

Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling

Evaluation Number 11

NASA Panel for Data Evaluation:

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ABSTRACT

This is the eleventh in a series of evaluated sets of rate constants and photochemical cross sections compiled by the NASA Panel for Data Evaluation. The primary application of the data is in the modeling of stratospheric processes, with particular emphasis on the ozone layer and its possible perturbation by anthropogenic and natural phenomena. Copies of this evaluation are available from the Jet Propulsion Laboratory, California Institute of Technology, Library Section, MS 111-120, 4800 Oak Grove Drive, Pasadena, California, 91109.

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CHEMICAL KINETICS AND PHOTOCHEMICAL DATA

FOR USE IN STRATOSPHERIC MODELING

INTRODUCTION

The present compilation of kinetic and photochemical data represents the eleventh evaluation prepared by the NASA Panel for Data Evaluation. The Panel was established in 1977 by the NASA Upper Atmosphere Research Program Office for the purpose of providing a critical tabulation of the latest kinetic and photochemical data for use by modelers in computer simulations of stratospheric chemistry. The previous publications appeared as follows:

<u>Evaluation</u>	<u>Reference</u>
1 NASA RP 1010, Chapter 1	(Hudson [1])
2 JPL Publication 79-27	(DeMore et al. [455])
3 NASA RP 1049, Chapter 1	(Hudson and Reed [2])
4 JPL Publication 81-3	(DeMore et al. [452])
5 JPL Publication 82-57	(DeMore et al. [450])
6 JPL Publication 83-62	(DeMore et al. [451])
7 JPL Publication 85-37	(DeMore et al. [446])
8 JPL Publication 87-41	(DeMore et al. [447])
9 JPL Publication 90-1	(DeMore et al. [448])
10 JPL Publication 92-20	(DeMore et al. [449])

The present composition of the Panel and the major responsibilities of each member are listed below:

W. B. DeMore, Chairman

D. M. Golden (three-body reactions, equilibrium constants)

R. F. Hampson (halogen chemistry)

C. J. Howard (HO_x chemistry, O(¹D) reactions, singlet O₂, metal chemistry, profiles)

C. E. Kolb (heterogeneous chemistry)

M. J. Kurylo (SO_x chemistry)

M. J. Molina (photochemical data)

A. R. Ravishankara (hydrocarbon oxidation, photochemical data)

S. P. Sander (NO_x chemistry)

As shown above, each Panel member concentrates his effort on a given area or type of data. Nevertheless, the final recommendations of the Panel represent a consensus of the entire Panel. Each member reviews the basis for all recommendations, and is cognizant of the final decision in every case. Communications regarding particular reactions may be addressed to the appropriate panel member.

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Copies of this evaluation may be obtained by requesting JPL Publication 94-26 from:

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BASIS OF THE RECOMMENDATIONS

The recommended rate data and cross sections are based on laboratory measurements. In order to provide recommendations that are as up-to-date as possible, preprints and written private communications are accepted, but only when it is expected that they will appear as published journal articles. In no cases are rate constants adjusted to fit observations of stratospheric concentrations. The Panel considers the question of consistency of data with expectations based on the theory of reaction kinetics, and when a discrepancy appears to exist this fact is pointed out in the accompanying note. The major use of theoretical extrapolation of data is in connection with three-body reactions, in which the required pressure or temperature dependence is sometimes unavailable from laboratory measurements, and can be estimated by use of appropriate theoretical treatment. In the case of important rate constants for which no experimental data are available, the panel may provide estimates of rate constant parameters based on analogy to similar reactions for which data are available.

RECENT CHANGES AND CURRENT NEEDS OF LABORATORY KINETICS

Format of the Evaluation

Some significant changes have been made in the ordering of reactions in the tables. Data are now presented in the order O_X , HO_X , NO_X , hydrocarbons, FO_X , ClO_X , BrO_X , IO_X , SO_X , and metal chemistry. The major differences between the present and the previous evaluation are that FO_X reactions have now been placed before ClO_X reactions, and a section on IO_X chemistry has been added. Individual reactions within a given section are ordered in the same sequence. These changes are expected to facilitate the location of data.

Changes or additions to Tables 1-3 are now indicated by shading instead of the previous practice of using symbols. A new entry is completely shaded, whereas a changed entry is shaded only where the change was made.

Appendix 1, listing heats of formation of many atmospheric species, has been updated and expanded. Appendix 2 now includes solar flux data as well as model-generated concentration profiles and J-values for important species in the upper atmosphere.

New reference software has been implemented in the present evaluation, which should improve the accuracy and completeness of the literature citations. The Panel is grateful to Dr. James B. Burkholder of the NOAA Aeronomy Laboratory for assistance in this process.

O_X Reactions

The kinetics of the O , O_2 , and O_3 system are relatively well-established. However, the $O + O_2 + M$ reaction remains of fundamental importance in atmospheric chemistry. This is because the extent of ozone destruction is determined by the relative rates of competing reactions such as $O + O_3$, $O + NO_2$, $O + OH$, and $O + ClO$. Additional studies of the ozone-forming reaction, or of its relative rate compared to the competing reactions, would be useful, especially at very low temperatures.

Reactions of Singlet Oxygen

$O(^1D)$ Reactions

The recommended rate coefficients for the $O(^1D)$ reactions correspond to the rate of removal of $O(^1D)$, which includes both chemical reactions and physical quenching of the excited O atoms. Details on the branching ratios and products are given in the notes.

The $O(^1D)$ reactions of 13 halocarbons have been added to this review. Some of these compounds are long-lived trace species for which the reaction with $O(^1D)$ in the stratosphere may represent a significant destruction process. There are new measurements that improve our database for several of the hydrohalocarbons. Some of the latter seem to exhibit an unexpected efficiency for physical quenching of $O(^1D)$.

The kinetic energy or hot atom effects of photolytically generated $O(^1D)$ are probably not important in the atmosphere, although the literature is rich with studies of these processes and with studies of the dynamics of many $O(^1D)$ reactions. The important atmospheric reactions of $O(^1D)$ include: (1) deactivation by major gases, N_2 and O_2 , which limit the $O(^1D)$ steady state concentrations; (2) reaction with trace gases, e.g., H_2O , CH_4 , and N_2O , which generate radicals; and (3) reaction with long lived trace gases, e.g., HCN , which have relatively slow atmospheric degradation rates. There are no data for the $O(^1D) + HCN$ reaction.

$O_2 (^1\Delta \text{ and } ^1\Sigma)$

Fourteen reactions of the ($a^1\Delta_g$) and ($b^1\Sigma_g^+$) excited states of molecular oxygen are reviewed. These states are populated via photochemical processes, mainly the UV photolysis of ozone and the reaction of $O(^1D)$ with O_2 . Over the years they have been proposed as contributors to various reaction schemes in the atmosphere, but as yet no significant role in the chemistry of the stratosphere has been demonstrated. The fate of most of these excited species is physical quenching by means of energy transfer processes. In the few cases where chemical reaction occurs, it is indicated in the corresponding note.

HO_x Reactions

The reaction of OH with HD has been added to this evaluation, otherwise there have been no changes in the database for HO_x chemistry since the last evaluation. The HO₂ + O₃ reaction rate coefficient remains one of the most significant uncertainties in the HO_x system. High quality data at low temperatures are needed for this key reaction.

NO_x Reactions

The changes to the database on NO_x reactions are relatively minor. There are new entries for the reactions NO₃ + NO₃ and electronically excited N₂ with O₂ and O₃. The N₂(A) + O₂ reaction has been suggested as being an important source of N₂O in the upper stratosphere and lower mesosphere. New work on the N + NO and N + NO₂ reactions has significantly improved the understanding of the temperature dependences of these reactions. There are minor changes to the recommendations for the reactions of NO₃ with OH and HO₂.

Hydrocarbon Oxidation

The rate coefficient for the reaction of OH with CH₄ has been revised slightly based on recent work. The new recommendation takes into account all the new data. Because of its use in the quantification of sources of methane based on isotopic information, the reaction of OH with CH₃D has been added. In light of some direct measurements, the rate coefficient for the reaction of OH with PAN is now quoted as an upper limit. This upper limit is much lower than the rate constant that was previously recommended. There have been additional studies on the reactions between peroxy radicals, and the current recommendations reflect the increased data base. In particular, we have recommended absorption cross sections for methyl and ethyl peroxy radicals (in the photochemistry section) and the recommended rate constants are based on these cross sections. The largest change in the rate constant is for the reaction between C₂H₅O₂ radicals. In addition to the above changes, many rate coefficients have been slightly modified to take recent work into account. The accuracy of many rate coefficients has improved and this is reflected in the revised rate constants.

Even though there have been many studies on the reactions between peroxy radicals, the use of only UV absorption to measure the rate coefficients has been a limiting factor. All peroxy radicals have similar absorption spectra and cross sections. Therefore, deconvolution of the measured absorbances into changes in concentrations of individual reactants is not unambiguous. Use of peroxy radical detection by methods other than UV absorption would be very beneficial.

The reactions of OH with CH₃CN and HCN also require further study, because both the rate and mechanism are uncertain. Studies of larger (>C₃) hydrocarbons, especially those containing oxygen, will be of interest in elucidating the hydrocarbon chemistry in the upper troposphere and the lower stratosphere. Such information is needed to assess the effects of aircraft emissions on ozone and climate.

Recently, attempts to identify and quantify the products of hydrocarbon reactions have increased. However, there are uncertainties in the products of several reactions that need clarification.

Halogen Reactions

The kinetics database for homogeneous reactions of halogen species has been expanded since the previous evaluation. Rate coefficients for the reaction of OH with ten C₃ and higher HFCs have been added, increasing to thirty-three the number of potential alternatives to the fully halogenated CFCs for which rate data for reaction with OH are now included. Rate coefficients for the reaction of chlorine atoms with nineteen of these species are now included. Note that rate coefficient data for the reaction of these species with O(¹D) are included in the O(¹D) section of Table 1. Halocarbon oxidation reactions have been added. Among these are reactions of CF₃O, CF₃O₂, and other substituted alkoxy and alkylperoxy radicals. A section on iodine chemistry has been added. There have been some changes in the recommendations for reactions included in the previous evaluation, in particular for reactions of OH with HFCs and HCFCs.

SO_x Reactions

The database on homogeneous sulfur chemistry has seen only minor changes in the recommendations for the reactions that were included in the previous evaluation. However, this section has undergone moderate expansion to include additional reactions of importance in the atmospheric oxidation of reduced sulfur compounds of natural and

anthropogenic origin. These new entries include oxidation reactions (O , O_3 , HO_2) for organic sulfur compounds through C_2 as well as the subsequent oxidation reactions of many of the organo-sulfur radicals formed in these processes. The database has also been expanded to include halogen atom and halogen oxide radical reactions with a number of the reduced sulfur compounds.

Metal Chemistry

New results indicate that the $Na + O_3$ reaction produces NaO in the first excited electronic state. This observation may help explain the apparent low yield in laboratory studies of Na D-line emission from the $NaO + O$ reaction, if the excited NaO lives long enough to react with O .

Sodium is deposited in the upper atmosphere by meteors along with larger amounts of silicon, magnesium, and iron; comparable amounts of aluminum, nickel, and calcium; and smaller amounts of potassium, chromium, manganese, and other elements. The interest is greatest in the alkali metals because they form the least stable oxides and thus free atoms can be regenerated through photolysis and reactions with O and O_3 . The other meteoric elements are expected to form more stable oxides. A review by Plane [1256] describes many aspects of atmospheric metal chemistry.

The total flux of alkali metals through the atmosphere is relatively small, e.g., one or two orders of magnitude less than CFCs. Therefore extremely efficient catalytic cycles are required in order for Na to have a significant effect on stratospheric chemistry. There are no measurements of metals or metal compounds in the stratosphere which indicate a significant role.

It has been proposed that the highly polar metal compounds may polymerize to form clusters and that the stratospheric concentrations of free metal compounds are too small to play a significant role in the chemistry.

Some studies have shown that the polar species NaO and $NaOH$ associate with abundant gases such as O_2 and CO_2 with very fast rates in the atmosphere. It has been proposed that reactions of this type will lead to the production of clusters with many molecules attached to the sodium compounds. In most cases thermal dissociation is slow, and photolysis competes with the association reactions and limits the cluster concentrations in daylight. If atmospheric sodium does form large clusters, it is unlikely that Na species can have a significant role in stratospheric ozone chemistry. In order to assess the importance of these processes, data are needed on the association rates and the photolysis rates involving the cluster species.

Photochemical Data

To reduce an important uncertainty in atmospheric modeling, high resolution measurements should be carried out as a function of temperature for the quantum yields for $O(^1D)$ production in the photolysis of ozone around 300 nm (i.e., in the Huggins bands). For Cl_2O_2 , the small absorption cross sections beyond 320 nm are potentially very important for photodissociation in the polar stratosphere, and need to be further studied. In addition, the photodissociation quantum yields for $ClONO_2$ at longer wavelengths (around 350 nm) should be further investigated.

Heterogeneous Chemistry

There is no longer any question that heterogeneous processes on the surfaces of polar stratospheric cloud particles play a critical role in the chemistry of the winter and spring polar stratospheres. Furthermore, there is increasing observational and modeling evidence that heterogeneous reactions on background sulfuric acid aerosols may play a very important role in stratospheric processes at mid-latitudes, particularly when stratospheric sulfate levels are elevated by major volcanic eruptions.

Polar heterogeneous chemical processes identified to date have a tendency to enhance the destruction of stratospheric ozone, primarily by converting relatively inactive "reservoir" species HCl and $ClONO_2$ to more active Cl_2 and $HOCl$, which are easily photolyzed to Cl and ClO . In some scenarios the heterogeneous reaction of $HOCl$ and N_2O_5 with HCl may also play an important role in promoting the production of more easily photolyzed species. In addition, interaction with PSC surfaces can remove N_2O_5 and HNO_3 vapor from the polar stratosphere, sequestering nitrogen oxides in the form of condensed phase nitric acid and, thus, reducing the normal mitigating effect gaseous NO_x can have on ClO_x -catalyzed ozone destruction. The net effect of these processes is a major buildup of ClO_x radicals in PSC-processed polar stratospheric air masses and, particularly over the Antarctic, a massive springtime destruction of stratospheric ozone.

Model calculations also suggest that the reaction of stratospheric N_2O_5 with liquid water in sulfuric acid aerosols to form HNO_3 can have a significant impact on NO_x/HNO_3 ratios in the lower mid-latitude stratosphere, bringing measured mid-latitude ozone losses into better agreement with observations. Models suggest that at current

mid-latitude ratios of NO_x/ClO_x this process increases ozone loss by lowering NO_x levels and thus reducing the scavenging of ClO by ClONO_2 formation. However, at higher NO_x/ClO_x ratios, such as those projected for mid-latitude regions impacted by the exhaust from a future high altitude supersonic aircraft fleet, the projected additional ozone loss from homogenous NO_x catalyzed destruction is greatly reduced or eliminated. Under some circumstances the reaction of ClONO_2 with sulfuric acid aerosol may also play a role in denitrification and the release of photolyzable chlorine species.

The stratosphere also contains carbonaceous soot from aircraft and rocket exhausts, alumina and other metal oxides from solid propellant rocket exhaust and spacecraft debris, and, possibly, sodium chloride from some volcanic eruptions. There is increasing interest in determining if and when heterogeneous processes on these relatively minor surfaces can influence stratospheric chemistry.

Heterogeneous processes involving the liquid water droplets and ice crystals found in tropospheric clouds and aircraft contrails and/or the sulfate aerosols found in the free troposphere may have a significant effect on the flux into the stratosphere of reactive species from partially oxidized hydrohalocarbons or aircraft exhaust. Proper modeling of these processes will be necessary to assess the atmospheric impact of reducing the use of partially chlorinated hydrocarbon solvents, replacing CFCs with HCFCs and HFCs, and the evolution of the civil aviation industry.

The laboratory study of heterogeneous processes relevant to the stratosphere is an immature field in comparison to the measurement of gas phase kinetic and photodissociation parameters. Heterogeneous experimental techniques are not yet as well developed and the interpretation of experimental data is significantly more complex. Nonetheless, over the past several years, a number of experimental groups have made very significant progress and data from complementary techniques are increasingly available to help determine when the quantification of heterogeneous kinetic processes has been successfully distinguished from complicating mass transport and surface saturation processes.

However, it is well to remember that quantitative application of laboratory results on heterogeneous processes to the stratosphere is not straightforward. First, there is still a significant level of uncertainty in both the detailed chemical and physical characteristics of the droplet and particle surfaces present in the stratosphere and in how faithful the laboratory simulation of these surfaces in various experimental configurations may be. Secondly, the proper incorporation of heterogeneous processes into models of stratospheric chemistry is very difficult and no current models incorporate formation of and reaction on droplet/particle surfaces in a fully coupled and self-consistent way. A great deal of effort will have to be expended before the modeling community is as adept at incorporating heterogeneous effects as they are in representing gas phase kinetic and photochemical processes.

Gas Phase Enthalpy Data (Appendix 1)

This table gives $\Delta H_f(298)$ values for a number of atmospheric species. Most of the recommendations are based upon data in the IUPAC Evaluation (Atkinson et al. [65]). Some of the values are different from the current IUPAC recommendations, reflecting recent studies that have not yet been accepted and incorporated into that publication. These data are presented without citation or reference to the original source.

Solar Flux and Species Profiles (Appendix 2)

A set of two figures representing solar fluxes has been added to this evaluation. One figure gives the solar flux from 110 to 600 nm above the atmosphere and the second gives the actinic flux from 180 to 400 nm at five altitudes from the surface to 50 km. We are grateful to Kenneth Minschwaner of NCAR (presently at the Department of Physics at New Mexico Institute of Mining and Technology) for providing these data.

A set of nine figures presenting model-calculated altitude profiles for stratospheric temperature, trace species concentrations, and photolysis rate coefficients is given. Some details of the model used to generate the profiles are given at the beginning of Appendix 2. The efforts of Peter S. Connell and other members of the LLNL are gratefully acknowledged for providing these profiles.

The data in the eleven figures are presented to provide "order of magnitude" values of important parameters for the purpose of evaluating stratospheric kinetics and photochemical processes. Since the profiles are sensitive to variations in season, hour of the day, latitude, and aerosol density, some care must be taken in how they are applied to specific problems. They are not intended to be standards.