer. In 1973, the rate constant for the important reaction:

$$O + NO_2 \rightarrow NO + O_2 \qquad (8)$$

was directly measured at stratospheric temperatures for the first time.[56] This rate constant at 230 K was shown to be a factor of 2 higher than the previously recommended value, which had been extrapolated from higher temperature data. Recent experimental work by Gierczak et al.[57] has led to further re-evaluation of this reaction, which has resulted in quantitative changes to our picture of the NO_x and HO_x budget in the lower stratosphere.

Most NO_x in the lower part of the stratosphere is in the form of gaseous nitric acid, $HONO_2$. The main process for removal of NO_x from the stratosphere is transport of this long-lived species. In 1982, there was an important revision[58] in the recommended value of the rate constant for the reaction

$$OH + HONO_2 \rightarrow H_2O + NO_3 \qquad (28)$$

as a result of the observation of a negative temperature dependence of the rate constant, which had been previously reported to be temperature independent.[59,60] This resulted in a much higher value of this rate constant at stratospheric temperatures. Recent work[61] has resulted in further advances in knowledge of the kinetics and mechanism of this reaction, showing that it has strong pressure and isotope effects and probably occurs via an H-bonded complex formed between OH and HNO_3. This lends support for the complex empirical expression recommended for the rate coefficient under atmospheric conditions.

The recommendation for the high- and low-pressure rate coefficients for the reaction

$$OH + NO_2 + M \rightarrow HONO_2 + M \qquad (29)$$

did not change for many years following the excellent kinetic data gathered in the late 1970s and early 1980s.[62,63] However, since the mid-1990s, changes in the recommendation have resulted from new experimental[64,65] and theoretical work.[66,67] There are essentially two groups of studies: those with higher rate constants and those with lower values. Since the reasons for the differences have not yet been identified, some uncertainties still remain, arising partly from the discovery of an additional channel for the reaction forming peroxynitrous acid, HOONO. The changes in the recommended temperature and pressure dependence of the rate coefficient for the reaction of OH with NO_2 is illustrated in Figure 3. The data are taken from the most recent NASA evaluation and show that, at temperatures and pressures relevant to the lower stratosphere, the rate constant for $HONO_2$ formation is significantly lower than previously recommended. At higher pressures, the additional HOONO-forming channel becomes significant, and the overall reaction rate is higher than previously recommended, although the $HONO_2$ formation rate is not affected. The preferred value of $k(1 \text{ bar}) = 1.2 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K, which applies to $HONO_2$ formation only, remains unchanged.

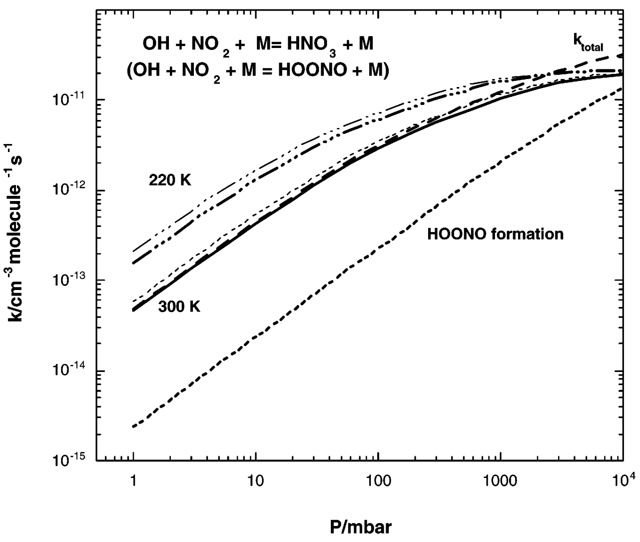

Figure 3. Temperature dependence of the rate coefficient for the reaction $OH + NO_2 + M \rightarrow$ products, at different pressures, illustrating the changes in the recommended rate coefficients for $HONO_2$ formation, as a result of recent new experimental data and theoretical analysis indicating the existence of a second channel in the reaction producing HOONO. The "thin" lines are calculated using the expressions recommended for the overall rate coefficient in JPL Evaluation No. 11(1994), and the "thick" lines are calculated using the expressions recommended in JPL Evaluation No. 14 (2003) for $HONO_2$ formation and the suggested expression for the second channel producing HOONO.

There is only limited information on the extent of formation of the HOONO isomer, as discussed by Golden and Smith,[67] and on its fate. However, it is clear that HOONO is unstable at lower tropospheric temperatures. While spectroscopic *in situ* detection still has not been reported in laboratory studies, non exponential OH decay kinetics above 400 K at pressures near 100 bar[68] provided clear evidence for its formation. It remains unclear whether HOONO efficiently converts to $HONO_2$ at lower pressures by an intramolecular process, or whether HOONO is a final reaction product. No recommendations have been made for the rate coefficients for HOONO formation, pending resolution of these issues.

The recently revised values for reactions of NO_x in the lowermost stratosphere lead to considerably better agreement between the calculated and observed partitioning between the various reactive nitrogen reservoirs in the lower stratosphere.[69] There is now much improved agreement between the NO_x/NO_y ratios obtained from concentrations of HNO_3, NO_2, and NO, measured from aircraft, and the ratios calculated from models, including the recently revised rate coefficients.

Another significant improvement resulted from the direct measurement in 1977 of the rate constant for the reaction $HO_2 + NO \rightarrow OH + NO_2$,[79] which was a factor of 30 higher than the previously recommended value, which had been based on indirect measurements. This change alone had profoundly significant effects on quantitative understanding of the production and loss of ozone in the stratosphere and the troposphere, as revealed in atmospheric chemical models.

The photochemistry of $HONO_2$ takes on a new significance in connection with the Cl-catalyzed polar O_3 depletion. The conversion of the active ClO radicals, formed as a result of heterogeneous chemistry on polar stratospheric clouds (see below), back to the inactive reservoir molecule, $ClONO_2$, is controlled by the slow release of NO_2 from $HONO_2$ photolysis. Cross sections for $HONO_2$ photolysis have now been determined at the low temperatures prevailing in the polar stratosphere.[71] A significant reduction in photolysis rate compared to that calculated from the room-temperature cross sections results from use of the proper temperature-dependent absorption cross sections.

4.4. Halogen Reactions

At the time of the Molina and Rowland hypothesis,[6] the only kinetic data on the key reactions involving Cl and ClO radicals were those obtained by M. A. A. Clyne and co-workers, who had made rapid progress toward understanding the elementary reactions of halogen atoms and halogen oxide radicals in the late 1960s.[72] A review in 1977 by Watson[73] of the kinetic data of ClO reactions of atmospheric interest showed that there were still major uncertainties in the data for many of the key reactions and photochemical processes. However, by that time, a large effort was being mounted by laboratory scientists to provide accurate rate coefficients and temperature dependences for the ClO_x reactions.

During the late 1970s, a number of new aspects of halogen chemistry had emerged. For example, an important role was identified for the temporary reservoir molecules, such as chlorine nitrate ($ClONO_2$),[74] in tying up active chlorine and so reducing the efficiency of the catalytic cycles which destroy ozone. Despite the expanding number of important gas-phase reactions needed to describe the stratospheric chemistry of chlorine species and its coupling with NO_x and HO_x chemistry, progress was good, so that by the time of the major international review—“Atmospheric Ozone 1985”—sponsored by the World Meteorological Organization (WMO),[75] it was concluded, “Most of these processes (i.e., major reactions of ClO) are now well understood...”. Earlier controversies, for example whether a second isomer of chlorine nitrate was formed in reaction of ClO with NO_2, had also been resolved.

The 1985 WMO assessment coincided with the discovery by Farman et al.[8] of the springtime Antarctic ozone hole and the suggestion that chlorine-catalyzed ozone destruction was responsible for the large ozone depletions observed there. This opened up many new challenges for the chemical kinetics community, especially as subsequent field observations[76] showed that the partitioning between the radical and reservoir species was totally different from the predictions of the then current theory. The presence of high concentrations of ClO in the polar vortex meant that reactions considered hitherto to be unimportant, such as the association of two ClO radicals to form a dimer, Cl_2O_2, became central to the ozone depletion chemistry. The subsequent photochemistry of Cl_2O_2 in the polar spring gives rise to ozone depletion by a completely different set of reactions:[77]

$$ClO + ClO + M \leftrightarrow Cl_2O_2 + M \quad (30,-30)$$

$$Cl_2O_2 + h\nu \rightarrow Cl + ClO_2 \quad (31)$$

$$ClO_2 + M \rightarrow Cl + O_2 + M \quad (32)$$

$$Cl + O_3 \rightarrow ClO + O_2 \quad (9)$$

In the1985 WMO assessment,[75] it appeared that gas-phase reactions alone controlled the partitioning of the halogen species between the reservoir molecules HCl, $ClONO_2$, HOCl, etc. It was noted, however, that heterogeneous reactions may play a significant role, for example, after volcanic eruptions, if certain surface reactions occurred efficiently. Foremost among the postulated reactions was the heterogeneous reaction between $ClONO_2$ and HCl, which was known to take place rapidly in the laboratory:

$$ClONO_2 + HCl \rightarrow Cl_2 + HONO_2 \quad (33)$$

It has now been established that the partitioning of chlorine in the polar springtime stratosphere is highly perturbed and that this is due to heterogeneous reactions such as reaction 33.[78] These reactions occur on the surface of polar stratospheric clouds, which were first firmly identified from satellite observations by McCormick et al.[79] in 1982. They result from the condensation of water and nitric acid at the low prevailing temperatures in the polar stratosphere. Heterogeneous processes can also lead to considerably reduced concentrations of NO_x encountered particularly in the polar winter stratosphere, due to the heterogeneous reaction

$$N_2O_5 + H_2O \rightarrow 2HONO_2 \quad (34)$$

In subsequent years, the kinetic data for these new gas-phase and heterogeneous reactions, which were not considered in previous evaluations, have been subject to intensive study. The situation was similar to that existing in the mid-1970s for the more conventional chlorine chemistry, and the kinetics community again responded quickly to the challenge of providing the required high quality data for this novel aspect of atmospheric chemistry. The task of the evaluation groups has been to draw together and assess the new information and to provide recommendations for the kinetics and mechanism of the key reactions. This has been straightforward for the gas-phase reactions, following the protocols and formats developed earlier. The task of evaluation of data for heterogeneous reactions has been less straightforward. First, the available data for individual reactions have been more diverse in both quality and extent. Second, the nature and definition of the substrate surfaces relevent for the atmosphere have been a source of considerable uncertainty, and third, the form of the parametrization of the reaction rates in atmospheric models has not reached a consensus. The evaluation activities in the heterogeneous atmospheric chemistry area have so far been limited, by and large, to compilation of the available data, with some comments on the methodology used and overall state of knowledge. A treatment of heterogeneous reactions occurring on liquid sulfuric acid particles, suitable for modeling such processes in the lower stratosphere, has been proposed by the NASA panel. Their most recent evaluation gives recommended data for the key parameters for calculation of reaction rates using the proposed model.

In the 1985 ozone assessment,[75] it was noted that the reactions of BrO_x radicals were generally less well defined and, in view of the concern about the growing use of Halons (bromochlorofluorocarbons) and the high catalytic efficiency for ozone destruction by BrO_x, there was a need for improvement in the database for the BrO_x cycles. Subsequently, the reactions of BrO have assumed added importance because of their role in polar ozone depletion in the stratosphere[80] and also in the springtime ozone loss in the Arctic tropospheric boundary layer, which appears to be entirely due to bromine-catalyzed ozone destruction.[81]

The kinetics and temperature dependences of the main reactions leading to the production, cycling, and removal of BrO_x radicals have now been established, and evaluations show that, with a few exceptions, the rate constants are reasonably well known, although uncertainties of several key reactions, such as $HO_2 + BrO \rightarrow HOBr + O_2$, remain large.[82] These data are also timely to assist in the interpretation of the growing number of field measurements being used to validate and develop models. For example, the discovery in 1986 of the unexpected atmospheric constituent, OClO,[83] could be easily rationalized in terms of its formation as a product of the BrO + ClO reaction.

A paper published by Solomon et al. in 1994[84] highlighted a possible role for iodine-catalyzed ozone loss in the lowermost stratosphere. The kinetics community was able to establish a reasonably reliable evaluated database for IO_x reactions within a relatively short time, using techniques and knowledge gained from earlier work on atmospheric halogen reactions. Models based on these evaluations were used to assess the role of short-lived iodo- and bromo-carbons in ozone loss for the most recent ozone assessment (WMO 2002).[85] These examples illustrate the capability of the kinetics community to respond rapidly to requirements of atmospheric modelers for new data for the prediction of ozone depletion due to halocarbons.

4.5. Reactions of Volatile Organic Compounds

The photochemical production of OH radicals in the troposphere leads to the oxidative degradation of organic chemicals emitted into the atmosphere, thus limiting their accumulation, which would lead to disruption of biogeochemical cycles and detrimental effects on the environment. Recognition of this has led to the development of atmospheric chemical models of increasing sophistication for the treatment of oxidation of volatile organic compounds (VOCs) in the atmosphere. The tropospheric removal of organic compounds by the OH radical is central to issues such as photochemical oxidant formation, acid precipitation, and the depletion of stratospheric ozone. The search is on for substitutes for CFCs, i.e., alternative hydrofluorocarbons and/or hydrochlorofluorocarbons which react sufficiently rapidly with the OH radical so that they are largely degraded in the troposphere. This has provided a further impetus to kinetics studies of VOCs oxidation, and evaluation of the data from these studies.

An understanding of the reactions of organic compounds in the atmosphere only began during the time period 1967−1971, with the first measurements of the rate constants for reaction of methane, ethane, and other alkanes with the OH radical[86] and with the realization that the OH radical was an important constituent of both the polluted and natural troposphere.[12,87,88] Combination of the kinetic data with estimates of the tropospheric OH radical concentrations led to the conclusion that OH radical reactions were of great importance in the degradation of organic compounds in both the natural and polluted troposphere. From 1971 onward, the kinetics and mechanisms of the gas-phase reactions of OH radicals and O_3 with organic compounds have been studied at a much accelerated pace, and a number of compilations and evaluations of the rate data have been conducted by the Riverside group.[88,90,91] In 1980, the potential importance of the NO_3 radical in the chemistry of the night-time troposphere was realized,[92,93] and this has been followed by numerous studies of the kinetics and mechanisms of NO_3 radical reactions with organic compounds.

In the 1970s, the chemistry of the clean troposphere was dealt with by consideration of only CH_4 and its major degradation products, HCHO, CH_3OOH, and CO.[94,95] The first evaluations carried out by the CODATA and NASA panels[30,96] confined their attention to this family of organic reactions only. When measurements of the tropospheric trace concentrations of non-methane hydrocarbons became available,[97] it was recognized that the chemistry of the C_2 and C_3 hydrocarbons (ethane, ethene, acetylene, propane, and propene) and of their degradation products, including CH_3COCH_3, CH_3CHO, and $CH_3C(O)ONO_2$ (PAN) needed to be considered in quantitative assessments of the chemistry of the troposphere. By 1992, the IUPAC panel[32] had expanded its coverage to include the reactions involved in the degradation of C_2 and C_4 hydrocarbon species, and isoprene (C_5H_8) degradation reactions are included in the latest evaluation. The philosophy of the scope of the database is to recommend rate parameters for sufficient elementary reactions to enable the mechanism of atmospheric degradation of a specific compound to final products to be described explicitly.

The expansion of the kinetic database for degradation of organic compounds continued in the 1990s, with the growing number of identified organic compounds of significance, especially from biogenic sources. In addition, it has become clear that tropospheric oxidation may occur at high altitudes (and hence low temperatures), where reaction rates and pathways may differ from those at the surface atmosphere. The large number of species and reactions involved in organic atmospheric chemistry currently provides a major challenge to scientists providing and evaluating kinetic data, and raises the issue of the role of a combined theoretical and experimental approach to definition of rate constants and mechanisms. Rate constants have been measured in the laboratory for many of these reactions. Consideration of the numerous experimental data reveals patterns of reactivity which can be recognized within a particular type of reaction (e.g., H-abstraction, addition to unsaturated C=C bonds) and which are related to molecular structure. This leads to the possibility of prediction of rate constants for molecules of known structure, but for which measurements may be experimentally difficult. Similarly, relationships may exist that allow prediction of the products and their yields for reactions that have a number of possible pathways.

A widely used approach is that of the structure–activity relationship (SAR), and this has been successfully used for prediction of OH reaction rates, for example by Atkinson.[98] Prediction of overall H-abstraction rate constants is based upon the estimation of $-CH_3$, $-CH_2{=}CH-$, and $-OH$ group rate constants for abstraction of H atoms from these groups, and these rate constants depend on the identity of the pendant substituents. A similar approach can be used to estimate rate constants for OH + alkene reactions, with summation of site-specific rate constants for addition and abstraction.

A different method for estimation of rate data uses correlation between the rate parameter of interest and a molecular property.[99,100] The latter may be experimentally determined properties (e.g., bond dissociation energy, ionization energy) or calculated properties (e.g., E_{HOMO}). If a tight correlation between measured rate coefficient and the molecular property can be established, this can form a general basis for predicting rate coefficients. To date, these methods have only been used as guidelines in the evaluation of experimental data and have not been used as a basis for recommendation of rate coefficents for reactions of VOCs. Considerable progress is possible in the future in this area.

In general contrast to the situation for the atmospheric reactions of inorganic species, there have been few major surprises in the development of the kinetic database for the gas-phase reactions of organic compounds with OH and NO_3 radicals and O_3. Rather, the past 20 years have been characterized by gradual refinement of the existing kinetic dataset, with few revisions of more than a factor of 2 in the room-temperature rate constants. Nevertheless, these refinements are significant, as exemplified by the changes in the rate coefficient recommended by the IUPAC panel between 1980[30] and the current recommendation for the reaction of OH with methane, which are illustrated in Figure 4. The lifetime of atmospheric methane with respect to removal by OH has been revised upward by about 20% as a result of the small change in the recommended rate constant at ~280 K, the mean temperature at which CH_4 is removed in the troposphere. There has also been an extension of the temperature and pressure ranges over which the rate constants have been measured. This reflects the improvements in the experimental techniques for the determination of rate constants. The greatest changes have occurred for those OH radical reactions which proceed by addition. This applies not only to classical addition reactions, such as OH addition to acetylene, ethene, and propene, but also to bimolecular reactions which appear to proceed by a hydrogen-bonded complex and give rise to strongly non-Arrhenius temperature dependencies, especially at low temperature. An example of this is the reaction of OH with acetone which has recently been the subject of several studies. These have led to changes in the recommended rate coefficient for the OH + $CH_3C(O)CH_3$ reaction at low temperatures for conditions in the upper troposphere. This is also illustrated in Figure 4, which is based on the most recent IUPAC recommendation compared with that recommended in 1997.[33]

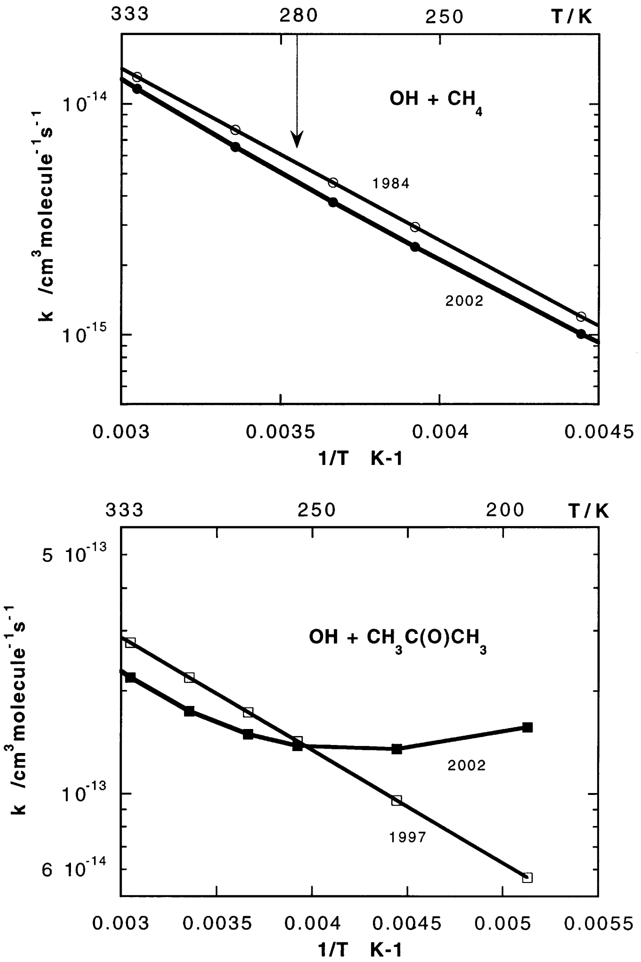

Figure 4. Temperature dependence of the rate coefficient for OH radical reactions with methane and acetone, covering the range of temperatures encountered in the troposphere: thick lines (filled points), current recommendations given by IUPAC; fine lines (open points), earlier recommendations. Note that changes influence directly the lifetimes of these gases in the troposphere.

Investigations of the reactions, under atmospheric conditions, of the initially formed radical species from the OH, NO_3, and O_3 reactions have also progressed significantly in recent years. Specifically, studies of the kinetics and mechanisms of the atmospheric reactions of alkyl (or substituted alkyl) radicals and of the subsequently formed peroxy and alkoxy radicals have been undertaken for a wide range of organic compounds, including the simple hydrocarbons, some biogenic VOCs, and halogenated organics (including those carbonyl compounds formed from the hydrofluorocarbons and hydrochlorofluorocarbons which are being utilized as CFC replacements).

There has also been an increasing amount of quantitative data concerning the absorption cross sections, photodissociation quantum yields, and products, all as a function of wavelength, for the photolysis of carbonyls and other oxygenated compounds formed as intermediate products of the tropospheric degradations of organic compounds. However, this is an area where more definitive work is required, especially for the quantum yields and dissociation products of simple carbonyls. The nature and further degradation of products has been particularly important for the CFC replacement compounds, and this was recognized early in the Alternative Fluorocarbon Environmental Acceptabilty (AFEAS) program.[101] There was a need to investigate whether any of the products of tropospheric degradation of the hydrofluorocarbons and hydrochlorofluorocarbons used as substitutes would either influence stratospheric ozone or have other undesirable environmental effects. Evaluations of the kinetics and mechanistic data from the laboratory studies initiated by this program have shown that the tropospheric degradation products of CFC substitutes will not lead to significant ozone loss in the stratosphere.[102] However, trifluoroacetic acid was identified as a product which could be of concern in the aqueous environment.

Compilation and evaluation of all these data for the purposes of atmospheric modeling presents a considerable challenge, and consequently a number of different initiatives have been undertaken to provide a data source for the atmospheric modeling and chemical kinetics communities, ranging from individual reviews such as those carried out by R. Atkinson and co-workers[89−91] to continuously updated resources such as the Master Chemical Mechanism, developed at the University of Leeds (UK),[103] and the IUPAC and NASA evaluations. The NASA data panel has recently expanded the scope of their evaluation to selected C_3 hydrocarbons and additional halogenated hydrocarbons. Additionally evaluations have been recently undertaken as specific one-off tasks, sponsored, for example, by the IGAC (International Global Atmospheric Chemistry project of IGBP) and SPARC (Stratospheric Processes And their Role in Climate project of WCRP) international programs, where atmospheric modeling plays a key component of the work-plan.

An example is the evaluation addressing the atmospheric chemistry of the four most abundant tropospheric organic peroxy radicals: CH_3O_2, $C_2H_5O_2$, $CH_3C(O)O_2$, and $CH_3C(O)CH_2O_2$.[104] The literature data for the atmospheric reactions of these radicals were evaluated, and published kinetic and product data were reinterpreted, or in some case reanalyzed using the new UV absorption cross sections, leading to a self-consistent set of kinetic, mechanistic, and spectroscopic data. Product studies were also evaluated. A set of peroxy radical reaction rate coefficients and products were recommended for use in atmospheric modeling.

5. Current and Future Prospects

The important role of data evaluation in atmospheric chemistry is illustrated well by the developments in recent years of national and international regulation of atmospheric pollutant emissions. Atmospheric chemists have demonstrated the importance of the concept of atmospheric lifetime in determining the impact of pollutant emissions, both in local air quality and in the global atmosphere. The concept of “reactivity” of VOCs in the generation of photochemical oxidants and its relationship to the VOC lifetime with respect to oxidation by reaction with OH was developed in the 1970s. This has subsequently led to the idea of photochemical oxidant creation potential (POCP) as a measure of the propensity of specific compounds for generation of secondary pollutants. The development of this concept by Derwent et al.[105] draws heavily on rate data and evaluations in formulating the explicit chemistry used, which is contained in a master chemical mechanism (MCM).[103] The MCM is now available for download on a website at the Data Center in the School of Chemistry, University of Leeds, UK (http://www.chem.leeds.ac.uk/Atmospheric/MCM/mcmproj.html).

The lifetime of longer lived pollutants, such as reactive greenhouse gases and halocarbons implicated in stratospheric ozone depletion, is a central factor in determining ozone depletion potentials (ODPs) and global warming potentials (GWPs) of these substances. These lifetimes scale closely with the rate coefficients for their reaction with hydroxyl radicals or with their photochemical destruction rates in the atmosphere. These potentials allow ranking of the pollutants according to their relative impact and therefore are useful instruments for the implementation of control of pollution. The work of evaluation groups has contributed significantly toward the optimum scientific basis and agreement on these relative impacts and the control measures used to ameliorate them.

The essential features of stratospheric gas-phase homogeneous chemistry, with the key reaction rates, were reasonably well understood and established by 1985. In recent years, great advances have been made in establishing quantitative chemical schemes controlling the concentrations of the key radical species involved in gas-phase oxidation in the troposphere. There remain areas of less well understood chemistry, such as tropospheric iodine, low temperature oxidation of organic compounds, and secondary aerosol formation. There also remains considerable work to be done in developing parametrizations and evaluating kinetic data for heterogeneous reactions on aerosols, cloud droplets, and ice surfaces. Evaluation of the kinetics database for chemistry involving polar stratospheric clouds and also aviation-derived soot aerosols has been actively pursued by the NASA panel. Evaluation of the rather sparse available data for kinetics of heterogeneous reactions involving aerosols characteristic of the lower atmosphere has not yet been done, although the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry have compiled the available rate data for a variety of tropospheric aerosols.

In the future, the efforts of laboratory scientists will continue to provide new data in response to the requirements of new scientific and societal issues in the field of atmospheric chemistry. The development of new and improved measurement techniques promises further advances in knowledge and improved kinetic data for gas-phase and heterogeneous reactions for atmospheric conditions. Evaluation groups are seeking new methods for updating and extending the portfolio of recommended rate coefficients, which will be necessary to maintain an effective and ongoing communication between laboratory scientists and atmospheric modelers. Recent years have seen great advances in the capability of theoretical chemistry. Calculated chemical structures, kinetic parameters, and reaction dynamics now provide an effective tool to help critical evaluation of experimental data and extend its application. Evaluation groups are already making more use of theory in reaching firm recommendations for rate data, especially in combustion chemistry, where experimental studies at the relevant temperatures and pressures are often not possible.

The establishment of Web-based material allows, for the first time, the opportunity of nearly continuous update of the evaluation, as well as easier access to the data. The development and implementation of protocols for the updating of the evaluation will be needed in future. Evaluation provides an especially important role in the interdisciplinary sciences such as atmospheric chemistry, where expertise in a single discipline needs to be concentrated at the working interface between disciplines. The new challenges of global environmental change, with chemistry−climate interactions as a central theme for international efforts in atmospheric science research, will increase the demands for access to evaluated, quality-assured, and quality-controlled data from the different disciplines, including chemical kinetics.

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