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Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling

Evaluation Number 10

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ABSTRACT

This is the tenth 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 tenth 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:

Evaluation Number	Reference
1	NASA RP 1010, Chapter 1 (Hudson, 1977)
2	JPL Publication 79-27 (DeMore et al., 1979)
3	NASA RP 1049, Chapter 1 (Hudson and Reed, 1979)
4	JPL Publication 81-3 (DeMore et al., 1981)
5	JPL Publication 82-57 (DeMore et al., 1982)
6	JPL Publication 83-62 (DeMore et al., 1983)
7	JPL Publication 85-37 (DeMore et al., 1985)
8	JPL Publication 87-41 (DeMore et al., 1987)
9	JPL Publication 90-1 (DeMore et al., 1990)

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 O_2, metal chemistry, profiles)

C. 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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The Chairman and Panel Members gratefully acknowledge the invaluable contributions of Ms. Grace Hallowell in the organization and production of this and previous evaluations.

Copies of this evaluation may be obtained by requesting JPL Publication 92-20 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

In the present evaluation the numbers of new (80) and changed (42) recommendations are greater than those of the previous evaluation, reflecting the continuing high level of activity in laboratory studies of atmospheric chemistry. Reactions of singlet molecular oxygen are included for the first time. Another new addition is an appendix of model-generated concentration profiles and J-values for important species in the upper atmosphere. The appendix listing heats of formation of many atmospheric species has been updated and expanded.

Although the database for homogeneous reaction kinetics of the stratosphere is by now relatively mature, it is well to remember that no rate constant is known to better than 10%, and many have uncertainties of 20% or more. The rate constant for the important reaction, $OH + CH_4$, has been corrected in the present evaluation by approximately 20%. This change is typical of that for many OH abstraction reactions, for which early measurements have often been erroneously high. Such changes are important because oxidation by OH is the principal removal path for many trace species, including man-made compounds such as the HCFCs (hydrochlorofluorocarbons). For reactions of this type, including Cl abstraction reactions, there is often some difficulty in reconciling high temperature (above 298 K) and low temperature (below 298 K) rate constant data. Early problems in evaluating the rate constant for the important $Cl + CH_4$ reaction were related to this situation. The frequent observation is that Arrhenius plots of the rate constant data show upward curvature at low temperatures which cannot be explained by tunneling or by expected departures from Arrhenius behavior. Some or perhaps all of these departures are due to secondary chemistry or reaction with walls and impurities. As a consequence, there is a continuing need for new techniques and approaches which minimize such errors.

As it is now well-recognized, the role of heterogeneous processes is one of the most uncertain areas of atmospheric modeling. Efforts have continued in many laboratories to quantify these effects and to provide a basis for their incorporation into the models. Substantial difficulties and uncertainties remain, however. Our evaluation of laboratory data for heterogeneous chemistry, which began in the previous evaluation, now includes a recommendation of preferred values rather than just a compilation of reported data.

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 are given in the notes.

The $O(^1D)$ reactions of 7 halocarbons have been added to this review. These compounds are generally 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 ($^1\Delta$ and $^1\Sigma$)

Fourteen reactions of the $(a^1\Delta_g)$ and $(b^1\Sigma^+_g)$ excited states of molecular oxygen have been added to this evaluation. 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

There has been no change in the database for HO_x chemistry since the last evaluation. The $HO_2 + O_3$ 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 of OH + HONO, NH + NO, NH + NO_2, and H + NO_2. The latter is a reaction commonly used in laboratory preparations of the hydroxyl radical. There are minor changes to the recommendations for the reactions NO + HO_2, NO + NO_3, OH + NH_3 and $NH_2 + O_2$ due to recently published work.

Hydrocarbon Oxidation

The major change in the recommendations for the hydrocarbon oxidation chemistry since the last evaluation is the value for the rate coefficient for the reaction of OH with CH_4, which has been reduced by approximately 20%. Even though this is a rather small numerical change, it is quite significant in the atmospheric budget and chemistry calculations. A few reactions dealing with atmospheric chemistry of ethane, peroxyacetyl nitrate (PAN), and simple organic acids have been added. In addition, small changes have been made for many rate coefficients. The accuracies of many rate coefficients have improved, and are reflected in the revised rate constants.

There still remain some areas of large uncertainties. The major such area is the reactions of peroxy radical reactions. Further work is needed to clarify the rate coefficients for many peroxy radicals. Use of peroxy radical detection by methods other than UV absorption would be very beneficial. Also, controlling the chemistry in the experimental system to minimize secondary reactions would be beneficial. The reactions involving PAN, CH_3CN, and HCN also require some attention. PAN reactions may be important in the evaluation of the atmospheric acceptability of supersonic and subsonic aircraft and in estimating the long range transport of odd nitrogen in the upper troposphere.

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 three propane-substituted HCFCs have been added, increasing to twenty-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 eighteen of these species have also been added. Note that rate coefficient data for the reaction of these halocarbons with $O(^1D)$ are included in the $O(^1D)$ section of Table 1. Rate coefficients have also been added for the reaction of chlorine atoms with PAN ($CH_3CO_3NO_2$), for the reaction of OH with CHF_2Br (a proposed replacement for Halons), and for the reaction of OH with $ClNO_2$. There have been only minor changes in the recommendations for reactions included in the previous evaluation, with the exception of the O + OClO reaction, for which the recommended bimolecular rate constant value has been significantly reduced and a termolecular reaction component forming ClO_3 has been included. With these additions and improvements, the kinetics database for homogeneous gas-phase reactions of halogen species appears to be well-established.

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 reactions involved in the oxidation of the radical products CH_3S, CH_3SS, and CH_3SSO. The database has also been expanded to include the reactions of SH with F_2, Cl_2, Br_2, and BrCl; the reactions of CS_2 and CH_3SH with Cl; as well as the reactions of H_2S with O_3, SO_3 with NH_3, and CH_3SCH_3 with N_2O_5.

Metal Chemistry

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 (1991) 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 CFMs. 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

In order to reduce an important source of uncertainty in atmospheric modeling calculations, high resolution measurements around 300 nm (i.e. in the Huggins bands) should be carried out for ozone absorption cross sections, quantum yields for O^1D production and their temperature dependency.

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 temperature dependency of the absorption cross sections in the 300 nm region may be very important for HNO_3, as well as for HO_2NO_2.

In the case of HCFCs, there are discrepancies among the available sets of UV absorption data on the magnitude of the temperature effect; further work in this area is still needed.

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 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.

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., 1989). 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.

Profiles (Appendix 2)

A set of nine figures presenting model-calculated altitude profiles for stratospheric temperature, trace species concentrations, and photolysis rate coefficients has been added to this publication. These data are given 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, and latitude, some care must be taken in how they are applied to specific problems. They are not intended to be standards for comparison with other model calculations. 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.

RATE CONSTANT DATA

In Table 1 (Rate Constants for Second Order Reactions) the reactions are grouped into the classes O_x, $O(^1D)$, Singlet O_2, HO_x, NO_x, Hydrocarbon Reactions, ClO_x, BrO_x, FO_x, SO_x, and metal reactions. The data in Table 2 (Rate Constants for Three-Body Reactions), while not grouped by class, are presented in the same order as the bimolecular reactions. Further, the presentation of photochemical cross section data follows the same sequence.

Bimolecular Reactions

Some of the reactions in Table 1 are actually more complex than simple two-body reactions. To explain the pressure and temperature dependences occasionally seen in reactions of this type, it is necessary to consider the bimolecular class of reactions in terms of two subcategories, direct (concerted) and indirect (non-concerted) reactions.

A direct or concerted bimolecular reaction is one in which the reactants A and B proceed to products C and D without the intermediate formation of an AB adduct which has appreciable bonding, i.e., no stable A-B molecule exists, and there is no reaction intermediate other than the transition state of the reaction, $(AB)^{\neq}$.

$$A + B \rightarrow (AB)^{\neq} \rightarrow C + D$$

The reaction of OH with CH_4 forming $H_2O + CH_3$ is an example of a reaction of this class.

Very useful correlations between the expected structure of the transition state $[AB]^{\neq}$ and the A-Factor of the reaction rate constant can be made, especially in reactions which are constrained to follow a well-defined approach of the two reactants in order to minimize energy requirements in the making and breaking of bonds. The rate constants for these reactions are well represented by the Arrhenius expression $k = A \exp(-E/RT)$ in the 200-300 K temperature range. These rate constants are not pressure dependent.

The indirect or non-concerted class of bimolecular reactions is characterized by a more complex reaction path involving a potential well between reactants and products, leading to a bound adduct (or reaction complex) formed between the reactants A and B:

$$A + B \leftrightarrow [AB]^* \rightarrow C + D$$

The intermediate $[AB]^*$ is different from the transition state $[AB]^{\neq}$, in that it is a bound molecule which can, in principle, be isolated. (Of course, transition states are involved in all of the above reactions, both forward and backward, but are not explicitly shown.) An example of this reaction type is ClO + NO, which normally produces Cl + NO_2. Reactions of the non-concerted type can have a more complex temperature dependence and can exhibit a pressure dependence if the lifetime of $[AB]^*$ is comparable to the rate of collisional deactivation of $[AB]^*$. This arises because the relative rate at which $[AB]^*$ goes to products C + D vs. reactants A + B is a sensitive function of its excitation energy. Thus, in reactions of this type, the distinction between the bimolecular and termolecular classification becomes less meaningful, and it is especially necessary to study such reactions under the temperature and pressure conditions in which they are to be used in model calculation, or, alternatively, to develop a reliable theoretical basis for extrapolation of data.

The rate constant tabulation for second-order reactions (Table 1) is given in Arrhenius form: $k(T) = A \exp((-E/R)(1/T))$ and contains the following information:

1. Reaction stoichiometry and products (if known). The pressure dependences are included, where appropriate.
2. Arrhenius A-factor.
3. Temperature dependence and associated uncertainty ("activation temperature" $E/R \pm \Delta E/R$).
4. Rate constant at 298 K.
5. Uncertainty factor at 298 K.
6. Note giving basis of recommendation and any other pertinent information.

Termolecular Reactions

Rate constants for third order reactions (Table 2) of the type $A + B \leftrightarrow [AB]^* \xrightarrow{M} AB$ are given in the form

$$k_0(T) = k_0^{300}(T/300)^{-n} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1},$$

(where $k_0{}^{300}$ has been adjusted for air as the third body), together with a recommended value of n. Where pressure fall-off corrections are necessary, an additional entry gives the limiting high pressure rate constant in a similar form:

$$k_\infty(T) = k_\infty^{300}(T/300)^{-m} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

To obtain the effective second-order rate constant for a given condition of temperature and pressure (altitude), the following formula is used:

$$k(Z) = k(M,T) = \left(\frac{k_0(T)[M]}{1 + (k_0(T)[M]/k_\infty(T))} \right) 0.6^{\{1 + [\log_{10}(k_0(T)[M]/k_\infty(T))]^2\}^{-1}}$$

The fixed value 0.6 which appears in this formula fits the data for all listed reactions adequately, although in principle this quantity may be different for each reaction, and also temperature dependent.

Thus, a compilation of rate constants of this type requires the stipulation of the four parameters, $k_0(300)$, n, $k_\infty(300)$, and m. These can be found in Table 2. The discussion that follows outlines the general methods we have used in establishing this table, and the notes to the table discuss specific data sources.

Low-Pressure Limiting Rate Constant [$k_0^x(T)$]

Troe (1977) has described a simple method for obtaining low-pressure limiting rate constants. In essence this method depends on the definition:

$$k_0^x(T) \equiv \beta_x k_{0,sc}^x(T)$$

Here sc signifies "strong" collisions, x denotes the bath gas, and β_x is an efficiency parameter ($0 < \beta < 1$), which provides a measure of energy transfer.

The coefficient β_x is related to the average energy transferred in a collision with gas x, $<\Delta E>_x$, via:

$$\frac{\beta_x}{1-\beta_x{}^{1/2}} = \frac{<\Delta E>_x}{F_E\, kT}$$

Notice that $<\Delta E>$ is quite sensitive to β. F_E is the correction factor of the energy dependence of the density of states (a quantity of the order of 1.1 for most species of stratospheric interest).

For many of the reactions of possible stratospheric interest reviewed here, there exist data in the low-pressure limit (or very close thereto), and we have chosen to evaluate and unify this data by calculating $k_{0,sc}^x(T)$ for the appropriate bath gas x and computing the value of β_x corresponding to the experimental value [Troe (1977)]. A compilation (Patrick and Golden, 1983) gives details for many of the reactions considered here.

From the β_x values (most of which are for N_2, i.e., β_{N2}), we compute $<\Delta E>_x$ according to the above equation. Values of $<\Delta E>_{N2}$ of approximately 0.3-1 kcal mole^{-1} are generally expected. If multiple data exist, we average the values of $<\Delta E>_{N2}$ and recommend a rate constant corresponding to the β_{N2} computed in the equation above.

Where no data exist we have estimated the low-pressure rate constant by taking $\beta_{N2} = 0.3$ at T = 300 K, a value based on those cases where data exist.

Temperature Dependence of Low-Pressure Limiting Rate Constants: n

The value of n recommended here comes from measurements or, in some cases, a calculation of $<\Delta E>_{N2}$ from the data at 300 K, and a computation of β_{N2} (200 K) assuming that $<\Delta E>_{N2}$ is independent of temperature in this range. This β_{N2} (200 K) value is combined with the computed value of k_0^{sc} (200 K) to give the expected value of the actual rate constant at 200 K. This latter in combination with the value at 300 K yields the value of n.

This procedure can be directly compared with measured values of k_0 (200 K) when those exist. Unfortunately, very few values at 200 K are available. There are often temperature-dependent studies, but some ambiguity exists when one attempts to extrapolate these down to 200 K. If data are to be extrapolated beyond the measured temperature range, a choice must be made as to the functional form of the temperature dependence. There are two general ways of expressing the temperature dependence of rate constants. Either the Arrhenius expression $k_0(T) = A\exp(-E/RT)$ or the form $k_0(T) = A' T^{-n}$ is employed. Since neither of these extrapolation techniques is soundly based, and since they often yield values that differ substantially, we have used the method explained earlier as the basis of our recommendations.

High-Pressure Limit Rate Constants $[k_\infty(T)]$

High-pressure rate constants can often be obtained experimentally, but those for the relatively small species of atmospheric importance usually reach the high-pressure limit at inaccessibly high pressures. This leaves two sources of these numbers, the first being guesses based upon some model, and the second being extrapolation of fall-off data up to higher pressures. Stratospheric conditions generally render reactions of interest much closer to the low-pressure limit, and thus are fairly insensitive to the high-pressure value. This means that while the extrapolation is long, and the value of $k_\infty(T)$ not very accurate, a "reasonable guess' of $k_\infty(T)$ will then suffice. In some cases we have declined to guess since the low-pressure limit is effective over the entire range of stratospheric conditions.

Temperature Dependence of High-Pressure Limit Rate Constants: m

There are very few data upon which to base a recommendation for values of m. Values in Table 2 are often estimated, based on models for the transition state of bond association reactions and whatever data are available.

Uncertainty Estimates

For second-order rate constants in Table 1, an estimate of the uncertainty at any given temperature may be obtained from the following expression:

$$f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$$

Note that the exponent is absolute value. An upper or lower bound (corresponding approximately to one standard deviation) of the rate constant at any temperature T can be obtained by multiplying or dividing the value of the rate constant at that temperature by the factor f(T). The quantities f(298) and $\Delta E/R$ are, respectively, the uncertainty in the rate constant at 298 K and in the Arrhenius temperature coefficient, as listed in Table 1. This approach is based on the fact that rate constants are almost always known with minimum uncertainty at room temperature. The overall uncertainty normally increases at other temperatures, because there are usually fewer data and it is almost always more difficult to make measurements at other temperatures. It is important to note that the uncertainty at a temperature T cannot be calculated from the expression $\exp(\Delta E/RT)$. The above expression for f(T) must be used to obtain the correct result.

The uncertainty represented by f(T) is normally symmetric; i.e., the rate constant may be greater than or less than the central value, k(T), by the factor f(T). In a few cases in Table 1 asymmetric uncertainties are given in the temperature coefficient. For these cases, the factors by which a rate constant are to be multiplied or divided to obtain, respectively, the upper and lower limits are not equal, except at 298 K where the factor is simply f(298 K). Explicit equations are given below for the case where the temperature dependence is (E/R +a, -b):

For T > 298 K, multiply by the factor

$$f(298\ \mathrm{K})e^{[a(1/298-1/T)]}$$

and divide by the factor

$$f(298\ \mathrm{K})e^{[b(1/298-1/T)]}$$

For T < 298 K, multiply by the factor

$$f(298\ \mathrm{K})e^{[b(1/T-1/298)]}$$

and divide by the factor

$$f(298\ \mathrm{K})e^{[a(1/T-1/298)]}$$

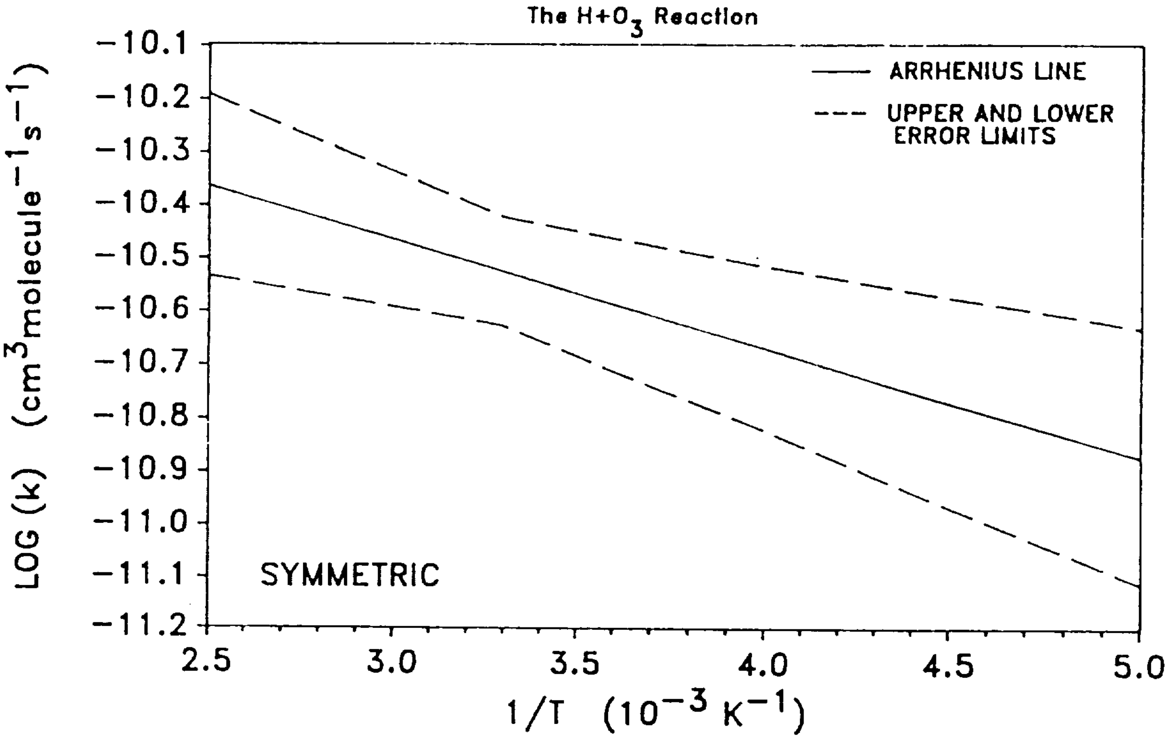
Examples of symmetric and asymmetric error limits are shown in Figure 1.

For three-body reactions (Table 2) a somewhat analogous procedure is used. Uncertainties expressed as increments to k_0 and k_∞ are given for these rate constants at room temperature. The additional uncertainty arising from the temperature extrapolation is expressed as an uncertainty in the temperature coefficients n and m.

The assigned uncertainties represent the subjective judgement of the Panel. They are not determined by a rigorous, statistical analysis of the database, which generally is too limited to permit such an analysis. Rather, the uncertainties are based on a knowledge of the techniques, the difficulties of the experiments, and the potential for systematic errors. There is obviously no way to quantify these "unknown" errors. The spread in results among different techniques for a given reaction may provide some basis for an uncertainty, but the possibility of the same, or compensating, systematic errors in all the studies must be recognized. Furthermore, the probability distribution may not follow the normal, Gaussian form. For measurements subject to large systematic errors, the true rate constant may be much further from the recommended value than would be expected based on a Gaussian distribution with the stated uncertainty. As an example, the recommended rate constants for the reactions HO_2 + NO and Cl + $ClONO_2$ have changed by factors of 30-50, occurrences which could not have been allowed for with any reasonable values of σ in a Gaussian distribution.

Units

The rate constants are given in units of concentration expressed as molecules per cubic centimeter and time in seconds. Thus, for first-, second-, and third-order reactions the units of k are s^{-1}, cm^3 $molecule^{-1}$ s^{-1}, and cm^6 $molecule^{-2}$ s^{-1}, respectively. Cross sections are expressed as cm^2 $molecule^{-1}$, base e.



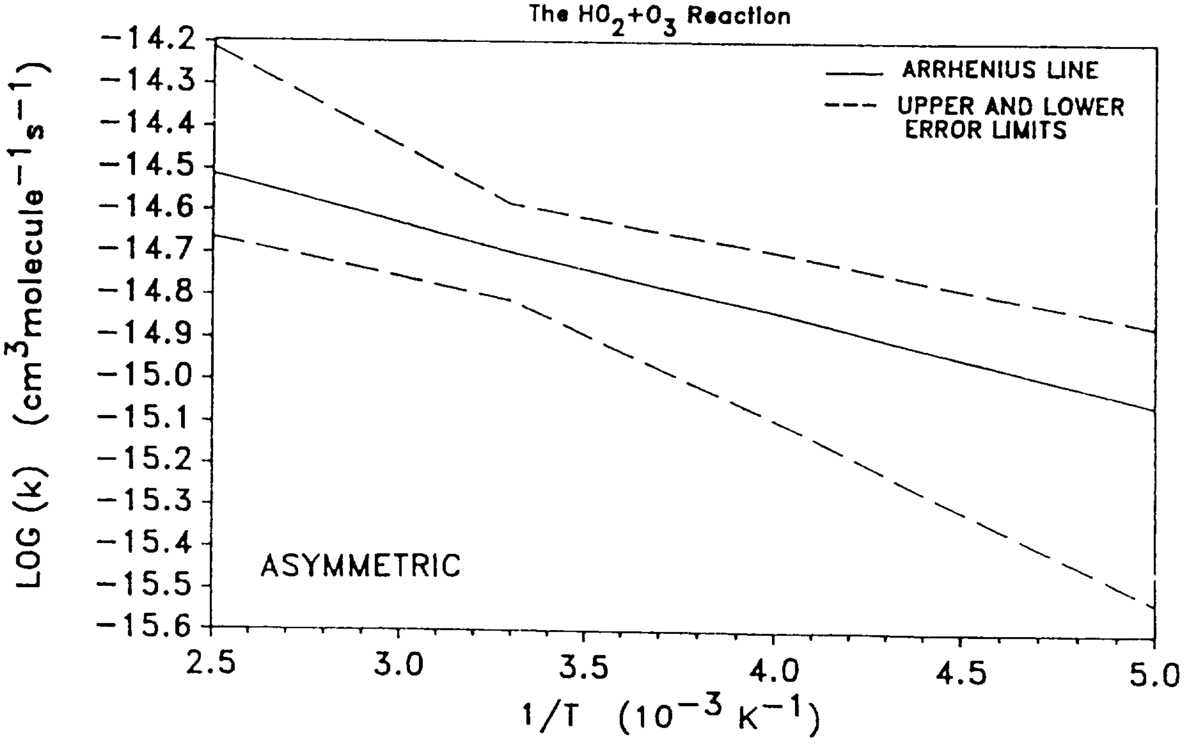


Figure 1. Symmetric and Asymmetric Error Limits

TABLE 1. RATE CONSTANTS FOR SECOND ORDER REACTIONS

	Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
	<u>O_x Reactions</u>					
	$O + O_2 \xrightarrow{M} O_3$	(See Table 2)				
	$O + O_3 \rightarrow O_2 + O_2$	8.0×10^{-12}	2060±250	8.0×10^{-15}	1.15	A1
	<u>$O(^1D)$ Reactions</u>					
	$O(^1D) + N_2O \rightarrow N_2 + O_2$	4.9×10^{-11}	0±100	4.9×10^{-11}	1.3	A2, A3
	$\rightarrow NO + NO$	6.7×10^{-11}	0±100	6.7×10^{-11}	1.3	A2, A3
	$O(^1D) + H_2O \rightarrow OH + OH$	2.2×10^{-10}	0±100	2.2×10^{-10}	1.2	A2, A4
	$O(^1D) + CH_4 \rightarrow OH + CH_3$	1.4×10^{-10}	0±100	1.4×10^{-10}	1.2	A2, A5
	$\rightarrow H_2 + CH_2O$	1.4×10^{-11}	0±100	1.4×10^{-11}	1.2	A2, A5
	$O(^1D) + H_2 \rightarrow OH + H$	1.0×10^{-10}	0±100	1.0×10^{-10}	1.2	A2, A6
&	$O(^1D) + N_2 \rightarrow O + N_2$	1.8×10^{-11}	-(110±100)	2.6×10^{-11}	1.2	A2
	$O(^1D) + N_2 \xrightarrow{M} N_2O$	(See Table 2)				
&	$O(^1D) + O_2 \rightarrow O + O_2$	3.2×10^{-11}	-(70±100)	4.0×10^{-11}	1.2	A2,A40
&	$O(^1D) + CO_2 \rightarrow O + CO_2$	7.4×10^{-11}	-(120±100)	1.1×10^{-10}	1.2	A2
	$O(^1D) + O_3 \rightarrow O_2 + O_2$	1.2×10^{-10}	0±100	1.2×10^{-10}	1.3	A2, A7
	$\rightarrow O_2 + O + O$	1.2×10^{-10}	0±100	1.2×10^{-10}	1.3	A2, A7
	$O(^1D) + HCl \rightarrow$ products	1.5×10^{-10}	0±100	1.5×10^{-10}	1.2	A8
	$O(^1D) + HF \rightarrow OH + F$	1.4×10^{-10}	0±100	1.4×10^{-10}	2.0	A9
	$O(^1D) + HBr \rightarrow$ products	1.5×10^{-10}	0±100	1.5×10^{-10}	2.0	A10
	$O(^1D) + Cl_2 \rightarrow$ products	2.8×10^{-10}	0±100	2.8×10^{-10}	2.0	A11
	$O(^1D) + CCl_4 \rightarrow$ products	3.3×10^{-10}	0±100	3.3×10^{-10}	1.2	A2, A12
	$O(^1D) + CFCl_3 \rightarrow$ products	2.3×10^{-10}	0±100	2.3×10^{-10}	1.2	A2, A12
	$O(^1D) + CF_2Cl_2 \rightarrow$ products	1.4×10^{-10}	0±100	1.4×10^{-10}	1.3	A2, A12
*	$O(^1D) + CF_4 \rightarrow CF_4 + O$	-	-	2.0×10^{-14}	1.5	A2, A13
	$O(^1D) + CCl_2O \rightarrow$ products	3.6×10^{-10}	0±100	3.6×10^{-10}	2.0	A2, A14

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
$O(^1D) + CFClO \rightarrow$ products	1.9×10^{-10}	0±100	1.9×10^{-10}	2.0	A2, A14
$O(^1D) + CF_2O \rightarrow$ products	7.4×10^{-11}	0±100	7.4×10^{-11}	2.0	A2, A14
$O(^1D) + NH_3 \rightarrow OH + NH_2$	2.5×10^{-10}	0±100	2.5×10^{-10}	1.3	A2, A15
# $O(^1D) + CF_3Cl \rightarrow$ products	8.7×10^{-11}	0±100	8.7×10^{-11}	1.3	A12,A33
# $O(^1D) + CF_2ClCFCl_2 \rightarrow$ products	2×10^{-10}	0±100	2×10^{-10}	2.0	A12,A34
# $O(^1D) + CF_3CCl_3 \rightarrow$ products	2×10^{-10}	0±100	2×10^{-10}	2.0	A12,A35
# $O(^1D) + CF_2ClCF_2Cl \rightarrow$ products	1.3×10^{-10}	0±100	1.3×10^{-10}	1.3	A12,A36
# $O(^1D) + CF_3CFCl_2 \rightarrow$ products	1×10^{-10}	0±100	1×10^{-10}	2.0	A12,A37
# $O(^1D) + CF_3CF_2Cl \rightarrow$ products	5×10^{-11}	0±100	5×10^{-11}	1.3	A12,A38
# $O(^1D) + c\text{-}C_4F_8 \rightarrow$ products	-	-	8×10^{-13}	1.3	A12,A39
$O(^1D) + CHFCl_2 \rightarrow$ products	1.9×10^{-10}	0±100	1.9×10^{-10}	1.3	A16, A12
* $O(^1D) + CHF_2Cl \rightarrow$ products	1.0×10^{-10}	0±100	1.0×10^{-10}	1.2	A17, A12
$O(^1D) + CHF_3 \rightarrow$ products	8.4×10^{-12}	0±100	8.4×10^{-12}	5.0	A18, A12
$O(^1D) + CH_2F_2 \rightarrow$ products	9.0×10^{-11}	0±100	9.0×10^{-11}	3.0	A19, A12
$O(^1D) + CH_3F \rightarrow$ products	1.4×10^{-10}	0±100	1.4×10^{-10}	2.0	A20, A12
* $O(^1D) + CHCl_2CF_3 \rightarrow$ products	2.0×10^{-10}	0±100	2.0×10^{-10}	1.3	A21, A12
* $O(^1D) + CHFClCF_3 \rightarrow$ products	8.6×10^{-11}	0±100	8.6×10^{-11}	1.3	A22, A12
* $O(^1D) + CHF_2CF_3 \rightarrow$ products	1.2×10^{-10}	0±100	1.2×10^{-10}	2.0	A23, A12
$O(^1D) + CH_2ClCF_2Cl \rightarrow$ products	1.6×10^{-10}	0±100	1.6×10^{-10}	2.0	A24, A12
* $O(^1D) + CH_2ClCF_3 \rightarrow$ products	1.2×10^{-10}	0±100	1.2×10^{-10}	1.3	A25, A12
* $O(^1D) + CH_2FCF_3 \rightarrow$ products	4.9×10^{-11}	0±100	4.9×10^{-11}	1.3	A26, A12
* $O(^1D) + CH_3CFCl_2 \rightarrow$ products	2.6×10^{-10}	0±100	2.6×10^{-10}	1.3	A27, A12
* $O(^1D) + CH_3CF_2Cl \rightarrow$ products	2.2×10^{-10}	0±100	2.2×10^{-10}	1.3	A28, A12
$O(^1D) + CH_3CF_3 \rightarrow$ products	1.0×10^{-10}	0±100	1.0×10^{-10}	3.0	A29, A12

Table 1. (Continued)

Reaction	A-Factor^a	E/R±(ΔE/R)	k(298 K)	f(298)^b	Notes
* $O(^1D) + CH_3CHF_2 \rightarrow$ products	$2.0x10^{-10}$	0±100	$2.0x10^{-10}$	1.3	A30, A12
* $O(^1D) + C_2F_6 \rightarrow O + C_2F_6$	-	-	$1.5x10^{-13}$	1.5	A31
* $O(^1D) + SF_6 \rightarrow$ products	-	-	$1.8x10^{-14}$	1.5	A32
	<u>Singlet O_2 Reactions</u>				
# $O_2(^1\Delta) + O \rightarrow$ products	-	-	$<2x10^{-16}$	-	A41
# $O_2(^1\Delta) + O_2 \rightarrow$ products	$3.6x10^{-18}$	220±100	$1.7x10^{-18}$	1.2	A42
# $O_2(^1\Delta) + O_3 \rightarrow O + 2O_2$	$5.2x10^{-11}$	2840±500	$3.8x10^{-15}$	1.2	A43
# $O_2(^1\Delta) + H_2O \rightarrow$ products	-	-	$4.8x10^{-18}$	1.5	A44
# $O_2(^1\Delta) + N \rightarrow NO + O$	-	-	$<9x10^{-17}$	-	A45
# $O_2(^1\Delta) + N_2 \rightarrow$ products	-	-	$<10^{-20}$	-	A46
# $O_2(^1\Delta) + CO_2 \rightarrow$ products	-	-	$<2x10^{-20}$	-	A47
# $O_2(^1\Sigma) + O \rightarrow$ products	-	-	$8x10^{-14}$	5.0	A48
# $O_2(^1\Sigma) + O_2 \rightarrow$ products	-	-	$3.9x10^{-17}$	1.5	A49
# $O_2(^1\Sigma) + O_3 \rightarrow$ products	$2.2x10^{-11}$	0±200	$2.2x10^{-11}$	1.2	A50
# $O_2(^1\Sigma) + H_2O \rightarrow$ products	-	-	$5.4x10^{-12}$	1.3	A51
# $O_2(^1\Sigma) + N \rightarrow$ products	-	-	$<10^{-13}$	-	A52
# $O_2(^1\Sigma) + N_2 \rightarrow$ products	$2.1x10^{-15}$	0±200	$2.1x10^{-15}$	1.2	A53
# $O_2(^1\Sigma) + CO_2 \rightarrow$ products	$4.2x10^{-13}$	0±200	$4.2x10^{-13}$	1.2	A54
	<u>HO_x Reactions</u>				
$H + O_2 \xrightarrow{M} HO_3$	(See Table 2)				
$H + O_3 \rightarrow OH + O_2$	$1.4x10^{-10}$	470±200	$2.9x10^{-11}$	1.25	B1
$H + HO_2 \rightarrow$ products	$8.1x10^{-11}$	0±100	$8.1x10^{-11}$	1.3	B2
$O + OH \rightarrow O_2 + H$	$2.2x10^{-11}$	-(120±100)	$3.3x10^{-11}$	1.2	B3
$O + HO_2 \rightarrow OH + O_2$	$3.0x10^{-11}$	-(200±100)	$5.9x10^{-11}$	1.2	B4

Table 1. (Continued)

	Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
	$O + H_2O_2 \rightarrow OH + HO_2$	1.4×10^{-12}	2000±1000	1.7×10^{-15}	2.0	B5
	$OH + HO_2 \rightarrow H_2O + O_2$	4.8×10^{-11}	-(250±200)	1.1×10^{-10}	1.3	B6
	$OH + O_3 \rightarrow HO_2 + O_2$	1.6×10^{-12}	940±300	6.8×10^{-14}	1.3	B7
	$OH + OH \rightarrow H_2O + O$	4.2×10^{-12}	240±240	1.9×10^{-12}	1.4	B8
	$\xrightarrow{M} H_2O_2$	(See Table 2)				
	$OH + H_2O_2 \rightarrow H_2O + HO_2$	2.9×10^{-12}	160±100	1.7×10^{-12}	1.2	B9
	$OH + H_2 \rightarrow H_2O + H$	5.5×10^{-12}	2000±400	6.7×10^{-15}	1.2	B10
&	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	2.3×10^{-13}	-(600±200)	1.7×10^{-12}	1.3	B11
	$\xrightarrow{M} H_2O_2 + O_2$	$1.7 \times 10^{-33}[M]$	-(1000±400)	$4.9 \times 10^{-32}[M]$	1.3	B11
&	$HO_2 + O_3 \rightarrow OH + 2O_2$	1.1×10^{-14}	$500\pm^{500}_{100}$	2.0×10^{-15}	1.3	B12
		<u>NO_x Reactions</u>				
	$N + O_2 \rightarrow NO + O$	1.5×10^{-11}	3600±400	8.5×10^{-17}	1.25	C1
	$N + O_3 \rightarrow NO + O_2$	-	-	$<2.0 \times 10^{-16}$	-	C2
&	$N + NO \rightarrow N_2 + O$	3.4×10^{-11}	0±100	3.4×10^{-11}	1.3	C3
	$N + NO_2 \rightarrow N_2O + O$	-	-	3.0×10^{-12}	3.0	C4
	$O + NO \xrightarrow{M} NO_2$	(See Table 2)				
	$O + NO_2 \rightarrow NO + O_2$	6.5×10^{-12}	-(120±120)	9.7×10^{-12}	1.1	C5
	$O + NO_2 \xrightarrow{M} NO_3$	(See Table 2)				
	$O + NO_3 \rightarrow O_2 + NO_2$	1.0×10^{-11}	0±150	1.0×10^{-11}	1.5	C6
	$O + N_2O_5 \rightarrow$ products	-	-	$<3.0 \times 10^{-16}$	-	C7
	$O + HNO_3 \rightarrow OH + NO_3$	-	-	$<3.0 \times 10^{-17}$	-	C8
	$O + HO_2NO_2 \rightarrow$ products	7.8×10^{-11}	3400±750	8.6×10^{-16}	3.0	C9
#	$H + NO_2 \rightarrow OH + NO$	4.0×10^{-10}	340±300	1.3×10^{-10}	1.3	C10
	$O_3 + NO \rightarrow NO_2 + O_2$	2.0×10^{-12}	1400±200	1.8×10^{-14}	1.2	C11

Table 1. (Continued)

	Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
*	$NO + HO_2 \rightarrow NO_2 + OH$	3.7×10^{-12}	-(250±80)	8.6×10^{-12}	1.2	C12
*	$NO + NO_3 \rightarrow 2NO_2$	1.5×10^{-11}	-(170±100)	2.6×10^{-11}	1.3	C13
	$OH + NO \xrightarrow{M} HONO$	(See Table 2)				
	$OH + NO_2 \xrightarrow{M} HNO_3$	(See Table 2)				
	$OH + NO_3 \rightarrow$ products	-	-	2.3×10^{-11}	2.0	C14
#	$OH + HONO \rightarrow H_2O + NO_2$	1.8×10^{-11}	$390\pm^{200}_{500}$	4.5×10^{-12}	1.5	C15
	$OH + HNO_3 \rightarrow H_2O + NO_3$	(See Note C16 and ≠ below)			1.3	C16
	$OH + HO_2NO_2 \rightarrow$ products	1.3×10^{-12}	$-(380\pm^{270}_{500})$	4.6×10^{-12}	1.5	C17
	$HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$	(See Table 2)				
	$HO_2 + NO_3 \rightarrow$ products	-	-	4.1×10^{-12}	2.0	C18
	$O_3 + NO_2 \rightarrow NO_3 + O_2$	1.2×10^{-13}	2450±150	3.2×10^{-17}	1.15	C19
	$O_3 + HNO_2 \rightarrow O_2 + HNO_3$	-	-	$<5.0\times10^{-19}$	-	C20
	$NO_2 + NO_3 \xrightarrow{M} N_2O_5$	(See Table 2)				
*	$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$	(See Note)				C21
	$N_2O_5 + H_2O \rightarrow 2HNO_3$	-	-	$<2.0\times10^{-21}$	-	C22
#	$NH + NO \rightarrow$ products	4.9×10^{-11}	0±300	4.9×10^{-11}	1.5	C23
#	$NH + NO_2 \rightarrow$ products	3.5×10^{-13}	-(1140±500)	1.6×10^{-11}	2.0	C24
*	$OH + NH_3 \rightarrow H_2O + NH_2$	1.7×10^{-12}	710±200	1.6×10^{-13}	1.2	C25
	$NH_2 + HO_2 \rightarrow$ products	-	-	3.4×10^{-11}	2.0	C26

≠ $OH + HNO_3$ pressure and temperature dependence fit by

$$k(M,T) = k_0 + \frac{k_3[M]}{1 + \dfrac{k_3[M]}{k_2}} \quad \text{with} \quad \left\{ \begin{array}{l} k_0 = 7.2\times10^{-15} \exp(785/T) \\ k_2 = 4.1\times10^{-16} \exp(1440/T) \\ k_3 = 1.9\times10^{-33} \exp(725/T) \end{array} \right.$$

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
$NH_2 + NO \rightarrow$ products	$3.8\text{x}10^{-12}$	-(450±150)	$1.7\text{x}10^{-11}$	2.0	C27
$NH_2 + NO_2 \rightarrow$ products	$2.1\text{x}10^{-12}$	-(650±250)	$1.9\text{x}10^{-11}$	3.0	C28
* $NH_2 + O_2 \rightarrow$ products	-	-	$<6.0\text{x}10^{-21}$	-	C29
$NH_2 + O_3 \rightarrow$ products	$4.3\text{x}10^{-12}$	930±500	$1.9\text{x}10^{-13}$	3.0	C30
	Hydrocarbon Reactions				
$OH + CO \rightarrow CO_2$	$1.5\text{x}10^{-13}(1+0.6P_{atm})$	0±300	$1.5\text{x}10^{-13}(1+0.6P_{atm})$	1.3	D1
* $OH + CH_4 \rightarrow CH_3 + H_2O$	$2.9\text{x}10^{-12}$	1820±200	$6.5\text{x}10^{-15}$	1.1	D2
* $OH + {}^{13}CH_4 \rightarrow {}^{13}CH_3 + H_2O$	(See Note)				D3
* $OH + C_2H_6 \rightarrow H_2O + C_2H_5$	$8.7\text{x}10^{-12}$	1070±100	$2.4\text{x}10^{-13}$	1.1	D4
* $OH + C_3H_8 \rightarrow H_2O + C_3H_7$	$1.1\text{x}10^{-11}$	700±100	$1.1\text{x}10^{-12}$	1.2	D5
$OH + C_2H_4 \rightarrow$ products	(See Table 2)				
$OH + C_2H_2 \rightarrow$ products	(See Table 2)				
$OH + H_2CO \rightarrow H_2O + HCO$	$1.0\text{x}10^{-11}$	0±200	$1.0\text{x}10^{-11}$	1.25	D6
$OH + CH_3OH \rightarrow$ products	$6.7\text{x}10^{-12}$	600±300	$8.9\text{x}10^{-13}$	1.2	D7
* $OH + C_2H_5OH \rightarrow$ products	$7.0\text{x}10^{-12}$	235±100	$3.2\text{x}10^{-12}$	1.3	D8
$OH + CH_3CHO \rightarrow CH_3CO + H_2O$	$6.0\text{x}10^{-12}$	-(250±200)	$1.4\text{x}10^{-11}$	1.4	D9
$OH + CH_3OOH \rightarrow$ products	$3.8\text{x}10^{-12}$	-(200±200)	$7.4\text{x}10^{-12}$	1.5	D10
# $OH + HC(O)OH \rightarrow$ products	$4.5\text{x}10^{-13}$	0±200	$4.5\text{x}10^{-13}$	1.3	D11
# $OH + CH_3C(O)OH \rightarrow$ products	$1.2\text{x}10^{-12}$	170±150	$6.8\text{x}10^{-13}$	1.5	D12
$OH + HCN \rightarrow$ products	$1.2\text{x}10^{-13}$	400±150	$3.1\text{x}10^{-14}$	3.0	D13
* $OH + CH_3CN \rightarrow$ products	$7.8\text{x}10^{-13}$	1050±200	$2.3\text{x}10^{-14}$	1.5	D14
# $OH + CH_3C(O)O_2NO_2 \rightarrow$ products	$1.1\text{x}10^{-12}$	650±400	$1.2\text{x}10^{-13}$	3.0	D15
$O_3 + C_2H_2 \rightarrow$ products	$1.0\text{x}10^{-14}$	4100±500	$1.0\text{x}10^{-20}$	3.0	D16
$O_3 + C_2H_4 \rightarrow$ products	$1.2\text{x}10^{-14}$	2630±100	$1.7\text{x}10^{-18}$	1.25	D17

Table 1. (Continued)

	Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
	$O_3 + C_3H_6 \rightarrow$ products	6.5×10^{-15}	1900±200	1.1×10^{-17}	1.2	D18
	$HO_2 + CH_2O \rightarrow$ adduct	6.7×10^{-15}	-(600±600)	5.0×10^{-14}	5.0	D19
&	$O + HCN \rightarrow$ products	1.0×10^{-11}	4000±1000	1.5×10^{-17}	10.0	D20
	$O + C_2H_2 \rightarrow$ products	3.0×10^{-11}	1600±250	1.4×10^{-13}	1.3	D21
	$O + H_2CO \rightarrow$ products	3.4×10^{-11}	1600±250	1.6×10^{-13}	1.25	D22
	$O + CH_3CHO \rightarrow CH_3CO + OH$	1.8×10^{-11}	1100±200	4.5×10^{-13}	1.25	D23
	$O + CH_3 \rightarrow$ products	1.1×10^{-10}	0±250	1.1×10^{-10}	1.3	D24
	$CH_3 + O_2 \rightarrow$ products	-	-	$<3.0\times10^{-16}$	-	D25
	$CH_3 + O_2 \xrightarrow{M} CH_3O_2$	(See Table 2)				
	$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$	-	-	$<2.0\times10^{-15}$	-	D26
	$C_2H_5 + O_2 \xrightarrow{M} C_2H_5O_2$	(See Table 2)				
	$CH_2OH + O_2 \rightarrow CH_2O + HO_2$			9.1×10^{-12}	1.3	D27
	$CH_3O + O_2 \rightarrow CH_2O + HO_2$	3.9×10^{-14}	900±300	1.9×10^{-15}	1.5	D28
#	$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$	3.1×10^{-14}	400±400	8.1×10^{-15}	2.0	D29
#	$C_2H_5O + NO \rightarrow$ products	(See Table 2)				
#	$C_2H_5O + NO_2 \rightarrow$ products	(See Table 2)				
	$HCO + O_2 \rightarrow CO + HO_2$	3.5×10^{-12}	-(140±140)	5.5×10^{-12}	1.3	D30
	$CH_3 + O_3 \rightarrow$ products	5.4×10^{-12}	220±150	2.6×10^{-12}	2.0	D31
	$CH_3O_2 + O_3 \rightarrow$ products	-	-	$<3.0\times10^{-17}$	-	D32
*	$CH_3O_2 + CH_3O_2 \rightarrow$ products	2.5×10^{-13}	-(190±190)	4.7×10^{-13}	1.5	D33
	$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	4.2×10^{-12}	-(180±180)	7.7×10^{-12}	1.5	D34
	$CH_3O_2 + NO_2 \xrightarrow{M} CH_3O_2NO_2$	(See Table 2)				
*	$CH_3O_2 + HO_2 \rightarrow$ products	3.8×10^{-13}	-(800±400)	5.6×10^{-12}	2.0	D35
#	$CH_3O_2 + CH_3C(O)O_2 \rightarrow$ products	1.4×10^{-11}	0±400	1.4×10^{-11}	2.0	D36

Table 1. (Continued)

	Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
*	$C_2H_5O_2 + C_2H_5O_2 \rightarrow$ products	1.5×10^{-13}	270±270	6.1×10^{-14}	2.0	D37
	$C_2H_5O_2 + NO \rightarrow$ products	8.9×10^{-12}	0±300	8.9×10^{-12}	1.3	D38
&	$C_2H_5O_2 + HO_2 \rightarrow$ products	6.5×10^{-13}	-(650±300)	5.8×10^{-12}	2.0	D39
#	$CH_3C(O)O_2 + CH_3C(O)O_2 \rightarrow$ products	2.5×10^{-12}	-(550±250)	1.6×10^{-11}	2.0	D40
	$CH_3C(O)O_2 + NO \rightarrow$ products	2.4×10^{-11}	0±200	2.4×10^{-11}	2.0	D41
	$CH_3C(O)O_2 + NO_2 \rightarrow$ products	(See Table 2)				
	$CH_3C(O)O_2 + HO_2 \rightarrow$ products	4.5×10^{-13}	-(1000±600)	1.3×10^{-11}	2.0	D42
&	$NO_3 + CO \rightarrow$ products	-	-	$<4.0\times10^{-19}$	-	D43
	$NO_3 + CH_2O \rightarrow$ products	-	-	5.8×10^{-16}	1.3	D44
	$NO_3 + CH_3CHO \rightarrow$ products	1.4×10^{-12}	1900±300	2.4×10^{-15}	1.3	D45
		<u>ClO_x Reactions</u>				
&	$Cl + O_3 + ClO + O_2$	2.9×10^{-11}	260±100	1.2×10^{-11}	1.15	E1
	$Cl + H_2 \rightarrow HCl + H$	3.7×10^{-11}	2300±200	1.6×10^{-14}	1.25	E2
	$Cl + CH_4 \rightarrow HCl + CH_3$	1.1×10^{-11}	1400±150	1.0×10^{-13}	1.1	E3
	$Cl + C_2H_6 \rightarrow HCl + C_2H_5$	7.7×10^{-11}	90±90	5.7×10^{-11}	1.1	E4
	$Cl + C_3H_8 \rightarrow HCl + C_3H_7$	1.4×10^{-10}	-(40±250)	1.6×10^{-10}	1.5	E5
	$Cl + C_2H_2 \rightarrow$ products	(See Table 2)				
&	$Cl + CH_3OH \rightarrow CH_2OH + HCl$	5.7×10^{-11}	0±250	5.7×10^{-11}	1.5	E6
	$Cl + CH_3CN \rightarrow$ products	-	-	$<2.0\times10^{-15}$	-	E7
	$Cl + CH_3Cl \rightarrow CH_2Cl + HCl$	3.3×10^{-11}	1250±200	4.9×10^{-13}	1.2	E8
#	$Cl + CH_2Cl_2 \rightarrow HCl + CHCl_2$	3.1×10^{-11}	1350±500	3.3×10^{-13}	2.0	E9
#	$Cl + CHCl_3 \rightarrow HCl + CCl_3$	4.9×10^{-12}	1240±500	7.6×10^{-14}	3.0	E10
#	$Cl + CHFCl_2 \rightarrow HCl + CFCl_2$	-	-	1.0×10^{-14}	3.0	E11
#	$Cl + CH_2FCl \rightarrow HCl + CHFCl$	2.1×10^{-11}	1390±500	1.9×10^{-13}	3.0	E12

Table 1. (Continued)

	Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
#	$Cl + CH_2F_2 \rightarrow HCl + CHF_2$	1.7×10^{-11}	1630±500	7.1×10^{-14}	3.0	E13
#	$Cl + CH_3F \rightarrow HCl + CH_2F$	4.8×10^{-12}	770±500	3.6×10^{-13}	1.5	E14
	$Cl + CH_3CCl_3 \rightarrow CH_2CCl_3 + HCl$	-	-	$<4.0\times10^{-14}$	-	E15
#	$Cl + CHCl_2CF_3 \rightarrow HCl + CCl_2CF_3$	-	-	1.2×10^{-14}	1.5	E16
#	$Cl + CHFClCF_3 \rightarrow HCl + CFClCF_3$	-	-	2.7×10^{-15}	2.0	E17
#	$Cl + CH_2ClCF_3 \rightarrow HCl + CHClCF_3$	1.8×10^{-12}	1710±500	5.9×10^{-15}	3.0	E18
#	$Cl + CHF_2CHF_2 \rightarrow HCl + CF_2CHF_2$	8.2×10^{-12}	2430±500	2.4×10^{-15}	3.0	E19
#	$Cl + CH_2FCF_3 \rightarrow HCl + CHFCF_3$	-	-	1.4×10^{-15}	3.0	E20
#	$Cl + CH_3CFCl_2 \rightarrow HCl + CH_2CFCl_2$	-	-	2.2×10^{-15}	1.5	E21
#	$Cl + CH_3CF_2Cl \rightarrow HCl + CH_2CF_2Cl$	-	-	3.9×10^{-16}	3.0	E22
#	$Cl + CH_2FCHF_2 \rightarrow HCl + CH_2FCF_2$	5.5×10^{-12}	1610±500	2.5×10^{-14}	3.0	E23
	$\rightarrow HCl + CHFCHF_2$	7.7×10^{-12}	1720±500	2.4×10^{-14}	3.0	E23
#	$Cl + CH_3CF_3 \rightarrow HCl + CH_2CF_3$	1.2×10^{-11}	3880±500	2.6×10^{-17}	5.0	E24
#	$Cl + CH_2FCH_2F \rightarrow HCl + CHFCH_2F$	2.6×10^{-11}	1060±500	7.5×10^{-13}	3.0	E25
#	$Cl + CH_3CHF_2 \rightarrow HCl + CH_3CF_2$	6.4×10^{-12}	950±500	2.6×10^{-13}	1.5	E26
	$\rightarrow HCl + CH_2CHF_2$	7.2×10^{-12}	2390±500	2.4×10^{-15}	3.0	E26
#	$Cl + CH_3CH_2F \rightarrow HCl + CH_3CHF$	1.8×10^{-11}	290±500	6.8×10^{-12}	3.0	E27
	$\rightarrow HCl + CH_2CH_2F$	1.4×10^{-11}	880±500	7.3×10^{-13}	3.0	E27
#	$Cl + CH_3CO_3NO_2 \rightarrow$ products	-	-	$<1\times10^{-14}$		E28
	$Cl + H_2CO \rightarrow HCl + HCO$	8.1×10^{-11}	30±100	7.3×10^{-11}	1.15	E29
	$Cl + H_2O_2 \rightarrow HCl + HO_2$	1.1×10^{-11}	980±500	4.1×10^{-13}	1.5	E30
	$Cl + HOCl \rightarrow Cl_2 + OH$	3.0×10^{-12}	130±250	1.9×10^{-12}	2.0	E31
	$Cl + HNO_3 \rightarrow$ products	-	-	$<2.0\times10^{-16}$	-	E32
	$Cl + HO_2 \rightarrow HCl + O_2$	1.8×10^{-11}	-(170±200)	3.2×10^{-11}	1.5	E33
	$\rightarrow OH + ClO$	4.1×10^{-11}	450±200	9.1×10^{-12}	2.0	E33

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
$Cl + Cl_2O \rightarrow Cl_2 + ClO$	9.8×10^{-11}	0±250	9.8×10^{-11}	1.2	E34
$Cl + OClO \rightarrow ClO + ClO$	3.4×10^{-11}	-(160±200)	5.8×10^{-11}	1.25	E35
* $Cl + ClOO \rightarrow Cl_2 + O_2$	2.3×10^{-10}	0±250	2.3×10^{-10}	3.0	E36
$\rightarrow ClO + ClO$	1.2×10^{-11}	0±250	1.2×10^{-11}	3.0	E36
$Cl + Cl_2O_2 \rightarrow$ products	-	-	1.0×10^{-10}	2.0	E37
$Cl + ClONO_2 \rightarrow$ products	6.8×10^{-12}	-(160±200)	1.2×10^{-11}	1.3	E38
$Cl + NO \xrightarrow{M} NOCl$	(See Table 2)				
$Cl + NO_2 \xrightarrow{M} ClONO\ (ClNO_2)$	(See Table 2)				
$Cl + NO_3 + ClO + NO_2$	2.6×10^{-11}	0±400	2.6×10^{-11}	2.0	E39
$Cl + N_2O + ClO + N_2$	(See Note)				E40
$Cl + ClNO \rightarrow NO + Cl_2$	5.8×10^{-11}	-(100±200)	8.1×10^{-11}	1.5	E41
$Cl + O_2 \xrightarrow{M} ClOO$	(See Table 2)				
$Cl + CO \xrightarrow{M} ClCO$	(See Table 2)				
$ClO + O \rightarrow Cl + O_2$	3.0×10^{-11}	-(70±70)	3.8×10^{-11}	1.2	E42
$ClO + NO + NO_2 + Cl$	6.4×10^{-12}	-(290±100)	1.7×10^{-11}	1.15	E43
$ClO + NO_2 \xrightarrow{M} ClONO_2$	(See Table 2)				
$ClO + NO_3 \rightarrow$ products	4.0×10^{-13}	0±400	4.0×10^{-13}	2.0	E44
$ClO + HO_2 \rightarrow HOCl + O_2$	4.8×10^{-13}	$-(700\pm^{250}_{700})$	5.0×10^{-12}	1.4	E45
$ClO + H_2CO \rightarrow$ products	~1.0×10^{-12}	>2100	<1.0×10^{-15}	-	E46
$ClO + OH \rightarrow$ products	1.1×10^{-11}	-(120±150)	1.7×10^{-11}	1.5	E47
$ClO + CH_4 \rightarrow$ products	~1.0×10^{-12}	>3700	<4.0×10^{-18}	-	E48
$ClO + H_2 \rightarrow$ products	~1.0×10^{-12}	>4800	<1.0×10^{-19}	-	E48
$ClO + CO \rightarrow$ products	~1.0×10^{-12}	>3700	<4.0×10^{-18}	-	E48

Table 1. (Continued)

	Reaction	A-Factor^{a}	E/R±(ΔE/R)	k(298 K)	f(298)^{b}	Notes
	$ClO + N_2O \rightarrow$ products	$\sim 1.0\times 10^{-12}$	>4300	$<6.0\times 10^{-19}$	-	E48
&	$ClO + ClO \rightarrow$ products	8.0×10^{-13}	1250±500	1.2×10^{-14}	2.0	E49
	$\xrightarrow{M} Cl_2O_2$	(See Table 2)				
*	$ClO + O_3 \rightarrow ClOO + O_2$			$<1.4\times 10^{-17}$	-	E50
	$\rightarrow OClO + O_2$	1.0×10^{-12}	>4000	$<1.0\times 10^{-18}$	-	E50
&	$ClO + CH_3O_2 \rightarrow$ products	(See Note)				E51
	$OH + Cl_2 \rightarrow HOCl + Cl$	1.4×10^{-12}	900±400	6.7×10^{-14}	1.2	E52
	$OH + HCl \rightarrow H_2O + Cl$	2.6×10^{-12}	350±100	8.0×10^{-13}	1.3	E53
	$OH + HOCl \rightarrow H_2O + ClO$	3.0×10^{-12}	500±500	5.0×10^{-13}	3.0	E54
	$OH + CH_3Cl \rightarrow CH_2Cl + H_2O$	2.1×10^{-12}	1150±200	4.4×10^{-14}	1.2	E55
	$OH + CH_2Cl_2 \rightarrow CHCl_2 + H_2O$	5.8×10^{-12}	1100±250	1.4×10^{-13}	1.2	E56
	$OH + CHCl_3 \rightarrow CCl_3 + H_2O$	4.3×10^{-12}	1100±200	1.1×10^{-13}	1.2	E57
	$OH + CCl_4 \rightarrow$ products	$\sim 1.0\times 10^{-12}$	>2300	$<5.0\times 10^{-16}$	-	E58
	$OH + CFCl_3 \rightarrow$ products	$\sim 1.0\times 10^{-12}$	>3700	$<5.0\times 10^{-18}$	-	E59
	$OH + CF_2Cl_2 \rightarrow$ products	$\sim 1.0\times 1$	>3600	$<6.0\times 10^{-18}$	2.0	E60
	$OH + CHFCl_2 \rightarrow CFCl_2 + H_2O$	1.2×10	1100±200	3.0×10^{-14}	1.2	E61
	$OH + CHF_2Cl \rightarrow CF_2Cl + H_2O$	1.2×10^{-12}	1650±300	4.7×10^{-15}	1.3	E62
	$OH + CH_2ClF \rightarrow CHClF + H_2O$	3.0×10^{-12}	1250±200	4.5×10^{-14}	1.2	E63
*	$OH + CH_3CCl_3 \rightarrow CH_2CCl_3 + H_2O$	1.8×10^{-12}	1550±150	1.0×10^{-14}	1.1	E64
*	$OH + CHCl_2CF_3 \rightarrow CCl_2CF_3 + H_2O$	7.7×10^{-13}	900±300	3.8×10^{-14}	1.3	E65
&	$OH + CHFClCF_3 \rightarrow CFClCF_3 + H_2O$	6.6×10^{-13}	1250±300	1.0×10^{-14}	1.3	E66
	$OH + CH_2ClCF_2Cl \rightarrow CHClCF_2Cl + H_2O$	3.6×10^{-12}	1600±400	1.7×10^{-14}	2.0	E67
	$OH + CH_2ClCF_3 \rightarrow CHClCF_3 + H_2O$	5.2×10^{-13}	1100±300	1.3×10^{-14}	1.3	E68
*	$OH + CH_3CFCl_2 \rightarrow CH_2CFCl_2 + H_2O$	1.3×10^{-12}	1600±300	6.0×10^{-15}	1.3	E69

Table 1. (Continued)

	Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
*	$OH + CH_3CF_2Cl \rightarrow CH_2CF_2Cl + H_2O$	1.4×10^{-12}	1800±200	3.3×10^{-15}	1.2	E70
#	$OH + CF_3CF_2CHCl_2 \rightarrow CF_3CF_2CCl_2 + H_2O$	1.5×10^{-12}	1250±200	2.3×10^{-14}	1.3	E71
#	$OH + CF_2ClCF_2CHFCl \rightarrow CF_2ClCF_2CFCl + H_2O$	5.5×10^{-13}	1250±200	8.3×10^{-15}	1.3	E72
#	$OH + CH_3CF_2CFCl_2 \rightarrow CH_2CF_2CFCl_2 + H_2O$	7.7×10^{-13}	1700±300	2.6×10^{-15}	2.0	E73
&	$OH + C_2Cl_4 \rightarrow$ products	9.4×10^{-12}	1200±200	1.7×10^{-13}	1.25	E74
&	$OH + C_2HCl_3 \rightarrow$ products	4.9×10^{-13}	-(450±200)	2.2×10^{-12}	1.25	E75
#	$OH + ClNO_2 \rightarrow HOCl + NO_2$	-	-	3.5×10^{-14}	3.0	E76
	$OH + ClONO_2 \rightarrow$ products	1.2×10^{-12}	330±200	3.9×10^{-13}	1.5	E77
	$O + HCl \rightarrow OH + Cl$	1.0×10^{-11}	3300±350	1.5×10^{-16}	2.0	E78
	$O + HOCl \rightarrow OH + ClO$	1.0×10^{-11}	2200±1000	6.0×10^{-15}	10.0	E79
	$O + ClONO_2 \rightarrow$ products	2.9×10^{-12}	800±200	2.0×10^{-13}	1.5	E80
	$O + Cl_2O \rightarrow ClO + ClO$	2.9×10^{-11}	630±200	3.5×10^{-12}	1.4	E81
*	$OClO + O \rightarrow ClO + O_2$	2.5×10^{-12}	950±300	1.0×10^{-13}	2.0	E82
	$OClO + O \xrightarrow{M} ClO_3$	(See Table 2)				
	$OClO + O_3 \rightarrow$ products	2.1×10^{-12}	4700±1000	3.0×10^{-19}	2.5	E83
	$OClO + OH \rightarrow HOCl + O_2$	4.5×10^{-13}	-(800±200)	6.8×10^{-12}	2.0	E84
	$OClO + NO \rightarrow NO_2 + ClO$	2.5×10^{-12}	600±300	3.4×10^{-13}	2.0	E85
	$Cl_2O_2 + O_3 \rightarrow$ products	-	-	$<1.0\times10^{-19}$	-	E86
	$Cl_2O_2 + NO \rightarrow$ products	-	-	$<2.0\times10^{-14}$	-	E87
&	$HCl + NO_3 \rightarrow HNO_3 + Cl$	-	-	$<5.0\times10^{-17}$	-	E88
	$HCl + ClONO_2 \rightarrow$ products	-	-	$<1.0\times10^{-20}$	-	E89
	$HCl + HO_2NO_2 \rightarrow$ products	-	-	$<1.0\times10^{-21}$	-	E90
	$H_2O + ClONO_2 \rightarrow$ products	-	-	$<2.0\times10^{-21}$	-	E91

Table 1. (Continued)

	Reaction	A-Factor^a	E/R±(ΔE/R)	k(298 K)	f(298)^b	Notes
&	$CF_2ClO_2 + NO \rightarrow CF_2ClO + NO_2$	3.1×10^{-12}	-(500±200)	1.6×10^{-11}	1.3	E92
&	$CFCl_2O_2 + NO \rightarrow CFCl_2O + NO_2$	3.5×10^{-12}	-(430±200)	1.5×10^{-11}	1.3	E93
&	$CCl_3O_2 + NO \rightarrow CCl_3O + NO_2$	5.7×10^{-12}	-(330±200)	1.7×10^{-11}	1.3	E94
		<u>BrO_x Reactions</u>				
	$Br + O_3 \rightarrow BrO + O_2$	1.7×10^{-11}	800±200	1.2×10^{-12}	1.2	F1
	$Br + H_2O_2 \rightarrow HBr + HO_2$	1.0×10^{-11}	>3000	$<5.0\times10^{-16}$	-	F2
	$Br + H_2CO \rightarrow HBr + HCO$	1.7×10^{-11}	800±200	1.1×10^{-12}	1.3	F3
	$Br + HO_2 \rightarrow HBr + O_2$	1.5×10^{-11}	600±600	2.0×10^{-12}	2.0	F4
	$Br + NO_2 \overset{M}{\rightarrow} BrNO_2$	(See Table 2)				
	$Br + Cl_2O \rightarrow BrCl + ClO$	2.0×10^{-11}	500±300	3.8×10^{-12}	2.0	F5
	$Br + OClO \rightarrow BrO + ClO$	2.6×10^{-11}	1300±300	3.4×10^{-13}	2.0	F6
	$Br + Cl_2O_2 \rightarrow$ products	-	-	3.0×10^{-12}	2.0	F7
	$BrO + O \rightarrow Br + O_2$	3.0×10^{-11}	0±250	3.0×10^{-11}	3.0	F8
&	$BrO + ClO \rightarrow Br + OClO$	1.6×10^{-12}	-(430±200)	6.8×10^{-12}	1.25	F9
	$\rightarrow Br + ClOO$	2.9×10^{-12}	-(220±200)	6.1×10^{-12}	1.25	F9
	$\rightarrow BrCl + O_2$	5.8×10^{-13}	-(170±200)	1.0×10^{-12}	1.25	F9
	$BrO + NO \rightarrow NO_2 + Br$	8.8×10^{-12}	-(260±130)	2.1×10^{-11}	1.15	F10
	$BrO + NO_2 \overset{M}{\rightarrow} BrONO_2$	(See Table 2)				
&	$BrO + BrO \rightarrow 2\,Br + O_2$	1.4×10^{-12}	-(150±150)	2.3×10^{-12}	1.25	F11
	$\rightarrow Br_2 + O_2$	6.0×10^{-14}	-(600±600)	4.4×10^{-13}	1.25	F11
	$BrO + O_3 \rightarrow Br + 2O_2$	$\sim1.0\times10^{-12}$	>1600	$<5.0\times10^{-15}$	-	F12
*	$BrO + HO_2 \rightarrow$ products	6.2×10^{-12}	-(500±500)	3.3×10^{-11}	3.0	F13
	$BrO + OH \rightarrow$ products	-	-	1.0×10^{-11}	5.0	F14
	$OH + Br_2 \rightarrow HOBr + Br$	4.2×10^{-11}	0±600	4.2×10^{-11}	1.3	F15

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
$OH + HBr \rightarrow H_2O + Br$	1.1×10^{-11}	0±250	1.1×10^{-11}	1.2	F16
* $OH + CH_3Br \rightarrow CH_2Br + H_2O$	3.6×10^{-12}	1430±150	3.0×10^{-14}	1.1	F17
# $OH + CHF_2Br \rightarrow CF_2Br + H_2O$	7.4×10^{-13}	1300±500	9.4×10^{-15}	3.0	F18
& $OH + CF_2Br_2 \rightarrow$ products	-	-	$<5.0 \times 10^{-16}$	-	F19
& $OH + CF_2ClBr \rightarrow$ products	-	-	$<1.5 \times 10^{-16}$	-	F20
& $OH + CF_3Br \rightarrow$ products	-	-	$<1.2 \times 10^{-16}$	-	F21
& $OH + CF_2BrCF_2Br \rightarrow$ products	-	-	$<1.5 \times 10^{-16}$	-	F22
$O + HBr \rightarrow OH + Br$	5.8×10^{-12}	1500±200	3.8×10^{-14}	1.3	F23
& $NO_3 + Br \rightarrow BrO + NO_2$	-	-	1.6×10^{-11}	2.0	F24
& $NO_3 + BrO \rightarrow$ products	-	-	1.0×10^{-12}	3.0	F25
& $NO_3 + HBr \rightarrow HNO_3 + Br$	-	-	$<1.0 \times 10^{-16}$	-	F26
	FO$_x$ Reactions				
$F + O_3 \rightarrow FO + O_2$	2.8×10^{-11}	230±200	1.3×10^{-11}	2.0	G1
$F + H_2 \rightarrow HF + H$	1.4×10^{-10}	500±200	2.6×10^{-11}	1.2	G2
$F + CH_4 \rightarrow HF + CH_3$	3.0×10^{-10}	400±300	8.0×10^{-11}	1.5	G3
$F + H_2O \rightarrow HF + OH$	1.4×10^{-11}	0±200	1.4×10^{-11}	1.3	G4
$F + O_2 \xrightarrow{M} FO_2$	(See Table 2)				
$F + NO \xrightarrow{M} FNO$	(See Table 2)				
$F + NO_2 \xrightarrow{M} FNO_2(FONO)$	(See Table 2)				
$F + HNO_3 \rightarrow HF + NO_3$	6.0×10^{-12}	-(400±200)	2.3×10^{-11}	1.3	G5
$NO + FO \rightarrow NO_2 + F$	2.6×10^{-11}	0±250	2.6×10^{-11}	2.0	G6
$FO + FO \rightarrow 2 F + O_2$	1.5×10^{-11}	0±250	1.5×10^{-11}	3.0	G7
$FO + O_3 \rightarrow F + 2 O_2$	(See Note)				G8
$\rightarrow FO_2 + O_2$	(See Note)				G8

Table 1. (Continued)

	Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
	$FO + NO_2 \xrightarrow{M} FONO_2$	(See Table 2)				
	$O + FO \rightarrow F + O_2$	5.0×10^{-11}	0±250	5.0×10^{-11}	3.0	G9
	$O + FO_2 \rightarrow FO + O_2$	5.0×10^{-11}	0±250	5.0×10^{-11}	5.0	G10
	$OH + CHF_3 \rightarrow CF_3 + H_2O$	1.5×10^{-12}	2650±500	2.1×10^{-16}	1.5	G11
*	$OH + CH_2F_2 \rightarrow CHF_2 + H_2O$	1.9×10^{-12}	1550±300	1.0×10^{-14}	1.3	G12
	$OH + CH_3F \rightarrow CH_2F + H_2O$	5.4×10^{-12}	1700±300	1.8×10^{-14}	1.2	G13
*	$OH + CHF_2CF_3 \rightarrow CF_2CF_3 + H_2O$	5.6×10^{-13}	1700±300	1.9×10^{-15}	1.3	G14
	$OH + CHF_2CHF_2 \rightarrow CF_2CHF_2 + H_2O$	8.7×10^{-13}	1500±500	5.7×10^{-15}	2.0	G15
&	$OH + CH_2FCF_3 \rightarrow CHFCF_3 + H_2O$	1.7×10^{-12}	1750±300	4.8×10^{-15}	1.3	G16
	$OH + CH_2FCHF_2 \rightarrow$ products	2.8×10^{-12}	1500±500	1.8×10^{-14}	2.0	G17
*	$OH + CH_3CF_3 \rightarrow CH_2CF_3 + H_2O$	1.6×10^{-12}	2100±300	1.4×10^{-15}	1.3	G18
	$OH + CH_2FCH_2F \rightarrow CHFCH_2F + H_2O$	1.7×10^{-11}	1500±500	1.1×10^{-13}	2.0	G19
&	$OH + CH_3CHF_2 \rightarrow$ products	1.5×10^{-12}	1100±200	3.7×10^{-14}	1.2	G20
	$OH + CH_3CH_2F \rightarrow$ products	1.3×10^{-11}	1200±300	2.3×10^{-13}	2.0	G21
	$CF_3O_2 + NO \rightarrow CF_3O + NO_2$	3.9×10^{-12}	-(400±200)	1.5×10^{-11}	1.3	G22
		<u>SO_x Reactions</u>				
	$OH + H_2S \rightarrow SH + H_2O$	6.0×10^{-12}	75±75	4.7×10^{-12}	1.2	H1
&	$OH + OCS \rightarrow$ products	1.1×10^{-13}	1200±500	1.9×10^{-15}	2.0	H2
&	$OH + CS_2 \rightarrow$ products	(See Note)	-	-	-	H3
	$OH + SO_2 \xrightarrow{M} HOSO_2$	(See Table 2)				
	$O + H_2S \rightarrow OH + SH$	9.2×10^{-12}	1800±550	2.2×10^{-14}	1.7	H4
	$O + OCS \rightarrow CO + SO$	2.1×10^{-11}	2200±150	1.3×10^{-14}	1.2	H5
	$O + CS_2 \rightarrow CS + SO$	3.2×10^{-11}	650±150	3.6×10^{-12}	1.2	H6
#	$O_3 + H_2S \rightarrow$ products	-	-	$< 2.0 \times 10^{-20}$	-	H7

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
$S + O_2 \rightarrow SO + O$	$2.3\text{x}10^{-12}$	0±200)	$2.3\text{x}10^{-12}$	1.2	H8
$S + O_3 \rightarrow SO + O_2$	-	-	$1.2\text{x}10^{-11}$	2.0	H9
$S + OH \rightarrow SO + H$	-	-	$6.6\text{x}10^{-11}$	3.0	H10
$SO + O_2 \rightarrow SO_2 + O$	$2.6\text{x}10^{-13}$	2400±500	$8.4\text{x}10^{-17}$	2.0	H11
$SO + O_3 \rightarrow SO_2 + O_2$	$3.6\text{x}10^{-12}$	1100±200	$9.0\text{x}10^{-14}$	1.2	H12
$SO + OH \rightarrow SO_2 + H$	-	-	$8.6\text{x}10^{-11}$	2.0	H13
$SO + NO_2 \rightarrow SO_2 + NO$	$1.4\text{x}10^{-11}$	0±50	$1.4\text{x}10^{-11}$	1.2	H14
$SO + ClO \rightarrow SO_2 + Cl$	$2.8\text{x}10^{-11}$	0±50	$2.8\text{x}10^{-11}$	1.3	H15
$SO + OClO \rightarrow SO_2 + ClO$	-	-	$1.9\text{x}10^{-12}$	3.0	H16
$SO + BrO \rightarrow SO_2 + Br$	-	-	$5.7\text{x}10^{-11}$	1.4	H17
$SO_2 + HO_2 \rightarrow$ products	-	-	$<1.0\text{x}10^{-18}$	-	H18
$SO_2 + CH_3O_2 \rightarrow$ products	-	-	$<5.0\text{x}10^{-17}$	-	H19
$SO_2 + NO_2 \rightarrow$ products	-	-	$<2.0\text{x}10^{-26}$	-	H20
$SO_2 + NO_3 \rightarrow$ products	-	-	$<7.0\text{x}10^{-21}$	-	H21
$SO_2 + O_3 \rightarrow SO_3 + O_2$	$3.0\text{x}10^{-12}$	>7000	$<2.0\text{x}10^{-22}$	-	H22
$SO_3 + H_2O \rightarrow H_2SO_4$	-	-	$<6.0\text{x}10^{-15}$	-	H23
$SO_3 + NO_2 \rightarrow$ products	-	-	$1.0\text{x}10^{-19}$	10.0	H24
# $SO_3 + NH_3 \rightarrow$ products	-	-	$6.9\text{x}10^{-11}$	3.0	H25
$Cl + H_2S \rightarrow HCl + SH$	$5.7\text{x}10^{-11}$	0±50	$5.7\text{x}10^{-11}$	1.3	H26
$Cl + OCS \rightarrow SCl + CO$	-	-	$<1.0\text{x}10^{-16}$	-	H27
# $Cl + CS_2 \rightarrow$ products	-	-	$<4.0\text{x}10^{-15}$	-	H28
# $Cl + CH_3SH \rightarrow CH_3S + HCl$	-	-	$1.4\text{x}10^{-10}$	1.4	H29
$ClO + OCS \rightarrow$ products	-	-	$<2.0\text{x}10^{-16}$	-	H30
$ClO + SO_2 \rightarrow Cl + SO_3$	-	-	$<4.0\text{x}10^{-18}$	-	H30

Table 1. (Continued)

	Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
	$SH + H_2O_2 \rightarrow$ products	-	-	$<5.0x10^{-15}$	-	H31
	$SH + O \rightarrow H + SO$	-	-	$1.6x10^{-10}$	5.0	H32
	$SH + O_2 \rightarrow OH + SO$	-	-	$<4.0x10^{-19}$	-	H33
&	$SH + O_3 \rightarrow HSO + O_2$	$9.0x10^{-12}$	280±200	$3.5x10^{-12}$	1.3	H34
	$SH + NO \xrightarrow{M} HSNO$	(See Table 2)				
&	$SH + NO_2 \rightarrow HSO + NO$	$2.9x10^{-11}$	-(240±100)	$6.5x10^{-11}$	1.3	H35
#	$SH + F_2 \rightarrow FSH + F$	$4.3x10^{-11}$	1390±200	$4.0x10^{-13}$	2.0	H36
#	$SH + Cl_2 \rightarrow ClSH + Cl$	$1.7x10^{-11}$	690±200	$1.7x10^{-12}$	2.0	H36
#	$SH + Br_2 \rightarrow BrSH + Br$	$6.0x10^{-11}$	-(160±160)	$1.0x10^{-10}$	2.0	H36
#	$SH + BrCl \rightarrow$ products	$2.3x10^{-11}$	-(350±200)	$7.4x10^{-11}$	2.0	H36
&	$HSO + O_2 \rightarrow$ products	-	-	$<2.0x10^{-17}$	-	H37
*	$HSO + O_3 \rightarrow$ products	-	-	$1.0x10^{-13}$	1.3	H38
	$HSO + NO \rightarrow$ products	-	-	$<1.0x10^{-15}$	-	H39
	$HSO + NO_2 \rightarrow HSO_2 + NO$	-	-	$9.6x10^{-12}$	2.0	H39
	$HSO_2 + O_2 \rightarrow HO_2 + SO_2$	-	-	$3.0x10^{-13}$	3.0	H40
	$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$	$1.3x10^{-12}$	330±200	$4.4x10^{-13}$	1.2	H41
	$CS + O_2 \rightarrow OCS + O$	-	-	$2.9x10^{-19}$	2.0	H42
	$CS + O_3 \rightarrow OCS + O_2$	-	-	$3.0x10^{-16}$	3.0	H43
	$CS + NO_2 \rightarrow OCS + NO$	-	-	$7.6x10^{-17}$	3.0	H43
&	$OH + CH_3SH \rightarrow$ products	$9.9x10^{-12}$	-(360±100)	$3.3x10^{-11}$	1.2	H44
&	$OH + CH_3SCH_3 \rightarrow H_2O + CH_2SCH_3$	$1.1x10^{-11}$	240±100	$4.9x10^{-12}$	1.2	H45
&	$OH + CH_3SSCH_3 \rightarrow$ products	$5.7x10^{-11}$	-(380±300)	$2.0x10^{-10}$	1.3	H46
	$NO_3 + H_2S \rightarrow$ products	-	-	$<8.0x10^{-16}$	-	H47
	$NO_3 + OCS \rightarrow$ products	-	-	$<1.0x10^{-16}$	-	H48

Table 1. (Continued)

Reaction	A-Factor^a	E/R±(ΔE/R)	k(298 K)	f(298)^b	Notes
$NO_3 + CS_2 \rightarrow$ products	-	-	$<4.0\text{x}10^{-16}$	-	H49
& $NO_3 + CH_3SH \rightarrow$ products	$4.4\text{x}10^{-13}$	-(210±210)	$8.9\text{x}10^{-13}$	1.25	H50
& $NO_3 + CH_3SCH_3 \rightarrow$ products	$1.9\text{x}10^{-13}$	-(500±200)	$1.0\text{x}10^{-12}$	1.2	H51
$NO_3 + CH_3SSCH_3 \rightarrow$ products	$1.3\text{x}10^{-12}$	270±270	$5.3\text{x}10^{-13}$	1.4	H52
# $N_2O_5 + CH_3SCH_3 \rightarrow$ products	-	-	$<1.0\text{x}10^{-17}$	-	H53
$CH_3S + O_2 \rightarrow$ products	-	-	$<3.0\text{x}10^{-18}$	-	H54
* $CH_3S + O_3 \rightarrow$ products	-	-	$5.4\text{x}10^{-12}$	1.3	H55
# $CH_3S + NO \rightarrow$ products	-	-	$<1.0\text{x}10^{-13}$	-	H56
& $CH_3S + NO_2 \rightarrow CH_3SO + NO$	-	-	$5.6\text{x}10^{-11}$	1.3	H57
* $CH_3SO + O_3 \rightarrow$ products	-	-	$6.0\text{x}10^{-13}$	1.5	H58
& $CH_3SO + NO_2 \rightarrow CH_3SO_2 + NO$	-	-	$1.2\text{x}10^{-11}$	1.4	H59
# $CH_3SS + O_3 \rightarrow$ products	-	-	$4.6\text{x}10^{-13}$	2.0	H60
# $CH_3SS + NO_2 \rightarrow$ products	-	-	$1.8\text{x}10^{-11}$	2.0	H61
# $CH_3SSO + NO_2 \rightarrow$ products	-	-	$4.5\text{x}10^{-12}$	2.0	H61
	Metal Reactions				
$Na + O_2 \xrightarrow{M} NaO_2$	(See Table 2)				
* $Na + O_3 \rightarrow NaO + O_2$	$7.3\text{x}10^{-10}$	0±200	$7.3\text{x}10^{-10}$	1.2	J1
$\rightarrow NaO_2 + O$	-	-	$<4.0\text{x}10^{-11}$	-	J1
* $Na + N_2O \rightarrow NaO + N_2$	$2.8\text{x}10^{-10}$	1600±400	$1.3\text{x}10^{-12}$	1.2	J2
$Na + Cl_2 \rightarrow NaCl + Cl$	$7.3\text{x}10^{-10}$	0±200	$7.3\text{x}10^{-10}$	1.3	J3
$NaO + O \rightarrow Na + O_2$	$3.7\text{x}10^{-10}$	0±400	$3.7\text{x}10^{-10}$	3.0	J4
$NaO + O_2 \xrightarrow{M} NaO_3$	(See Table 2)				
$NaO + O_3 \rightarrow NaO_2 + O_2$	$1.6\text{x}10^{-10}$	0±400	$1.6\text{x}10^{-10}$	2.0	J5
$\rightarrow Na + 2O_2$	$6.0\text{x}10^{-11}$	0±800	$6.0\text{x}10^{-11}$	3.0	J5

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
$NaO + H_2 \rightarrow NaOH + H$	2.6×10^{-11}	0±600	2.6×10^{-11}	2.0	J6
$NaO + H_2O \rightarrow NaOH + OH$	2.2×10^{-10}	0±400	2.2×10^{-10}	2.0	J7
$NaO + NO \rightarrow Na + NO_2$	1.5×10^{-10}	0±400	1.5×10^{-10}	4.0	J8
$NaO + CO_2 \overset{M}{\rightarrow} NaCO_3$	(See Table 2)				
$NaO + HCl \rightarrow$ products	2.8×10^{-10}	0±400	2.8×10^{-10}	3.0	J9
$NaO_2 + NO \rightarrow NaO + NO_2$	-	-	$<10^{-14}$	-	J10
$NaO_2 + HCl \rightarrow$ products	2.3×10^{-10}	0±400	2.3×10^{-10}	3.0	J11
$NaOH + HCl \rightarrow NaCl + H_2O$	2.8×10^{-10}	0±400	2.8×10^{-10}	3.0	J12
$NaOH + CO_2 \overset{M}{\rightarrow} NaHCO_3$	(See Table 2)				

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty factor at 298 K. To calculate the uncertainty at other temperatures, use the expression:

$$f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$$

Note that the exponent is absolute value.

& Indicates a change in the Note.
* Indicates a change from the previous Panel evaluation (JPL 90-1).
# Indicates a new entry that was not in the previous evaluation.

NOTES TO TABLE 1

A1. $O + O_3$. The recommended rate expression is from Wine et al. (1983) and is a linear least squares fit of all data (unweighted) from Davis et al. (1973b), McCrumb and Kaufman (1972), West et al. (1978), Arnold and Comes (1979), and Wine et al. (1983).

A2. $O(^1D)$ Reactions. These recommendations are based on averages of the absolute rate constant measurements reported by Streit et al. (1976), Davidson et al. (1977) and Davidson et al. (1978) for N_2O, H_2O, CH_4, H_2, N_2, O_2, O_3, $CCl4$, $CFCl_3$, CF_2Cl_2, NH_3, and CO_2; by Amimoto et al. (1978), Amimoto et al. (1979), and Force and Wiesenfeld (1981a,b) for N_2O, H_2O, CH_4, N_2, H_2, O_2, O_3, CO_2, CCl_4, $CFCl_3$, CF_2Cl_2, and CF_4; by Wine and Ravishankara (1981, 1982, 1983) for N_2O, H_2O, N_2, H_2, O_3, CO_2, and CF_2O; by Brock and Watson (private communication, 1980) for N_2, O_2 and CO_2; by Lee and Slanger (1978 and 1979) for H_2O and O_2; by Gericke and Comes (1981) for H_2; and by Shi and Barker (1990) for N_2 and CO_2. The weight of the evidence from these studies indicates that the results of Heidner and Husain (1973), Heidner et al. (1973) and Fletcher and Husain (1976a, 1976b) contain a systematic error. For the critical atmospheric reactants, such as N_2O, H_2O, and CH_4, the recommended absolute rate constants are in good agreement with the previous relative measurements when compared with N_2 as the reference reactant. A similar comparison with O_2 as the reference reactant gives somewhat poorer agreement.

A3. $O(^1D) + N_2O$. The branching ratio for the reaction of $O(^1D)$ with N_2O to give $N_2 + O_2$ or $NO + NO$ is an average of the values reported by Davidson et al. (1979); Volltrauer et al. (1979); Marx et al. (1979) and Lam et al. (1981), with a spread in $k(NO + NO)/k(TOTAL) = 0.52 - 0.62$. The recommended branching ratio agrees well with earlier measurements of the quantum yield from N_2O photolysis (Calvert and Pitts 1966b). The $O(^1D)$ translational energy and temperature dependence effects are not clearly resolved. Wine and Ravishankara (1982) have determined that the yield of $O(^3P)$ from $O(^1D) + N_2O$ is <4.0%. The uncertainty for this reaction includes factors for both the overall rate coefficient and the branching ratio. A direct measurement by Greenblatt and Ravishankara (1990) of the NO yield from the $O(^1D) + N_2O$ reaction in the presence of airlike mixtures agrees very well with the value predicted using the recommended $O(^1D)$ rate constants for N_2, O_2, and N_2O and the $O(^1D) + N_2O$ product branching ratio. These authors suggest that their results support the recommendations and reduce the uncertainty in the collected rate parameters by over a factor of two.

A4. $O(^1D) + H_2O$. Measurements of the $O_2 + H_2$ product yield were made by Zellner et al. (1980) (1 + 0.5 or -1)% and by Glinski and Birks (1985) (0.6 + 0.7 or -0.6)%. Wine and Ravishankara (1982) have determined that the yield of $O(^3P)$ from $O(^1D) + H_2O$ is <(4.9±3.2)%.

A5. $O(^1D) + CH_4$. The branching ratio for the reaction of $O(^1D)$ with CH_4 to give $OH + CH_3$ or $CH_2O + H_2$ is from Lin and DeMore (1973). A molecular beam study by Casavecchia et al. (1980) indicates that an additional path forming CH_3O (or CH_2OH) + H may be important. This possibility requires further investigation. Wine and Ravishankara (1982) have determined that the yield of $O(^3P)$ from $O(^1D) + CH_4$ is <4.3%.

A6. $O(^1D) + H_2$. Wine and Ravishankara (1982) have determined the yield of $O(^3P)$ is <4.9%. The major products are H + OH.

A7. $O(^1D) + O_3$. The branching ratio for reaction of $O(^1D)$ with O_3 to give $O_2 + O_2$ or $O_2 + O + O$ is from Davenport et al. (1972). This is supported by measurements of Amimoto et al. (1978) who reported that on average one ground state O is produced per $O(^1D)$ reaction with O_3. It seems unlikely that this could result from 100% quenching of the $O(^1D)$ by O_3.

A8. $O(^1D) + HCl$. The recommendation is the average of measurements by Davidson et al. (1977) and Wine et al. (1986). Product studies by the latter indicate: $O(^3P) + HCl$(9±5)%; $H + ClO$(24±5)%; and $OH + Cl$(67±10)%.

A9. $O(^1D) + HF$. Rate coefficient and product yield measured by Wine et al. (1984, private communication). The $O(^3P)$ yield is less than 4%.

A10. $O(^1D) + HBr$. Rate coefficient and products measured by Wine et al. (1986). Product yields: $HBr + O(^3P)$ (20±7)%, $H + BrO$ <4.5%, and $OH + Br$ (80±12)%.

A11. $O(^1D) + Cl_2$. Rate coefficient and $O(^3P)$ product measured by Wine et al. (1985a). Product yields: $Cl_2 + O(^3P)$ (25±10)%. The balance is probably $ClO + Cl$. An earlier indirect study by Freudenstein and Biedenkapp (1976) is in reasonable agreement on the yield of ClO.

A12. $O(^1D)$ + halocarbons. The halocarbon rate constants are for the total disappearance of $O(^1D)$ and probably include physical quenching. Products of the reactive channels may include $CX_3O + X$, $CX_2O + X_2$, and $CX_3 + XO$, where X = H, F, or Cl in various combinations. Chlorine and hydrogen are more easily displaced than fluorine from halocarbons. Some values have been reported for the fractions of the total rate of disappearance of $O(^1D)$ proceeding through physical quenching and reactive channels. For CCl_4: quenching = (14±6)% and reaction = (86±6)%, (Force and Wiesenfeld, 1981a); for $CFCl_3$: quenching = (25±10)%, ClO formation = (60±15)% (Donovan, private communication, 1980); for CF_2Cl_2: quenching = (14±7)% and reaction = (86±14)% (Force and Wiesenfeld, 1981a), quenching = (20±10)%, ClO formation = (55±15)% (Donovan, private communication, 1980).

A13. $O(^1D) + CF_4$. (CFC-14) The recommendation is based upon the measurement by Ravishankara et al. (1992) who report 92±8% physical quenching. Force and Wiesenfeld (1981a) measured a quenching rate coefficient about 10 times larger. Shi and Barker (1990) report an upper limit that is consistent with the recommendation. The small rate coefficient for this reaction makes it vulnerable to interference from reactant impurities. For this reason the recommendation should probably be considered an upper limit.

A14. $O(^1D) + CCl_2O$, CFClO and CF_2O. For the reactions of $O(^1D)$ with CCl_2O and CFClO the recommended rate constants are derived from data of Fletcher and Husain (1978). For consistency, the recommended values for these rate constants were derived using a scaling factor (0.5) which corrects for the difference between rate constants from the Husain Laboratory and the recommendations for other $O(^1D)$ rate constants in this table. The recommendation for CF_2O is from the data of Wine and Ravishankara (1983). Their result is preferred over the value of Fletcher and Husain (1978) because it appears to follow the pattern of decreased reactivity with increased fluorine substitution observed for other halocarbons. These reactions have been studied only at 298 K. Based on consideration of similar $O(^1D)$ reactions, it is assumed that E/R equals zero, and therefore the value shown for the A-factor has been set equal to k(298 K).

A15. $O(^1D) + NH_3$. Sanders et al. (1980a) have detected the products $NH(a^1\Delta)$ and OH formed in the reaction. They report the yield of $NH(a^1\Delta)$ is in the range 3-15% of the amount of OH detected.

A16. $O(^1D) + CHFCl_2$ (HCFC-21). The recommendation is based upon the measurement by Davison et al. (1978) of the total rate coefficient (physical quenching and reaction).

A17. $O(^1D) + CHF_2Cl$ (HCFC-22). The recommendation is based upon the measurements by Davidson et al. (1978) and Warren et al. (1991) of the total rate coefficient. A measurement of the rate of reaction (halocarbon removal) relative to the rate of reaction with N_2O by Green and Wayne (1976/77a) agrees very well with this value when the $O(^1D) + N_2O$ recommendation is used to obtain an absolute value. A relative measurement by Atkinson et al. (1976) gives a rate coefficient about a factor of two higher. Addison et al. (1979) reported the following product yields: ClO 55±10%, CF_2 45±10%, $O(^3P)$ 28 +10 or -15%, and OH 5%, where the $O(^3P)$ comes from a branch yielding CF_2 and HCl. Warren et al. (1991) also report a yield of $O(^3P)$ of 28±6%, which they interpret as the product of physical quenching.

A18. $O(^1D) + CHF_3$. (HFC-23) The recommendation is based upon the measurement of Force and Wiesenfeld (1981a) who also reported that the rate coefficient is partitioned between physical quenching

(77%) and reactive loss of CHF_3 (23%). The recommendation has a large error limit because it seems inconsistent with the recommended value for the analogous compound CHF_2CF_3.

A19. $O(^1D) + CH_2F_2$. (HFC-32) The recommendation is based upon the relative rate measurement of Green and Wayne (1976/77a) who measured the loss of CH_2F_2 relative to the loss of N_2O. The recommendation for N_2O is used to obtain an estimated rate coefficient for reactive loss of CH_2F_2, 4.6×10^{-11}. This has been increased by a factor of two to obtain the recommendation based on the assumption that physical quenching will account for about 50% of the total $O(^1D)$ loss. This estimate is made by analogy to the data for CHF_3 and CH_3F from Force and Wiesenfeld (1981a).

A20. $O(^1D) + CH_3F$. (HFC-41) The recommendation is based upon the measurement of Force and Wiesenfeld (1981a) who also reported that the rate coefficient is partitioned between physical quenching (25%) and reactive loss of CH_3F (75%).

A21. $O(^1D) + CHCl_2CF_3$. (HCFC-123) The recommendation is based upon measurements by Warren et al. (1991). The relative rate measurement of Green and Wayne (1976/77a) who measured the loss of $CHCl_2CF_3$ relative to the loss of N_2O agrees well with the recommendation when the recommendation for N_2O is used. Warren et al. report 21±8% physical quenching.

A22. $O(^1D) + CHClFCF_3$. (HCFC-124) The recommendation is based upon the measurement of Warren et al. (1991) who report 31±10% physical quenching.

A23. $O(^1D) + CHF_2CF_3$. (HFC-125) The recommendation is based upon the measurement of Warren et al. (1991) who report 85+15/-22% physical quenching. Green and Wayne (1976/77a) measured the loss of CHF_2CF_3 relative to the loss of N_2O and report a loss corresponding to about 40% of the recommended rate coefficient. This reaction is much faster than one would predict by analogy to similar compounds, such as CH_2FCF_3.

A24. $O(^1D) + CH_2ClCF_2Cl$. (HCFC-132b) The recommendation is based upon the relative rate measurement of Green and Wayne (1976/77a) who measured the loss of CH_2ClCF_2Cl relative to the loss of N_2O. The recommendation for N_2O is used to obtain the value given. It is assumed that there is no physical quenching.

A25. $O(^1D) + CH_2ClCF_3$. (HCFC-133a) The recommendation is based upon the measurement of Warren et al. (1991) who report 20±5% physical quenching. This agrees with Green and Wayne (1976/77a) who measured the loss of CH_2ClCF_3 relative to the loss of N_2O, when the recommendation for N_2O is used.

A26. $O(^1D) + CH_2FCF_3$. (HFC-134a) The recommendation is based on the measurement of Warren et al. (1991) who report 94+6/-10% physical quenching. The predominance of physical quenching is surprising, considering the presence of C-H bonds which are usually reactive to $O(^1D)$.

A27. $O(^1D) + CH_3CFCl_2$. (HCFC-141b) The recommendation is based upon the measurement of Warren et al. (1991) who report 31±5% physical quenching.

A28. $O(^1D) + CH_3CF_2Cl$. (HCFC-142b) The recommendation is based upon the measurement of Warren et al. (1991) who report 26±5% physical quenching. This agrees very well with Green and Wayne (1976/77a) who measured the loss of CH_3CF_2Cl relative to the loss of N_2O, when the recommendation for N_2O is used.

A29. $O(^1D) + CH_3CF_3$. (HFC-143a) The recommendation is based upon the relative rate measurement of Green and Wayne (1976/77a) who measured the loss of CH_3CF_3 relative to the loss of N_2O. The recommendation for N_2O is used to obtain the value given. It is assumed that there is no physical quenching, although the reported physical quenching by CH_2FCF_3 and CH_3CHF_2 suggests possible quenching.

A30. $O(^1D) + CH_3CHF_2$. (HFC-152a) The recommendation is based on the measurements of Warren et al. (1991) who report 54±7% physical quenching.

A31. $O(^1D) + C_2F_6$. (CFC-116) The recommendation is based on a measurement by Ravishankara et al. (1992) who report 85±15% physical quenching. The small rate coefficient for this reaction makes it vulnerable to interference from reactant impurities. For this reason the recommendation should probably be considered an upper limit.

A32. $O(^1D) + SF_6$. The recommendation is based upon measurements by Ravishankara et al. (1992) who report 32±10% physical quenching. The small rate coefficient for this reaction makes it vulnerable to interference from reactant impurities. For this reason the recommendation should probably be considered an upper limit.

A33. $O(^1D) + CF_3Cl$. (CFC-13) New Entry. The recommendation is based on the measurement by Ravishankara et al. (1992) who report 31±10% physical quenching.

A34. $O(^1D) + CF_2ClCFCl_2$. (CFC-113) New Entry. The recommendation is an estimate based on analogy to similar compounds.

A35. $O(^1D) + CF_3CCl_3$. (CFC-113a) New Entry. The recommendation is an estimate based on analogy to similar compounds.

A36. $O(^1D) + CF_2ClCF_2Cl$. (CFC-114) New Entry. The recommendation is based on the measurement by Ravishankara et al. (1992) who report 25±9% physical quenching.

A37. $O(^1D) + CF_3CFCl_2$. (CFC-114a) New Entry. The recommendation is an estimate based on analogy to similar compounds.

A38. $O(^1D) + CF_3CF_2Cl$. (CFC-115) New Entry. The recommendation is based on the measurement by Ravishankara et al. (1992) who report 70±7% physical quenching.

A39. $O(^1D) + c\text{-}C_4F_8$. New Entry. The recommendation for perfluorocyclobutane is based upon the measurement by Ravishankara et al. (1992) who report 100+0/-15% physical quenching. The small rate coefficient for this reaction makes it vulnerable to interference from reactant impurities. For this reason the recommendation should probably be considered an upper limit.

A40. $O(^1D) + O_2$. The deactivation of $O(^1D)$ by O_2 leads to the production of $O_2(^1\Sigma)$ with an efficiency of 80±20%: Noxon (1970), Biedenkapp and Bair (1970), Snelling (1974), and Lee and Slanger (1978). The $O_2(^1\Sigma)$ is produced in the v=0, 1, and 2 vibrational levels in the amounts 60%, 40%, and <3%, Gauthier and Snelling (1974) and Lee and Slanger (1978).

A41. $O_2(^1\Delta) + O$. New Entry. The recommendation is based on the upper limit reported by Clark and Wayne (1969b).

A42. $O_2(^1\Delta) + O_2$. New Entry. The recommendation is the average of eight room temperature measurements: Steer et al. (1969), Findlay and Snelling (1971b), Borrell et al. (1977), Leiss et al. (1978), Tachibana and Phelps (1981), Billington and Borrell (1986), Raja et al. (1986), and Wildt et al. (1988). The temperature dependence is derived from the data of Findlay and Snelling and Billington and Borrell. Several other less direct measurements of the rate coefficient agree with the recommendation including Clark and Wayne (1969a), Findlay et al. (1969), and McLaren et al. (1981). Wildt et al. (1989) report observations of weak emissions in the near IR due to collision induced radiation.

A43. $O_2(^1\Delta) + O_3$. New Entry. The recommendation is the average of the room temperature measurements of Clark et al. (1970), Findlay and Snelling (1971a), Becker et al. (1972), and Collins et al. (1973). Several less direct measurements agree well with the recommendation, (McNeal and Cook (1967), Wayne and Pitts (1969), and Arnold and Comes (1980)). The temperature dependence is from Findlay and Snelling and Becker et al. who agree very well, although both covered a relatively small temperature range. An earlier study by Clark et al. covered a much larger range, and found a much smaller temperature coefficient. The reason for this discrepancy is not clear. The yield of O + $2O_2$ products appears to be close to unity, based on many studies of the quantum yield of O_3 destruction near the peak of the Hartley band. For example, measurements of the number of O_3 molecules destroyed per photon absorbed: Von Ellenrieder et al. (1971), Lissi and Heicklen (1972/73), and references cited therein and measurements of O_3 loss and O atom temporal profiles in pulsed experiments Klais et al. (1980b) and Arnold and Comes (1980).

A44. $O_2(^1\Delta) + H_2O$. New Entry. The recommendation is the average of the measurements reported by Becker et al. (1971) and Findlay and Snelling (1971b). An earlier study by Clark and Wayne (1969a) reported a value about three times larger.

A45. $O_2(^1\Delta) + N$. New Entry. The recommendation is an upper limit based upon the measurement reported by Westenberg et al. (1970b) who used ESR to detect $O_2(X^3\Sigma$ and $a^1\Delta)$, $O(^3P)$ and $N(^4S)$ with a discharge flow reactor. They used an excess of $O_2(^1\Delta)$ and measured the decay of N and the appearance of O at 195 and 300 K. They observed that the reaction of N with $O_2(^1\Delta)$ is somewhat slower than its reaction of $O_2(^3\Sigma)$. The recommended rate constant value for the latter provides the basis for the recommendation. Clark and Wayne (1969b, 1970) and Schmidt and Schiff (1973) reported observations of an $O_2(^1\Delta)$ reaction with N that is about 30 times faster than the recommended limit. Schmidt and Schiff attribute the observed loss of $O_2(^1\Delta)$ in excess N to a rapid energy exchange with some constituent in discharged nitrogen, other than N.

A46. $O_2(^1\Delta) + N_2$. New Entry. The recommendation is based upon the measurements by Findlay et al. (1969) and Becker et al. (1971). Other studies obtained higher values for an upper limit: Clark and Wayne (1969a) and Steer et al. (1969).

A47. $O_2(^1\Delta) + CO_2$. New Entry. The recommendation is based on the measurements reported by Findlay and Snelling (1971b) and Leiss et al. (1978). Upper limit rate coefficients reported by Becker et al. (1971), McLauren et al. (1981), and Singh et al. (1985) are consistent with the recommendation.

A48. $O_2(^1\Sigma) + O$. New Entry. The recommendation is based on the measurement reported by Slanger and Black (1979).

A49. $O_2(^1\Sigma) + O_2$. New Entry. The recommendation is the average of values reported by Martin et al. (1976), Lawton et al. (1977), and Lawton and Phelps (1978) who are in excellent agreement. Measurements by Thomas and Thrush (1975), Chatha et al. (1979), and Knickelbein et al. (1987) are in reasonable agreement with the recommendation. Knickelbein et al. report an approximate unit yield of $O_2(^1\Delta)$ product.

A50. $O_2(^1\Sigma) + O_3$. New Entry. The recommendation is based upon the room temperature measurements of Gilpin et al. (1971), Slanger and Black (1979), Choo and Leu (1985b), and Shi and Barker (1990). Measurements by Snelling (1974), Amimoto and Wiesenfeld (1980), Ogren et al. (1982), and Turnipseed et al. (1991b) are in very good agreement with the recommendation. The temperature dependence is derived from the results of Choo and Leu. The yield of O + $2O_2$ products is reported to be 70±20% by Slanger and Black and Amimoto and Wiesenfeld.

A51. $O_2(^1\Sigma) + H_2O$. New Entry. The recommendation is the average of room temperature measurements reported by Stuhl and Niki (1970), Filseth et al. (1970), Wildt et al. (1988), and Shi and Barker (1990). These data cover a range of about a factor of two. Measurements reported by O'Brien and Myers (1970), Derwent and Thrush (1971), and Thomas and Thrush (1975) are in good agreement with the recommendation. Wildt et al. (1988) report that the yield of $O_2(^1\Delta) \geq 90\%$.

A52. $O_2(^1\Sigma) + N$. New Entry. The recommendation is based on the limit reported by Slanger and Black (1979).

A53. $O_2(^1\Sigma) + N_2$. New Entry. The recommendation is the average of measurements reported by Izod and Wayne (1968), Stuhl and Welge (1969), Filseth et al. (1970), Martin et al. (1976), Kohse-Höinghaus and Stuhl (1980), Choo and Leu (1985b), Wildt et al. (1988), and Shi and Barker (1990). Less direct measurements reported by Noxon (1970), Myers and O'Brien (1970), and Chatha et al. (1979) are consistent with the recommendation. Kohse-Hoinghaus and Stuhl observed no significant temperature dependence over the range 203-349 K.

A54. $O_2(^1\Sigma) + CO_2$. New Entry. The recommendation is the average of measurements reported by Filseth et al. (1970), Davidson et al. (1972/73), Avilés et al. (1980), Muller and Houston (1981), Choo and Leu (1985b), Wildt et al. (1988), and Shi and Barker (1990) at room temperature. The temperature dependence is from the work of Choo and Leu. Muller and Houston and Singh and Setser (1985) give evidence that $O_2(^1\Delta)$ is a product. Wildt et al. report that the yield of $O_2(^1\Delta) \geq 90\%$.

B1. $H + O_3$. The recommendation is an average of the results of Lee et al. (1978b) and Keyser (1979), which are in excellent agreement over the 200-400 K range. An earlier study by Clyne and Monkhouse (1977) is in very good agreement on the T dependence in the range 300-560 K but lies about 60% below the recommended values. Although we have no reason not to believe the Clyne and Monkhouse values, we prefer the two studies that are in excellent agreement, especially since they were carried out over the T range of interest. Recent results by Finlayson-Pitts and Kleindienst (1979) agree well with .the present recommendations. Reports of a channel forming $HO_2 + O$ (Finlayson-Pitts and Kleindienst, 1979: ~25%, and Force and Wiesenfeld, 1981b: ~40%) have been contradicted by other studies (Howard and Finlayson-Pitts, 1980: <3%; Washida et al., 1980a: <6%; Finlayson-Pitts et al., 1981: <2%); and Dodonov et al., 1985: <0.3%). Secondary chemistry is believed to be responsible for the observed O-atoms in this system. Washida et al. (1980c) measured a low limit (<0.1%) for the production of singlet molecular oxygen in the reaction $H + O_3$.

B2. $H + HO_2$. There are five studies of this reaction: Hack et al. (1978), Hack et al. (1979c), Thrush and Wilkinson (1981b), Sridharan et al. (1982) and Keyser (1986). Related early work and combustion studies are referenced in the Sridharan et al. paper. All five studies used discharge flow systems. It is difficult to obtain a direct measurement of the rate constant for this reaction because both reactants are radicals and the products OH and O are very reactive toward the HO_2 reactant. The recommendation is based on the data of Sridharan et al. and Keyser because their measurements were the most direct and required the fewest corrections. The other measurements, $(5.0\pm1.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} by Thrush and Wilkinson (1981b) and $(4.65\pm1) \times 10^{-11}$ by Hack et al. (1979c) are in reasonable agreement with the recommended value. Three of the studies reported the product channels: (a) 2OH, (b) $H_2O + O$, and (c) $H_2 + O_2$. Hack et al. (1978) $k_a/k = 0.69$, $k_b/k \leq 0.02$, and $k_c/k = 0.29$; Sridharan et al. (1982) $k_a/k = 0.87\pm0.04$, $k_b/k = 0.02\pm0.02$, $k_c/k = 0.09\pm.045$; and Keyser (1986) $k_a/k = 0.90\pm0.04$, $k_b/k = 0.02\pm0.02$, and $k_c/k = 0.08\pm0.04$. Hislop and Wayne (1977), Keyser et al. (1985), and Michelangeli et al. (1988) reported on the yield of $O_2\ (b^1\Sigma)$ formed in channel (c) as $(2.8\pm1.3) \times 10^{-4}$, $<8 \times 10^{-3}$, and $<2.1 \times 10^{-2}$ respectively of the total reactions. Keyser found the rate coefficient and product yields to be independent of temperature for $245 < T < 300$ K.

B3. $O + OH$. The rate constant for $O + OH$ is a fit to three temperature dependence studies: Westenberg et al. (1970a), Lewis and Watson (1980), Howard and Smith (1981). This recommendation is consistent with earlier work near room temperature as reviewed by Lewis and Watson (1980) and with the recent measurements of Brune et al. (1983). The ratio $k(O + HO_2)/k(O + OH)$ measured by Keyser (1983) agrees with the rate constants recommended here.

B4. $O + HO_2$. The recommendation for the $O + HO_2$ reaction rate constant is the average of five studies at room temperature (Keyser, 1982, Sridharan et al., 1982, Ravishankara et al., 1983b, Brune et al., 1983 and Nicovich and Wine, 1987) fitted to the temperature dependence given by Keyser (1982) and Nicovich and Wine (1987). Earlier studies by Hack et al. (1979a) and Burrows et al. (1977, 1979) are not considered, because the $OH + H_2O_2$ reaction was important in these studies and the value used for its rate constant in their analyses has been shown to be in error. Data from Lii et al. (1980c) are not used, because they are based on only four experiments and involve a curve fitting procedure that appears to be insensitive to the desired rate constant. Data from Ravishankara et al. (1983b) at 298 K show no dependence on pressure between 10 and 500 torr N_2. The ratio k(O + HO_2)/k(O + OH) measured by Keyser (1983) agrees with the rate constants recommended here. Sridharan et al. (1985) showed that the reaction products correspond to abstraction of an oxygen atom from HO_2 by the O reactant. Keyser et al. (1985) reported <1% O_2 ($b^1\Sigma$) yield.

B5. O + H_2O_2. There are two direct studies of the O + H_2O_2 reaction: Davis et al. (1974c) and Wine et al. (1983). The recommended value is a fit to the combined data. Wine et al. suggest that the earlier measurements may be too high because of secondary chemistry. The A-factor for both data sets is quite low compared to similar atom-molecule reactions. An indirect measurement of the E/R by Roscoe (1982) is consistent with the recommendation.

B6. OH + HO_2. A study by Keyser (1988) appears to resolve a discrepancy between low pressure discharge flow experiments which all gave rate coefficients near 7 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} : Keyser (1981), Thrush and Wilkinson (1981a), Sridharan et al. (1981, 1984), Temps and Wagner (1982), and Rozenshtein et al. (1984), and atmospheric pressure studies which gave rate coefficients near 11 x 10^{-11}: Lii et al. (1980a), Hochanadel et al. (1980), DeMore (1982), Cox et al. (1981), Burrows et al. (1981), and Kurylo et al. (1981). Laboratory measurements using a discharge flow experiment and a chemical model analysis of the results by Keyser (1988) demonstrate that the previous discharge flow measurements were probably subject to interference from small amounts of O and H. In the presence of excess HO_2 these atoms generate OH and result in a rate coefficient measurement which falls below the true value. The temperature dependence is from Keyser (1988) who covered the range 254 to 382 K. A flow tube study by Schwab et al. (1989) reported k = (8.0 +3/-4) x 10^{-11} in agreement with the recommendation. These workers measured the concentrations of HO_2, OH, O, and H and used a computer model of the relevant reactions to test for interference. A flow tube study by Dransfeld and Wagner (1986) employing isotope labelled ^{18}OH reactant obtained k = (11±2) x 10^{-11} in good agreement with the recommendation. They attributed about half of the reactive events to isotope scrambling because control experiments with ^{16} OH gave k = 6 x 10^{-11}. It should be noted that their control experiments were subject to the errors described by Keyser (1988) due to the presence of small amounts of H and O whereas their ^{18}OH measurements were not. Kurylo et al. (1981) found no evidence of significant scrambling in isotope studies of the OH and HO_2 reaction. An additional careful study of the reaction temperature dependence would be useful.

B7. OH + O_3. The recommendation for the OH + O_3 rate constant is based on the room temperature measurements of Kurylo (1973) and Zahniser and Howard (1980) and the temperature dependence studies of Anderson and Kaufman (1973), Ravishankara et al. (1979b) and Smith et al. (1984). Kurylo's value was adjusted (-8%) to correct for an error in the ozone concentration measurement (Hampson and Garvin, 1977). The Anderson and Kaufman rate constants were normalized to k = 6.2 x 10^{-14} cm^3 $molecule^{-1}$ s^{-1} at 295 K as suggested by Chang and Kaufman (1978).

B8. OH + OH. The recommendation for the OH + OH reaction is the average of six measurements near 298 K: Westenberg and de Haas (1973a), McKenzie et al. (1973), Clyne and Down (1974), Trainor and von Rosenberg (1974), Farquharson and Smith (1980), and Wagner and Zellner (1981). The rate constants for these studies all fall between (1.4 and 2.3) x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. The temperature dependence is from Wagner and Zellner, who reported rate constants for the range T = 250-580 K.

B9. OH + H_2O_2. The recommendation is a fit to the temperature dependence studies of Keyser (1980b), Sridharan et al. (1980), Wine et al. (1981c), Kurylo et al. (1982b), and Vaghjiani et al. (1989). The data from these studies have been revised to account for the H_2O_2 UV absorption cross section recommendations in this evaluation. The first two references contain a discussion of some possible reasons for the discrepancies with earlier work and an assessment of the impact of the new value on other kinetic studies. All of these measurements agree quite well and overlap one another. Measurements by Lamb et al. (1983) agree at room temperature but indicate a quite different temperature dependence with k increasing slightly with decreasing temperature. Their data were not incorporated in the fit. A measurement at room temperature by Marinelli and Johnston (1982a) agrees well with the recommendation.

B10. $OH + H_2$. The $OH + H_2$ reaction has been the subject of numerous studies (see Ravishankara et al. (1981b) for a review of experimental and theoretical work). The recommendation is fixed to the average of nine studies at 298 K: Greiner (1969), Stuhl and Niki (1972), Westenberg and de Haas (1973c), Smith and Zellner (1974), Atkinson et al. (1975), Overend et al. (1975), Tully and Ravishankara (1980), Zellner and Steinert (1981), and Ravishankara et al. (1981b).

B11. $HO_2 + HO_2$. Two separate expressions are given for the rate constant for the $HO_2 + HO_2$ reaction. The effective rate constant is given by the sum of these two equations. This reaction has been shown to have a pressure independent bimolecular component and a pressure dependent termolecular component. Both components have negative temperature coefficients. The bimolecular expression is obtained from data of Cox and Burrows (1979), Thrush and Tyndall (1982a,b), Kircher and Sander (1984), Takacs and Howard (1984, 1986), Sander (1984) and Kurylo et al. (1986). Data of Rozenshtein et al. (1984) are consistent with the low pressure recommendation but they report no change in k with pressure up to 1 atm. Earlier results of Thrush and Wilkinson (1979) are inconsistent with the recommendation. The termolecular expression is obtained from data of Sander et al. (1982), Simonaitis and Heicklen (1982), and Kurylo et al. (1986) at room temperature and Kircher and Sander (1984) for the temperature dependence. This equation applies to M = air. On this reaction system there is general agreement among investigators on the following aspects of the reaction at high pressure (P ~1 atm): (a) the HO_2 UV absorption cross section: Paukert and Johnston (1972), Cox and Burrows (1979), Hochanadel et al. (1980), Sander et al. (1982), Kurylo et al. (1987a), and Crowley et al. (1991); (b) the rate constant at 300K: Paukert and Johnston (1972), Hamilton and Lii (1977), Cox and Burrows (1979), Lii et al. (1979), Tsuchiya and Nakamura (1979), Sander et al. (1982), Simonaitis and Heicklen (1982), Kurylo et al. (1986), Andersson et al. (1988), and Crowley et al. (1991) (all values fall in the range (2.5 to 4.7) x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}); (c) the rate constant temperature dependence: Cox and Burrows (1979), Lii et al. (1979), and Kircher and Sander (1984); (d) the rate constant water vapor dependence: Hamilton (1975), Hochanadel et al. (1972), Hamilton and Lii (1977), Cox and Burrows (1979), DeMore (1979), Lii et al. (1981), Sander et al. (1982), and Andersson et al. (1988); (e) the H/D isotope effect: Hamilton and Lii (1977) and Sander et al. (1982); and (f) the formation $H_2O_2 + O_2$ as the major products at 300 K: Su et al. (1979b), Niki et al. (1980a), Sander et al. (1982), and Simonaitis and Heicklen (1982). Sahetchian et al. (1982, 1987) give evidence for the formation of a small amount of H_2 (~10%) at temperatures near 500 K but Baldwin et al. (1984) and Ingold (1988) give evidence that the yield must be much less. Glinski and Birks (1985) report an upper limit of 1% H_2 yield at a total pressure of about 50 torr and 298 K, but their experiment may have interference from wall reactions. A smaller limit to H_2 production (0.01%) was later determined in the same laboratory (Stephens et al., 1989). For systems containing water vapor, the multiplicative factor given by Lii et al. (1981) and Kircher and Sander (1984) can be used: 1 + 1.4 x 10^{-21} $[H_2O]$ exp(2200/T). Lightfoot et al. (1988) reported atmospheric pressure measurements over the temperature range 298-777 K that are in agreement with the recommended value at room temperature but indicate an upward curvature in the Arrhenius plot at elevated temperature. A high temperature study by Hippler et al. (1990) confirms the strong curvature.

B12. $HO_2 + O_3$. There are four studies of this reaction using flow tube reactors: Zahniser and Howard (1980) at 245 to 365 K, Manzanares et al. (1986) at 298 K, Sinha et al. (1987) at 243 to 413 K, and Wang et al. (1988a) at 233 to 400 K. The data of Sinha et al. was given somewhat greater weight in the evaluation because this study did not employ an OH radical scavenger. The other studies fall close to the recommendation. All of the temperature dependence studies show some curvature in the Arrhenius plot with the E/R decreasing at lower temperature. The recommendation incorporates only data at temperatures less than 300 K and is not valid for T > 300 K and is uncertain at T < 230 K, where there are no data. Zahniser and Nelson (private communication, 1991) observe curvature in the Arrhenius plot at low temperatures. High quality low temperature data are needed for this reaction. Indirect studies using the $HO_2 + HO_2$ reactions as a reference (Simonaitis and Heicklen, 1973; DeMore and Tschuikow-Roux, 1974; and DeMore, 1979) give results that fall below the recommendation, when current data are used for the reference rate coefficient.

C1. $N + O_2$. The recommended expression is derived from a least squares fit to the data of Kistiakowsky and Volpi (1957), Wilson (1967), Becker et al. (1969), Westenberg et al. (1970b), Clark and Wayne (1970), Winkler et al. (1986) and Barnett et al. (1987). k(298 K) is derived from the Arrhenius expression and is in excellent agreement with the average of all of the room temperature determinations.

C2. $N + O_3$. The recommendation is based on the results of Barnett et al. (1987). The value of $(1.0 \pm 0.2) \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} reported by Barnett et al. should probably be considered an upper limit rather than a determination. The low values reported by Barnett et al., Stief et al. (1979) and Garvin and Broida (1963) cast doubt on the much faster rates reported by Phillips and Schiff (1962), and Chen and Taylor (1961).

C3. N + NO. There is relatively poor agreement between the temperature dependence studies of Clyne and McDermid (1975), who obtain E/R ~ 400 K over the range 298-670 K using discharge flow - mass spectroscopy and Lee et al. (1978c) who observe no temperature dependence between 200 and 400 K using the discharge flow - resonance fluorescence and flash photolysis - resonance fluorescence techniques. The recommendation for the temperature dependence is based on Lee et al. because the better sensitivity of the resonance fluorescence method for $N(^4S)$ reduces the possibility of interference from secondary reactions, and because of the relatively large experimental scatter in the data of Clyne and McDermid. There is clearly a need for additional temperature dependence data. The room temperature value is from these studies and the data of Sugawara et al. (1980), Cheah and Clyne (1980) and Husain and Slater (1980).

C4. $N + NO_2$. The Panel accepts the results of Clyne and Ono (1982) for the value of the rate constant at 298 K. This is a factor of 2 higher than that reported by Clyne and McDermid (1975). However, Clyne and Ono consider that the more recent study is probably more reliable. Husain and Slater (1980) reported a room temperature rate constant of 3.8×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, which is a factor of 12 greater than the value reported by Clyne and Ono. This high value may indicate the presence of catalytic cycles, as discussed by Clyne and McDermid, and Clyne and Ono. There are no studies of the temperature dependence of the rate constant. The reaction products are taken to be $N_2O + O$ (Clyne and McDermid). A recent study by Iwata et al. (1986) suggested an upper limit of 3.3×10^{-13} cm^3 $molecule^{-1}$ s^{-1} for the corresponding reaction involving $N(^2D)$ and $N(^2P)$ atoms (sum of all reaction channels).

C5. $O + NO_2$. k(298 K) is based on the results of Davis et al. (1973a), Slanger et al. (1973), Bemand et al. (1974), Ongstad and Birks (1986) and Geers-Muller and Stuhl (1987). The recommendation for E/R is from Davis et al., Ongstad and Birks, and Geers-Muller and Stuhl with the A-factor adjusted to give the recommended k(298 K) value.

C6. $O + NO_3$. Based on the study of Graham and Johnston (1978) at 298 K and 329 K. While limited in temperature range, the data indicate no temperature dependence. Furthermore, by analogy with the reaction of O with NO_2, it is assumed that this rate constant is independent of temperature. Clearly, temperature dependence studies are needed.

C7. $O + N_2O_5$. Based on Kaiser and Japar (1978).

C8. $O + HNO_3$. The upper limit reported by Chapman and Wayne (1974) is accepted.

C9. $O + HO_2NO_2$. The recommended value is based on the study of Chang et al. (1981). The large uncertainty in E/R and k at 298 K are due to the fact that the recommendation is based on a single study.

C10. $H + NO_2$. New Entry. The recommended value of k_{298} is derived from the studies of Wagner et al. (1976), Bemand and Clyne (1977), Clyne and Monkhouse (1977), Michael et al. (1979c) and Ko and Fontijn (1991). The temperature dependence is from the studies of Wagner et al. and Ko and Fontijn. The data from Wategaonkar and Setser (1989) and Agrawalla et al. (1981) were not considered.

C11. $O_3 + NO$. The recommended Arrhenius expression is a least squares fit to the data reported by Birks et al. (1976), Lippmann et al. (1980), Ray and Watson (1981b), Michael et al. (1981) and Borders and Birks (1982) at and below room temperature, with the data at closely spaced temperatures reported in Lippmann et al. and Borders and Birks being grouped together so that these five studies are weighted equally. This expression fits all the data within the temperature range 195-304 K reported in these five studies to within 20%. Only the data between 195 and 304 K were used to derive the recommended Arrhenius expression, due to the observed non-linear Arrhenius behavior (Clyne et al. (1964), Clough and Thrush (1967), Birks et al., Michael et al. and Borders and Birks). Clough and Thrush, Birks et al., Schurath et al. (1981), and Michael et al. have all reported individual Arrhenius parameters for each of the two primary reaction channels. The range of values for k at stratospheric temperatures is somewhat larger than would be expected for such an easy reaction to study. The measurements of Stedman and Niki (1973a) and Bemand et al. (1974) at 298 K are in excellent agreement with the recommended value of k at 298 K.

C12. HO_2 +NO. Changed from JPL 90-1. The recommendation for HO_2 +NO is based on the average of seven measurements of the rate constant near room temperature: Howard and Evenson (1977), Leu (1979b), Howard (1979), Glaschick-Schimpf et al. (1979), Hack et al. (1980), Thrush and Wilkinson (1981a) and Jemi-Alade and Thrush (1990). All of these are in quite good agreement. An earlier study, Burrows et al. (1979) has been disregarded because of an error in the reference rate constant, k (OH + H_2O_2). The room temperature study of Rozenshtein et al. (1984) has also been disregarded due to an inadequate treatment of possible secondary reactions. The temperature dependence is from the data of Howard (1979), Leu (1979b) and Howard (1980). Since all of these studies were carried out at low pressures, a direct study at higher pressures is needed.

C13. NO + NO_3. Changed from JPL 90-1. The recommendation is based on the studies of Hammer et al. (1986), Sander and Kircher (1986) and Tyndall et al. (1991a) which are in excellent agreement.

C14. OH + NO_3. The recommendation is derived from an average of the results of Boodaghians et al. (1988) and the 298 K results of Mellouki et al. (1988a). The reaction products are probably HO_2 + NO_2.

C15. OH + HONO. New Entry. The recommended rate expression is derived from the work of Jenkin and Cox (1987) which supersedes the earlier room temperature study of Cox et al. (1976b). Recent unpublished results from the Ravishankara group suggest that the reaction may have a small negative temperature dependence.

C16. OH + HNO_3. The intensive study of this reaction over the past few years has significantly reduced many of the apparent discrepancies among (a) the early studies yielding a low, temperature independent rate constant (Smith and Zellner, 1975 and Margitan et al., 1975); (b) more recent work (mostly flash photolysis) with a k(298) approximately 40% larger, and a strong negative T dependence below room temperature (Wine et al., 1981b; Kurylo et al., 1982a; Margitan and Watson, 1982; Marinelli and Johnston, 1982a; Ravishankara et al., 1982; Jourdain et al., 1982; C. A. Smith et al., 1984; Jolly et al., 1985 (298 K); Stachnik et al., 1986); and (c) recent discharge low studies yielding the lower value for k(298 K) but showing substantial negative T dependence (Devolder et al., 1984; Connell and Howard, 1985). Major features of the data are (1) a strong negative T dependence below room temperature, (2) a much weaker temperature dependence above room temperature, possibly leveling off around 500 K, and (3) small, measurable pressure dependence which becomes greater at low temperature. The pressure dependence has been determined by Margitan and Watson (1982) over the ranges 20-100 torr and 225-298 K and by Stachnik et al. (1986) at pressures of 10, 60 and 730 torr at 298 K. The two studies are in excellent agreement. Their "low pressure limit" agrees well with the average $k(298\ K) = 1.0 \times 10^{-13}\ cm^3\ molec^{-1}\ s^{-1}$ derived from the four low pressure discharge flow studies. The value measured for pressures typical of the other flash photolysis studies (20-50 torr) also agrees well. The two pressure dependence studies indicate that the high pressure limit is approximately 50% greater than the low pressure limit at 298 K, and about a factor of 2 greater at 240 K. Thus, over the narrow pressure ranges explored in most flash photolysis studies, the P dependence can be represented by combining a low pressure (bimolecular) limit, k_o, with a Lindemann-Hinshelwood expression for the P dependence:

$$k(M,T) = k_o + \frac{k_3[M]}{1 + \frac{k_3[M]}{k_2}} \quad \text{with} \quad \left\{ \begin{array}{l} k_0 = 7.2\text{x}10^{-15}\ \exp(785/T) \\ k_2 = 4.1\text{x}10^{-16}\ \exp(1440/T) \\ k_3 = 1.9\text{x}10^{-33}\ \exp(725/T) \end{array} \right.$$

The coefficients k_3 and k_2 are the termolecular and high pressure limits for the "association" channel. The value of k at high pressures is the sum $k_o + k_2$. The weak pressure dependence and weak T dependence above 300 K explain many of the apparent discrepancies for all the data (including the 1975 studies), except for a few minor features which are probably due to the normally encountered experimental scatter. The Smith and Zellner flash photolysis values are low compared to other flash systems (closer to the flow studies), although the difference is not unusual (~30%). Conversely, the Jourdain et al. flow study is high relative to the other ones. The Connell and Howard T dependence (below 300 K) is significantly weaker than the other studies. The failure of Smith et al. to observe a pressure effect between 50 and 760 torr, even at 240 K, is in sharp conflict with the effect seen by Stachnik et al. over the same range in a much more detailed study. Jolly et al., also could not detect a pressure dependence between 1 torr (M = HNO_3) and 600 torr (M = SF_6) at 298 K. Nelson et al. (1981), Jourdain et al. and Ravishankara et al. have all shown that within experimental error the yield of NO_3 (per OH removed) is unity at 298 K, with similar results at 250 K (Ravishankara et al.).

C17. $OH + HO_2NO_2$. The recommendation for both k at 298 K and the Arrhenius expression is based upon the data of Trevor et al. (1982), Barnes et al. (1981), C. A. Smith et al. (1984) and Barnes et al. (1986b). Trevor et al. studied this reaction over the temperature range 246-324 K and reported a temperature invariant value of 4.0×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, although a weighted least squares fit to their data yields an Arrhenius expression with an E/R value of (193±193) K. In contrast, Smith et al. studied the reaction over the temperature range 240-300 K and observed a negative temperature dependence with an E/R value of -(650±30) K. The early Barnes et al. study (1981) was carried out only at room temperature and 1 torr total pressure while their most recent study was performed in the pressure range 1-300 torr N_2 and temperature range 268-295 K with no rate constant variation being observed. In addition, k_{298} derived in Barnes et al. (1981) was revised upward in the later study from 4.1×10^{-12} to 5.0×10^{-12} due to a change in the rate constant for the reference reaction. The values of k at 298 K from the four studies are in excellent agreement. An unweighted least squares fit to the data from the above-mentioned studies yields the recommended Arrhenius expression. The less precise value for k at 298 K reported by Littlejohn and Johnston (1980) is in fair agreement with the recommended value. The error limits on the recommended E/R are sufficient to encompass the results of both Trevor et al. and Smith et al. It should be noted that the values of k at 220 K deduced from the two studies differ by a factor of 2. Clearly additional studies of k as a function of temperature and the identification of the reaction products are needed.

C18. $HO_2 + NO_3$. The recommendation at 298 K is obtained from a least squares fit to the 298 K data of Mellouki et al. (1988a) and the temperature dependence data of Hall et al. (1988) below 333 K.

C19. $O_3 + NO_2$. The recommended expression is derived from a least squares fit to the data of Davis et al. (1974b), Graham and Johnston (1974), Huie and Herron (1974) and Cox and Coker (1983). The data of Verhees and Adema (1985) and Stedman and Niki (1973a) were not considered because of systematic discrepancies with the other studies.

C20. $O_3 + HNO_2$. Based on Kaiser and Japar (1977) and Streit et al. (1979).

C21. $NO_2 + NO_3$. Changed from JPL 90-1. The existence of the reaction channel forming $NO + NO_2 + O_2$ has not been firmly established. However, studies of N_2O_5 thermal decomposition that monitor NO_2 (Daniels and Johnston, 1921; Johnston and Tao, 1951; Cantrell et al., 1988) and NO (Hjorth et al., 1989, and Cantrell et al., 1990a) require reaction(s) that decompose NO_3 into $NO = O_2$. The rate constant from the first three studies is obtained from the product kK_{eq} where K_{eq} is the equilibrium constant for $NO_2 + NO_3 = N_2O_5$ while for the latter two studies the rate constant is obtained from the ratio $k/k(NO + NO_3)$ where $k(NO + NO_3)$ is the rate constant for the reaction $NO + NO_3 \rightarrow 2NO_2$. Using K_{eq} and $k(NO + NO_3)$ from this evaluation, the rate expression that best fits the data from all five studies is 4.5×10^{-14} exp (-1260/T) cm^3 $molecule^{-1}$ s^{-1} with an overall uncertainty factor of 2.

C22. $N_2O_5 + H_2O$. The recommended value at 298 K is based on the studies of Tuazon et al. (1983a), Atkinson et al. (1986) and Hjorth et al. (1987). Sverdrup et al. (1987) obtained an upper limit that is a factor of four smaller than that obtained in the other studies, but the higher upper limit is recommended because of the difficulty of distinguishing between homogeneous and heterogeneous processes in the experiment. See Table 57 for heterogeneous rate data for this reaction.

C23. NH + NO. New Entry. The recommendation is derived from the room temperature results of Hansen et al. (1976), Cox et al. (1985) and Harrison et al. (1986). The temperature dependence is from Harrison et al.

C24. $NH + NO_2$. New Entry. The recommendation is derived from the temperature dependence study of Harrison et al. (1986).

C25. $OH + NH_3$. Changed from JPL 90-1. The recommended value at 298 K is the average of the values reported by Stuhl (1973b), Smith and Zellner (1975), Perry et al. (1976b), Silver and Kolb (1980), Stephens (1984) and Diau et al. (1990). The values reported by Pagsberg et al. (1979) and Cox et al. (1975) were not considered because these studies involved the analysis of a complex mechanism and the results are well outside the error limits implied by the above six direct studies. The results of Kurylo (1973) and Hack et al. (1974) were not considered because of their large discrepancies with the other direct studies (factors of 3.9 and 1.6 at room temperature, respectively). Because the Arrhenius plot displays considerable curvature, the temperature dependence is based only on the data below 300 K, i.e. the studies of Smith and Zellner (1975) and Diau et al. (1990), and the A-factor has been selected to fit the recommended room temperature value.

C26. $NH_2 + HO_2$. There is a fairly good agreement on the value of k at 298 K between the direct study of Kurasawa and Lesclaux (1980b), and the relative studies of Cheskis and Sarkisov (1979) and Pagsberg et al. (1979). The recommended value is the average of the values reported in these three studies. The identity of the products is not known; however, Kurasawa and Lesclaux suggest that the most probable reaction channels give either $NH_3 + O_2$ or $HNO + H_2O$ as products.

C27. $NH_2 + NO$. The recommended value for k at 298 K is the average of the values reported by Gordon et al. (1971), Gehring et al. (1973), Lesclaux et al. (1975), Hancock et al. (1975), Sarkisov et al. (1978), Hack et al. (1979b), Stief et al. (1982), Silver and Kolb (1982), and Whyte and Phillips (1983). The values reported in these studies for k at 298 K range from 8.3 to 27.0 ($\times 10^{-12}$) cm^3 $molecule^{-1}$ s^{-1}, which is not particularly satisfactory. The results tend to separate into two groups. The flash photolysis results average 1.9×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, while those obtained using the discharge flow technique average 0.9×10^{-11} cm^3 $molecule^{-1}$ s^{-1}. The apparent discrepancy cannot be due simply to a pressure effect as the pressure ranges of the flash photolysis and discharge flow studies overlapped, and none of the studies observed a pressure dependence for k. There have been four studies of the temperature dependence of k. Each study reported k to decrease with increasing temperature, i.e. $T^{-1.25}$ (Lesclaux et al. from 300-500 K), $T^{-1.85}$ (Hack et al. from 210-503 K), $T^{-1.67}$ (Stief et al. from 216-480 K) and $T^{-2.3}$ exp(-684/T) (Silver and Kolb from 294-1215 K). The recommended temperature dependence is taken to be a weighted average of the data below 500 K from all four studies. The expression is: $k = 1.6 \times 10^{-11} (T/298)^{-1.5}$ for the temperature range 210-500 K. There are many possible product channels for this reaction. Strong evidence against the formation of H atoms exists. Both Silver and Kolb (1982) and Andresen et al. (1982) report substantial yields of OH of 40% and ≥65%, respectively, in disagreement with Stief et al. (1982), Hall et al. (1986) and Dolson (1986) who observed room temperature OH yields of <22%, 13±2% and <15%, respectively. In addition, Andresen et al. set a lower limit of ≥29% of the channel $N_2 + H_2O$.

C28. $NH_2 + NO_2$. There have been four studies of this reaction (Hack et al., 1979b; Kurasawa and Lesclaux, 1979; Whyte and Phillips, 1983; and Xiang et al., 1985). There is very poor agreement among these studies both for k at 298 K (factor of 2.3) and for the temperature dependence of k ($T^{-3.0}$ and $T^{-1.3}$). The recommended values of k at 298 K and the temperature dependence of k are averages of the results reported in these four studies. Hack et al. have shown that the predominant reaction channel (>95%) produces $N_2O + H_2O$. Just as for the $NH_2 + NO$ reaction, the data for this reaction seem to indicate a factor of two discrepancy between flow and flash techniques, although the database is much smaller.

C29. $NH_2 + O_2$. Changed from JPL 90-1. This reaction has several product channels which are energetically possible including $NO + H_2O$ and $HNO + OH$. With the exception of the studies of Hack et al. (1982) and Jayanty et al. (1976) and several studies at high temperature, there is no evidence for a reaction. The following upper limits have been measured (cm^3 $molecule^{-1}$ s^{-1}): 3×10^{-18} (Lesclaux and Demissy, 1977), 8×10^{-15} (Pagsberg et al., 1979), 1.5×10^{-17} (Cheskis and Sarkisov, 1979), 3×10^{-18} (Lozovsky et al., 1984), 1×10^{-17} (Patrick and Golden, 1984b) and 7.7×10^{-18} (Michael et al., 1985b) and 6×10^{-21} (Tyndall et al., 1991b). The recommendation is based on the study of Tyndall et al. which was sensitive to reaction paths leading to the products NO, NO_2 and N_2O. The reaction forming NH_2O_2 cannot be ruled out, but is apparently not important in the atmosphere.

C30. $NH_2 + O_3$. There is poor agreement among the recent studies of Cheskis et al. (1985), k(298) = 1.5×10^{-13} cm^3 s^{-1}, Patrick and Golden (1984b), k(298) = 3.25×10^{-13} cm^3 s^{-1}, Hack et al. (1981), 1.84×10^{-13} cm^3 s^{-1}, Bulatov et al. (1980), 1.2×10^{-13} cm^3 s^{-1}, and Kurasawa and Lesclaux (1980a), 0.63×10^{-13} cm^3 s^{-1}. The very low value of Kurasawa and Lesclaux may be due to regeneration of NH_2 from secondary reactions (see Patrick and Golden), and it is disregarded here. The discharge flow value of Hack et al. is nearly a factor of two less than the recent Patrick and Golden flash photolysis value. The large discrepancy between Bulatov et al. and Patrick and Golden eludes explanation. The recommendation is the k(298) average of these four studies, and E/R is an average of Patrick and Golden (1151 K) with Hack et al. (710 K).

D1. OH + CO. The recommendation allows for an increase in k with pressure. The zero pressure value was derived by averaging all direct low pressure determinations [those listed in Baulch et al. (1980) and the values reported by Dreier and Wolfrum (1980), Husain et al. (1981), Ravishankara and Thompson (1983), Paraskevopoulos and Irwin (1984), Hofzumahaus and Stuhl (1984), Fritz and Zellner, private communication (1987)]. The results of Jonah et al. (1984) are too high and were not included. An increase in k with pressure has been observed by a large number of investigators [Overend and Paraskevopoulos (1977a), Perry et al. (1977), Chan et al. (1977), Bierman et al. (1978), Cox et al. (1976b), Butler et al. (1978), Paraskevopoulos and Irwin (1982b, 1984), DeMore, (1984), Hofzumahaus and Stuhl (1984), Fritz and Zellner (1987), Hynes et al. (1986a), Stachnik and Molina, private communication (1987), and Wahner and Zetzsch, private communication (1987)]. In addition, Niki et al. (1984) have measured k relative to OH + C_2H_4 in one atmosphere of air by following CO_2 production using FTIR. The recommended 298 K value was obtained by using a weighted non-linear least squares analysis of all pressure dependent data in N_2 [Paraskevopoulos and Irwin (1984); DeMore (1984), Hofzumahaus and Stuhl (1984), and Hynes et al. (1986a)] as well as those in air [Fritz and Zellner (1987), Niki et al. (1985), Hynes et al. (1986a), Stachnik and Molina (1987), Wahner and Zetzsch (1987)] to the form k = (A+BP)/(C+DP) where P is pressure in atmosphere. The data were best fit with D = 0 and therefore a linear form is recommended. Previous controversy regarding the effect of small amounts of O_2 (Bierman et al., 1978) has been resolved and is attributed to secondary reactions [(DeMore (1984), Hofzumahaus and Stuhl (1984)]. The results of Butler et al. (1978) have to be re-evaluated in the light of refinements in the rate coefficient for the OH + H_2O_2 reaction. The corrected rate coefficient is in approximate agreement with the recommended value. Currently, there are no indications to suggest that the presence of O_2 has any effect on the rate coefficient other than as a third body. The E/R value in the pressure range 50-760 torr has been shown to be essentially zero between 220 and 298 K by Hynes et al. (1986a), and Stachnik and Molina (private communications, 1987). Further substantiation of the temperature independence of k at 1 atm. may be worthwhile. The uncertainty factor is for 1 atm. of air. In the presence of O_2, the HOCO intermediate is converted to $HO_2 + CO_2$ (DeMore, 1984). Beno et al. (1985) observe an enhancement of k with water vapor which is in conflict with the flash photolysis studies, e.g., Ravishankara and Thompson (1983), Paraskevopoulos and Irwin (1984), and Hynes et al. (1986a).

D2. OH + CH_4. This reaction has been investigated by many workers over past few decades because of its importance in combustion and atmospheric processes [Greiner (1970b), Davis et al. (1974a), Margitan et al. (1974), Zellner and Steinert (1976), Tully and Ravishankara (1980), Jeong and Kaufman (1982), Jonah et al. (1984), and Madronich and Felder (1985)]. The Arrhenius plot for this rate coefficient is curved and there is very little data at temperatures below 298 K. Extrapolation of the higher temperature data to the lower atmospheric temperatures is likely to cause errors. Furthermore, at lower temperatures, the rate coefficient is small and, hence, its measurements are easily influenced by the presence of impurities and occurrence of secondary reactions. Recently, Vaghjiani and Ravishankara (1991) have investigated this reaction using a pulsed laser photolysis-laser induced fluorescence apparatus. They found k(298 K) to be ~20% lower than the previous recommendation. They attribute the previously measured higher values to secondary reactions of OH with CH_3 radicals and partly to the presence of impurities. They have extensively measured the rate coefficient at the lower atmospheric temperatures and obtain a slightly higher E/R than the previously recommended value. The current recommendation is based on their results. The results of Vaghjiani and Ravishankara agree with most previous data obtained at T>400 K where the rate coefficient is significantly larger and hence not influenced by the above mentioned problems.

D3. OH + $^{13}CH_4$ (k_{13}). This reaction has been studied relative to the OH + CH_4 (k_{12}) reaction, since the ratio of the rate coefficients k_{12}/k_{13} is the quantity needed for identifying methane sources. Rust and Stevens (1980), Davidson et al. (1987), and Cantrell et al. (1990c) have measured k_{12}/k_{13} at 298 K to be 1.003, 1.010, and 1.0055, respectively. Cantrell et al.'s data supersede the results of Davidson et al.. The recommended value of 1.005 ± 0.002 is based on the results of Rust and Stevens and Cantrell et al.. Cantrell et al. find k_{12}/k_{13} to be independent of temperature between 273 and 353 K.

D4. OH + C_2H_6. There are seventeen studies of this reaction at 298 K, [Greiner (1970a), Howard and Evenson (1976b), Overend et al. (1975), Lee and Tang (1982), Leu (1979b), Tully et al. (1983), Jeong et al. (1984), Tully et al. (1986), Nielsen et al. (1986), Zabarnick et al. (1988), Wallington et al. (1987), Smith et al. (1984), Baulch et al. (1985), Bourmada et al. (1987), Abbatt et al. (1990), Schiffman et al. (1991), and Talukdar et al. (1991c)]. The recommended value is obtained by averaging the results of the recent investigations by Tully et al. (1986), Wallington et al. (1987), Abbatt et al. (1990), Schiffman et al. (1991), and Talukdar et al. (1991). These investigations are believed to have smaller errors and yield 298 K values which are ~15% lower than the previous recommendation. When the measurements were not carried out at exactly 298 K, we have recalculated k using an E/R of 1070 K. The temperature dependence of the rate coefficient below 298 K has been measured only by Jeong et al., Wallington et al., and Talukdar et al. The last two studies are in excellent agreement. The recommended E/R is obtained from an analysis of the data of Wallington et al. and Talukdar et al.

D5. OH + C_3H_8. There are many measurements of the rate coefficients at 298 K. In this evaluation we have considered only the direct measurements [Greiner (1970a), Tully et al. (1983), Droege and Tully (1986), Schmidt et al. (1985), Baulch et al. (1985), Bradley et al. (1973), Abbatt et al. (1990), Schiffman et al. (1991), and Talukdar et al. (1991)]. The 298 K value is the average of these nine studies. Greiner (1970a), Tully et al. (1983), Droege and Tully (1986) and Talukdar et al. (1991c) have measured the temperature dependence of this reaction. The recommended E/R was obtained from a linear least squares analysis of the data of Droege and Tully below 400 K and the data of Talukdar et al. The A factor was adjusted to reproduce k(298 K). This reaction has two possible channels, i.e., abstraction of the primary and the secondary H-atom. Therefore, non-Arrhenius behavior is exhibited over a wide temperature range, as shown by Tully et al. and Droege and Tully. The branching ratios were estimated from the latter study:

$$k_{primary} = 6.3 \times 10^{-12} \exp(-1050/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
$$k_{secondary} = 6.3 \times 10^{-12} \exp(-580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

These numbers are in reasonable agreement with the older data of Greiner.

D6. OH + H_2CO. The value for k(298 K) is the average of those determined by Atkinson and Pitts (1978), Stief et al. (1980), Temps and Wagner (1984), and Zabarnick et al. (1988). The value reported by Morris and Niki (1971) agrees within the stated uncertainty. There are two relative values which are not in agreement with the recommendations. The value of Niki et al. (1987b) relative to OH + C_2H_4 is higher while the value of Smith (1978) relative to OH + OH is lower. The latter data are also at variance with the negligible temperature dependence observed in the two flash photolysis studies. The combined data set suggests E/R = 0. The abstraction reaction shown in the table is the major channel [Temps and Wagner (1984), Niki et al. (1984)]; other channels may contribute to a small extent [Horowitz et al. (1978)].

D7. OH + CH_3OH. The recommended value for k(298 K) is the average of seven direct studies [Overend and Paraskevopoulos (1978), Ravishankara and Davis (1978), Hagele et al. (1983), Meier et al. (1984), Greenhill and O'Grady (1986), Wallington and Kurylo (1987), and Hess and Tully (1989)]. Indirect measurements by Campbell et al. (1976), Barnes et al. (1982), Tuazon et al. (1983b) and Kloppfer et al. (1986) are in good agreement with the recommended value. The temperature dependence of k has been measured by Hagele et al., Meier et al., Greenhill and O'Grady, Wallington and Kurylo, and Hess and Tully. The recommended value of E/R was calculated using the results obtained in the temperature range of 240 to 400 K by Greenhill and O'Grady (1986) and Wallington and Kurylo (1987), the only investigators who have measured k below 298 K. Hess and Tully report a curved Arrhenius plot over the temperature range 298 - 1000 K, while Meier et al. do not observe such a curvature. This reaction has two pathways: abstraction of the H-atom from the methyl group or from the OH group. The results of Hagele et al., Meier et al., and Hess and Tully suggest that H abstraction from the methyl group is the dominant channel below room temperature.

D8. OH + C_2H_5OH. The recommended value for k(298 K) is the average of those reported by Campbell et al. (1976), Overend and Paraskevopoulos (1978), Ravishankara and Davis (1978), Cox and Goldstone (1982), Kerr and Stocker (1986), Wallington and Kurylo (1987), and Hess and Tully (1988). The value reported by Meier et al. is nearly a factor of two lower than that recommended here. The recommended value of E/R was obtained by using the data of Wallington and Kurylo, and Hess and Tully. The A-factor has been adjusted to yield the recommended value of k(298 K). At atmospheric temperatures, H-atom abstraction from the CH_2 group is the dominant channel [Meier et al. (1985), Hess and Tully (1988)].

D9. OH + CH_3CHO. There are six measurements of this rate coefficient at 298 K [Morris et al. (1971), Niki et al. (1978b), Atkinson and Pitts (1978), Kerr and Sheppard (1981), Semmes et al. (1985), and Michael et al. (1985a)]. The recommended value of k(298 K) is the average of these measurements. Atkinson and Pitts, Semmes et al., and Michael et al. measured the temperature dependence of this rate coefficient and found it to exhibit a negative temperature dependence. The recommended E/R is the average value of these studies. The A-factor has been adjusted to yield the recommended value of k(298 K).

D10. OH + CH_3OOH. The recommended value for k(298 K) is the average of the rate coefficients measured by Niki et al. (1983) and Vaghjiani and Ravishankara (1989a), which differ by nearly a factor of two. Niki et al. measured the rate coefficient relative to that for OH with C_2H_4 (= 8.0×10^{-12} cm^3 $molecule^{-1}$ s^{-1}) by monitoring CH_3OOH disappearance using an FTIR system. Vaghjiani and Ravishankara monitored the disappearance of OH, OD, and ^{18}OH in excess CH_3OOH in a pulsed photolysis-LIF system. They measured k between 203 and 423 K and report a negative activation energy with E/R = -190 K; the recommended E/R is based on their results. The reaction of OH with CH_3OOH occurs via abstraction of H from the oxygen end to produce the CH_3OO radical and from the CH_3 group to produce the CH_2OOH radical, as originally proposed by Niki et al. and confirmed by Vaghjiani and Ravishankara. CH_2OOH is unstable and falls apart to CH_2O and OH within a few microseconds. The possible reaction of CH_2OOH with O_2 is unimportant under atmospheric conditions (Vaghjiani and Ravishankara). The recommended branching ratios are,

$$OH + CH_3OOH \rightarrow CH_3O_2 + H_2O \qquad (a)\ 70\%$$
$$OH + CH_3OOH \rightarrow CH_2OOH + H_2O \qquad (b)\ 30\%,$$

(from Vaghjiani and Ravishankara) and are nearly independent of temperature.

D11. OH + HC(O)OH. New Entry. The recommended value of k(298 K) is the average of those measured by Wine et al. (1985b), Jolly et al. (1986), and Dagaut et al. (1988c). Zetzsch and Stuhl (1982) have also measured k(298 K), to be ~50% lower than the recommended value. The temperature dependence of k has been studied only by Wine et al., who observed a very small negative activation energy. In the absence of confirmatory studies, a temperature independent k is recommended. Based on the study of Wine et al., where the rate coefficient for the OH + HC(O)OH reaction was found to be the same as that for OH + DC(O)OH reaction, and the study of Jolly et al., where the formic acid dimer was found to be unreactive toward OH, the reaction appears to proceed via abstraction of the acidic H atom. Wine et al. also found that H atoms are produced in the reaction, which is consistent with the formation of HC(O)O that would rapidly fall apart to CO_2 and H. Wine et al., also raise the possibility that, in the atmosphere, the formic acid could be hydrogen bonded to a water molecule and its reactivity with OH could be lowered.

D12. OH + $CH_3C(O)OH$. New Entry. The recommended k(298 K) was obtained from the average of the values obtained by Zetzsch and Stuhl (1982) and Dagaut et al. (1988c). The temperature dependence has been studied only by Dagaut et al., and is recommended. Dagaut et al. observe that the acetic acid dimer reacts twice as fast as the monomer, and attribute this to the reactivity of the acid group being unaltered upon dimerization. However, this observation is inconsistent with the non-reactivity of the formic acid dimer but is consistent with the reaction proceeding mainly via the abstraction of the H from the alkyl group.

D13. OH + HCN. This reaction is pressure dependent. The recommended value is the high pressure limit measured by Fritz et al. (1984) using a laser photolysis-resonance fluorescence apparatus. Phillips (1978) studied this reaction using a discharge flow apparatus at low pressures and found the rate coefficient to have reached the high pressure limit at ~10 torr at 298 K. Fritz et al.'s results contradict this finding. They agree with Phillip's measured value, within a factor of two, at 7 torr but they find k to increase further with pressure. The products of the reaction are unknown.

D14. OH + CH_3CN. This rate coefficient has been measured as a function of temperature by Harris et al. (1981) between 298 and 424 K, Kurylo and Knable (1984) between 250 and 363 K, Rhasa (1983) between 295 and 520 K, and Hynes and Wine (1991) between 256 and 388 K. In addition, the 298 K value has been measured by Poulet et al. (1984a). The 298 K results of Harris et al. are in disagreement with all other measurements and therefore have not been included. The recommended 298 K value is a weighted average of all other studies. The temperature dependence was computed using the results of Kurylo and Knable (250-363 K), the lower temperature values (i.e., 295-391 K) of Rhasa, and the data of Hynes and Wine (256-388 K). Three points are worth noting: (a) Rhasa observed a curved Arrhenius plot even in the temperature range of 295-520 K and therefore extrapolation of the recommended expression could lead to large errors, (b) Hynes and Wine observed a pressure dependent increase of k(298 K) which levels off at about 1 atmosphere. This observation is contradictory to the results of other investigations. (c) Hynes and Wine have carried out extensive pressure, temperature, O_2 concentration, and isotope variations in this reaction. They postulate that the reaction proceeds via addition as well as abstraction pathways. They observe OH regeneration in the presence of O_2. The recommended k(298 K) and E/R are applicable for only lower tropospheric conditions. Because of the unresolved questions of pressure dependence and reaction mechanism, the recommended value may not be applicable under upper tropospheric and stratospheric conditions.

D15. OH + $CH_3C(O)O_2NO_2$ (PAN). New Entry. This reaction has been studied by three groups of investigators, Winer et al. (1977), Wallington et al. (1984), and Tsalkani et al. (1988). Winer et al. obtained only an upper limit for the rate coefficient. The recommended value is a weighted average of the results from Wallington et al. and Tsalkani et al. Tsalkani et al. noted that their system was very ill-behaved and obtained a value of k(298 K) that is a factor of ~2 lower than that obtained by Wallington et al. The pulsed photolysis study of Wallington et al. yielded consistent results and their results are weighted more heavily in this evaluation. PAN is unstable and a very difficult molecule to handle. Also, it is difficult to get rid of the solvent in which it is prepared. Therefore, measuring PAN concentrations and avoiding impurities are very difficult. Our recommendation reflects this difficulty. The recommended k(298 K) is consistent with the upper limit of Winer et al. The temperature dependence of this reaction has been studied only by Wallington et al., and is recommended. The products of the reaction are not known. Further measurements of the rate coefficients and information on the reaction pathways are needed.

D16. O_3 + C_2H_2. The database for this reaction is not well established. Room temperature measurements (Cadle and Schadt, 1953; DeMore, 1969; DeMore, 1971; Stedman and Niki, 1973b; Pate et al, 1976; and Atkinson and Aschmann, 1984) disagree by as much as an order of magnitude. It is probable that secondary reactions involving destruction of ozone by radical products resulted in erroneously high values for the rate constants in several of the previous measurements. The present recommendation for k(298 K) is based on the room temperature value of Atkinson and Aschmann (1984), which is the lowest value obtained and therefore perhaps the most accurate. The temperature dependence is estimated, based on an assumed A-factor of 1.0 x 10^{-14} cm^3 s^{-1} similar to that for the O_3 + C_2H_4 reaction and corresponding to the expected 5-membered ring structure for the transition state (DeMore, 1969, 1971). Further studies, particularly of the temperature dependence, are needed. Major products in the gas phase reaction are CO, CO_2, and HCOOH, and chemically-activated formic anhydride has been proposed as an intermediate of the reaction (DeMore, 1971, and DeMore and Lin, 1973). The anhydride intermediates in several alkyne ozonations have been isolated in low temperature solvent experiments (DeMore and Lin, 1971).

D17. O_3 + C_2H_4. The rate constant of this reaction is well established over a wide temperature range, 178 to 360 K. Our recommendation is taken from that of IUPAC (1989), which is based on the data of DeMore (1969), Stedman et al. (1973), Herron and Huie (1974), Japar et al. (1974, 1976), Toby et al. (1976), Su et al. (1980), Adeniji et al. (1981), Kan et al. (1981), Atkinson et al. (1982), and Bahta et al. (1984).

D18. $O_3 + C_3H_6$. The rate constant of this reaction is well established over the temperature range 185 to 360 K. The present recommendation is based largely on the data of Herron and Huie (1974), in the temperature range 235-362 K. (Note that a typographical error in Table 2 of that paper improperly lists the lowest temperature as 250 K, rather than the correct value, 235 K.) The recommended Arrhenius expression agrees within 25% with the low temperature (185-195 K) data of DeMore (1969), and is consistent with, but slightly lower (about 40%) than the data of Adeniji et al. (1981) in the temperature range 260-294 K. Room temperature measurements of Cox and Penkett (1972), Stedman et al. (1973), Japar et al. (1974, 1976), and Atkinson et al. (1982) are in good agreement (10% or better) with the recommendation.

D19. $HO_2 + CH_2O$. There is sufficient evidence to suggest that HO_2 adds to CH_2O [Su et al. (1979b,c), Veyret et al. (1982), Zabel et al. (1987), Barnes et al. (1985), and Veyret et al. (1989)]. The recommended k(298 K) is the average of values obtained by Su et al. (1979c), Veyret et al. (1982), and Veyret et al. (1989). The temperature dependence observed by Veyret et al. (1989) is recommended. The value reported by Barnes et al. at 273 K is consistent with this recommendation. The adduct $HO_2{\bullet}CH_2O$ seems to isomerize to $HOCH_2OO$ reasonably rapidly and reversibly. There is a great deal of discrepancy between measured values of the equilibrium constants for this reaction.

D20. O + HCN. Because it is a very slow reaction, there are no studies of this reaction below 450 K. Davies and Thrush (1968) studied this reaction between 469 and 574 K while Perry and Melius (1984) studied it between 540 and 900 K. Results of Perry and Melius are in agreement with those of Davies and Thrush. Our recommendation is based on these two studies. The higher temperature (T>1000 K) combustion related studies [Roth et al. (1980), Szekely et al. (1984), and Louge and Hanson (1984)] have not been considered. This reaction has two reaction pathways: $O + HCN \rightarrow H + NCO$, $\Delta H = -2$ kcal/mol (k_a); and $O + HCN \rightarrow CO + NH$ (k_b), $\Delta H = -36$ kcal/mol. The branching ratio k_a/k_b for these two channels has been measured to be ~2 at T = 860 K. The branching ratio at lower temperatures, which is likely to vary significantly with temperature, is unknown.

D21. $O + C_2H_2$. The value at 298 K is an average of ten measurements [Arrington et al. (1965), Sullivan and Warneck (1965), Brown and Thrush (1967), Hoyermann et al. (1967, 1969), Westenberg and deHaas (1969b), James and Glass (1970), Stuhl and Niki (1971), Westenberg and deHaas (1977), and Aleksandrov et al. (1981)]. There is reasonably good agreement among these studies. Arrington et al. (1965) did not observe a temperature dependence, an observation which was later shown to be erroneous by Westenberg and deHaas (1969b). Westenberg and deHaas (1969b), Hoyermann et al. (1969) and Aleksandrov et al. (1981) are the only authors who have measured the temperature dependence below 500 K. Westenberg and deHaas observed a curved Arrhenius plot at temperatures higher than 450 K. In the range 194-450 K, Arrhenius behavior provides an adequate description and the E/R obtained by a fit of the data from these three groups in this temperature range is recommended. The A-factor was calculated to reproduce k(298 K). This reaction can have two sets of products, i.e., $C_2HO + H$ or $CH_2 + CO$. Under molecular beam conditions C_2HO has been shown to be the major product. The study by Aleksandrov et al. using a discharge flow-resonance fluorescence method (under undefined pressure conditions) indicates that the $C_2HO + H$ channel contributes no more than 7% to the net reaction at 298 K, while a similar study by Vinckier et al. (1985) suggests that both CH_2 and C_2HO are formed.

D22. $O + H_2CO$. The recommended values for A, E/R and k(298 K) are the averages of those determined by Klemm (1979) (250 to 498 K) using flash photolysis-resonance fluorescence, by Klemm et al. (1980) (298 to 748 K) using discharge flow-resonance fluorescence, and Chang and Barker (1979) (296 to 436 K) using discharge flow-mass spectrometry techniques. All three studies are in good agreement. The k(298 K) value is also consistent with the results of Niki et al. (1969), Herron and Penzhorn (1969), and Mack and Thrush (1973). Although the mechanism for $O + H_2CO$ has been considered to be the abstraction reaction yielding OH + HCO, Chang and Barker suggest that an additional channel yielding $H + HCO_2$ may be occurring to the extent of 30% of the total reaction. This conclusion is based on an observation of CO_2 as a product of the reaction under conditions where reactions such as $O + HCO \rightarrow H + CO_2$ and $O + HCO \rightarrow OH + CO$ apparently do not occur. This interesting suggestion needs independent confirmation.

D23. $O + CH_3CHO$. The recommended k(298 K) is the average of three measurements by Cadle and Powers (1967), Mack and Thrush (1974), and Singleton et al. (1977), which are in good agreement. Cadle and Powers and Singleton et al. studied this reaction as a function of temperature between 298 and 475 K and obtained very similar Arrhenius parameters. The recommended E/R value was obtained by considering both sets of data. This reaction is known to proceed via H-atom abstraction [Mack and Thrush (1974), Avery and Cvetanovic (1965), and Singleton et al. (1977)].

D24. O + CH_3. The recommended k(298 K) is the weighted average of three measurements by Washida and Bayes (1976), Washida (1980), and Plumb and Ryan (1982b). The E/R value is based on the results of Washida and Bayes (1976), who found k to be independent of temperature between 259 and 341 K.

D25. $CH_3 + O_2$. This bimolecular reaction is not expected to be important based on the results of Baldwin and Golden (1978a), who found $k < 5 \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} for temperatures up to 1200 K. Klais et al. (1979) failed to detect OH (via $CH_3 + O_2 \rightarrow CH_2O + OH$) at 368 K and placed an upper limit of 3×10^{-16} cm^3 $molecule^{-1}$ s^{-1} for this rate coefficient. Bhaskaran et al. (1979) measured $k = 1x10^{-11}$ exp (-12,900/T) cm^3 $molecule^{-1}$ s^{-1} for $1800 < T < 2200$ K. The latter two studies thus support the results of Baldwin and Golden. Studies by Selzer and Hayes (1983) and Plumb and Ryan (1982b) confirm the low value for this rate coefficient. Previous studies of Washida and Bayes (1976) are superseded by those of Selzer and Bayes. Plumb and Ryan have placed an upper limit of 3×10^{-16} cm^3 $molecule^{-1}$ s^{-1} based on their inability to find HCHO in their experiments. A study by Zellner and Ewig (1988) suggests that this reaction is important at combustion temperature but is unimportant for the atmosphere.

D26. $C_2H_5 + O_2$. This recommendation is taken from IUPAC (1989).

D27. $CH_2OH + O_2$. The rate coefficient was first measured directly by Radford (1980) by detecting the HO_2 product in a laser magnetic resonance spectrometer. The wall loss of CH_2OH could have introduced a large error in this measurement. Radford also showed that the previous measurement of Avramenko and Kolesnikova (1961) was in error. Wang et al. (1984) measured a value of 1.4×10^{-12} cm^3 $molecule^{-1}$ s^{-1} by detecting the HO_2 product. Recently, Dobe et al. (1985), Grotheer et al. (1985), Payne et al. (1988), Grotheer et al. (1988) and Nesbitt et al. (1988) have measured k(298 K) to be close to 1.0×10^{-11} cm^3 $molecule^{-1}$ s^{-1} under conditions where wall losses are small. This reaction appears to exhibit a very complex temperature dependence. Based on the recent data of Grotheer et al. (1988) and Nesbitt et al. (1988), k appears to increase from 200 K to approximately 250 K in an Arrhenius fashion, levels off at approximately 300 K, decreases from 300 to 500 K, and finally increases as temperature is increased. This complex temperature dependence is believed to be due to the formation of a $CH_2(OH) \bullet O_2$ adduct which can isomerize to $CH_2O \bullet HO_2$ or decompose to reactants. The $CH_2O \bullet HO_2$ isomer can also decompose to CH_2O and HO_2 or reform the original adduct. At temperatures less than 250 K, the data of Nesbitt et al. suggests an E/R value of ~1700 K.

D28. $CH_3O + O_2$. The recommended value for k(298 K) is the average of those reported by Lorenz et al. (1985) and Wantuck et al. (1987). The recommended E/R was obtained using the results of Gutman et al. (1982) (413 to 608 K), Lorenz et al. (1985) (298 to 450 K), and Wantuck et al. (1987) (298 to 498 K). These investigators have measured k directly under pseudo-first order conditions by following CH_3O via laser induced fluorescence. Wantuck et al. measured k up to 973 K and found the Arrhenius plot to be curved; only their lower temperature data are used in the fit to obtain E/R. The A factor has been adjusted to reproduce the recommended k(298 K). The previous high temperature measurements [Barker et al. (1977) and Batt and Robinson (1979)] are in reasonable agreement with the derived expression. This value is consistent with the 298 K results of Cox et al. (1980), obtained from an end product analysis study, and with the upper limit measured by Sanders et al. (1980b). The A-factor appears to be too low for a hydrogen atom transfer reaction. The Arrhenius plot is curved at higher temperature (Wantuck et al.). The reaction may be more complicated than a simple abstraction. At 298 K, the products of this reaction are HO_2 and CH_2O as shown by Niki et al. (1981).

D29. $C_2H_5O + O_2$. New Entry. The recommendation is based on the pulsed laser photolysis study of Gutman et al.. (1982) who directly monitored the removal of C_2H_5O via laser induced fluorescence in a excess of O_2. They measured k at only two temperatures, all above 298 K. The 298 K value deduced from an indirect study by Zabarnick and Heicklen (1985) is in reasonable agreement with the recommended value.

D30. $HCO + O_2$. The value of k(298 K) is the average of the determinations by Washida et al. (1974), Shibuya et al. (1977), Veyret and Lesclaux (1981), and Langford and Moore (1984). There are three measurements of k where HCO was monitored via the intracavity dye laser absorption technique (Reilly et al. (1978), Nadtochenko et al. (1979), and Gill et al. (1981)). Even though there is excellent agreement between these three studies, they yield consistently lower values than those obtained by other techniques. There are several possible reasons for this discrepancy: (a) The relationship between HCO concentration and laser attenuation in an intracavity absorption experiment might not be linear, (b) there could have been depletion of O_2 in the static systems that were used (as suggested by Veyret and Lesclaux), and (c) these experiments were designed more for the study of photochemistry than kinetics. Therefore, these values are not included in obtaining the recommended value. The recommended temperature dependence is essentially identical to that measured by Veyret and Lesclaux. We have expressed the temperature dependence in an Arrhenius form even though Veyret and Lesclaux preferred a T^n form ($k = 5.5 \times 10^{-11}\ T^{-(0.4\pm0.3)}$ cm^3 $molecule^{-1}$ s^{-1}).

D31. $CH_3 + O_3$. The recommended A-factor and E/R are those obtained from the results of Ogryzlo et al. (1981). The results of Simonaitis and Heicklen (1975), based on an analysis of a complex system, are not used. Washida et al. (1980b) used $O + C_2H_4$ as the source of CH_3. Studies on $O + C_2H_4$ reaction [Buss et al. (1981), Kleinermanns and Luntz (1981), Hunziker et al. (1981), and Inoue and Akimoto (1981)] have shown this reaction to be a poor source of CH_3. Therefore, the results of Washida et al. are also not used.

D32. $CH_3O_2 + O_3$. There are no direct studies of this reaction. The quoted upper limit is based on indirect evidence obtained by Simonaitis and Heicklen (1975).

D33. $CH_3O_2 + CH_3O_2$. This reaction has been studied at 298 K by Hochanadel et al. (1977), Parkes (1977), Anastasi et al. (1978), Kan et al. (1979), Sanhueza et al. (1979), Cox and Tyndall (1980), Sander and Watson (1981c), Basco and Parmer (1985), McAdam et al. (1987), Kurylo and Wallington (1987), Jenkin et al. (1988), Lightfoot et al. (1990a), and Simon et al. (1990b). All the above determinations used UV absorption techniques to monitor CH_3O_2 and hence measured k/σ, where σ is the absorption cross section for CH_3O_2 at the monitored wavelength. Therefore, the derived value of k critically depends on the value of σ that is used. Even though there is good agreement between the measured values of k/σ, there are large discrepancies (approximately a factor of 2) between the values of σ measured by Hochanadel et al., Parkes, Sander and Watson, Adachi et al. (1980), McAdam et al., Kurylo et al. (1987a), and Simon et al. To obtain the recommended k value at 298 K, an average value of σ at 250 nm, 4.0×10^{-18} cm^2 (obtained by averaging the results of Sander and Watson, Kurylo and Wallington as amended in Dagaut and Kurylo (1990), Lightfoot et al., and Jenkin et al.) was chosen. The value of k(298 K) was derived using this value of σ and the weighted average value of k/σ at 250 nm measured by Cox and Tyndall, Jenkin et al., Sander and Watson, McAdam et al., Kurylo and Wallington, Lightfoot et al., and Simon et al. The recommended temperature dependence was calculated by using the results of Sander and Watson, Kurylo and Wallington, Lightfoot et al. (at temperatures between 228 and 420 K), and Jenkin and Cox (1990), using a value of σ independent of T. It has been recently shown by Lightfoot and Jemi-Alade (1991) that σ is essentially invariant with temperature. It is not clear whether the above procedure of recalculating k using an average value of σ is valid. Therefore, the quoted error limits encompass the values of k calculated by various authors. This reaction has four possible sets of products, i.e.,

$CH_3O_2 + CH_3O_2 \rightarrow 2CH_3O + O_2$	k_a ; $k_a/k = 0.3$ at 298 K
$CH_3O_2 + CH_3O_2 \rightarrow CH_2O + CH_3OH + O_2$	k_b ; $k_b/k = 0.6$ at 298 K
$CH_3O_2 + CH_3O_2 \rightarrow CH_3OOCH_3 + O_2$	k_c ; $k_c/k = 0.1$ at 298 K
$CH_3O_2 + CH_3O_2 \rightarrow CH_3OOH + CH_2O_2$	k_d ; $k_d/k = 0.0$ at 298 K

FTIR studies by Kan et al. (1980) and Niki et al. (1981) are in reasonable agreement on branching ratios at 298 K; $k_a/k \sim 0.35$, $k_b/k \sim 0.55$. The recent study by Lightfoot et al. also yields $k_a/k \cong 0.35$ while Horie et al. (1990) obtain 0.30. The last two groups see a large decrease of k_a/k with decreasing temperature, which may be expressed as $(k_a/k) = 1/[1 + \{exp(1130/T)\}/19]$. The results of Ballod et al. (1989) are in fair agreement with this trend. Channel (d) was suggested by Nangia and Benson (1980), but there is no experimental data to suggest its occurrence [Khursan et al..(1990)]. Because of the existence of multiple pathways, the temperature dependence of k may be complex. Further work is required on both the temperature dependence and the variation of branching ratios with temperature. It should be noted that the recommended value depends on the branching ratios.

D34. CH_3O_2 + NO. The value of k(298 K) is the average of those determined by Sander and Watson (1980), Ravishankara et al. (1981a), Cox and Tyndall (1980), Plumb et al. (1981), Simonaitis and Heicklen (1981) and Zellner et al. (1986). Values lower by more than a factor of two have been reported by Adachi and Basco (1979) and Simonaitis and Heicklen (1979). The former direct study was probably in error because of interference by CH_3ONO formation. The results of Simonaitis and Heicklen (1979) and Plumb et al. (1979) are assumed to be superseded by their more recent values. Ravishankara et al. (1981a) and Simonaitis and Heicklen (1981) have measured the temperature dependence of k over limited temperature ranges. The recommended A-factor and E/R were obtained by a least squares analysis of the data from these two studies. The value of k(218 K) obtained by Simonaitis and Heicklen (1981) is not included; however, the large error bounds allow the calculated value of k at 218 K to overlap that measured by Simonaitis and Heicklen. Ravishankara et al. (1981a) find that the reaction channel leading to NO_2 accounts for at least 80% of the reaction. Zellner et al. (1986) have measured the yield of CH_3O to be 1.0±0.2. These results, in conjunction with the indirect evidence obtained by Pate et al. (1974), confirm that NO_2 formation is the major reaction path, at least at low pressures.

D35. $CH_3O_2 + HO_2$. The rate coefficient at 298 K has been measured by Cox and Tyndall (1979, 1980), Moortgat et al. (1986), McAdam et al. (1987), Kurylo et al. (1987b), Jenkin et al. (1988), and Lightfoot et al. (1990b). In all the studies, except that of Jenkin et al., both CH_3O_2 and HO_2 have been monitored via UV absorption. Jenkin et al. used IR absorption of HO_2 and UV absorption of CH_3O_2 to obtain the rate constants. Because of overlapping absorption spectra of CH_3O_2 and HO_2 and the unavoidable occurrence of the $CH_3O_2 + CH_3O_2$ and $HO_2 + HO_2$ reactions along with the $CH_3O_2 + HO_2$ reaction, the extraction of the rate coefficient requires modelling of the system and reliance on the UV cross sections of both CH_3O_2 and HO_2. The agreement between the values of k obtained by all these groups is not very good. Part of the differences are definitely due to different values of the UV cross sections used in various studies. Contribution from secondary reactions may also be partly responsible for the differences. Unfortunately, it is not feasible to correct the reported values to a common set of cross sections. Therefore, the average of values from Cox and Tyndall, Moortgat et al., McAdam et al., Kurylo and Wallington, Jenkin et al., and Lightfoot et al. are used to obtain the recommended value. Cox and Tyndall, Dagaut et al. (1988a), and Lightfoot et al., have measured the temperature dependence of this rate coefficient. The recommended E/R was obtained by plotting ln $(k_{(T)}/k_{298})$ vs 1/T from these studies. This method looks for only the E/R value in each data set. The A-factor was calculated to reproduce k(298 K). The studies by the above groups have indicated that this reaction is not affected by pressure or nature of the buffer gas.

Jenkin et al. suggest that a substantial fraction of the reaction may yield $H_2O + CH_2O + O_2$ rather than $CH_3OOH + O_2$. The lower value of k measured by monitoring CH_3OOH formation by Moortgat et al. and Kan et al. (1980) is consistent with the occurrence of the second channel and the lower value of k measured when CH_3OOH product yield is monitored. However, the recent work of Wallington (1991) indicates that CH_3OOH is the dominant (>92%), if not the only, product. Further work on measurement of k without reliance on UV absorption cross sections and branching ratios where CH_2O is monitored is needed.

D36. $CH_3O_2 + CH_3C(O)O_2$. New Entry. The reaction has been investigated by Addison et al. (1980), Moortgat et al. (1986), and Moortgat et al. (1989a) using UV absorption in conjunction with investigations of the $CH_3C(O)O_2$ self-reaction. The rate coefficient obtained by Addison et al. is a factor of ~5 lower than those measured by Moortgat et al. (1986). It is believed that this lower value is due to the use of low UV absorption cross sections, which were poorly known at the time of this study [Moortgat et al. (1989)]. The recommended value is that obtained by Moortgat et al. (1989), which is in excellent agreement with the value of Moortgat et al. (1986). The temperature dependence of k has been studied by Moortgat et al. (1989) and is recommended.

The reaction has two pathways,

$$CH_3C(O)O_2 + CH_3O_2 \rightarrow CH_3C(O)O + CH_3O + O_2 \qquad (a)$$
$$CH_3C(O)O_2 + CH_3O_2 \rightarrow CH_3C(O)OH + CH_2O + O_2 \qquad (b).$$

Moortgat et al. (1989) have extracted from their measurements the following T dependence for the individual rate coefficients over a very limited temperature range near 298 K:

$$k_a = 1.8 \times 10^{-9} \exp[-(1800 \pm 1100)/T]\ cm^3\ molecule^{-1}\ s^{-1}$$
$$k_b = 4.1 \times 10^{-15} \exp[(2100 \pm 1200)/T]\ cm^3\ molecule^{-1}\ s^{-1}.$$

Note that these rate coefficients have large uncertainties and should be used only for $250 < T < 350$ K. Pathway (a) was originally proposed by Weaver et al. (1976) while pathway (b) was proposed by Moortgat et al. (1989).

D37. $C_2H_5O_2 + C_2H_5O_2$. The recommended value of k(298 K) was derived from the studies of Adachi et al. (1979), Anastasi et al. (1979), Munk et al. (1986), Cattell et al. (1986), Anastasi et al. (1987), and Wallington et al. (1988a). All the above determinations used UV absorption to monitor $C_2H_5O_2$ and hence measured k/σ, where σ is the absorption cross section of $C_2H_5O_2$ at the monitoring wavelength. These investigators also measured the σ that was used in evaluating the rate coefficient. There are large discrepancies in the measured values of σ. For this evaluation, we have used the reported value of k rather than evaluating a mean value of k/σ and converting it to k, using a preferred value of σ. In all these experiments the observed rate coefficient is higher than the true rate coefficient because of secondary reactions involving HO_2. HO_2 is formed by the reaction of CH_3CH_2O with O_2, and reacts with $C_2H_5O_2$ to enhance the observed rate coefficient (see Wallington et al. for further discussion). Based on product branching ratios discussed below, which determine the magnitude of the necessary correction, the recommended rate coefficient is 0.6 times the average observed rate coefficient. The recommended value of E/R was obtained from the results of Anastasi et al. (1979), Wallington et al. (1988a), Anastasi (1987), and Cattell et al. (1986). The observed products [Niki et al. (1982)], suggest that at 298K the channel to yield $2\ C_2H_5O + O_2$ accounts for about 60% of the reaction; the channel to yield $CH_3CHO + C_2H_5OH + O_2$ accounts for about 40% of the reaction; and the channel to yield $C_2H_5O_2C_2H_5 + O_2$ accounts for less than 5% of the reaction. These branching ratios were used above to obtain the true rate coefficient from the observed rate coefficient.

D38. $C_2H_5O_2 + NO$. The recommended value is that reported by Plumb et al. (1982). The value reported by Adachi and Basco (1979), which is a factor of three lower than the Plumb et al. value, was not used. The rate coefficient for the $CH_3O_2 + NO$ reaction measured by Basco and co-workers [Adachi et al. (1979)], using the same apparatus, is much lower than the value recommended here. The temperature dependence of the $C_2H_5O_2 + NO$ rate coefficient has not been measured. However, by analogy with the $CH_3O_2 + NO$ reaction, the E/R is expected to be near zero, with a small negative value being likely.

D39. $C_2H_5O_2 + HO_2$. New Entry. The recommended value is the average of those measured by Cattell et al. (1986) and Dagaut et al. (1988b). In both experiments the rate coefficient was obtained by modeling the reaction system. Also, the calculated rate coefficients depended on the UV absorption cross sections of both $C_2H_5O_2$ and HO_2. As mentioned earlier, the absorption cross section of $C_2H_5O_2$ is not well-defined. The agreement between the two studies, however, is reasonable. The recommended E/R is that measured by Dagaut et al. Wallington and Japar (1990) have shown that $C_2H_5O_2H$ and O_2 are the only products of this reaction.

D40. $CH_3C(O)O_2 + CH_3C(O)O_2$. New Entry. This reaction has been studied by Addison et al. (1980), Basco and Parmar (1985), and Moortgat et al. (1989a), using UV absorption techniques. The recommended value is that obtained by Moortgat et al. As pointed out by Moortgat et al., the six times lower value of k obtained by Addison et al. is likely due to the use of incorrect UV absorption cross sections for the peroxyradical, which were poorly defined when the study was carried out. The k obtained by Basco and Parmar is ~2 times lower than the recommended value. This discrepancy is possibly due to neglecting the UV absorption of CH_3O_2 in their data analysis [Moortgat et al. (1989a)]. The recommended temperature dependence is that measured by Moortgat et al. Addison et al. reported the formation of O_3, which was attributed to the reaction channel which produces $CH_3C(O)OCH_3C(O) + O_3$. Moortgat et al.

place an upper limit of 2% for this channel. The main products of this reaction appear to be $CH_3C(O)O$ + O_2. The $CH_3C(O)O$ radicals rapidly decompose to give CH_3 and CO_2.

D41. $CH_3C(O)O_2$ + NO. New Entry. This rate coefficient has been determined relative to that for the addition reaction of $CH_3C(O)O_2$ with NO_2 by Cox et al. (1976c), Cox and Roffey (1977), Hendry and Kenley (1977), Kirchner et al. (1990), and Tuazon et al. (1991). The pressure and temperatures employed in these studies are not all the same. The recommended value for the addition reaction of $CH_3C(O)O_2$ with NO_2 has been used to place all these relative values on an absolute scale. The obtained values are in reasonable agreement and show that the rate coefficient is independent of pressure. The recommended value was obtained by a weighted (depending on the number of determinations) average of the results from all the investigators. The study of Kirchner et al. shows that the rate coefficient is independent of temperature, at least within the small range of 304 to 321 K. Based on analogy with other RO_2 + NO reactions, the E/R is recommended to be zero. The product of the reaction is most likely $CH_3C(O)O$ and NO_2.

D42. $CH_3C(O)O_2$ + HO_2 . New Entry. The recommendation is based on Moortgat et al. (1989b), the only measurement of this rate coefficient. They measured UV absorption at 210 and 260 nm as a function of time in a flash photolysis system and fitted the observed 210 and 260 nm absorption temporal profiles to a set of reactions involving $CH_3C(O)O_2$, CH_3O_2, and HO_2. The recommended temperature dependence is also from this study. The rate coefficient obtained in such a measurement is dependent on the UV absorption cross sections of all the absorbers and all their reactions. Hence, any change in these parameters can change the calculated rate coefficient. The recommended k and E/R are consistent with those for similar peroxy radical reactions. There are two possible channels for this reaction:

$$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OOH + O_2 \qquad (a)$$
$$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OH + O_3 \qquad (b)$$

Niki et al. (1985) measured k_b/k to be 0.25 which agrees reasonably with 0.33 measured by Moortgat et al. Moortgat et al. also found that k_b/k did not vary with temperature. A temperature independent value of 0.3 is recommended for k_b/k.

D43. NO_3 + CO. The upper limit is based on the results of Hjorth et al. (1986), who monitored isotopically labeled CO loss in the presence of NO_3 by FTIR. Burrows et al. (1985b) obtained an upper limit of 4 x 10^{-16} cm^3 $molecule^{-1}$ s^{-1}, which is consistent with the Hjorth et al. study. Products are expected to be NO_2 + CO_2, if the reaction occurs.

D44. NO_3 + CH_2O. There are three measurements of this rate coefficient at 298 K: Atkinson et al. (1984a), Cantrell et al. (1985), and Hjorth et al. (1988). The value reported by Atkinson et al. (1984a), k = (3.23 ± 0.26) x 10^{-16} cm^3 $molecule^{-1}$ s^{-1}, is corrected to 5.8 x 10^{-16} cm^3 $molecule^{-1}$ s^{-1} to account for the different value of the equilibrium constant for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reaction that was measured subsequent to this study by the same group using the same apparatus. This correction is in accordance with their suggestion [Tuazon et al. (1984)]. The value reported by Cantrell et al., and Hjorth et al. k = 6.3 x 10^{-16} cm^3 $molecule^{-1}$ s^{-1} and (5.4±1.1) x 10^{-16} cm^3 $molecule^{-1}$ s^{-1}, respectively, are in good agreement with the corrected value of Atkinson et al. The recommended value is the average of these three studies. Cantrell et al. have good evidence to suggest that HNO_3 and CHO are the products of this reaction. The temperature dependence of this rate coefficient is unknown.

D45. NO_3 + CH_3CHO. There are four measurements of this rate constant: Morris and Niki (1974), Atkinson et al. (1984a), Cantrell et al. (1986), Dlugokencky and Howard (1989). The value reported by Atkinson et al. (1984a), k = (1.34±0.28) x 10^{-15} cm^3 $molecule^{-1}$ s^{-1}, is corrected to 2.4 x 10^{-15} cm^3 $molecule^{-1}$ s^{-1} as discussed for the NO_3 + H_2CO reaction above and as suggested by Tuazon et al. (1984). The recommended value is the average of the values obtained by Atkinson et al., Cantrell et al., and Dlugokencky and Howard. The results of Morris and Niki agree with the recommended value when their original data is re-analyzed using a more recent value for the equilibrium constant for the reaction $NO_2 + NO_3 \leftrightarrow N_2O_5$ as shown by Dlugokencky and Howard. Dlugokencky and Howard have studied the temperature dependence of this reaction. Their measured value of E/R is recommended. The A-factor has been calculated to yield the k(298 K) recommended here. Morris and Niki, and Cantrell et al. observed the formation of HNO_3 and PAN in their studies, which strongly suggests that HNO_3 and CH_3CO are the products of this reaction.

E1. Cl + O_3. The results reported for k(298 K) by Watson et al. (1976), Zahniser et al. (1976), Kurylo and Braun (1976) and Clyne and Nip (1976a) are in good agreement, and have been used to determine the preferred value at this temperature. The values reported by Leu and DeMore (1976) (due to the wide error limits) and Clyne and Watson (1974a) (the value is inexplicably high) are not considered. The four Arrhenius expressions are in fair agreement within the temperature range 205-300 K. In this temperature range, the rate constants at any particular temperature agree to within 30-40%. Although the values of the activation energy obtained by Watson et al. and Kurylo and Braun are in excellent agreement, the value of k in the study of Kurylo and Braun is consistently (~17%) lower than that of Watson et al. This may suggest a systematic underestimate of the rate constant, as the values from the other three agree so well at 298 K. A more disturbing difference is the scatter in the values reported for the activation energy (338-831 cal/mol). However, there is no reason to prefer any one set of data to any other; therefore, the preferred Arrhenius expression shown above was obtained by computing the mean of the four results between 205 and 298 K. Inclusion of higher temperature (≤466 K) experimental data would yield the following Arrhenius expression: $k = (3.4 \pm 1.0) \times 10^{-11} \exp(-310 \pm 76/T)$. Results of the study by Nicovich et al. (1990b) show non-Arrhenius behavior over the temperature range 189-385 K. These results are in good agreement with the present recommendation above about 250 K, but at lower temperatures they are faster than the recommendation although still within its stated uncertainty down to about 220 K. DeMore (1991) directly determined the ratio k(Cl + O_3)/k(Cl + CH_4) at 197-217 K to be within 15% of that calculated from the absolute rate constant values recommended here.

Vanderzanden and Birks (1982) have interpreted their observation of oxygen atoms in this system as evidence for some production (0.1-0.5%) of O_2 ($^1\Sigma_g^+$) in this reaction. The possible production of singlet molecular oxygen in this reaction has also been discussed by DeMore (1981), in connection with the Cl_2 photosensitized decomposition of ozone. However Choo and Leu (1985a) were unable to detect $O_2(^1\Sigma)$ or $O_2(^1\Delta)$ in the Cl + O_3 system and set upper limits to the branching ratios for their production of 5×10^{-4} and 2.5×10^{-2}, respectively. They suggested two possible mechanisms for the observed production of oxygen atoms, involving reactions of vibrationally excited ClO radicals with O_3 or with Cl atoms, respectively. Burkholder et al. (1989) in a study of infrared line intensities of the ClO radical present evidence in support of the second mechanism. In their experiments with excess Cl atoms, the vibrationally excited ClO radicals produced in the Cl + O_3 reaction can react with Cl atoms to give Cl_2 and oxygen atoms which can. then remove additional ClO radicals. These authors point out the possibility for systematic error from assuming a 1:1 stoichiometry for $[Cl)]:[O_3]_o$ when using the Cl + O_3 reaction as a quantitative source of ClO radicals for kinetic and spectroscopic studies.

E2. Cl + H_2. This Arrhenius expression is based on the data below 300 K reported by Watson et al. (1975), Lee et al. (1977), Miller and Gordon (1981), and Kita and Stedman (1982). The results of these studies are in excellent agreement below 300 K; the data at higher temperatures are in somewhat poorer agreement. The results of Watson et al., Miller and Gordon, and Kita and Stedman agree well (after extrapolation) with the results of Benson et al. (1969) and Steiner and Rideal (1939) at higher temperatures. For a discussion of the large body of rate data at high temperatures, see the review by Baulch et al. (1980). Miller and Gordon and Kita and Stedman also measured the rate of the reverse reaction, and found the ratio to be in good agreement with equilibrium constant data.

E3. Cl + CH_4. The values reported from the thirteen absolute rate coefficient studies for k at 298 K fall in the range (0.99 to 1.48) x 10^{-13}, with a mean value of 1.15 x 10^{-13}. However, based upon the stated confidence limits reported in each study, the range of values far exceeds that to be expected. A preferred average value of 1.0 x 10^{-13} can be determined from the absolute rate coefficient studies for k at 298 K by giving equal weight to the values reported in Lin et al. (1978a), Watson et al. (1976), Manning and Kurylo (1977); Whytock et al. (1977), Zahniser et al. (1978), Michael and Lee (1977), Keyser (1978), and Ravishankara and Wine (1980). The values derived for k at 298 K from the competitive chlorination studies of Pritchard et al. (1954), Knox (1955), Pritchard et al. (1955), Knox and Nelson (1959), and Lin et al. (1978a) range from (0.95-1.13) x 10^{-13}, with an average value of 1.02 x 10^{-13}. The preferred value of 1.0 x 10^{-13} was obtained by taking a mean value from the most reliable absolute and relative rate coefficient studies.

There have been nine absolute studies of the temperature dependence of k. In general the agreement between most of these studies can be considered to be quite good. However, for a meaningful analysis of the reported studies it is best to discuss them in terms of two distinct temperature regions, (a) below 300 K, and (b) above 300 K. Three resonance fluorescence studies have been performed over the temperature range ~200-500 K [Whytock et al. (1977), Zahniser et al. (1978) and Keyser (1978)] and in each case a strong nonlinear Arrhenius behavior was observed. Ravishankara and Wine (1980) also noted nonlinear Arrhenius behavior over a more limited temperature range. This behavior tends to explain partially the large variance in the values of E/R reported between those other investigators who predominantly studied this reaction below 300 K [Watson et al. (1976) and Manning and Kurylo (1977)] and those who only studied it above 300 K [Clyne and Walker (1973), Poulet et al. (1974), and Lin et al. (1978a)]. The agreement between all studies below 300 K is good, with values of (a) E/R ranging from 1229-1320 K, and (b) k(230 K) ranging from (2.64-3.32) x 10^{-14}. The mean of the two discharge flow values [Zahniser et al. (1978) and Keyser (1978)] is 2.67 x 10^{-14}, while the mean of the four flash photolysis values [Watson et al. (1976), Manning and Kurylo (1977), Whytock et al. (1977), and Ravishankara and Wine (1980)] is 3.22 x 10^{-14} at 230 K. There have not been any absolute studies at stratospheric temperatures other than those which utilized the resonance fluorescence technique. Ravishankara and Wine (1980) have suggested that the results obtained using the discharge flow and competitive chlorination techniques may be in error at the lower temperatures (<240 K) due to a non-equilibration of the $^2P_{1/2}$ and $^2P_{3/2}$ states of atomic chlorine. Ravishankara and Wine observed that at temperatures below 240 K the apparent bimolecular rate constant was dependent upon the chemical composition of the reaction mixture; i.e., if the mixture did not contain an efficient spin equilibrator, e.g. Ar or CCl_4, the bimolecular rate constant decreased at high CH_4 concentrations. The chemical composition in each of the flash photolysis studies contained an efficient spin equilibrator, whereas this was not the case in the discharge flow studies. However, the reactor walls in the discharge flow studies could have been expected to have acted as an efficient spin equilibrator. Consequently, until the hypothesis of Ravishankara and Wine is proven it is assumed that the discharge flow and competitive chlorination results are reliable.

Above 300 K the three resonance fluorescence studies reported (a) "averaged" values of E/R ranging from 1530-1623 K, and (b) values for k(500 K) ranging from (7.74-8.76) x 10^{-13}. Three mass spectrometric studies have been performed above 300 K with E/R values ranging from 1409-1790 K. The data of Poulet et al. (1974) are sparse and scattered, that of Clyne and Walker (1973) show too strong a temperature dependence (compared to all other absolute and competitive studies) and k(298 K) is ~20% higher than the preferred value at 298 K, while that of Lin et al. (1978a) is in fair agreement with the resonance fluorescence results.

In conclusion, it should be stated that the best values of k from the absolute studies, both above and below 300 K, are obtained from the resonance fluorescence studies. The competitive chlorination results differ from those obtained from the absolute studies in that linear Arrhenius behavior is observed. This difference is the major discrepancy between the two types of experiments. The values of E/R range from 1503 to 1530 K, and k(230 K) from (2.11-2.54) x 10^{-14} with a mean value of 2.27 x 10^{-14}. It can be seen from the above discussion that the average values at 230 K are: 3.19 x 10^{-14} (flash photolysis), 2.67 x 10^{-14} (discharge flow) and 2.27 x 10^{-14} (competitive chlorination). These differences increase at lower temperatures. Until the hypothesis of Ravishankara and Wine (1980) is re-examined, the preferred Arrhenius expression attempts to best fit the results obtained between 200 and 300 K from all sources. The average value of k at 298 K is 1.04 x 10^{-13}, and at 230 K is 2.71 x 10^{-14} (this is a simple mean of the three average values). The preferred Arrhenius expression yields values similar to those obtained in the discharge flow-resonance fluorescence studies. If only flash photolysis-resonance fluorescence results are used then an alternate expression of 6.4 x 10^{-12} (exp(-1200/T)) can be obtained (k(298 K) = 1.07 x 10^{-13}, and k(230 K) = 3.19 x 10^{-14}).

E4. Cl + C_2H_6. The absolute rate coefficients reported in all four studies [Davis et al. (1970), Manning and Kurylo (1977), Lewis et al. (1980), and Ray et al. (1980)] are in good agreement at 298 K. The value reported by Davis et al. was probably overestimated by ~10% (the authors assumed that I_f was proportional to $[Cl]^{0.9}$, whereas a linear relationship between I_f and [Cl] probably held under their experimental conditions). The preferred value at 298 K was taken to be a simple mean of the four values (the value reported by Davis et al. was reduced by 10%), i.e., 5.7×10^{-11}. The two values reported for E/R are in good agreement; E/R = 61 K (Manning and Kurylo) and E/R = 130 K (Lewis et al.). A simple least squares fit to all the data would unfairly weight the data of Lewis et al. due to the larger temperature range covered. Therefore, the preferred value of $7.7 \times 10^{-11} \exp(-90/T)$ is an expression which best fits the data of Lewis et al. and Manning and Kurylo between 220 and 350 K.

E5. Cl + C_3H_8. This recommendation is based on results over the temperature range 220-607 K reported in the discharge flow-resonance fluorescence study of Lewis et al. (1980). These results are consistent with those obtained in the competitive chlorination studies of Pritchard et al. (1955), Knox and Nelson (1959), Atkinson and Aschmann (1985), and Wallington et al. (1988).

E6. Cl + CH_3OH. This recommendation is based on the 200-500 K results of Michael et al. (1979b) by the flash photolysis-resonance technique and the 298 K results of Payne et al. (1987) by the discharge flow-mass spectrometry technique. Product analysis and isotopic substitution have established that the reaction mechanism consists of abstraction of a hydrogen atom from the methyl group rather than from the hydroxyl group. See Radford (1980), Radford et al. (1981), Meier et al. (1984), and Payne et al. (1987). This reaction has been used as a source of CH_2OH and as a source of HO_2 by the reaction of CH_2OH with O_2. The results obtained in the competitive chlorination studies of Wallington et al. (1988c), Lightfoot et al. (1990b) and Nelson et al. (1990b) are consistent with the recommendation.

E7. Cl + CH_3CN. The recommendation accepts the upper limit at room temperature reported by Kurylo and Knable (1984) using flash photolysis-resonance fluorescence. Poulet et al. (1984a) used discharge flow-mass spectrometry and reported the expression $k = 3.5 \times 10^{-11} \exp(-2785/T)$ over the temperature range 478-723 K. They also reported a room temperature value of 9×10^{-15}, which is a factor of 3 greater than that calculated from their expression. It appears likely that their room temperature observations were strongly influenced by heterogeneous processes. It should be noted that their extrapolated room temperature value is approximately equal to Kurylo and Knable's upper limit. Olbregts et al. (1984) reported values near 400 K that agree with results of Poulet et al.

E8. Cl + CH_3Cl. The results reported by Clyne and Walker (1973) and Manning and Kurylo (1977) are in good agreement at 298 K. However, the value of the activation energy measured by Manning and Kurylo is significantly lower than that measured by Clyne and Walker. Both groups of workers measured the rate constant for the Cl + CH_4 and, similarly, the activation energy measured by Manning and Kurylo was significantly lower than that measured by Clyne and Walker. It is suggested that the discharge flow-mass spectrometric technique was in this case subject to a systematic error, and it is recommended that the flash photolysis results be used for stratospheric calculations in the 200-300 K temperature range (see discussion of the Cl + CH_4 studies). In the discussion of the Cl + CH_4 reaction it was suggested that some of the apparent discrepancy between the results of Clyne and Walker and the flash photolysis studies can be explained by nonlinear Arrhenius behavior. However, it is less likely that this can be invoked for this reaction as the pre-exponential A-factor (as measured in the flash photolysis studies) is already $\sim 3.5 \times 10^{-11}$ and the significant curvature which would be required in the Arrhenius plot to make the data compatible would result in an unreasonably high value for A ($>2 \times 10^{-10}$). Results of the relative rate study of Wallington et al. (1990b) are in good agreement with the recommended value.

E9. Cl + CH_2Cl_2. New Entry. The recommended value is based on results of the relative rate study of Tschuikow-Roux et al. (1988) normalized to the value of the rate constant for the reference reaction (Cl + CH_4) recommended in this evaluation. The room temperature value is in good agreement with results of the relative rate study of Niki et al. (1980b). The higher results of Clyne and Walker (1973) were not used.

E10. Cl + $CHCl_3$. New Entry. The recommended value is based on results of the relative rate study of Knox (1962) normalized to the values of the rate constants for the two reference reactions (Cl + CH_4 and Cl + CH_3Cl) recommended in this evaluation. The higher results of Clyne and Walker (1973) were not used.

E11. Cl + $CHFCl_2$ (HCFC-21). New Entry. The recommended value is based on results of the relative rate study of Glavas and Heicklen (1985) normalized to the value of the rate constant for the reference reaction (Cl + NO + M) recommended in this evaluation.

E12. Cl + CH_2FCl (HCFC-31). New Entry. The recommended value is based on results of the relative rate study of Tschuikow-Roux et al. (1988) normalized to the value of the rate constant for the reference reaction (Cl + CH_4) recommended in this evaluation.

E13. Cl + CH_2F_2 (HFC-32). New Entry. The recommended value is based on results of the relative rate study of Tschuikow-Roux et al. (1985b) normalized to the value of the rate constant for the reference reaction (Cl + CH_4) recommended in this evaluation.

E14. Cl + CH_3F (HFC-41). New Entry. The recommended value is based on results of the direct study of Manning and Kurylo (1977) using the flash photolysis-resonance fluorescence technique. The results of the relative rate study of Tschuikow-Roux et al. (1988) are in good agreement at room temperature but show a stronger temperature dependence, which is encompassed within the error limits.

E15. Cl + CH_3CCl_3. There has been only one study of this rate, that by Wine et al. (1982), using a laser flash photolysis-resonance fluorescence technique. It was concluded that the presence of a reactive impurity accounted for a significant fraction of the Cl removal, and therefore only upper limits to the rate were reported for the temperature range 259-356 K. This reaction is too slow to be of any importance in atmospheric chemistry.

E16. Cl + $CHCl_2CF_3$ (HCFC-123). New Entry. The recommended value is based on results of the direct study of Warren and Ravishankara (private communication) using the pulsed photolysis-resonance fluorescence technique, and the relative rate study of Wallington and Hurley (1992) at room temperature.

E17. Cl + $CHFClCF_3$ (HCFC-124). New Entry. The recommended value is based on results of the direct study of Warren and Ravishankara (private communication) using the pulsed photolysis-resonance fluorescence technique.

E18. Cl + CH_2ClCF_3 (HCFC-133a). New Entry. The recommended value is based on results of the direct study of Jourdain et al. (1978b) using the discharge flow-mass spectrometric technique to monitor the decay of the HCFC in the presence of a large excess of Cl atoms.

E19. Cl + CHF_2CHF_2 (HFC-134). New Entry. The recommended value is based on results of the relative rate study of Yano and Tschuikow-Roux (1986) normalized to the value of the rate constant for the reference reaction (Cl + C_2H_6) recommended in this evaluation.

E20. Cl + CH_2FCF_3 (HFC-134a). New Entry. The recommended value is based on results of the relative rate study of Wallington and Hurley (1992).

E21. Cl + CH_3CFCl_3 (HCFC-141b). New Entry. The recommended value is based on results of the relative rate study of Warren and Ravishankara (private communication) using the pulsed photolysis-resonance fluorescence technique and the relative rate study of Wallington and Hurley (1992) at room temperature.

E22. Cl + CH_3CF_2Cl (HCFC-142b). New Entry. The recommended value is based on results of the relative rate study of Wallington and Hurley (1992).

E23. Cl + CH_2FCHF_2 (HFC-143). New Entry. The recommended values for the two reaction channels are based on results of the relative rate study of Tschuikow-Roux et al. (1985b) normalized to the value of the rate constant for the reference reaction (Cl + CH_4) recommended in this evaluation.

E24. Cl + CH_3CF_3 (HFC-143a). New Entry. The recommended value is based on results of the relative rate study of Tschuikow-Roux et al. (1985b) normalized to the value of the rate constant for the reference reaction (Cl + CH_4) recommended in this evaluation.

E25. Cl + CH_2FCH_2F (HFC-152). New Entry. The recommended value is based on results of the relative rate study of Yano and Tschuikow-Roux (1986) normalized to the value of the rate constant for the reference reaction (Cl + C_2H_6) recommended in this evaluation.

E26. Cl + CH_3CHF_2 (HFC-152a). New Entry. The recommended values for the two reaction channels are based on results of the relative rate study of Yano and Tschuikow-Roux (1986) normalized to the value of the rate constant for the reference reaction (Cl + C_2H_6) recommended in this evaluation. The overall rate constant value is in good agreement with results of the relative rate study of Wallington and Hurley (1992) at room temperature.

E27. Cl + CH_3CH_2F (HFC-161). New Entry. The recommended values for the two reaction channels are based on results of the relative rate study of Tschuikow-Roux et al. (1985b) normalized to the value of the rate constant for the reference reaction (Cl + CH_4) recommended in this evaluation.

E28. Cl + $CH_3CO_3NO_2$ (PAN). New Entry. The recommended value is based on results of the relative rate study of Wallington et al. (1990b). In this study no reaction of PAN was observed in the presence of Cl atoms. These results are preferred over the results of the direct study of Tsalkani et al. (1988) using a discharge flow system with EPR detection of Cl atom decay (in which study the authors reported a rate constant of (3.7±1.7) x 10^{-13} cm^3 $molecule^{-1}$ s^{-1}). In both studies the major impurity in the PAN samples would be the alkane solvent. The presence of 0.1% tridecane in the PAN sample used by Tsalkani et al. could account for the observed Cl atom decay; however, solvent impurities in the PAN sample would be of no consequence in the relative rate study of Wallington et al.

E29. Cl + H_2CO. The results from five of the six published studies [Michael et al. (1979a), Anderson and Kurylo (1979), Niki et al. (1978a), Fasano and Nogar (1981) and Poulet et al. (1981)] are in good agreement at ~298 K, but ~50% greater than the value reported by Foon et al. (1979). The preferred value at 298 K was obtained by combining the absolute values reported by Michael et al., Anderson and Kurylo, and Fasano and Nogar, with the values obtained by combining the ratio of k(Cl + H_2CO)/k(Cl + C_2H_6) reported by Niki et al. (1.3±0.1) and by Poulet et al. (1.16±0.12) with the preferred value of 5.7 x 10^{-11} for k(Cl + C_2H_6) at 298 K. The preferred value of E/R was obtained from a least squares fit to all the data reported in Michael et al. and in Anderson and Kurylo. The A-factor was adjusted to yield the preferred value at 298 K.

E30. Cl + H_2O_2. The absolute rate coefficients determined at ~298 K by Watson et al. (1976), Leu and DeMore (1976), Michael et al. (1977), Poulet et al. (1978a) and Keyser (1980a) range in value from (3.6-6.2) x 10^{-13}. The studies of Michael et al., Keyser, and Poulet et al. are presently considered to be the most reliable. The preferred value for the Arrhenius expression is taken to be that reported by Keyser. The A-factor reported by Michael et al. is considerably lower than that expected from theoretical considerations and may possibly be attributed to decomposition of H_2O_2 at temperatures above 300 K. The data of Michael et al. at and below 300 K are in good agreement with the Arrhenius expression reported by Keyser. More data are required before the Arrhenius parameters can be considered to be well-established. Heneghan and Benson (1983), using mass spectrometry, confirmed that this reaction proceeds only by the abstraction mechanism giving HCl and HO_2 as products.

E31. Cl + HOCl. This recommendation is based on results over the temperature range 243-365 K using the discharge flow-mass spectrometric technique in the only reported study of this rate, Cook et al. (1981a). Ennis and Birks (1985) have measured the product distribution in a discharge flow-mass spectrometric system and found that the major reaction channel is that to give the products Cl_2 + OH with a yield of 91±6%.

E32. Cl + HNO_3. The recommended upper limit at room temperature is that reported in the recent study of Wine et al. (1988), in which long path laser absorption spectroscopy was used to look for the appearance of NO_3 following the pulsed laser photolysis of Cl_2-HNO_3 mixtures and no evidence for NO_3 production was observed. In the same study a less sensitive upper limit was derived from monitoring Cl atom decay by resonance fluorescence. A less sensitive upper limit was also found in the recent discharge flow-EPR study of Zagogianni et al. (1987). Higher values obtained in earlier studies [Leu and DeMore (1976), Kurylo et al. (1983b), and Clark et al. (1982)] as well as the higher temperature results of Poulet et al. (1978a) are not used.

E33. Cl + HO_2. The recommendations for the two reaction channels are based upon the results by Lee and Howard (1982) using a discharge flow system with laser magnetic resonance detection of HO_2, OH and ClO. The total rate constant is temperature independent with a value of $(4.2\pm0.7) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 250-420 K. This value for the total rate constant is in agreement with the results of indirect studies relative to Cl + H_2O_2 [Leu and DeMore (1976), Poulet et al. (1978a), Burrows et al. (1979)] or to Cl + H_2 [Cox (1980)]. The contribution of the reaction channel producing OH + ClO (21% at room temperature) is much higher than the upper limit reported by Burrows et al. (1% of total reaction). Cattell and Cox (1986) using a molecular modulation-UV absorption technique over the pressure range 50-760 torr report results in good agreement with those of Lee and Howard both for the overall rate constant and for the relative contribution of the two reaction channels. The rate constant for the channel producing ClO + OH can be combined with that for the reaction ClO + OH > Cl + HO_2 to give an equilibrium constant from which a value of the heat of formation of HO_2 at 298 K of 3.0 kcal/mol can be derived.

E34. Cl + Cl_2O. The preferred value was determined from two independent absolute rate coefficient studies reported by Ray et al. (1980), using the discharge flow-resonance fluorescence and discharge flow-mass spectrometric techniques. This value has been confirmed by Burrows and Cox (1981) who determined the ratio $k(Cl + Cl_2O)/k(Cl + H_2) = 6900$ in modulated photolysis experiments. The earlier value reported by Basco and Dogra (1971a) has been rejected. The Arrhenius parameters have not been experimentally determined; however, the high value of k at 298 K precludes a substantial positive activation energy.

E35. Cl + OClO. The recent data of Toohey (1988) are in good agreement with the results of Bemand et al. (1973) at room temperature, and the recommended value at room temperature is the mean of the values reported in these two studies. The slight negative temperature dependence reported by Toohey (1988) is accepted but with error limits that encompass the temperature independence reported in the earlier study.

E36. Cl + ClOO. The recommended value is based on the results of recent studies by Mauldin et al. (1992) and Baer et al. (1991), in which studies ClOO was formed by the pulsed photolysis of Cl_2/O_2 mixtures and its overall loss rate was monitored by UV absorption. In both studies k was found to be independent of temperature. These results are preferred over the results of the earlier, indirect studies of Johnston et al. (1969), Cox et al. (1979), and Ashford et al. (1978). The earlier studies did show that the predominant reaction pathway is that yielding Cl_2 + O_2 as products. From the branching ratio data of Cox et al., Ashford et al., and Nicholas and Norrish (1968), it can be estimated that this reaction channel constitutes 95% of the overall reaction with ClO + ClO the products of the minor (5%) reaction channel.

E37. Cl + Cl_2O_2. The recommended value is that determined by Friedl (private communication, 1989) in a study using a DF-MS technique. It is in agreement with the value reported by Cox and Hayman (1988) in a study using a static photolysis technique with photodiode array UV spectroscopy.

E38. Cl + $ClONO_2$. Flash photolysis/resonance fluorescence studies by Margitan (1983a) and by Kurylo et al. (1983a), which are in good agreement, show that the rate constant for this reaction is almost two orders of magnitude faster than that indicated by the previous work of Kurylo and Manning (1977) and Ravishankara et al. (1977b). It is probable that the slower reaction observed by Kurylo and Manning was actually O + $ClNO_3$, not Cl + $ClNO_3$. The preferred value averages the results of the two new studies.

E39. Cl + NO_3. The recommended value at room temperature is based on the recent discharge flow-EPR study of Mellouki et al. (1987). The results of this direct absolute rate study are preferred over results of the earlier relative rate studies of Cox et al. (1984a), Burrows et al. (1985b), and Cox et al. (1987), in all of which NO_3 was monitored in the photolysis of Cl_2-$ClONO_2$-N_2 mixtures. Complications in the chemistry of the earlier systems probably contributed to the spread in reported values. This radical-

radical reaction is expected to have negligible temperature dependence, which is consistent with the results from the study of Cox et al. (1987) in which the complications must have been temperature-independent.

E40. Cl + N_2O. This rate coefficient has been determined in a study of the halogen-catalyzed decomposition of nitrous oxide at about 1000 K by Kaufman et al. (1956). The largest value reported was 10^{-17} cm^3 $molecule^{-1}$ s^{-1}, with an activation energy of 34 kcal/mol. Extrapolation of these results to low temperature shows that this reaction cannot be of any significance in atmospheric chemistry.

E41. Cl + ClNO. Recent studies have significantly improved the database for this rate constant. The discharge flow-resonance fluorescence study of Abbatt et al. (1989) provides the first reliable data on the temperature dependence. The laser photolysis-LMR study of Chasovnikov et al. (1987) provides rate data for each Cl atom spin state, and they attribute the low value reported by Nelson and Johnston (1981) in a laser flash photolysis-resonance fluorescence study to reaction of the Cl $^2P_{1/2}$ state. Adsorption and decomposition of ClNO on the walls of their static system may account for the very low value of Grimely and Houston (1980). The results of Clyne and Cruse (1972) in a discharge flow-resonance fluorescence study are significantly lower than all recent results. The recommended value at room temperature is the mean of the values reported by Abbatt et al. (1989), Chasovnikov et al. (1987), Nesbitt et al. (1987), and Kita and Stedman (1982). The recommended temperature dependence is from the study of Abbatt et al. (1989).

E42. ClO + O. Recently there have been five studies of this rate constant over an extended temperature range using a variety of techniques: Leu (1984b); Margitan (1984b); Schwab et al. (1984); Ongstad and Birks (1986); and Nicovich et al. (1988). The recommended value is based on a least squares fit to the data reported in these studies and in the earlier studies of Zahniser and Kaufman (1977) and Ongstad and Birks (1984). Values reported in the early studies of Bemand et al. (1973) and Clyne and Nip (1976b) are significantly higher and were not used in deriving the recommended value. Leu and Yung (1987) were unable to detect $O_2(^1\Sigma)$ or $O_2(^1\Delta)$ and set upper limits to the branching ratios for their production of 4.4 x 10^{-4} and 2.5 x 10^{-2} respectively.

E43. ClO + NO. The absolute rate coefficients determined in the four discharge flow-mass spectrometric studies [Clyne and Watson (1974a), Leu and DeMore (1978), Ray and Watson (1981a) and Clyne and MacRobert (1980)] and the discharge flow laser magnetic resonance study Lee et al. (1982) are in excellent agreement at 298 K, and are averaged to yield the preferred value. The value reported by Zahniser and Kaufman (1977) from a competitive study is not used in the derivation of the preferred value as it is about 33% higher. The magnitudes of the temperature dependences reported by Leu and DeMore (1978) and Lee et al. are in excellent agreement. Although the E/R value reported by Zahniser and Kaufman (1977) is in fair agreement with the other values, it is not considered as it is dependent upon the E/R value assumed for the Cl + O_3 reaction. The Arrhenius expression was derived from a least squares fit to the data reported by Clyne and Watson, Leu and DeMore, Ray and Watson, Clyne and MacRobert and Lee et al.

E44. ClO + NO_3 The recommended value is based on results reported by Cox et al. (1984a) and by Cox et al. (1987) in the only reported studies of this reaction. Both studies used the modulated photolysis of Cl_2 + $ClONO_2$ mixtures. In the new study a small temperature dependence is reported, but because of uncertainties in the data a temperature-independent value is recommended in this evaluation.

E45. ClO + HO_2 . There have now been five studies of this rate constant. Three were low pressure discharge flow studies, each using a different experimental detection technique (Reimann and Kaufman, 1978; Stimpfle et al., 1979; Leck et al., 1980), and two were molecular modulation studies; at one atmosphere (Burrows and Cox, 1981), and over the pressure range 50-760 torr (Cattell and Cox, 1986). The 298 K values reported, in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, are: 3.8±0.5 (Reimann and Kaufman), 6.3±1.3 (Stimpfle et al.), 4.5±0.9 (Leck et al.), 5.4 (Burrows and Cox), and 6.2±1.5 (Cattell and Cox). The recommended value is the mean of these values. The study of Cattell and Cox over an extended pressure range when combined with results of the low pressure discharge flow studies seems to indicate that this reaction exhibits no pressure dependence at room temperature. The only temperature dependence study (Stimpfle et al.) resulted in a non-linear Arrhenius behavior. The data were best described by a four parameter equation of the form $k = Ae^{-B/T} + CT^n$, possibly suggesting that two different mechanisms may be occurring. The expression forwarded by Stimpfle et al. was $3.3 \times 10^{-11} \exp(-850/T) + 4.5 \times 10^{-12} (T/300)^{-3.7}$. Two possible preferred values can be suggested for the temperature dependence of k; (a) an expression of the form suggested by Stimpfle et al., but where the values of A and C are adjusted to yield a value of 5.0×10^{-12} at 298 K, or (b) a simple Arrhenius expression which fits the data obtained at and below 300 K (normalized to 5.0×10^{-12} at 298 K). The latter form is preferred. The two most probable pairs of reaction products are, (1) $HOCl + O_2$ and (2) $HCl + O_3$. Leu (1980b) and Leck et al. used mass spectrometric detection of ozone to place upper limits of 1.5% (298 K) and 3.0% (248 K); and 2.0% (298 K), respectively, on k_2/k. Burrows and Cox report an upper limit of 0.3% for k_2/k at 300 K.

E46. $ClO + H_2CO$. Poulet et al. (1980) have reported an upper limit of 10^{-15} cm^3 $molecule^{-1}$ s^{-1} for k at 298 K using the discharge flow-EPR technique.

E47. $ClO + OH$. The recommended value is based on a fit to the 219-373 K data of Hills and Howard (1984), the 243-298 K data of Burrows et al. (1984a), and the 298 K data of Poulet et al. (1986a). Data reported in the studies of Ravishankara et al. (1983a), and Leu and Lin (1979) were not used in deriving the recommended value because in these studies the concentration of ClO was not determined directly. The results of Burrows et al. are temperature-independent while those of Hills and Howard show a slight negative temperature dependence. The fraction of total reaction yielding $HO_2 + Cl$ as products has been determined by Leu and Lin (>0.65); Burrows et al. (0.85±0.2); Hills and Howard (0.86±0.14); and Poulet et al. (0.98±0.12). The latest study gives an upper limit of 0.14 for the branching ratio to give $HCl + O_2$ as products. The uncertainties in all studies allow for the possibility that the HCl yield is indeed zero.

E48. ClO Reactions. These upper limits are based on the data of Walker (reported in Clyne and Watson, 1974a). The upper limits shown for k(298) were actually determined from data collected at either 587 or 670 K. The Arrhenius expressions were estimated based on this ~600 K data.

E49. $ClO + ClO$. There are three bimolecular channels for this reaction: $ClO + ClO \rightarrow OClO + Cl$ (k_1); $ClO + ClO \rightarrow Cl + ClOO$ (k_2); and $ClO + ClO \rightarrow Cl_2 + O_2$ (k_3). The recommended values given here are for the total rate coefficient at low pressures. They are based largely on results obtained in the discharge flow studies of Clyne and Coxon (1968), Clyne and White (1971) and Clyne et al. (1975). Note that the rate constant is here defined as $-d(ClO)/dt = 2k(ClO)^2$. Molecular modulation studies of Hayman et al. (1986) and Cox and Derwent (1979) have given a similar temperature dependence but somewhat lower rate constant values. The product branching ratios and their dependence on temperature and pressure are not well established. The low pressure results indicate that k_2 and k_3 are both important, while k_1 represents only about 10 percent of the total reaction. Results of the recent molecular modulation study of Simon et al. (1990a) are significantly different indicating an equal partitioning among the three reaction channels. Moreover, the overall rate constant value is nearly twice as large as that reported by Clyne and co-workers. This new work raises questions. However, we prefer to leave unchanged the present recommendation which is based on the low pressure studies of Clyne and co-workers -- the higher pressure used in the study of Simon et al. (1990a) may result in complications in the chemistry. These new results are encompassed within the stated uncertainty limits. The reaction exhibits both bimolecular and termolecular reaction channels (see entry for this reaction in Table 2). The termolecular reaction, presumably to give the dimer, dominates at pressures higher than about 10 torr; however, the role of the dimer in the overall reaction is unclear - whether it is merely in equilibrium with ClO or decomposes to give the same products given in the bimolecular reaction channels. Some product branching ratio data have been derived from studies of the chlorine photosensitized decomposition of ozone. In these systems there are uncertainties concerning the need for some reaction of the Cl_2O_2 complex in order to account for the strong temperature dependence of the ozone quantum yield and also concerning the possible role of ClO complex formation with O_2 and subsequent reactions of the ClO-O_2 complex. The equilibrium constant for formation of the Cl_2O_2 dimer is given in Table 3.

E50. $ClO + O_3$. There are two possible channels for this reaction: $ClO + O_3 \rightarrow ClOO + O_2$ (k_1); and $ClO + O_3 \rightarrow OClO + O_2$ (k_2). The recommended upper limit for k_1 at 298 K is based on results of the recent study by Stevens and Anderson (1990). These authors also report that $k_1 = (4\pm2) \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} at 413 K. These data can be combined to derive the Arrhenius parameters $A = 2 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}

and E/R > 3600 K. The upper limit for k_2 is based on results reported by DeMore et al. (1976) and Wongdontri-Stuper et al. (1979); the Arrhenius parameters for k_2 were estimated.

E51. $ClO + CH_3O_2$. There are two possible channels for this reaction: $ClO + CH_3O_2 \rightarrow ClOO + CH_3O$ (k_1); and $ClO + CH_3O_2 \rightarrow OClO + CH_3O$ (k_2). DeMore (1991) reported the results of a study of the photolysis of $Cl_2/CH_4/O_3/O_2/N_2$ mixtures at $\lambda > 320$ nm, with products monitored by UV-VIS and FTIR absorption spectroscopy. The following upper limits at 200 K were derived: $k_1 < 4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $k_2 < 1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}. These results are preferred over the low temperature value suggested by Simon et al. (1989) (which was based on results of their room temperature study) because the newer results provide more direct information on the rate of this reaction at low temperatures.

E52. $OH + Cl_2$. The recommended room temperature value is the average of the results reported by Boodaghians et al. (1987), Loewenstein and Anderson (1984), Ravishankara et al. (1983a), and Leu and Lin (1979). The temperature dependence is from Boodaghians et al. Loewenstein and Anderson determined that the exclusive products are Cl + HOCl.

E53. OH + HCl. The recommended value is based on a least squares fit to the data reported in the recent studies by Molina et al. (1984), Keyser (1984), and Ravishankara et al. (1985b). In these studies particular attention was paid to the determination of the absolute concentration of HCl by UV and IR spectrophotometry. Earlier studies by Takacs and Glass (1973c), Zahniser et al. (1974), Smith and Zellner (1974), Ravishankara et al. (1977a), Hack et al. (1977), Husain et al. (1981), Cannon et al. (1984), Husain et al. (1984), and Smith and Williams (1986) had reported somewhat lower room temperature values.

E54. OH + HOCl. In the only reported study of this system Ennis and Birks (1988) reported the value of this rate constant at room temperature to lie in the range (1.7 - 9.5) x 10^{-13} cm^3 molecule^{-1} s^{-1}. A temperature dependent expression has been estimated by choosing a pre-exponential factor by analogy with the $OH + H_2O_2$ reaction and selecting the midpoint of the experimental range for the room temperature rate constant. The large uncertainty factor is needed to encompass the entire range.

E55. $OH + CH_3Cl$. The preferred values were obtained using only absolute rate coefficient data. The data of Howard and Evenson (1976a), Davis et al. (1976), Perry et al. (1976a), Paraskevopoulos et al. (1981) and Jeong and Kaufman (1982) are in good agreement and were used to determine the preferred values. The preferred Arrhenius expression was derived from a least squares fit to the data below 400 K. Results of a new study by Taylor et al. (1989) over the temperature range 295-800 K are in good agreement with the recommendation at room temperature, but values extrapolated to stratospheric temperatures are substantially lower than the recommendation.

E56. $OH + CH_2Cl_2$. The data of Howard and Evenson (1976a), Perry et al. (1976), Davis et al. (1976) and Jeong and Kaufman (1982) are in reasonable agreement. The temperature dependence data of Davis et al. tend to somewhat smaller values than those of Jeong and Kaufman but the resulting activation energies are in good agreement. The preferred Arrhenius expression was derived from a least squares fit to the data below 400 K. The recommended room temperature value was derived from the Arrhenius expression at 298 K. Results of a new study by Taylor et al. (1989) over the temperature range 298-775 K are in reasonable agreement with the recommendation at room temperature and when extrapolated to stratospheric temperatures.

E57. $OH + CHCl_3$. The preferred values were obtained using only absolute rate coefficient data. The accuracy of the $OH + CH_4/OH + CHCl_3$ study (Cox et al., 1976a) was probably no better than a factor of 2. The data of Howard and Evenson (1976a), Davis et al. (1976) and Jeong and Kaufman (1982) are in good agreement and were used to determine the preferred values. The preferred Arrhenius expression was derived from a least squares fit to the data below 400 K. Results of a new study by Taylor et al. (1989) over the temperature range 295-775 K are in good agreement with the recommendation at room temperature, but values extrapolated to stratospheric temperatures are higher than the recommendation.

E58. $OH + CCl_4$. The recommended upper limit at room temperature is based on the upper limit reported in the competitive study by Cox et al. (1976a). The value given there has been increased by a factor of four to allow for uncertainties in the number of NO molecules oxidized. The recommendation is compatible with the less sensitive upper limits reported by Howard and Evenson (1976a) and Clyne and Holt (1979a). None of these investigators reported any evidence for reaction between these species. The A-factor was estimated and a lower limit for E/R was derived.

E59. OH + $CFCl_3$. The A-factor was estimated, and a lower limit was derived for E/R by using the upper limit reported for the rate constant by Chang and Kaufman (1977b) at about ~480 K. This expression is quite compatible with the upper limits reported by Atkinson et al. (1975), Howard and Evenson (1976a), Cox et al. (1976a) and Clyne and Holt (1979b). None of the investigators reported any evidence for reaction.

E60. OH + CF_2Cl_2. The A-factor was estimated, and a lower limit was derived for E/R by using the upper limit reported for the rate constant by Chang and Kaufman (1977b) at about ~480 K. This expression is quite compatible with the upper limits reported by Atkinson et al. (1975), Howard and Evenson (1976a), Cox et al. (1976a) and Clyne and Holt (1979b). None of the investigators reported any evidence for reaction.

E61. OH + $CHFCl_2$ (HCFC-21). Absolute rate coefficient data for this reaction have been reported by Howard and Evenson (1976a), Perry et al. (1976a), Watson et al. (1977), Chang and Kaufman (1977a), Clyne and Holt (1979b), Paraskevopoulos et al. (1981) and Jeong and Kaufman (1982). The database is well established and there have been no new data recently. The preferred values are derived from a fit to all data below 400 K except the rate constants of Clyne and Holt (1979b) which have a significantly larger temperature dependence than all the other studies. The rate constants from the latter study are consistently larger than those obtained in all other studies.

E62. OH + CHF_2Cl (HCFC-22). Absolute rate coefficient data for this reaction have been reported by Howard and Evenson (1976a), Atkinson et al. (1975), Watson et al. (1977), Chang and Kaufman (1977a), Handwerk and Zellner (1978), Clyne and Holt (1979b), Paraskevopoulos et al. (1981) and Jeong and Kaufman (1982). The database is well established and there have been no new data recently. The preferred values are derived from a fit to all data below 400 K except the rate constants of Clyne and Holt (1979b), which have a significantly larger temperature dependence than all the other studies.

E63. OH + CH_2FCl (HCFC-31). The data for this reaction are in excellent agreement. The recommended Arrhenius expression was derived from the room temperature data of Howard and Evenson (1976a) and Paraskevopoulos et al. (1981), and the temperature dependence data of Watson et al. (1977), Handwerk and Zellner (1978) and Jeong and Kaufman (1982) below 400 K.

E64. OH + CH_3CCl_3. The k(298K) recommendation is based on absolute rate studies of Talukdar et al. (1992) and Finlayson-Pitts et al. (1992), and a relative rate study (CH_4 as reference) of DeMore (1992). The temperature dependence is that of Talukdar et al. (1992). These recent studies indicate both a lower k(298K) and E/R than was reported in earlier studies: Nelson et al. (1990a), Jeong and Kaufman (1979), and Kurylo et al. (1979).

E65. OH + $CHCl_2CF_3$ (HCFC-123). The preferred rate expression is derived from the temperature dependence data below 400 K of Nielsen (1991), Gierczak et al. (1991), Liu et al. (1990), Watson et al. (1979), and the room temperature data of Howard and Evenson (1976b). The data of Brown et al. (1990a) and Clyne and Holt (1979b) were not considered. The recommended value of k_{298} is derived from the temperature dependence expression.

E66. OH + $CHFClCF_3$ (HCFC-124). The preferred rate expression is derived from the temperature dependence data of Gierczak et al. (1991), Watson et al. (1979), and the room temperature data of Howard and Evenson (1976b). The recommended value of k_{298} is derived from the temperature dependence expression.

E67. OH + CH_2ClCF_2Cl (HCFC-132b). The recommended temperature dependence was derived from the data of Watson et al. (1979b) which were corrected by these authors for the presence of alkene impurities. The data of Jeong et al. (1984), indicating substantially faster rate constants may have been affected by such impurities and hence were not included in deriving the recommendation. The preferred value of k_{298} was derived from the recommended Arrhenius expression.

E68. OH + CH_2ClCF_3 (HCFC-133a). The temperature dependence of the preferred rate expression was derived from the data of Handwerk and Zellner (1978). The recommended value of k_{298} is the average of the values of Howard and Evenson (1976b) and Handwerk and Zellner (1978) adjusted to 298 K. The data of Clyne and Holt (1979b) were not used in deriving this recommendation.

E69. OH + CH_3CFCl_2 (HCFC-141b). The preferred rate expression is significantly different from that in NASA (1990) due to the recent data of Talukdar et al. (1991a) and Zhang et al. (1992a). The above review was based on the results of Liu et al. (1990) and the preliminary data of Talukdar et al. which showed noticeable curvature in the Arrhenius plots. The reaction rate at the lowest temperature, being so slow, is most likely to be affected by impurities. The use of higher-purity samples and improved OH detection sensitivity in the studies of Talukdar et al. and Zhang et al. resolved the problem of Arrhenius curvature. The new results imply an A-factor which is more consistent with similar H-abstractions by OH. The temperature dependence expression is derived from the data of Zhang et al. (1992a), Liu et al. (1990) at 330 K and above, and the data of Talukdar et al. above 253 K. The temperature dependence data of Brown et al. (1990a) were not considered because the relatively large rate constants and Arrhenius curvature are suggestive of sample impurities. The recommended value of k_{298} is obtained from the temperature dependence expression.

E70. OH + CH_3CF_2Cl (HCFC-142b). The recommended rate expression is derived from a fit to the temperature dependence data of Geirczak et al. (1991), Liu et al. (1990), Watson et al. (1977), Handwerk and Zellner (1978), the 270 K data of Zhang et al. (1992a) and the room temperature data of Howard and Evenson (1976b), and Paraskevopoulos et al. (1981). The data from Brown et al. (1990a) and Clyne and Holt (1979b) were not considered. The value of k_{298} was derived from the rate expression.

E71. OH + $CF_3CF_2CHCl_2$ (HCFC-225ca). The preferred rate expression is derived from the temperature dependence data of Nelson et al. (1992) and Zhang et al. (1991). The data of Brown et al. (1990b) were ignored. The recommended value of k_{298} is obtained from the temperature dependence expression.

E72. OH + CF_2ClCF_2CHFCl (HCFC-225cb). The preferred rate expression is derived from the temperature dependence data of Nelson et al. (1992) and Zhang et al. (1991). The recommended value of k_{298} is obtained from the temperature dependence expression.

E73. OH + $CH_3CF_2CFCl_2$ (HCFC-243cc). The preferred rate expression is derived from the temperature dependence data of Nelson et al. (1992). The recommended value of k_{298} is obtained from the temperature dependence expression.

E74. OH + C_2Cl_4. The preferred value at 298 K is a mean of the value reported by Howard (1976) and Chang and Kaufman (1977a). The value reported by Winer et al. (1976), which is more than a factor of 10 greater, is rejected. The preferred Arrhenius parameters are those of Chang and Kaufman. Kirchner et al. (1990) report a room temperature rate constant in good agreement with the recommended value and Arrhenius parameters in reasonable agreement with the recommended values.

E75. OH + C_2HCl_3. The preferred value at 298 K is a mean of the values reported by Howard (1976) and Chang and Kaufman (1977a). The value derived from a relative rate coefficient study by Winer et al. (1976) is a factor of ~2 greater than the other values and is not considered in deriving the preferred value at 298 K. The Arrhenius parameters are based on those reported by Chang and Kaufman (the A-factor is reduced to yield the preferred value at 298 K). Kirchner et al. (1990) report a room temperature rate constant and Arrhenius parameters in reasonable agreement with the recommended values.

E76. OH + $ClNO_2$. The recommended value is based on results of the direct study of Ganske et al. (1991) using the discharge flow-resonance fluorescence technique. Mass spectrometric studies showed HOCl to be the major product with no evidence for production of $HONO_2$ or Cl_2.

E77. OH + $ClONO_2$. The results reported by Zahniser et al. (1977) and Ravishankara et al. (1977b) are in good agreement at ~245 K (within 25%), considering the difficulties associated with handling $ClONO_2$. The preferred value is that of Zahniser et al. Neither study reported any data on the reaction products.

E78. O + HCl. Fair agreement exists between the results of Brown and Smith (1975), Wong and Belles (1971), Ravishankara et al. (1977a), Hack et al. (1977) and Singleton and Cvetanovic (1981) at 300 K (some of the values for k(300 K) were obtained by extrapolation of the experimentally determined Arrhenius expressions), but these are a factor of ~7 lower than that of Balakhnin et al. (1971). Unfortunately, the values reported for E/R are in complete disagreement, ranging from 2260-3755 K. The preferred value was based on the results reported by Brown and Smith, Wong and Belles, Ravishankara et al., Hack et al. and Singleton and Cvetanovic but not those reported by Balakhnin et al.

E79. O + HOCl. There are no experimental data; this is an estimated value based on rates of O-atom reactions with similar compounds.

E80. O + $ClONO_2$. The results reported by Molina et al. (1977b) and Kurylo (1977) are in good agreement, and this data has been used to derive the preferred Arrhenius expression. The value reported by Ravishankara et al. (1977b) at 245 K is a factor of 2 greater than those from the other studies, and this may possibly be attributed to (a) secondary kinetic complications, (b) presence of NO_2 as a reactive impurity in the $ClONO_2$, or (c) formation of reactive photolytic products. None of the studies reported identification of the reaction products. The room temperature result of Adler-Golden and Wiesenfeld (1981) is in good agreement with the recommended value.

E81. O + Cl_2O. The recommendation averages the results of Miziolek and Molina (1978) for 236-295 K with the approximately 30 percent lower values of Wecker et al. (1982) over the same temperature range. Earlier results by Basco and Dogra (1971c) and Freeman and Phillips (1968) have not been included in the derivation of the preferred value due to data analysis difficulties in both studies.

E82. OClO + O. The recommended value is based on results of the DF-RF study of Gleason et al. (1991). Over the temperature range from 400 K down to 240 K their data are well fitted by this Arrhenius expression, but at lower temperatures down to 200 K their data show an abrupt change to a negative temperature dependence. At 200 K the value measured is a factor of 3 higher than that calculated from the Arrhenius expression. Similar results were obtained in a recent study (Toohey, Avallone, and Anderson, private communication). Over the temperature range 413 - 273 K their data showed a temperature dependence very similar to that reported by Gleason et al. over the same temperature range. Moreover as the temperature was lowered further their rate constant values also levelled off and then increased at the lowest temperature. Their rate constant values were nearly 50% lower than the values of Gleason et al. from 400 K down to 273 K and 30% lower at 253 K. Colussi (1990), using a laser flash photolysis - resonance fluorescence technique over an extended pressure range, reported a value of the bimolecular rate coefficient at room temperature 50% higher than the recommended value. Colussi et al. (1992) extended these measurements down to 248 K; in contrast to the positive temperature dependence over this temperature range reported by Gleason et al. (1991), these authors report a negative temperature dependence. The bimolecular rate constants reported by Colussi et al. (1992) are not directly measured but are derived quantities which are consistent with fall off curves fitted to the experimental data over the pressure range 20 - 600 torr. It appears that the experiments of Bemand et al. (1973), which provided the basis for the previously recommended value (a factor of 5 higher than the present recommendation), were complicated by secondary chemistry. The results of Colussi (1990) and Colussi et al. (1992) over an extended pressure range demonstrate the importance of the termolecular reaction $O + OClO + M \rightarrow ClO_3 + M$ (see entry for this reaction in Table 2). It should be noted that the termolecular rate constants derived by Gleason et al. (1991) on the basis of their low temperature data are not consistent with the termolecular rate constant expression recommended in this evaluation (factor of 3 difference), which expression is based on the results of Colussi (1990) and Colussi et al. (1992).

E83. OClO + O_3. The recommended value is based on results over the temperature range 262-296 K reported by Wongdontri-Stuper et al. (1979). Within the indicated uncertainty limits it also encompasses the somewhat lower room temperature result of Birks et al. (1977).

E84. OClO + OH. The recommended value is that reported by Poulet et al. (1986b), the only reported study of this rate constant, using a discharge flow system in which OH decay was measured by LIF or EPR over the temperature range 293-473 K. Product HOCl was detected by modulated molecular beam mass spectrometry. The branching ratio for the channel to produce HOCl + O_2 was determined to be close to unity, but experimental uncertainty would allow it to be as low as 0.80.

E85. OClO + NO. The Arrhenius expression was estimated based on 298 K data reported by Bemand, Clyne and Watson (1973).

E86. $Cl_2O_2 + O_3$. The recommended upper limit is that determined by DeMore and Tschuikow-Roux (1990). It refers to a temperature of 195 K and while the reaction possibly could be faster at higher temperatures, the value of the rate at the higher temperatures would be of no significance because of the thermal decomposition of the dimer.

E87. Cl_2O_2 + NO. The recommended upper limit is that determined by Friedl (private communication, 1989) in a study using a DF-MS technique.

E88. HCl + NO_3. The recommended upper limit is that reported by Mellouki et al. (1989) in a study using DF-EPR techniques. This upper limit shows that this reaction is of negligible importance in stratospheric chemistry. Somewhat lower upper limits have been reported by Cantrell et al. (1987b) and Canosa-Mas et al. (1989); the latter study also reports Arrhenius parameters at higher temperatures (333-473 K).

E89. HCl + $ClONO_2$. Recently, results of four studies of the kinetics of this system have been published, in which the following upper limits to the homogeneous bimolecular rate constant were reported: 1×10^{-19} cm^3 $molecule^{-1}$ s^{-1} by a static wall-less long-path UV absorption technique and a steady-state flow FTIR technique (Molina et al., 1985); 5×10^{-18} using a flow reactor with FTIR analysis (Friedl et al., 1986); and 8.4×10^{-21} using a static photolysis system with FTIR analysis (Hatakeyama and Leu, 1986 and Leu et al., 1989), and 1.5×10^{-19} by FTIR analysis of the decay of $ClONO_2$ in the presence of HCl in large-volume (2500 and 5800 liters) Teflon or Teflon-coated chambers (Atkinson et al., 1987). Earlier, Birks et al. (1977) had reported a higher upper limit. All studies found this reaction to be catalyzed by surfaces. The differences in the reported upper limits can be accounted for in terms of the very different reactor characteristics and detection sensitivities of the various studies. The homogeneous reaction is too slow to have any significant effect on atmospheric chemistry.

E90. HCl + HO_2NO_2. This upper limit is based on results of static photolysis-FTIR experiments reported by Leu et al. (1989).

E91. H_2O + $ClONO_2$. This recommendation is based on the upper limits to the homogeneous bimolecular rate constant reported by Atkinson et al. (1986), and by Hatakeyama and Leu (1986, 1989). Atkinson et al. observed by FTIR analysis the decay of $ClONO_2$ in the presence of H_2O in large-volume (2500 and 5800 liters) Teflon or Teflon-coated chambers. Their observed decay rate gives an upper limit to the homogeneous gas phase rate constant, and they conclude that the decay observed is due to heterogeneous processes. Hatakeyama and Leu, using a static photolysis system with FTIR analysis, derive a similar upper limit. Rowland et al. (1986) concluded that the decay they observed resulted from rapid heterogeneous processes. The homogeneous reaction is too slow to have any significant effect on atmospheric chemistry.

E92. CF_2ClO_2 + NO. The recommended value is based on results reported by Dognon et al. (1985) for the temperature range 230-430 K, using a pulsed laser photolysis - time resolved mass spectrometry technique. Measurement of NO_2 yields showed that CF_2ClO and NO_2 are the major products. The alkoxy radical produced (CF_2ClO) decomposes spontaneously to yield a carbonyl (CF_2O) plus a Cl atom.

E93. $CFCl_2O_2$ + NO. The recommended value is based on results reported by Dognon et al. (1985) for the temperature range 230-430 K, using a pulsed laser photolysis - time resolved mass spectrometry technique. It is in good agreement with the room temperature value reported by Lesclaux and Caralp (1984). Measurement of NO_2 yields by Dognon et al. showed that $CFCl_2O$ and NO_2 are the major products. The alkoxy radical produced ($CFCl_2O$) decomposes spontaneously to yield a carbonyl (CFClO) plus a Cl atom.

E94. CCl_3O_2 + NO. The recommended value is based on results reported by Dognon et al. (1985) for the temperature range 230-430 K, using a pulsed laser photolysis - time resolved mass spectrometry technique. It is in good agreement with the room temperature value reported by Ryan and Plumb (1984). Measurement of NO_2 yields by Dognon et al. showed that CCl_3O and NO_2 are the major products. The alkoxy radical produced (CCl_3O) decomposes spontaneously to yield a carbonyl (CCl_2O) plus a Cl atom.

F1. Br + O_3. The results reported for k(298 K) by Clyne and Watson (1975), Leu and DeMore (1977), Michael et al. (1978), Michael and Payne (1979), and Toohey et al. (1987b) are in excellent agreement. The preferred value at 298 K is derived by taking a simple mean of these five values. The temperature dependences reported for k by Leu and DeMore and by Toohey et al. are in good agreement, but they can only be considered to be in fair agreement with those reported by Michael et al. and Michael and Payne. The preferred value was synthesized to best fit all the data reported from these five studies. The new results of Nicovich et al. (1990b) are in excellent agreement with this recommendation.

F2. Br + H_2O_2. The recommended upper limit to the value of the rate constant at room temperature is based on results reported in the study by Toohey et al. (1987) using a discharge flow-laser magnetic resonance technique. Their upper limit determined over the temperature range 298-378 K is consistent with less sensitive upper limits determined by Leu (1980a) and Posey et al. (1981) using the discharge flow-mass spectrometric technique. The much higher value reported by Heneghan and Benson (1983) may result from the presence of excited Br atoms in the very low pressure reactor. The pre-exponential factor was chosen to be consistent with that for the Cl + H_2O_2 rate constant, and the E/R value was fitted to the upper limit at 298 K.

F3. Br + H_2CO. There have been two studies of this rate constant as a function of temperature; Nava et al. (1981), using the flash photolysis-resonance fluorescence technique, and Poulet et al. (1981), using the discharge flow-mass spectrometric technique. These results are in reasonably good agreement. The Arrhenius expression was derived from a least squares fit to the data reported in these two studies. The higher room temperature value of Le Bras et al. (1980) using the discharge flow-EPR technique has been shown to be in error due to secondary chemistry (Poulet et al.).

F4. Br + HO_2. This recommendation is based on results obtained over the 260-390 K temperature range in the recent study by Toohey et al. (1987), using a discharge flow system with LMR detection of HO_2 decay in excess Br. The room temperature value reported in this study is a factor of three higher than that reported by Poulet et al. (1984b) using LIF and MS techniques and is an order of magnitude larger than the value of Posey et al. (1981). The uncertainty in E/R is set to encompass the value E/R = 0, as for other radical-radical reactions. A new value determined by Laverdet et al. (1990) using DF-EPR techniques is in good agreement with this recommendation. The reactions of Br atoms with H_2O_2, HCHO, and HO_2 are all slower than the corresponding reactions of Cl atoms by one to two orders of magnitude.

F5. Br + Cl_2O. The recommended value is that reported by Sander and Friedl (1989). It was derived by observing the formation of ClO using long path UV absorption following the flash photolysis of a Br_2 - Cl_2O mixture.

F6. Br + OClO. The recommended value at room temperature is the mean of the values reported by Clyne and Watson (1977) and Toohey (1988). In the earlier study correction for the effect of the rapid reverse reaction was required. The temperature dependence reported by Toohey (1988) is accepted but with increased error limits.

F7. Br + Cl_2O_2. The recommended value is that determined by Friedl (private communication, 1989) in a study using a DF-MS technique.

F8. BrO + O. The preferred value is based on the value reported by Clyne et al. (1976). This value appears to be quite reasonable in light of the known reactivity of ClO radicals with atomic oxygen. The temperature dependence of k is expected to be small for an atom-radical process, e.g., O + ClO.

F9. BrO + ClO. There has recently been a substantial improvement in the database for this rate coefficient. Friedl and Sander (1989) using DF/MS techniques measured the overall rate constant over the temperature range 220-400 K and also over this temperature range determined directly branching ratios for the reaction channels producing BrCl and OClO. The same authors in a separate study using flash photolysis-ultraviolet absorption techniques (Sander and Friedl, 1989) determined the overall rate constant over the temperature range 220-400 K and pressure range 50-750 torr and also determined at 220 K and 298 K the branching ratio for OClO production. The results by these two independent techniques are in excellent agreement, with the overall rate constant showing a negative temperature dependence. Toohey and Anderson (1988) using DF/RF/LMR techniques reported room temperature values of the overall rate constant and the branching ratio for OClO production. They also found evidence for the direct production of BrCl in a vibrationally excited π state. Poulet et al. (1990) using DF/MS techniques reported room temperature values of the overall rate constant and branching ratios for OClO and BrCl production. Overall room temperature rate constant values reported also include those from the DF/MS study of Clyne and Watson (1977) and the very low value derived in the flash photolysis study of Basco and Dogra (1971b) using a different interpretation of the reaction mechanism. The recommended Arrhenius expressions for the individual reaction channels are taken from the study of Friedl and Sander (1989). This study and the very recent study of Turnipseed et al. (1991a) contain the most comprehensive sets of rate constant and branching ratio data. The overall rate constants reported in these two studies are in good agreement (20%) at room temperature and in excellent agreement at stratospheric temperatures. Both studies report that OClO production by channel (1) accounts for 60% of the overall reaction at 200 K. Both studies report a BrCl yield by channel (3) of about 8%, relatively independent of temperature. The recommended expressions are consistent with the body of data from all studies except those of Hills et al. (1988) and Basco and Dogra (1971b).

F10. BrO + NO. The results of the three low pressure mass spectrometric studies (Clyne and Watson, 1975; Ray and Watson, 1981a; Leu, 1979a) and the high pressure UV absorption study (Watson et al. 1979a), which all used pseudo first-order conditions, are in excellent agreement at 298 K, and are thought to be much more reliable than the earlier low pressure UV absorption study (Clyne and Cruse, 1970b). The results of the two temperature dependence studies are in good agreement and both show a small negative temperature dependence. The preferred Arrhenius expression was derived from a least squares fit to all the data reported in the four recent studies. By combining the data reported by Watson et al. with those from the three mass spectrometric studies, it can be shown that this reaction does not exhibit any observable pressure dependence between 1 and 700 torr total pressure. The temperature dependences of k for the analogous ClO and HO_2 reactions are also negative, and are similar in magnitude.

F11. BrO + BrO. There are two possible bimolecular channels for this reaction: $BrO + BrO \rightarrow 2Br + O_2$ (k_1) and $BrO + BrO \rightarrow Br_2 + O_2$ (k_2). The total rate constant for disappearance of BrO ($k = k_1 + k_2$) has been studied by a variety of techniques, including discharge flow-ultraviolet absorption (Clyne and Cruse, 1970a), discharge flow-mass spectrometry (Clyne and Watson, 1975; Turnipseed et al. 1990; and Lancar et al. 1991) and flash photolysis-ultraviolet absorption (Basco and Dogra, 1971b; Sander and Watson, 1981b). Since this reaction is second order in [BrO], those studies monitoring [BrO] by ultraviolet absorption required the value of the cross section σ to determine k. There is substantial disagreement in the reported values of σ. Although the magnitude of σ is dependent upon the particular spectral transition selected and instrumental parameters such as spectral bandwidth, the most likely explanation for the large differences in the reported values of σ is that the techniques (based on reaction stoichiometries) used to determine σ in the early studies were used incorrectly (see discussion by Clyne and Watson). The study of Sander and Watson used totally independent methods to determine the values of σ and (σ/k). The recommendations for k_1 and k_2 are consistent with a recommendation of $k = 1.14 \times 10^{-12} \exp(+255/T)$ cm^3 $molecule^{-1}$ s^{-1}. This temperature dependence is the average of the corrected value from Sander and Watson and from Turnipseed et al., and the pre-exponential factor has been chosen to fit the value of $k(298\ K) = 2.7 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, which is the average of the values reported by Clyne and Watson (the mass spectrometric study where knowledge of σ is not required), by Sander and Watson (the latest absorption study) by Turnipseed et al. and by Lancar et al. There was no observable pressure dependence from 50 to 475 torr in the study by Sander and Watson. Cox et al. (1982) used the molecular modulation technique with ultraviolet absorption to derive a temperature independent value of k_2 which is 50 percent greater than the 298 K value recommended here.

The partitioning of the total rate constant into its two components, k_1 and k_2, has been measured at room temperature by Sander and Watson (1981b), Turnipseed et al. (1990) and Lancar et al. (1991), by Jaffe and Mainquist (1980) from 258 to 333 K, and by Cox et al. (1982) from 278 to 348 K. All are in agreement that $k_1/k = 0.84 \pm 0.03$ at 298 K. In the temperature dependent studies the quantum yield for the bromine photosensitized decomposition of ozone was measured. Jaffe and Mainquist observed a strong, unexplained dependence of the quantum yield at 298 K on [Br_2], and their results were obtained at much higher [Br_2] values than were those of Cox et al. This make a comparison of results difficult. From an analysis of both sets of temperature dependent data, the following expressions for k_1/k were derived: 0.98 exp(-44/T) (Jaffe and Mainquist); 1.42 exp(-163/T) (Cox et al.); and 1.18 exp(-104/T) (mean value). This mean value has been combined with the expression for k_1 shown in the table. The expression for k_2 results from the numerical values of k_2 at 200 K and 300 K derived from the evaluation of these expressions for k_1 and for $k = (k_1 + k_2)$. In a very recent study (Mauldin, Wahner, and Ravishankara, private communication) the overall rate constant was observed to be pressure dependent at 220 K, at which temperature an additional, short-lived, absorption feature was observed and was tentatively attributed to the dimer Br_2O_2.

F12. BrO + O_3. Based on a study reported by Sander and Watson (1981b). Clyne and Cruse (1970a) reported an upper limit of 8×10^{-14} cm^3 $molecule^{-1}$ s^{-1} for this reaction. Both studies reported that there is no evidence for this reaction. The analogous ClO reaction has a rate constant of $<10^{-18}$ cm^3 $molecule^{-1}$ s^{-1}.

F13. BrO + HO_2. The preferred value is based on the study of Poulet et al (1992) in which BrO decay in excess HO_2 was monitored by DF/MS. The only product observed was HOBr; however, the possible production of HBr requires further study. These new results are preferred over the previous study of Cox and Sheppard (1982) by molecular modulation-UV absorption in which a much lower value (factor of 6) was reported. The temperature dependence is our estimate, based on analogy with the ClO + HO_2 reaction.

F14. BrO + OH. Value chosen to be consistent with k(ClO + OH), due to the absence of any experimental data.

F15. OH + Br_2. The recommended room temperature value is the average of the values reported by Boodaghians et al. (1987), Loewenstein and Anderson (1984), and Poulet et al. (1983). The temperature independence is from Boodaghians et al. Loewenstein and Anderson determined that the exclusive products are Br + HOBr.

F16. OH + HBr. The preferred value at room temperature is the average of the values reported by Ravishankara et al. (1979a) using FP-RF, by Jourdain et al. (1981) using DF-DPR, by Cannon et al. (1984) using FP-LIF, and by Ravishankara et al. (1985a) using LFP-RF and LFP-LIF techniques. In this latest study the HBr concentration was directly measured in-situ in the slow flow system by UV absorption. The rate constant determined in this re-investigation is identical to the value recommended here. The data of Ravishankara et al. (1979a) show no dependence on temperature over the range 249-416 K. Values reported by Takacs and Glass (1973a) and by Husain et al. (1981) are a factor of two lower and were not included in the derivation of the preferred value.

F17. OH + CH_3Br. The recommended value is derived from an analysis of results of the studies of Mellouki et al. (1992) and Zhang et al (1992b). The results of these extensive studies are in excellent agreement and are preferred over the higher values reported in the earlier studies of Davis et al. (1976) and Howard and Evensen (1976a).

F18. OH + CHF_2Br. New Entry. The recommended value is based on results of the direct study of Talukdar et al. (1991b) using two techniques: pulsed laser photolysis with LIF detection of OH and discharge flow-LMR detection of OH. These results are preferred over the consistently higher results by Brown et al. (1990b).

F19. OH + CF_2Br_2. The recommended upper limit at room temperature is the upper limit reported by Burkholder et al. (1991) in a study using pulsed photolysis-LIF and DF-LMR techniques.

F20. OH + CF_2ClBr. The recommended upper limit at room temperature is the upper limit reported by Burkholder et al. (1991) in a study using pulsed photolysis-LIF and DF-LMR techniques. A less sensitive upper limit was reported by Clyne and Holt (1979a).

F21. $OH + CF_3Br$. The recommended upper limit at room temperature is the upper limit reported by Burkholder et al. (1991) in a study using pulsed photolysis-LIF and DF-LMR techniques. A less sensitive upper limit was reported by LeBras and Combourieu (1978).

F22. $OH + CF_2BrCF_2Br$. The recommended upper limit at room temperature is the upper limit reported by Burkholder et al. (1991) in a study using pulsed photolysis-LIF and DF-LMR techniques.

F23. $O + HBr$. Results of the flash photolysis-resonance fluorescence study of Nava et al. (1983) for 221-455 K and the laser flash photolysis-resonance fluorescence study of Nicovich and Wine (1989) for 250-402 K provide the only data at stratospheric temperatures. Results have also been reported by Singleton and Cvetanovic (1978) for 298-554 K by a phase-shift technique, and discharge flow results of Brown and Smith (1975) for 267-430 K and of Takacs and Glass (1973b) at 298 K. The preferred value is based on the results of Nava et al., those of Nicovich and Wine and those of Singleton and Cvetanovic over the same temperature range, since these results are less subject to complications due to secondary chemistry than are the results using discharge flow techniques. The uncertainty at 298 K has been set to encompass these latter results.

F24. $NO_3 + Br$. The recommended value is that reported by Mellouki et al. (1989) in a study using DF-DPR techniques.

F25. $NO_3 + BrO$. The recommended value is the geometric mean of the lower and upper limits reported by Mellouki et al. (1989) in a study using DF-DPR techniques. These reported limits are encompassed within the indicated uncertainty limits.

F26. $NO_3 + HBr$. The recommended upper limit is the upper limit reported by Mellouki et al. (1989) in a study using DF-EPR techniques. This upper limit shows that this reaction is of negligible importance in stratospheric chemistry. Canosa-Mas et al. (1989) reported a value which is consistent, within experimental error, with the upper limit of Mellouki et al.

G1. $F + O_3$. The only experimental data are those reported by Wagner et al. (1972). The value appears to be quite reasonable in view of the well-known reactivity of atomic chlorine with O_3.

G2. $F + H_2$. The value of k at 298 K seems to be well established with the results reported by Zhitneva and Pshezhetskii (1978), Heidner et al. (1979, 1980), Wurzberg and Houston (1980), Dodonov et al. (1971), Clyne et al. (1973), Bozzelli (1973), Igoshin et al. (1974), Clyne and Hodgson (1985) and Stevens et al. (1989) being in excellent agreement (range of k being $2.3\text{-}3.0 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}). The preferred value at 298 K is taken to be the mean of the values reported in these references. Values of E/R range from 433-595 K (Heidner et al.; Wurzberg and Houston; Igoshin et al.; and Stevens et al.). The preferred value of E/R is derived from a fit to the data in these studies. The A-factor was chosen to fit the recommended room temperature value.

G3. $F + CH_4$. The three absolute rate coefficients determined by Wagner et al. (1971), Clyne et al. (1973) and Kompa and Wanner (1972) at 298 K are in good agreement; however, this may be somewhat fortuitous as the ratios of $k(F + H_2)/k(F + CH_4)$ determined by these same groups can only be considered to be in fair agreement, 0.23, 0.42 and 0.88. The values determined for k (298) from the relative rate coefficient studies are also in good agreement with those determined in the absolute rate coefficient studies, and the value of 0.42 reported for $k(F + H_2)/k(F + CH_4)$ by Foon and Reid (1971) is in good agreement with that reported by Clyne et al. Fasano and Nogar (1982) determined the absolute room temperature rate coefficient, and the rate coefficient relative to that of the reaction $F + D_2$. The preferred value for k (298) is a weighted mean of all the results. The magnitude of the temperature dependence is somewhat uncertain. The preferred Arrhenius parameters are based on the data reported by Wagner et al., and Foon and Reid, and the preferred Arrhenius parameters of the $F + H_2$ reaction. This reaction has been reviewed by both Foon and Kaufman (1975) and Jones and Skolnik (1976). The A-factor may be too high.

G4. $F + H_2O$. The recommended temperature-independent value is based on results reported in the recent study by Stevens et al. (1989) over the temperature range 240-373 K using a discharge flow system with chemical conversion of fluorine atoms to deuterium atoms and detection of the latter by resonanace fluorescence. This value is in excellent agreement with the room temperature results of Frost et al.

(1986) and Walther and Wagner (1983). The latter authors in a limited temperature dependent study reported an E/R value of 400 K. Although these data have not been included in the derivation of the preferred value, with the exception of the one low temperature data point, they are encompassed within the indicated uncertainty limits.

G5. F + HNO_3. The recommendation is based on results of the temperature-dependent study of Wine et al. (1988) and the room temperature results of Mellouki et al. (1987) and Rahman et al. (1988). The values at room temperature are in good agreement. The study of Wine et al. (1988) was over the temperature range 260-373 K. Below 320 K the data were fitted with the Arrhenius expression recommended here, whereas at higher temperatures a temperature-independent value was found, suggesting the occurrence of different mechanisms in the two temperature regimes.

G6. NO + FO. This is the value reported by Ray and Watson (1981a) for k at 298 K using the discharge flow-mass spectrometric technique. The temperature dependence of k is expected to be small for such a radical-radical reaction. The temperature dependences of k for the analogous ClO and BrO reactions (Table 1) are small and negative.

G7. FO + FO. The value of k(FO + FO) reported by Clyne and Watson (1974b) was obtained in a more direct manner than that of Wagner et al. (1972), and as such is less susceptible to error due to the presence of complicating secondary reactions. The value recommended in this assessment is a weighted average of the two studies. From the data of Wagner et al. it can be seen that the dominant reaction channel is that producing 2F + O_2. However, their database is not adequate to conclude that this is the only process.

G8. FO + O_3. The FO + O_3 reaction has two possible pathways which are exothermic, resulting in the production of F + $2O_2$ or FO_2 + O_2. Although this reaction has not been studied in a simple direct manner, two studies of complex chemical systems have reported some kinetic information about it. Starrico et al. (1962) measured quantum yields for ozone destruction in F_2/O_3 mixtures, and attributed the high values, ~4600, to be due to the rapid regeneration of atomic fluorine via the $FO + O_3 \rightarrow F + 2O_2$ reaction. However, their results are probably also consistent with the chain propagation process being $FO + FO \rightarrow 2F + O_2$ (the latter reaction has been studied twice (Wagner et al., 1972; Clyne and Watson, 1974b), and although the value of $[F]_{produced}/[FO]_{consumed}$ is known to be close to unity, it has not been accurately determined. Consequently it is impossible to ascertain from the experimental results of Starrico et al. whether or not the high quantum yields for ozone destruction should be attributed to the FO + O_3 reaction producing either F + $2O_2$ or FO_2 + O_2 (this process is also a chain propagation step if the resulting FO_2 radical preferentially reacts with ozone rather than with either FO or itself). Wagner et al. utilized a low pressure discharge flow-mass spectrometric system to study the F + O_3 and FO + FO reactions by directly monitoring the time history of the concentrations of F, FO and O_3. They concluded that the FO + O_3 reaction was unimportant in their system. However, their paper does not present enough information to warrant this conclusion. Indeed, their value of k(FO + FO) of 3×10^{-11} is about a factor of 4 greater than that reported by Clyne and Watson, which may possibly be attributed to either reactive impurities being present in their system, e.g., $O(^3P)$, or the FO + O_3 reactions being not of negligible importance in their study. Consequently, it is not possible to determine a value for the FO + O_3 reaction rate constant from existing experimental data. It is worth noting the analogous ClO + O_3 reactions are extremely slow ($<10^{-18}$ cm^3 $molecule^{-1}$ s^{-1}) (DeMore et al., 1976), and upper limits of 8×10^{-14} (Clyne and Cruse, 1970a) and 5×10^{-15} cm^3 $molecule^{-1}$ s^{-1} (Sander and Watson, 1981b) have been reported for BrO + O_3.

G9. O + FO. This estimate is probably accurate to within a factor of 3, and is based upon the assumption that the reactivity of FO is similar to that of ClO and BrO. The temperature dependence of the rate constant is expected to be small, as for the analogous ClO reaction.

G10. O + FO_2. No experimental data. The rate constant for such a radical-atom process is expected to approach the gas collision frequency, and is not expected to exhibit a strong temperature dependence.

G11. OH + CHF_3 (HFC-23). The recommendation is based on three data points: the room temperature points of Howard and Evenson (1976a), and the 387 K and 410 K points of Jeong and Kaufman (1982). The data of Clyne and Holt (1979b) were not considered because of the large disparity with other studies. Because of experimental complications associated with the measurement of rate constants near 10^{-16} cm^3 $molecule^{-1}$ s^{-1}, the k_{298} determinations of Howard and Evenson (1976a) and Nip et al. (1979) should be considered upper limits. The Howard and Evenson value, being the smaller of the two, was therefore used as the basis for the k_{298} recommendation.

G12. $OH + CH_2F_2$ (HFC-32). The temperature dependence of the preferred rate expression is derived from the data of Jeong and Kaufman (1982), Talukdar et al. (1991a) below 400 K and the room temperature data of Howard and Evenson (1976a) and Nip et al. (1979). Although the data of Clyne and Holt (1979b) are consistent with the data from the other studies, this study is not included in the least squares fit. The recommendation for k_{298} is derived from the Arrhenius line.

G13. $OH + CH_3F$ (HFC-41). The temperature dependence of the preferred rate expression is derived from the data of Jeong and Kaufman (1982) below 400 K. The recommendation for k_{298} is derived from the average of the room temperature data of Jeong and Kaufman (1982), Howard and Evenson (1976a) and Nip et al (1979).

G14. $OH + CHF_2CF_3$ (HFC-125). The preferred rate expression is derived from the temperature dependence data of Talukdar et al. (1991a) and the room temperature data of Martin and Paraskevopoulos (1983) and DeMore (1992). Due to the large discrepancy between the room temperature rate constant of Clyne and Holt (1979b) and those of Martin and Paraskevopoulos and Talukdar et al., the Clyne and Holt data were ignored. The data from Brown et al. (1990a) were not considered due to the likelihood of impurities. The preferred value of k_{298} is taken from the recommended temperature dependence.

G15. $OH + CHF_2CHF_2$ (HFC-134). For the preferred rate expression, the data of Clyne and Holt (1979b) were rejected in favor of an estimated temperature dependence. The recommended value of k_{298} was obtained by adjusting the 294 K value of Clyne and Holt (1979b) to 298 K.

G16. $OH + CH_2FCF_3$ (HFC-134a). The preferred rate expression was derived from the data of Gierczak et al. (1991) above 243 K, Liu et al. (1990), the 270 K data of Zhang et al. (1992a) and the room temperature data of Martin and Paraskevopoulos (1983) and DeMore (1992). The data of Jeong et al. (1984), Brown et al. (1990a), and Clyne and Holt (1979b) were not considered. The recommended value of k_{298} is obtained from the temperature dependence expression.

G17. $OH + CH_2FCHF_2$ (HFC-143). The only temperature dependence data for this reaction are those of Clyne and Holt (1979b). Due to the large discrepancy between the room temperature rate constant of Clyne and Holt (1979b) and that measured by Martin and Paraskevopoulos (1983), and the generally poor agreement between the Clyne and Holt data and that of other workers for several other halomethanes and haloethanes, the Clyne and Holt data were not used in deriving this recommendation. The preferred value of k_{298} is taken from Martin and Paraskevopoulos (1983). The temperature dependence was estimated.

G18. $OH + CH_3CF_3$ (HFC-143a). The only temperature dependence data for this reaction are those of Talukdar et al. (1991a) and Clyne and Holt (1979b). Due to the large discrepancy between the room temperature rate constant of Clyne and Holt (1979b) and that measured by Martin and Paraskevopoulos (1983), and the generally poor agreement between the Clyne and Holt data and that of other workers for several other halomethanes and haloethanes, the Clyne and Holt data were ignored. The recommended rate expression is derived from a fit to the temperature dependence data of Talukdar et al. for $T \geq 251$ K and the room temperature point of Martin and Paraskevopoulos. The recommended value of k_{298} is derived from the rate expression.

G19. $OH + CH_2FCH_2F$ (HFC-152). The preferred rate expression is derived by fitting an estimated temperature dependence to the room temperature data of Martin and Paraskevopoulos (1983).

G20. $OH + CH_3CHF_2$ (HFC-152a). The preferred rate expression is derived from the temperature dependence data of Nielsen (1991), Gierczak et al. (1991), Liu et al. (1990) and the room temperature data of Howard and Evenson (1976b), Handwerk and Zellner (1978), and Nip et al. (1979). The data of Brown et al. (1990a) and Clyne and Holt (1979b) were not considered. The recommended value of k_{298} is derived from the rate expression.

G21. $OH + CH_3CH_2F$ (HFC-161). There are no temperature dependence data for this reaction. The temperature dependence of the recommended expression was derived by analogy with members of the homologous series which includes the $OH + C_2H_6$ and $OH + CH_3CHF_2$ reactions. The value of k_{298} was taken from the study of Nip et al. (1979). Singleton et al. (1980) determined that 85 ± 3% of the abstraction by OH is from the fluorine substituted methyl group.

G22. $CF_3O_2 + NO$. The recommended value for the reaction of NO with this perhalogenated methylperoxy radical is based on the results reported by Dognon et al. (1985) for the temperature range 230-430 K. It is in good agreement with the room temperature value reported by Plumb and Ryan (1982a). Dognon et al. have shown that NO_2 is the major product in this reaction.

H1. $OH + H_2S$. The values of k(298 K) and E/R are derived from a composite unweighted least squares fit to the individual data points of Perry et al. (1976b), Cox and Sheppard (1980), Wine et al. (1981a), Leu and Smith (1982a), Michael et al. (1982), Lin (1982), Lin et al. (1985), Barnes et al. (1986a), and Lafage et al. (1987). The studies of Leu and Smith (1982a), Lin et al. (1985), Lin (1982), and Lafage et al. (1987) show a slight parabolic temperature dependence of k with a minimum occurring near room temperature. However, with the error limits stated in this evaluation, all data are fit reasonably well by an Arrhenius expression. Lafage et al. and Michael et al. discuss the results in terms of a two channel reaction scheme involving direct H atom abstraction and complex (adduct) formation. Lafage et al. analyzed their results above room temperature to yield an apparent E/R = 400K for the abstraction channel in good agreement with the E/R value determined above room temperature by Westenberg and de Haas (1973b). The results of these latter workers lie systematically higher (by about 70%), presumably due to secondary reactions. The room temperature value measured by Stuhl (1974) lies just outside the 2σ error limit set for k(298 K).

H2. $OH + OCS$. The value of k(298 K) is an average of the determinations by Wahner and Ravishankara (1987) and Cheng and Lee (1986). The room temperature rate constants from these studies are a factor of three higher than the earlier determination by Leu and Smith (1981). As discussed in the later studies, this difference may be due to an overcorrection of the Leu and Smith data to account for OH reaction with H_2S impurities and also to possible regeneration of OH. Nevertheless, the uncertainty factor at 298 K has been set to encompass the earlier study within 2σ. The work by Wahner and Ravishankara (1987) supersedes the study of Ravishankara et al. (1980b), which minimized complications due to secondary and/or excited state reactions presumably interfering with the experiments of Atkinson et al. (1978) and of Kurylo (1978b). The upper limit for k(298 K) reported by Cox and Sheppard (1980) is too insensitive to permit comparison with the more recent studies. The room temperature measurements of Wahner and Ravishankara demonstrate the lack of an effect of total pressure (or O_2 partial pressure) on the rate constant and are supported by the more limited pressure and O_2 studies of Cheng and Lee. The recommendation for E/R is based on the study of Cheng and Lee who determined a value considerably lower than reported by Leu and Smith, although this difference may be due in part to the earlier mentioned overcorrection of the data by these latter authors.

Product observations by Leu and Smith indicate that SH is a primary product of this reaction and tentatively confirm the suggestion of Kurylo and Laufer (1979) that the predominant reaction pathway is to produce $SH + CO_2$ through a complex (adduct) mechanism similar to that observed for the $OH + CS_2$ reaction. However, the absence of an O_2/pressure effect for OH + OCS is in marked contrast with the strong dependence seen in studies of $OH + CS_2$ (see note H3).

Experiments by Greenblatt and Howard (1989) have shown that oxygen atom exchange in the reaction of ^{18}OH with OCS is relatively unimportant, leading to an upper limit of 1×10^{-15} being set on the rate constant of the exchange reaction.

H3. $OH + CS_2$. There is a consensus of experimental evidence that this reaction proceeds very slowly as a direct bimolecular process. Wine et al. (1980) set an upper limit on k(298 K) of 1.5×10^{-15} cm^3 $molecule^{-1}$ s^{-1}. A consistent upper limit is also reported by Iyer and Rowland (1980) for the rate of direct product of OCS, suggesting that OCS and SH are primary products of the bimolecular process. This mechanistic interpretation is further supported by the studies of Leu and Smith (1982b) and of Biermann et al. (1982), which set somewhat higher upper limits on k(298 K). The more rapid reaction rates measured by Atkinson et al. (1978), Kurylo (1978b), and Cox and Sheppard (1980) may be attributable to severe complications arising from excited state and secondary chemistry in their photolytic systems. The Cox and Sheppard study in particular may have been affected by the reaction of electronically excited CS_2 (produced via the 350 nm photolysis) with O_2 (in the one atmosphere synthetic air mixture) as well as by the accelerating effect of O_2 on the OH + CS_2 reaction itself, which has been observed by other workers as summarized below. The possible importance of electronically excited CS_2 reactions in the tropospheric oxidation of CS_2 to OCS has been discussed by Wine et al. (1981d).

An accelerating effect of O_2 on the OH + CS_2 reaction rate has been observed by Jones et al. (1982), Barnes et al. (1983), and Hynes et al. (1988) along with a near unity product yield for SO_2 and OCS. In the latter two studies the effective bimolecular rate constant was found to be a function of total pressure (O_2 + N_2) as well and exhibited an appreciably negative temperature dependence. These observations are consistent with the formation of a long-lived adduct as postulated by Kurylo (1978b) and Kurylo and Laufer (1979) followed by its reaction with O_2:

$$\mathrm{OH} + \mathrm{CS_2} + \mathrm{M} \underset{k_b}{\overset{k_a}{\leftrightarrow}} \mathrm{HOCS_2} + \mathrm{M}$$

$$\mathrm{HOCS_2} + \mathrm{O_2} \xrightarrow{k_c} \mathrm{Products}$$

Hynes et al. (1988), Murrells et al. (1990), Becker et al. (1990), and Bulatov et al. (1988) have, in fact, directly observed the approach to equilibrium in this reversible adduct formation. In the Hynes et al. study, the equilibrium constant was measured as a function of temperature and the heat of formation of $HOCS_2$ was calculated (-27.4 kcal/mole). A rearrangement of this adduct followed by dissociation into OCS and SH corresponds to the bimolecular (low k) channel referred to earlier. Hynes et al. (1988) measured the rate constant for this process in the absence of O_2 (at approximately one atmosphere of N_2) to be $< 8 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}. Hynes et al. (1988) and Murrells et al. (1990) agree quite well on the value of k_c with an average value of 2.7×10^{-14} being reported independent of temperature and pressure. The effective second order rate constant for CS_2 or OH removal in the above reaction scheme can be expressed as

$$1/k_{eff} = (k_b/k_a k_c)(1/P_{O2}) + (1/k_a)(1/P_M)$$

where P_{O2} is the partial pressure of O_2 and P_M equals $P_{O2} + P_{N2}$. The validity of this expression requires that k_a and k_b are invariant with the P_{O2}/P_{N2} ratio. A 1/k vs $1/P_{O2}$ plot of the data of Jones et al. (1982) taken at atmospheric pressure exhibits marked curvature, suggesting a more complex mechanistic involvement of O_2; whereas the data of Barnes et al. (1983) and Hynes et al. (1988) are more satisfactorily represented by this analytical expression. Nevertheless, while the qualitative features of the data from all three laboratories agree, there are some quantitative inconsistencies. First, under similar conditions of O_2 and N_2 pressures, the Barnes et al. rate constants lie approximately 60% higher than those of Jones et al. and up to a factor of two higher than those derived by Hynes et al. Secondly, two fits each of both the Barnes et al. and Hynes et al. data can be made: one at fixed P_M and varying P_{O2}, and the other at fixed P_{O2} and varying P_M (i.e., varying added N_2). Within each data set, rate constants calculated from both fits agree reasonably well for mole fractions of O_2 near 0.2 (equivalent to air) but disagree by more than a factor of two for measurements in a pure O_2 system. Finally, the temperature dependence (from 264 - 293 K) of the k_{eff} values from Barnes et al. varies systematically from an E/R of -1300 K for experiments in pure O_2 (at 700 torr total pressure) to -2900 K for experiments in a 50 torr O_2 plus 650 torr N_2 mixture. An Arrhenius fit of the Hynes et al. data (from 251 - 348 K) recorded in synthetic air at 690 torr yields an E/R = -3300 K, although the data show marked curvature over the temperature range of study. These observations suggest that k_a and k_b may not be independent of the identity of M. For this reason, we limit our recommendation to air mixtures (i.e., $P_{O2}/P_{N2} = 0.25$) at atmospheric pressure. Since most CS_2 is oxidized within the atmospheric boundary layer, such restriction does not limit the applicability of this recommendation in atmospheric modeling.

The present recommendation accepts the measurements of Hynes et al. (1988) which appear to be the most sensitive of the three investigations. Thus, k(298 K) is derived from the Arrhenius fit of the data near room temperature.

$$k(298\ K) = 1.2 \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$$

The uncertainty factor, f(298) = 1.5, encompasses the results of Barnes et al. (1983) within 2σ. To compute values of k below 298 K we have accepted the analysis of Hynes et al.

$$k(T) = \{1.25 \times 10^{-16} \exp(4550/T)\}/\{T + 1.81 \times 10^{-3} \exp(3400/T)\}$$

This recommendation is only valid for one atmosphere pressure of air. It is interesting to note that measurements by Hynes et al. (1988) at approximately 250 K and 700 torr total pressure result in k_{eff} values that are independent of the amount of O_2 for partial pressures between 145 - 680 torr. This suggests that the adduct is quite stable with respect to dissociation into the reactants ($OH + CS_2$) at this low temperature and the effective rate constant for reactant removal approaches the elementary rate constant for adduct formation.

From a mechanistic viewpoint, the primary products of reaction c determine the products of CS_2 oxidation in air. Lovejoy et al. (1990a) have shown that the yields of both HO_2 and SO_2 are equal and near unity. Together with the earlier mentioned unity yield of OCS, these observations suggest that the oxidation equation

$$OH + CS_2 + 2O_2 \rightarrow OCS + HO_2 + SO_2$$

describes this atmospheric system. Insight into the specific reaction pathways can be gleaned from the study of Lovejoy et al. (1990b) in which k_c for the reaction of $DOCS_2 + O_2$ was found to be the same as that for $HOCS_2$, indicating that simple H atom abstraction is not the likely process. These authors have also found that ^{18}O from ^{18}OH ends up on SO_2, suggesting that direct OH attack on the S atom is followed by a complex reaction pathway involving O_2. Additional work involving direct intermediate observations would be helpful in elucidating this reaction mechanism.

H4. $O + H_2S$. This recommendation is derived from an unweighted least squares fit of the data of Singleton et al. (1979) and Whytock et al. (1976). The results of Slagle et al. (1978) show very good agreement for E/R in the temperature region of overlap (300 - 500 K) but lie systematically higher at every temperature. The uncertainty factor at 298 K has been chosen to encompass the room temperature rate constant values of Slagle et al. (1978) and Hollinden et al. (1970). Other than the 263 K data point of Whytock et al. and the 281 K point of Slagle et al., the main body of rate constant data below 298 K comes from the study of Hollinden et al., which indicates a dramatic change in E/R in this temperature region. Thus, ΔE/R was set to account for these observations. Such a non-linearity in the Arrhenius plot might indicate a change in the reaction mechanism from abstraction (as written) to addition. An addition channel (resulting in H atom displacement) has been proposed by Slagle et al. (1978), Singleton et al. (1979), and Singleton et al. (1982). In the latter two studies, an upper limit of 20% was placed on the displacement channel. Direct observations of product HSO was made in the reactive scattering experiments of Clemo et al. (1981) and Davidson et al. (1982). A threshold energy of 3.3 kcal/mole was observed (similar to the activation energy measured in earlier studies) suggesting the importance of this direct displacement channel. Addition products from this reaction have been seen in a matrix by Smardzewski and Lin (1977). Further kinetic studies in the 200 - 300 K temperature range as well as quantitative direct mechanistic information could clarify these issues. However, this reaction is thought to be of limited importance in stratospheric chemistry.

H5. O + OCS. The value of k(298 K) is the average of the determinations by Westenberg and de Haas (1969a), Klemm and Stief (1974), Wei and Timmons (1975), Manning et al. (1976), and Breckenridge and Miller (1972). The recommended value of E/R is the average value taken from the first three listed studies. Hsu et al. (1979) report that this reaction proceeds exclusively by a stripping mechanism.

H6. $O + CS_2$. The value of k(298 K) is an average of the rate constants determined by Wei and Timmons (1975), Westenberg and de Haas (1969a), Slagle et al. (1974a), Callear and Smith (1967), Callear and

Hedges (1970), Homann et al. (1968), and Graham and Gutman (1977). The E/R value is an average of the determinations by Wei and Timmons and Graham and Gutman. The ΔE/R has been set to encompass the limited temperature data of Westenberg and de Haas. The principal reaction products are thought to be CS + SO. However, Hsu et al. (1979) report that 1.4% of the reaction at 298 K proceeds through a channel yielding CO + S_2 and calculate a rate constant for the overall process in agreement with that recommended. Graham and Gutman (1977) have found that 9.6% of the reaction proceeds to yield OCS + S at room temperature.

H7. O_3 + H_2S. New Entry. This upper limit was determined by Becker et al. (1975) from measurements of the rates of SO_2 production and O_3 consumption. The heterogeneous reaction between H_2S and O_3 is far more efficient in most laboratory systems.

H8. S + O_2. This recommendation is based primarily on the study of Davis et al. (1972). Modest agreement at 298 K is found in the studies of Fair and Thrush (1969) Fair et al. (1971), Donovan and Little (1972), and Clyne and Townsend (1975). The study by Clyne and Whitefield (1979), which indicates a slightly negative E/R between 300 and 400 K, is encompassed by the assigned uncertainty limits.

H9. S + O_3. This recommendation accepts the only available experimental data of Clyne and Townsend (1975). In this study the authors measure a value of the rate constant for S + O_2 in reasonable agreement with that recommended above. The assigned error limit reflects both this ancillary agreement and the need for independent confirmation.

H10. S + OH. This recommendation is based on the single study by Jourdain et al. (1979). Their measured value for k(298 K) compares favorably with the recommended value of k(O + OH) when one considers the slightly greater exothermicity of the present reaction.

H11. SO + O_2. This recommendation is based on the low temperature measurements of Black et al. (1982a, 1982b). The room temperature value accepts the results of the more recent paper as recommended by the authors. The uncertainties cited reflect the need for further confirmation and the fact that these results lie significantly higher than an extrapolation of the higher temperature data of Homann et al. (1968). A room temperature upper limit on k set by Breckenridge and Miller (1972) is consistent with the Black et al. data.

H12. SO + O_3. The value of k(298 K) is an average of the determinations by Halstead and Thrush (1966), Robertshaw and Smith (1980), and Black et al. (1982a, 1982b) using widely different techniques. The value of E/R is an average of the values reported by Halstead and Thrush and Black et al. (1982b), with the A-factor recalculated to fit the recommendation for k(298 K).

H13. SO + OH. The value recommended for K(298 K) is an average of the determinations by Fair and Thrush (1969) and Jourdain et al. (1979). Both sets of data have been corrected using the present recommendation for the O + OH reaction.

H14. SO + NO_2. The value of k(298 K) is an average of the determinations by Clyne and MacRobert (1980), Black et al. (1982a), and Brunning and Stief (1986a), which agree quite well with the rate constant calculated from the relative rate measurements of Clyne et al. (1966). The Arrhenius parameters are taken from Brunning and Stief.

H15. SO + ClO. The value of k(298 K) is an average of the determinations by Clyne and MacRobert (1981) and Brunning and Stief (1986a). The temperature independence is taken from the latter study with the A-factor recalculated to fit the k(298 K) recommendation.

H16. SO + OClO. This recommendation is based on the single room temperature study by Clyne and MacRobert (1981). The uncertainty reflects the absence of any confirming investigation.

H17. SO + BrO. This recommendation is based on the measurements of Brunning and Stief (1986b) performed under both excess BrO and excess SO conditions. The rate constant is supported by the lower limit assigned by Clyne and MacRobert (1981) from measurements of SO_2 production.

H18. $SO_2 + HO_2$. This upper limit is based on the atmospheric pressure study of Graham et al. (1979). A low pressure laser magnetic resonance study by Burrows et al. (1979) places a somewhat higher upper limit on k(298 K) of 4×10^{-17} (determined relative to $OH + H_2O_2$). Their limit is based on the assumption that the products are OH and SO_3. The weight of evidence from both studies suggests an error in the earlier determination by Payne et al. (1973).

H19. $SO_2 + CH_3O_2$. This recommendation accepts the results from the study of Sander and Watson (1981a), which is believed to be the most appropriate for stratospheric modeling purposes. These authors conducted experiments using much lower CH_3O_2 concentrations than employed in the earlier investigations of Sanhueza et al. (1979) and Kan et al. (1979), both of which resulted in k(298 K) values approximately 100 times greater. A later report by Kan et al. (1981) postulates that these differences are due to the reactive removal of the $CH_3O_2SO_2$ adduct at high CH_3O_2 concentrations prior to its reversible decomposition into CH_3O_2 and SO_2. They suggest that such behavior of $CH_3O_2SO_2$ or its equilibrated adduct with O_2 ($CH_3O_2SO_2O_2$) would be expected in the studies yielding high k values, while decomposition of $CH_3O_2SO_2$ into reactants would dominate in the Sander and Watson experiments. It does not appear likely that such secondary reactions involving CH_3O_2, NO, or other radical species would be rapid enough, if they occur under normal stratospheric conditions to compete with the adduct decomposition. This interpretation, unfortunately, does not explain the high rate constant derived by Cocks et al. (1986) under conditions of low [CH_3O_2].

H20. $SO_2 + NO_2$. This recommendation is based on the study of Penzhorn and Canosa (1983) using second derivative UV spectroscopy. While these authors actually report a measured value for k(298 K), their observations of strong heterogeneous and water vapor catalyzed effects prompt us to accept their measurement as an upper limit. This value is approximately two orders of magnitude lower than that for a dark reaction observed by Jaffe and Klein (1966), much of which may have been due to heterogeneous processes. Penzhorn and Canosa suggest that the products of this reaction are $NO + SO_3$.

H21. $SO_2 + NO_3$. This recommended upper limit for k(298 K) is based on the study by Daubendiek and Calvert (1975). Considerably higher upper limits have been derived by Burrows et al. (1985b), Wallington et al. (1986a), Canosa-Mas et al. (1988), and Dlugokencky and Howard (1988).

H22. $SO_2 + O_3$. This recommendation is based on the limited data of Davis et al. (1974b) at 300 K and 360 K in a stopped flow investigation using mass spectrometric and uv spectroscopic detection.

H23. $SO_3 + H_2O$. This recommendation is based on the measurements of Wang et al. (1988b). Although these authors attempted to exclude any heterogeneous effects from their experiments, they conclude that their measurements must still be viewed as yielding an upper limit to the gas phase homogeneous reaction rate constant. An earlier reported higher rate constant value by Castleman et al. (1975) may have resulted from an underestimation of the effects of heterogeneous reactions.

H24. $SO_3 + NO_2$. This recommendation is based on the study of Penzhorn and Canosa (1983) using second derivative UV spectroscopy. These authors observe the production of a white aerosol, which they interpret to be the adduct NSO_5. This claim is supported by ESCA spectra.

H25. $SO_3 + NH_3$. New Entry. This recommendation is based on the single study by Shen et al. (1990). The uncertainty reflects the absence of any confirming investigation.

H26. $Cl + H_2S$. The value of k(298 K) is an average of the determinations by Nesbitt and Leone (1980) (which refines the data of Braithwaite and Leone (1978)), Clyne and Ono (1983), Clyne et al. (1984), and Nava et al. (1985). The zero activation energy is derived from the data of Nava et al. with the A-factor calculated to agree with the recommended value for k(298 K). Lu et al. (1986) also measure a temperature independent rate constant, and their larger value of k(298 K) = 10.5×10^{-11} may be indicative of a slight pressure dependence of the reaction since their experiments were performed at 4000 torr.

H27. Cl + OCS. This upper limit is based on the minimum detectable decrease in atomic chlorine measured by Eibling and Kaufman (1983). Based on the observation of product SCl, these authors set a lower limit on k(298 K) of 10^{-18} for the reaction as written. Considerably higher upper limits on k(298 K) were determined in the studies of Clyne et al. (1984) and Nava et al. (1985).

H28. $Cl + CS_2$. New Entry. This upper limit for the overall reaction is based on determinations by Nicovich et al. (1990c) and Wallington et al. (1991). The first authors confirm that the reaction proceeds via reversible adduct formation as suggested by Martin et al. (1987). The much larger rate constant values determined by Martin et al. may possibly be attributed to reactive impurities in the CS_2 sample. Nicovich et al. set an upper limit on the rate constant for the adduct (CS_2Cl) reacting with O_2 of 2.5×10^{-16} at room temperature.

H29. $Cl + CH_3SH$. New Entry. This recommendation is an average of of the room temperature determinations of Mellouki et al. (1988b) and Nesbitt and Leone (1980). Nesbitt and Leone (1981) report that less than 2% of the reaction occurs via abstraction of an H atom from the CH_3 group.

H30. $ClO + OCS$; $ClO + SO_2$. These recommendations are based on the discharge flow mass spectrometric data of Eibling and Kaufman (1983). The upper limit on k(298 K) for ClO + OCS was set from the minimum detectable decrease in ClO. No products were observed. The upper limit on k(298 K) for $ClO + SO_2$ is based on the authors' estimate of their detectability for SO_3. The upper limit for this same reaction based on the minimum detectable decrease in ClO was not used due to the potential problem of ClO reformation from the $Cl + O_3$ source reaction.

H31. $SH + H_2O_2$. This recommended upper limit for k(298 K) is based on the single study of Friedl et al. (1985). Their value is calculated from the lack of SH decay (measured by laser-induced fluorescence) and the lack of OH production (measured by resonance fluorescence). The three possible product channels yield: $H_2S + HO_2$, HSOH + OH, and $HSO + H_2O$.

H32. SH + O. This recommendation accepts the results of Cupitt and Glass (1975). The large uncertainty reflects the absence of any confirming investigation.

H33. $SH + O_2$. This upper limit for k(298 K) is based on the study by Stachnik and Molina (1987) utilizing experiments sensitive to the production of OH. Somewhat higher upper limits of 1.0×10^{-17} and 1.5×10^{-17} were assigned by Friedl et al. (1985) and Wang et al. (1987) respectively from the detection sensitivities for OH detection and SH decay respectively. An even higher upper limit by Black (1984), based on the lack of SH decay, may have been complicated by SH regeneration. Much less sensitive upper limits have been calculated by Tiee et al. (1981), Nielsen (1979), and Cupitt and Glass (1975). Stachnik and Molina (1987) also report a somewhat higher upper limit ($< 1.0 \times 10^{-18}$) for the rate constant for the sum of the two $SH + O_2$ reaction channels (producing OH + SO and $H + SO_2$).

H34. $SH + O_3$. The value for k(298 K) is an average of the determinations by Friedl et al. (1985) (laser induced fluorescence detection of SH), Schonle et al. (1987) (mass spectrometric detection of reactant SH and product HSO) as revised by Schindler and Benter (1988), and Wang and Howard (1990) (laser magnetic resonance detection of SH). The temperature dependence is from Wang and Howard with the A-factor calculated to agree with the recommended value for k(298 K). $\Delta E/R$ reflects the fact that the temperature dependence comes from measurements above room temperature and, thus, extrapolation to lower temperatures may be subject to additional uncertainties. Wang and Howard report observing a minor reaction channel that produces $H + SO + O_2$.

H35. $SH + NO_2$. This recommendation accepts the measurements of Wang et al. (1987). These authors suggest that the lower values of k(298 K) reported by Black (1984), Friedl et al. (1985), and Bulatov et al. (1985) are due to SH regeneration from the H_2S source compound. In the study by Stachnik and Molina (1987), attempts were made at minimizing such regeneration and a value of k(298 K) was reported significantly higher than that from the earlier studies, but still 30% lower than that measured by Wang et al. who used two independent SH source reactions. A slightly higher rate constant measured by Schonle et al. (1987) as revised by Schindler and Benter (1988) has not been recommended due to the somewhat more limited database for their determination. The reaction as written represents the most exothermic channel. In fact, HSO has been detected as a product by Leu and Smith (1982a), Bulatov et al. (1985), Schonle et al. (1987), and Wang et al. (1987). The absence of a primary deuterium isotope effect, as observed by Wang et al. (1987), coupled with the large magnitude of the rate constant suggests that the (four-center intermediate) channels producing SO + HNO and OH + SNO are of minor importance. No evidence for a three body combination reaction was found by either Black (1984) or Friedl et al. (1985). Based on a pressure independence of the rate constant between 30 - 300 torr, Black set an upper limit of 7.0 x 10^{-31} for the termolecular rate constant. Similarly, Stachnik and Molina (1987) saw no change in decay rate between 100 and 730 torr with O_2 (although these O_2 experiments were designed primarily to limit SH regeneration).

H36. SH + F_2; SH + Cl_2; SH + Br_2; SH + BrCl. New Entries. The recommendations for these reactions are derived from the data of Fenter and Anderson (1991) for the SD radical. The uncertainties have been increased over those estimated by the investigators to reflect the absence of any confirming investigations and the influence of the secondary isotope effect. For the BrCl reaction, the channel producing ClSD + Br was found to be described by the rate expression k = 2.3 x 10^{-11} exp(100/T).

H37. HSO + O_2. This recommendation is based on the study by Lovejoy et al. (1987), who employed laser magnetic resonance monitoring of HSO in a discharge flow system. The upper limit thus derived for k(298 K) is nearly two orders of magnitude lower than measured by Bulatov et al. (1986).

H38. HSO + O_3. This recommendation is based on the determinations by Friedl et al. (1985) and Wang and Howard (1990). In the first study, performed at higher O_3 concentrations, greater quantities of HSO were produced in the flow tube and SH approached a steady state due to its generation via HSO + O_3. The rate constant for this reaction was thus determined relative to SH + O_3 from measurements of the steady state SH concentration as a function of the initial SH concentration. In the second study, the rate constant and its branching ratio were measured at two temperatures. At room temperature, the overall rate constant is in excellent agreement with that of Friedl et al.

The lack of an isotope effect when SD was employed in the Friedl et al. study suggests that the products of the HSO + O_3 reaction are SH + $2O_2$ (analogous to those for HO_2 + O_3). However, Wang and Howard found that only 70% of the reaction leads to HS formation. In addition, their observations of HO_2 production in the presence of O_2 suggests the existence of a reaction channel producing HSO_2 + O_2 followed by $HSO_2 + O_2 \rightarrow HO_2 + SO_2$. At the present time, no recommendation is given for the product channels. Further mechanistic work is suggested since it is important to understand whether this reaction in the atmosphere leads to HS regeneration or to oxidation of the sulfur.

H39. HSO + NO; HSO + NO_2. The recommendations for these reactions are based on the study by Lovejoy et al. (1987) in which laser magnetic resonance was used to monitor HSO in a discharge flow system. Their upper limit for the NO reaction is a factor of 25 lower than the rate constant measured by Bulatov et al. (1985) using intracavity laser absorption at pressures between 10 and 100 torr. Since it is unlikely that this reaction rate undergoes a factor of 25 increase between 1 torr (the pressure of the Lovejoy et al. work) and 10 torr, the higher rate constant may be due to secondary chemistry associated with the HSO production methods employed.

The recommendation for the NO_2 reaction is a factor of two higher than the rate constant reported by Bulatov et al. (1984). Lovejoy et al. have attributed this difference to HSO regeneration under the experimental conditions used by Bulatov et al. (1984). The product assignment for this reaction is discussed in note H40.

H40. HSO_2 + O_2. This recommendation is based on the rate of HO_2 formation measured by Lovejoy et al. (1987) upon addition of O_2 to the HSO + NO_2 reaction system. While HSO_2 was not observed directly, a consideration of the mechanistic possibilities for HSO + NO_2, coupled with measurements of the HO_2 production rate at various O_2 pressures, led these authors to suggest that HSO_2 is both a major product of the HSO + NO_2 reaction and a precursor for HO_2 via reaction with O_2.

H41. $HOSO_2$ + O_2. This recommendation is based on the studies of Gleason et al. (1987) and Gleason and Howard (1988) in which the $HOSO_2$ reactant was monitored using a chemical ionization mass spectrometric technique. Gleason and Howard conducted their measurements over the 297-423 K temperature range in the only temperature dependence investigation. Thus, $\Delta E/R$ has been increased from their quoted limits to account for the potential uncertainties in extrapolating their data to subambient temperatures. The value of k(298 K) derives further support from the studies of Margitan

(1984a) and Martin et al. (1986), both of whom used modeling fits of OH radical decays in the OH + SO_2 + M reaction system in the presence of O_2 and NO. In this latter analysis, the $HOSO_2$ reacts with O_2 yielding HO_2, which subsequently regenerates OH through its reaction with NO. The infrared spectrum of $HOSO_2$ has been recorded in low temperature matrix isolation experiments by Hashimoto et al. (1984) and Nagase et al. (1988). Mass spectrometric detection of $HOSO_2$ in the gas phase has also been reported by Egsgaard et al. (1988).

H42. CS + O_2. The recommendation given for k(298 K) is based on the work of Black et al. (1983) using laser induced fluorescence to monitor CS. This value agrees with the somewhat less precise determination by Richardson (1975) using OCS formation rates. The latter author presents evidence that this reaction channel dominates over the one producing SO + CO by more than a factor of 10. Measurements by Richardson at 293 K and 495 K yield an E/R of 1860 K. However, use of this activation energy with the recommended value of k(298 K) results in an unusually low Arrhenius A-factor of 1.5×10^{-16}. In view of this, no recommendation is given for the temperature dependence.

H43. CS + O_3; CS + NO_2. The k(298 K) recommendations for both reactions accept the results of Black et al. (1983) who used laser induced fluorescence to monitor the CS reactant in a room temperature experiment. The uncertainty factors reflect the absence of any confirming measurements.

H44. OH + CH_3SH. This recommendation is based on a composite fit to the data of Atkinson et al. (1977b), Wine et al. (1981a), Wine et al. (1984a), and Hynes and Wine (1987), which are in excellent agreement. The results from the relative rate study of Barnes et al. (1986) are in agreement with this recommendation and indicate that the higher value of Cox and Sheppard (1980) is due to complications resulting from the presence of O_2 and NO in their reaction system. MacLeod et al. (1983, 1984) and Lee and Tang (1983) obtained rate constants at 298K approximately 50% lower than recommended here. These authors also obtained lower values for the ethanethiol reaction in comparison with results from studies upon which the methanethiol recommendation is made. Wine et al. (1984a) present evidence that this reaction proceeds via adduct formation to produce a species that is thermally stable over the temperature range and time scales of the kinetic measurements. Tyndall and Ravishankara (1989) have determined the yield of CH_3S (via laser induced fluorescence) to be unity, indicating that any adduct must be short lived (less than 100 μs). Longer lifetimes would have led to anomalies in the OH decay kinetics used for the rate constant determinations. Hynes and Wine (1987) failed to observe any effect of O_2 on the measurement rate constant.

H45. OH + CH_3SCH_3. This recommendation averages the results of Hynes et al. (1986b), Wine et al. (1981a), and Hsu et al. (1987c). The earlier higher rate constant values of Atkinson et al. (1978) and Kurylo (1978a) are presumably due to reactive impurities, while those of MacLeod et al. (1983) were most likely overestimated because of heterogeneous reactions. Absolute determinations lower than those recommended were obtained by Martin et al. (1985), Wallington et al. (1986b), and Nielsen et al. (1989). While the reasons for these differences are not readily apparent, these results are encompassed within the 2σ error limits of the 298 K recommendation. Hynes et al. (1986b) have demonstrated the importance of a second reaction channel involving addition of OH to dimethyl sulfide. The adduct formed decomposed rapidly, so that in the absence of any adduct scavenger, only the direct abstraction channel is measured. The recommendation given is for the abstraction reaction only. In the presence of O_2, however, the adduct reacts to form a variety of products. An increase in k with increasing O_2 concentration has been clearly observed by Hynes et al. (1986b), Wallington et al. (1986b), Barnes et al. (1988), and Nielsen et al. (1989). This O_2 effect has been suggested as an explanation for the higher rate constants obtained in many of the earlier relative rate studies. Hynes et al. (1986b) give the following expression for the observed rate constant in one atmosphere of air:

$$k_{obs} = \{T \exp(-234/T) + 8.46 \times 10^{-10} \exp(7230/T) + 2.68 \times 10^{-10} \exp(7810/T)\} / \{1.04 \times 10^{11}\, T + 88.1 \exp(7460/T)\}$$

H46. OH + CH_3SSCH_3. This recommendation is based on the study of Wine et al. (1981a). The room temperature relative rate study by Cox and Sheppard (1980) is in good agreement with the recommended value. The value of ΔE/R reflects the existence of only one temperature dependence investigation. Domine and Ravishankara (1989) have observed both CH_3S (via laser induced fluorescence) and

CH_3SOH (via photoionization mass spectrometry) as products of this reaction. At 298 K, the yield of CH_3S alone was quantified at approximately 30%.

H47. $NO_3 + H_2S$. This recommendation accepts the upper limit set by Dlugokencky and Howard (1988) based on experiments in which NO_3 loss was followed in the presence of large concentrations of H_2S. Less sensitive upper limits for the rate constant have been reported by Wallington et al. (1986a) and Cantrell et al. (1987b).

H48. $NO_3 + OCS$. This upper limit is based on the relative rate data of MacLeod et al. (1986).

H49. $NO_3 + CS_2$. This upper limit is based on the study of Burrows et al. (1985b). A somewhat higher upper limit was derived in the relative rate data of MacLeod et al. (1986).

H50. $NO_3 + CH_3SH$. The recommended values are derived from a composite fit to the data of Wallington et al. (1986a), Rahman et al. (1988), and Dlugokencky and Howard (1988). The room temperature rate constant derived in the relative rate experiments of MacLeod et al. (1986) is in good agreement with the recommended value. The suite of investigations shows the rate constant to be pressure independent over the range 1 - 700 torr. Dlugokencky and Howard place an upper limit of 5% on the production of NO_2 via this reaction at low pressure.

H51. $NO_3 + CH_3SCH_3$. The recommended values are derived from a composite fit to the data of Wallington et al. (1986a), Tyndall et al. (1986), and Dlugokencky and Howard (1988). The relative rate study of Atkinson et al. (1984b) yields a rate constant at room temperature in good agreement with that recommended. The experimental data from all investigations demonstrate the pressure independence of the rate constant over the range 1 - 740 torr. A recent room temperature study by Daykin and Wine (1990) is also in agreement with the recommended value. Evidence to date indicates a pressure independence of the rate constant despite the temperature dependence and observed products being consistent with the formation of an NO_3-CH_3SCH_3 adduct.

H52. $NO_3 + CH_3SSCH_3$. The recommended values were derived from a composite fit to the data of Wallington et al. (1986a) and Dlugokencky and Howard (1988). The investigation by Atkinson et al. (1988) indicates that the relative rate technique cannot be considered as yielding reliable rate data for this reaction due to chemical complexities. Thus, the much lower room temperature results from the study of MacLeod et al. (1986) can be considered to be erroneous.

H53. $N_2O_5 + CH_3SCH_3$. New Entry. This recommendation is based on the value estimated by Tyndall and Ravishankara (1991) from the study by Atkinson et al. (1984b).

H54. $CH_3S + O_2$. This upper limit is based on the study by Tyndall and Ravishankara (1989a). Somewhat higher upper limits were derived in the earlier studies of Balla et al. (1986) and Black and Jusinski (1986).

H55. $CH_3S + O_3$. This recommendation is based on the room temperature determinations of Tyndall and Ravishankara (1989b) and Domine et al. (1992). The latter authors measured the yield of CH_3SO to be 15% at low pressure and use this value to revise the corrections of the earlier investigation to account for CH_3S regeneration by $CH_3SO + O_3$. A failure to observe significant reaction in the study by Black and Jusinski (1986) is interpreted as due to rapid regeneration of CH_3S in their system.

H56. $CH_3S + NO$. New Entry. The upper limit for the bimolecular reaction between CH_3S and NO is based on estimates by Balla et al. (1986) who conducted a temperature dependence study of the termolecular reaction.

H57. $CH_3S + NO_2$. This recommendation averages the results of Tyndall and Ravishankara (1989a) and Domine et al. (1990). An earlier study by Balla et al. (1986) yielded a room temperature rate constant nearly a factor of two higher, which may be attributed to secondary reactions at higher radical concentrations. Tyndall and Ravishankara determined the NO yield to be (80 ± 20)%. Together with the unity yield of CH_3SO obtained by Domine et al., this implies that the primary reaction channel is as written.

H58. $CH_3SO + O_3$. This recommendation is based on the study by Domine et al. (1992). It is supported by the study of Tyndall and Ravishankara (1989b) in which the rate constant was derived from a complex analysis of the $CH_3S + O_3$ reaction system. Domine et al. place the direct yield of CH_2SO at approximately 10% and that of CH_3S at 13% at low pressure.

H59. $CH_3SO + NO_2$. This recommendation is based on the direct measurements of Domine et al. (1990). The results are supported by somewhat less direct measurements of Tyndall and Ravishankara (1989a) and Mellouki et al. (1988b).

H60. $CH_3SS + O_3$. New Entry. This recommendation is based on the discharge flow photoionization mass spectroscopy study by Domine et al. (1992). The uncertainty factor reflects the absence of any confirming investigations. The rate constant ratio for the reactions of CH_3SS with O_3 and NO_2 is consistent with the rate constant ration for the corresponding CH_3S reactions.

H61. $CH_3SS + NO_2$; $CH_3SSO + NO_2$. These recommendations are based on the discharge flow photoionization mass spectroscopy study by Domine et al. (1991). The rate constant ratio for these two reactions agrees with that observed for other RS/RSO radicals with NO_2. The assigned uncertainties reflect this agreement but acknowledge the absence of any confirming investigation. In the Domine et al. study, CH_3SSO was produced by reacting away all CH_3SS with high NO_2 concentrations. Thus, as expected, O atom transfer may be the primary channel in the CH_3SS reaction.

J1. $Na + O_3$. The recommendation is based on the measurements of Ager et al. (1986) and Worsnop et al. (1991). The data of Worsnop et al. is taken from their Table II because the values in the abstract and text are in error (Worsnop, private communication, 1991). The data of Worsnop et al. supersedes earlier work from that laboratory (Silver and Kolb, 1986a). Measurements made by Husain et al. (1985) at 500 K are consistent with the recommendation but are not included because they did not recognize that secondary chemistry, $NaO + O_3 \rightarrow Na + 2O_2$, interferes with the rate coefficient measurement. Worsnop et al. (1991) observe no significant temperature dependence from 214-294 K. Ager et al. (1986) estimate that the $NaO_2 + O$ product channel $\leq 5\%$.

J2. $Na + N_2O$. The recommendation incorporates the data of Husain and Marshall (1985), Ager et al. (1986), Plane and Rajasekhar (1989), and Worsnop et al. (1991). Silver and Kolb (1986a) measured a rate coefficient at 295 K that is lower and is superceded by Worsnop et al. (1991). Earlier, less direct studies are discussed by Ager et al. (1986). The NaO product does not react significantly with N_2O at room temperature [k (for $Na + N_2 + O_2$ products) $\leq 10^{-16}$ and k (for $NaO_2 + N_2$ products) $\leq 2 \times 10^{-15}$ Ager et al.].

J3. $Na + Cl_2$. Two measurements of the rate coefficient for this reaction are in excellent agreement: Silver (1986) and Talcott et al. (1986). The recommended value is the average of these room temperature results.

J4. $NaO + O$. The recommendation is based on a measurement at 573 K by Plane and Husain (1986). They reported that $\leq 1\%$ of the Na product is in the 3^2P excited state.

J5. $NaO + O_3$. This reaction was studied by Silver and Kolb (1986a) and Ager et al. (1986), who agree on the rate coefficient and branching ratio. This agreement may be fortuitous because Silver and Kolb used an indirect method and an analysis based on their rate coefficient for the $Na + O_3$ reaction which is about 1/2 that reported by Ager et al. Ager et al. employed a somewhat more direct measurement but the study is complicated by a chain reaction mechanism in the Na/O_3 system.

J6. $NaO + H_2$. The recommendation is based on a measurement by Ager and Howard (1987a). They also reported a significant $Na + H_2O$ product channel and that a small fraction of the Na from this channel is in the 3^2P excited state.

J7. $NaO + H_2O$. The recommendation is based on a measurement by Ager and Howard (1987a).

J8. NaO + NO. The recommendation is based on an indirect measurement reported by Ager et al. (1986).

J9. NaO + HCl. There is only one indirect measurement of the rate coefficient for this reaction, that from the study by Silver et al. (1984a). They indicate that the products are NaCl and OH, although some NaOH and Cl production is not ruled out.

J10. NaO_2 + NO. This reaction is endothermic. The upper limit recommended is from an experimental study by Ager et al. (1986).

J11. NaO_2 + HCl. The recommendation is based on a measurement reported by Silver and Kolb (1986b). They indicated that the products are NaCl + HO_2, but NaOOH + Cl may be possible products.

J12. NaOH + HCl. The recommendation is based on the study by Silver et al. (1984a), which is the only published study of this reaction.

TABLE 2. RATE CONSTANTS FOR THREE-BODY REACTIONS

	Reaction	Low Pressure Limit[a] $k_o(T) = k_o^{300} (T/300)^{-n}$		High Pressure Limit[b] $k_\infty(T) = k_\infty^{300} (T/300)^{-m}$		Notes
		k_o^{300}	n	k_∞^{300}	m	
&	$O + O_2 \xrightarrow{M} O_3$	(6.0±0.5) (-34)	2.3±0.5	-	-	1
	$O(^1D) + N_2 \xrightarrow{M} N_2O$	(3.5±3.0) (-37)	$0.6^{+2.0}_{-0.6}$	-	-	2
	$H + O_2 \xrightarrow{M} HO_2$	(5.7±0.5) (-32)	1.6±0.5	(7.5±4.0) (-11)	0±1.0	3
	$OH + OH \xrightarrow{M} H_2O_2$	(6.9±3.0) (-31)	$0.8^{+2.0}_{-0.8}$	(1.5±0.5) (-11)	0±0.5	4
&	$O + NO \xrightarrow{M} NO_2$	(9.0±2.0) (-32)	1.5±0.3	(3.0±1.0) (-11)	0±1.0	5
	$O + NO_2 \xrightarrow{M} NO_3$	(9.0±1.0) (-32)	2.0±1.0	(2.2±0.3) (-11)	0±1.0	6
	$OH + NO \xrightarrow{M} HONO$	(7.0±2.0) (-31)	2.6±1.0	(1.5±1.0) (-11)	0.5±0.5	7
	$OH + NO_2 \xrightarrow{M} HNO_3$	(2.6±0.3) (-30)	3.2±0.7	(2.4±1.2) (-11)	1.3±1.3	8
	$HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$	(1.8±0.3) (-31)	3.2±0.4	(4.7±1.0) (-12)	1.4±1.4	9
*	$NO_2 + NO_3 \xrightarrow{M} N_2O_5$	(2.2±0.5) (-30)	3.9±1.0	(1.5±0.8) (-12)	0.7±0.4	10
	$Cl + NO \xrightarrow{M} ClNO$	(9.0±2.0) (-32)	1.6±0.5	-	-	11
	$Cl + NO_2 \xrightarrow{M} ClONO$	(1.3±0.2) (-30)	2.0±1.0	(1.0±0.5) (-10)	1.0±1.0	12
	$\xrightarrow{M} ClNO_2$	(1.8±0.3) (-31)	2.0±1.0	(1.0±0.5) (-10)	1.0±1.0	12
&	$Cl + O_2 \xrightarrow{M} ClOO$	(2.7±1.0) (-33)	1.5±0.5	-	-	13
	$Cl + CO \xrightarrow{M} ClCO$	(1.3±0.5) (-33)	3.8±0.5	-	-	14
	$Cl + C_2H_2 \xrightarrow{M} ClC_2H_2$	(8.0±1.0) (-30)	3.5±0.5	(1.0±0.5) (-10)	2.6±0.5	15
*	$ClO + ClO \xrightarrow{M} Cl_2O_2$	(1.9±0.5) (-32)	3.9±1.0	(7.0±1) (-12)	0±1.0	16
&	$ClO + NO_2 \xrightarrow{M} ClONO_2$	(1.8±0.3) (-31)	3.4±1.0	(1.5±0.7) (-11)	1.9±1.9	17
#	$O + OClO \xrightarrow{M} ClO_3$	(1.9±0.5) (-31)	1.1±1.0	(3.1±0.8) (-11)	0±1.0	18
#	$Br + NO_2 \xrightarrow{M} BrNO_2$	(4.2±0.8) (-31)	2.4±0.5	(2.7±0.5) (-11)	0±1.0	19
*	$BrO + NO_2 \xrightarrow{M} BrONO_2$	(5.2±0.5) (-31)	3.0±0.8	(9.0±1.0) (-12)	2.3±1.0	20

Table 2. (Continued)

Reaction	Low Pressure Limit[a] $k_o(T) = k_o^{300}\ (T/300)^{-n}$		High Pressure Limit[b] $k_\infty(T) = k_\infty^{300}\ (T/300)^{-m}$		Notes
	k_o^{300}	n	k_∞^{300}	m	
$F + O_2 \xrightarrow{M} FO_2$	(4.4±0.4) (-33)	1.2±0.5	-	-	21
$F + NO \xrightarrow{M} FNO$	(5.9±3.0) (-32)	1.7±1.7	-	-	22
$F + NO_2 \xrightarrow{M}$ products	(1.1±0.6) (-30)	2.0±2.0	(3.0±2.0) (-11)	1.0±1.0	23
$FO + NO_2 \xrightarrow{M} FONO_2$	(2.6±2.0) (-31)	1.3±1.3	(2.0±1.0) (-11)	1.5±1.5	24
$CH_3 + O_2 \xrightarrow{M} CH_3O_2$	(4.5±1.5) (-31)	3.0±1.0	(1.8±0.2) (-12)	1.7±1.7	25
* $C_2H_5 + O_2 \xrightarrow{M} C_2H_5O_2$	(1.5±1.0) (-28)	3.0±1.0	(8.0±1.0) (-12)	0±1.0	26
# $CH_3O + NO \xrightarrow{M} CH_3ONO$	(1.35±0.5) (-29)	3.8±1	(3.6±1.6) (-11)	0.6±1.0	27
# $CH_3O + NO_2 \xrightarrow{M} CH_3ONO_2$	(2.8±0.6) (-29)	4.0±2.0	(2.0±0.4) (-11)	1.0±1.0	28
# $C_2H_5O + NO \xrightarrow{M} C_2H_5ONO$	(2.0±1.0) (-27)	4.0±2.0	(4.4±0.4) (-11)	1.0±1.0	29
# $C_2H_5O + NO_2 \xrightarrow{M} C_2H_5ONO_2$	(2.0±1.0) (-27)	4.0±2.0	(2.8±0.4) (-11)	1.0±1.0	30
$CH_3O_2 + NO_2 \xrightarrow{M} CH_3O_2NO_2$	(1.5±0.8) (-30)	4.0±2.0	(6.5±3.2) (-12)	2.0±2.0	31
& $OH + SO_2 \xrightarrow{M} HOSO_2$	(3.0±1.0) (-31)	3.3±1.5	(1.5±10.5) (-12)	$0\pm^{0}_{2}$	32
* $OH + C_2H_4 \xrightarrow{M} HOCH_2CH_2$	(1.0±0.6) (-28)	0.8±2.0	(8.8±0.9) (-12)	$0\pm^{0}_{2}$	33
$OH + C_2H_2 \xrightarrow{M} HOCHCH$	(5.5±2.0) (-30)	0.0±0.2	(8.3±1.0) (-13)	$-2\pm^{2}_{1}$	34
$CF_3 + O_2 \xrightarrow{M} CF_3O_2$	(1.5±0.3) (-29)	4.0±2.0	(8.5±1.0) (-12)	1.0±1.0	35
# $CF_2Cl + O_2 \xrightarrow{M} CF_2ClO_2$	(3.0±1.5) (-30)	4.0±2.0	(3±2) (-12)	1.0±1.0	36
$CFCl_2 + O_2 \xrightarrow{M} CFCl_2O_2$	(5.0±0.8) (-30)	4.0±2.0	(6.0±1.0) (-12)	1.0±1.0	37
* $CCl_3 + O_2 \xrightarrow{M} CCl_3O_2$	(1.0±0.7) (-30)	6.0±2.0	(2.5±2.0) (-12)	1.0±1.0	38
& $CFCl_2O_2 + NO_2 \xrightarrow{M} CFCl_2O_2NO_2$	(3.5±0.5) (-29)	5.0±1.0	(6.0±1.0) (-12)	2.5±1.0	39
# $CF_2ClO_2 + NO_2 \xrightarrow{M} CF_2ClO_2NO_2$	(3.5±1.8) (-29)	5.0±1.0	(5.2±1.0) (-12)	2.5±1.0	40
# $CH_3C(O)O_2 + NO_2 \xrightarrow{M} CH_3C(O)O_2NO_2$	(8±4) (-29)	7.0±2.0	(12±2)(-12)	1.0±1.0	41

Table 2. (Continued)

	Reaction	Low Pressure Limit[a] $k_0(T) = k_0^{300} (T/300)^{-n}$		High Pressure Limit[b] $k_\infty(T) = k_\infty^{300} (T/300)^{-m}$		
		k_0^{300}	n	k_∞^{300}	m	Notes
	$CF_3O_2 + NO_2 \rightarrow CF_3O_2NO_2$	(2.2±0.5) (-29)	5.0±1.0	(6.0±1.0) (-12)	2.5±1.0	42
	$CCl_3O_2 + NO_2 \rightarrow CCl_3O_2NO_2$	(5.0±1.0) (-29)	5.0±1.0	(6.0±1.0) (-12)	2.5±1	43
	$HS + NO \xrightarrow{M} HSNO$	(2.4±0.4) (-31)	3.0±1.0	(2.7±0.5) (-11)	0 0±2	44
#	$CH_3S + NO \xrightarrow{M} CH_3SNO$	(3.2±0.4) (-29)	4.0±1	(3.9±0.6) (-11)	2.7±1.0	45
&	$Na + O_2 \xrightarrow{M} NaO_2$	(2.4±0.5) (-30)	1.2±0.5	(4.0±2.0) (-10)	0±1.0	46
	$NaO + O_2 \xrightarrow{M} NaO_3$	(3.5±0.7) (-30)	2.0±2.0	(5.7±3.0) (-10)	0±1.0	47
	$NaO + CO_2 \xrightarrow{M} NaCO_3$	(8.7±2.6) (-28)	2.0±2.0	(6.5±3.0) (-10)	0±1.0	48
	$NaOH + CO_2 \xrightarrow{M} NaHCO_3$	(1.3±0.3) (-28)	2.0±2.0	(6.8±4.0) (-10)	0±1.0	49

Note: $k(Z) = k(M,T) = \left(\frac{k_0(T)[M]}{1 + (k_0(T)[M]/k_\infty(T))} \right) 0.6^{\{1 + [\log_{10} (k_0(T)[M]/k_\infty(T))]^2\}^{-1}}$

The values quoted are suitable for air as the third body, M.

[a] Units are cm^6/molecule^2-sec.

[b] Units are cm^3/molecule-sec.

* Indicates a change from the previous Panel evaluation (JPL 90-1).

& Indicates a change in the Note.

# Indicates a new entry that was not in the previous evaluation.

NOTES TO TABLE 2

1. $O + O_2$. Low-pressure limit and T-dependence are an average of Klais, Anderson, and Kurylo (1980a) and Lin and Leu (1982). The result is in agreement with most previous work (see references therein) and with the recent study of Hippler et al. (1990). Kaye (1986) has calculated isotope effects for this reaction, using methods similar to those discussed in the Introduction; Troe (1977), Patrick and Golden (1983).

   Croce de Cobos and Troe (1984) are in agreement with earlier work. Rawlins et al. (1987) report values in Ar between 80 and 150K that extrapolate to agreement with the recommended values.

2. $O(^1D) + N_2$. Low-pressure limit from Kajimoto and Cvetanovic (1976). The T-dependence is obtained by assuming a constant β. The rate constant is extremely low in this special system due to electronic curve crossing.

3. $H + O_2$. Kurylo (1972), Wong and Davis (1974) and Hsu et al. (1987) are averaged to obtain the low pressure limiting value at 300K. The first two studies include T-dependence, as does a recent study by Hsu et al. (1979). The recommended value is chosen with constant $<\Delta E>_{N_2} \sim .05$ kcal mole^{-1}. This very low number reflects rotational effects. The high pressure limit is from Cobos et al. (1985). The temperature dependence is estimated. Cobos et al. (1985) estimate $m = -0.6$, which is within our uncertainty. Recent high temperature measurements in Ar by Pirraglia et al. (1989) are in good agreement.

4. OH + OH. Zellner et al. (1988) have studied this reaction at 253, 298, and 353K at pressures between 26 and 1100 mbar of N_2. They report

   $$k_o(T) = (6.9 \, ^{+1.4}_{-2.5}) \times 10^{-31} \, (T/298)^{-0.8} \, cm^6 \, s^{-1}$$

   $$k_\infty(T) = 1.5 \times 10^{-11} \, (T/298)^{0} \, cm^3 \, s^{-1}$$

   The unsymmetrical error limits in k_o (298) take into account contributions from $H + OH \rightarrow H_2O$. Error limits were not reported for other parameters. The recommended error limits are estimates.

   Trainor and von Rosenberg (1974) report a value at 300K that is lower by a factor of 2.7.

5. O + NO. Low-pressure limit and n from direct measurements of Schieferstein et al. (1983) and their re-analysis of the data of Whytock et al. (1976). Error limits encompass other studies. High-pressure limit and m from Baulch et al. (1980) and Baulch et al. (1982), slightly modified. Recent shock tube measurements by Yarwood et al. (1991) in argon from 300-1300K are consistent with these values.

6. $O + NO_2$. Values of rate constants and temperature dependences from the evaluation of Baulch et al. (1980). They use $F_c = 0.8$ to fit the measured data at 298 K, but our value of $F_c = 0.6$ gives a similar result. In a supplementary review, Baulch et al. (1982) suggest a slight temperature dependence for F_c, which would cause their suggested value to rise to $F_c = 0.85$ at 200 K.

7. OH + NO. The low-pressure limit rate constant has been reported by Anderson and Kaufman (1972), Stuhl and Niki (1972), Morley and Smith (1972), Westenberg and de Haas (1972), Anderson et al. (1974), Howard and Evenseon (1974), Harris and Wayne (1975), Atkinson et al. (1975), Overend et al. (1976), Anastasi and Smith (1978), and Burrows et al. (1983). The general agreement is good, and the recommended value is a weighted average, with heavy weighting to the work of Anastasi and Smith. The reported high pressure limit rate constant is generally obtained from extrapolation. The recommended value is a weighted average of the reports in Anastasi and Smith (1978) and Anderson et al. (1974). [Both cis and trans--HONO are expected to be formed.]

8. $OH + NO_2$. The low-pressure limit is from Anderson et al. (1974), who report $n = 2.5$ $(240 < T/K < 450)$; Howard and Evenson (1974): Anastasi and Smith (1976), who report $n = 2.6$ $(220 < T/K < 550)$; and

Wine et al. (1979), who support these values over the range ($247 < T/K < 352$). The recommended value of n = 3.2 comes from $<\Delta E>_{N_2}$ = 0.55 kcal mole^{-1}. (This value is consistent with the experiments.) Burrows et al. (1983) confirm the value of k at 295 K. The high-pressure limit and T-dependence come from RRKM model of Smith and Golden (1978), although the error limits have been expanded to encompass m = 0. Robertshaw and Smith (1982) have measured k up to 8.6 atmospheres of CF_4. Their work suggests that k_∞ might be higher than suggested here (~50%). This might also be due to other causes (i.e., isomer formation or involvement of excited electronic states). Burkholder et al. (1987) have shown that $HONO_2$ is the only isomer formed (yield - $.75\pm^{.25}_{.10}$). The recommendation here fits all data over the range of atmospheric interest.

9. $HO_2 + NO_2$. Kurylo and Ouellette (1986) have remeasured the 300K range constants. Kurylo and Ouellette (1987) have also remeasured the temperature dependence. The recommended values are taken from this latter reference wherein their data were combined with that of Sander and Peterson (1984). The recommended k_0 (300 k) is consistent with Howard (1977). Other studies by Simonaitis and Heicklen (1978) and Cox and Patrick (1979) are in reasonable agreement with the recommendation.

10. $NO_2 + NO_3$. Data with N_2 as the bath gas from Kircher et al. (1984), Croce de Cobos et al. (1987a) (up to P = 5 atm), Smith et al. (1985), Burrows et al. (1985a), and Wallington et al. (1987a) were used to obtain k_0^{300} and k_∞^{300}. Values from Croce de Cobos et al. (1984) at pressures above 10 atm are 30% higher than the curve used herein. The values of n and m are from Kircher et al. (1984) and Orlando et al. (1991b). The study of Fowles et al. (1982) is noted, but not used. Johnston et al. (1986) have reviewed this reaction.

    Data for the reverse reaction have been obtained by Connell and Johnston (1979) and Viggiano et al. (1981). (These two data sets are in reasonable agreement under overlapping conditions.) These data may be compared to the suggested parameters by multiplying by the recently redetermined equilibrium constant given in Table 3. The agreement is good. If the previous value of the equilibrium constant is used, the agreement is less than good.

11. Cl + NO. Low-pressure limit from Lee et al. (1978a), Clark et al. (1966), Ashmore and Spencer (1959), and Ravishankara et al. (1978). Temperature dependence from Lee et al. (1978a) and Clark et al. (1966).

12. $Cl + NO_2$. Low-pressure limit and T-dependence from Leu (1984a). (Assuming similar T-dependence in N_2 and He.) Leu (1984a) confirms the observation of Niki et al. (1978c) that both ClONO and $ClNO_2$ are formed, with the former dominating. This has been explained by Chang et al. (1979a), with detailed calculations in Patrick and Golden (1983). The temperature dependence is as predicted in Patrick and Golden (1983). The latter work extends to 200 torr and the high pressure limit was chosen to fit these measurements. The temperature dependence of the high pressure limit is estimated.

13. $Cl + O_2$. Nicovich et al. (1991) measure k=(9 ± 3) x 10^{-33} cm^6 molecule^{-2}s^{-1} at T = 187 ± 6K in O_2. Using the methods described in Patrick and Golden (1983), but adjusting the thermochemistry of ClO_2 such that S^o_{298} = 64.3 cal mol^{-1} K^{-1} and $\Delta H_{f,298}$ = 23.3 ± 0.6 kcal mol^{-1} (See note 6 of Table 3). We calculate 5.4 x 10^{-33} cm^6 molecule^{-2} s^{-1} at T = 185K with collisional efficiency of the bath gas taken from the formula $[\beta/(1-\beta^{1/2})] = <\Delta E>/F_E kT$ and $<\Delta E> \sim 0.5$ kcal mole^{-1} (i.e., $\beta_{185} = .42$ and $\beta_{300} = .30$). Since O_2 may be particularly efficient for this process we use this calculation with broader error limits. The value from the calculation at 300K (i.e., 2.7 x 10^{-33} cm^6 molec^{-2} s^{-1}) compares with an older value of Nicholas and Norrish (1968) of 1.7 x 10^{-33} in an $N_2 + O_2$ mixture. The temperature dependence is from the calculation. Baer et al. (1991) report a value at 298 K in good agreement with the value recommended here. But the temperature dependence is strikingly different as noted by the authors.

14. Cl + CO → ClCO. From Nicovich et al. (1990a) who measured the process in N_2 for $185 \leq T/K \leq 260$.

15. Cl + C_2H_2. Brunning and Stief (1985) measured k from 210 to 361 K in Ar between 10 and 300 torr. Experiments in N_2 at 296K were used to scale the low-pressure limiting rate constant. They report:

$$ko = (1.0 \pm 0.2) \times 10^{-29} (T/300)^{-3.50 \pm 0.05}$$

$$k_\infty = (4.7 \pm 0.9) 10^{-11} (T/300)^{-2.63 \pm 0.05}$$

Wallington et al. (1990a) measured k at 295K in air between 50 and 5800 torr. They report for a combination of their data and the 296K, N_2 data of Brunning and Stief:

$$k_o = (6.1 \pm 0.8) \times 10^{-30}$$

$$k_\infty = (1.9 \pm 0.3) \times 10^{-10}$$

The values recommended here, place heavier weight on the data at pressures below an atmosphere. The temperature dependence is from Brunning and Stief with increased error limits. These values are compatible with earlier studies at Poulet et al. (1973), Atkinson and Aschmann (1985), Lee and Rowland (1977) and Wallington et al. (1988b).

16. ClO + ClO. Sander et al. (1989) and Trolier et al. (1990) measured this reaction at 200-260K in 20-600 torr nitrogen and oxygen. The results are generally consistent with a Patrick and Golden (1983) type calculation within a factor of 2, using thermodynamics consistent with the equilibrium constant measurements of Cox and Hayman (1988). At low temperature and pressure, the rate constants of Trolier et al. (1990) exceed those of Sander et al. (1989) and the calculation, suggesting a possible additional route. The recommended values are an average of these two studies. The error limits encompass both sets of results.

Hayman et al. (1986) report a higher value at higher temperatures that is not consistent in the above sense. Other previous measurements, such as Cox and Derwent (1979), Basco and Hunt (1979) and Walker (1972) and Johnston et al. (1969) range from 1-5 x 10^{-32} cm^6 s^{-1} with N_2 or O_2 as third bodies. Birk et al. (1989) have reported that the major dimerization product is chlorine peroxide. Recent studies of DeMore and Tschuikow-Roux (1990), Slanina and Uhlik (1991) and Stanton et al. (1991) support this observation.

17. ClO + NO_2. Several independent low-pressure determinations (Zahniser et al., 1977; Birks et al., 1977; Leu et al., 1977; Lee et al., 1982) of the rate of ClO disappearance via the ClO + NO_2 + M reaction are in excellent agreement and give an average k_o (300) near 1.8 x 10^{-31} cm^6 s^{-1}. No product identification was carried out, and it was assumed that the reaction gave chlorine nitrate, $ClONO_2$. In contrast, direct measurements of the rate of thermal decomposition of $ClONO_2$ (Knauth, 1978; Schone et al., 1979; and recently Anderson and Fahey, 1990), when combined with the accepted thermochemistry give a value lower by a factor of three. It is concluded that earlier measurements of the heat of formation are incorrect and the value 5.5 kcal $mole^{-1}$ evaluated from the kinetics by Anderson and Fahey (1990) is accepted.

Earlier explanations to the effect that the low-pressure ClO disappearance studies measured not only a reaction forming $ClONO_2$, but another channel forming an isomer, such as $OClNO_2$, ClOONO, or OClONO (Chang et al., 1979a; Molina et al., 1980a) are obviated by the above and work of Margitan (1983b), Cox et al. (1984b), and Burrows et al. (1985a) which indicates that there are no isomers of $ClONO_2$ formed. Wallington and Cox (1986) confirm current values, but are unable to explain the effect of OClO observed by both Molina et al. (1980a) and themselves.

The high-pressure limit rate constants and their temperature dependence are from the model of Smith and Golden (1978). The recommended rate constants fit measured rate data for the disappearance of reactants (Cox and Lewis, 1979; Dasch et al., 1981). Data from Handwerk and Zellner (1984) indicate a slightly lower k_{∞}.

18. O + OClO. New Entry. The recommendation is based on recent data of Colussi et al. (1991) and Colussi (1990) who measured the pressure dependence between 248 and 312K. Their results are consistent with calculations. A zero pressure rate constant of $(1.6 \pm 0.4) \times 10^{-13}$ cm^3 s^{-1} is reported for the chemical activation channel producing ClO + O_2, and their value of $\Delta H_f^o(ClO_3) = 52$ kcal $mole^{-1}$ is derived at 298K.

19. Br+NO_2. New Entry. The recommended values are from a study by Kreutter et al. (1991). Their k_o value agrees with the measurement of Mellouki et al. (1989) at 300K. A Patrick and Golden (1983) type calculation using the known structure of the more stable $BrNO_2$ isomer and the measured equilibrium by Kreutter et al. (1991) underpredicts k_o by an order of magnitude. Participation by other electronic states and isomers such as BrONO merits further consideration, in keeping with the chlorine analog.

20. BrO + NO_2. Earlier measurements at 300 K from Sander et al. (1981) are combined with recent work of Thorn et al. (1989) who measured the rate constant at pressures from 16 to 800 torr of N_2 and at 268, 298, and 346 K. A recent study by Danis et al. (1990) reports $k_o = (3.8 \pm 0.8) \times 10^{-31}$ $(T/298)^{-2.4 \pm 0.5}$ for $M=O_2$. The recommended value for n is taken from Thorn et al. (1989) and Danis et al. (1990). The value of k_o seems large and possible isomer formation cannot be ignored even though similar suggestions for ClO + NO_2 are not important.

21. F + O_2. A recent study by Pagsberg et al. (1987) reports k_0 in Argon = 4.38×10^{-33} $(T/300)^{-1.2}$. This is in good agreement with earlier values of Smith and Wrigley (1980), Smith and Wrigley (1981), Shamonina and Kotov (1979), Arutyhonov et al. (1976) and slightly lower than the values of Chen et al. (1977) and Chegodaev et al. (1978). Lyman and Holland (1988) report a slightly lower value in Ar and 298K. We assume that $\beta_{Ar} = \beta_{N2}$ at all temperatures.

    Pagsberg et al. (1987), also determined the equilibrium constant and thus ΔH_f (FO_2). See Note 11 of Table 3. A calculation such as described in Patrick and Golden (1983), using the new value yields: $k_o = 1.06 \times 10^{-33}$ $(T/300)^{-1.5}$ using $\beta_{N2} = 0.3$ (i.e., $<\Delta E> = 2kJ\ mol^{-1}$). This is not good agreement.

22. F + NO. Parameters estimated from strong collision calculations with $<\Delta E>$ set at .42 kcal/$mole^{-1}$, yielding b = 0.30 at 300 K and $\beta = 0.38$ at 200 K.

23. F + NO_2. Experimental data of Fasano and Nogar (1983) were used to determine both the high and low pressure limits at 300 K. They fit their data to an expression such as recommended here.

    Treatment of the data for this system requires knowledge of the relative stabilities of FNO_2 and FONO. Patrick and Golden (1983) assumed that the difference between these would be the same as between the $ClNO_2$ isomers. Thus, they concluded that k_{300}^{0} $(FNO_2) = 8.9 \times 10^{-31}$ and k_{300}^{0} (FONO) = 2.4×10^{-30}, and that FONO would be formed ~3 times more favorably than FNO_2. We have found an error of a factor of four in their calculations, which would predict k_{300}^{0} (FONO) $\simeq 1.06 \times 10^{-29}$, and thus an overwhelming amount of FONO. The measured value is k ~1.06×10^{-30}, which is one-tenth of the predicted value.

    A calculation at the MP-3/6-31G* level by Evleth (private communication, 1984) indicates that the FONO is much more than 10 kcal mol^{-1} less stable than FNO_2 and that its rate of formation can be ignored. Thus, we have k(exp) = k$(FNO_2) = 1.06 \times 10^{-30}$.

    The value of n = 2 is from Patrick and Golden, and the value of m is a rough estimate from similar reactions.

24. $FO + NO_2$. Low-pressure limit from strong collision calculation and $\beta = 0.33$. T-dependence from resultant $<\Delta E> = .523$ kcal mole^{-1}. High-pressure limit and T-dependence estimated. Once again (see Note 20) multiple channels could be important here, which would mean that the reaction between FO and NO_2 could be much faster, since these values consider only $FONO_2$ formation.

25. $CH_3 + O_2$. Low-pressure limit from Seltzer and Bayes (1983). (These workers determined the rate constants as a function of pressure in N_2, Ar, O_2, and He. Only the N_2 points were used directly in the evaluation, but the others are consistent.) Plumb and Ryan (1982b) report a value in He which is consistent within error limits with the work of Seltzer and Bayes. Pilling and Smith (1985) have measured this process in Ar (32-490 torr). Their low pressure limiting rate constant is consistent with this evaluation, but their high pressure value is a little low. Cobos et al. (1985) have made measurements in Ar and N_2 from 0.25 to 150 atmospheres. They report parameters somewhat different than recommended here, but their data are reproduced well by the recommended values. The work of Laguna and Baughcum (1982) seems to be in the fall-off region. Results of Pratt and Wood (1984) in Ar are consistent with this recommendation, although the measurements are indirect. Their T-dependence is within our estimate. As can be seen from Patrick and Golden (1983), the above value leads to a very small β, ~.02, and thus temperature dependence is hard to calculate. The suggested value has been changed from the previous evaluation to accommodate the values of Keiffer et al. (1987) who measure the process in Ar between 20 and 600 torr and in the range $334 \leq T/K \leq 582$. Ryan and Plumb (1984) suggest that the same type of calculation as employed by Patrick and Golden yields a reasonable value of β. We have not been able to reproduce their results. The high pressure rate constant fits the data of Cobos et al. (1985). The temperature dependence is an estimate. (Data of van den Bergh and Callear (1971), Hochanadel et al. (1977), Basco et al. (1972), Washida and Bayes (1976), Laufer and Bass (1975), and Washida (1980) are also considered.) The fit to Keiffer et al. (1987) is very good, suggesting that the temperature dependence for the high pressure limit is also reasonable.

26. $C_2H_5 + O_2$. A relative rate study by Kaiser et al. (1990) yields:

$k_\infty = (9.2 \pm 0.9) \times 10^{-12}$ cm^3 molecule^{-1}s^{-1}

$k_0 = (6.5 \pm 2.0) \times 10^{-29}$ cm^6 molecule^{-2}s^{-1} in He at 298K and pressures between 3 and 1500 torr. Their k_∞ agrees with the value calculated by Wagner et al. (1990) ($k_\infty = 7 \times 10^{-12}$ cm^3 molecule^{-1}s^{-1}) using variational RRKM theory. The extrapolation to the low pressure limit is difficult due to the complex potential energy surface, but agrees with a Patrick and Golden (1983) type calculation using $\Delta H^o_0 = 32.4$ kcal mol^{-1}. The recommended values use the calculated temperature dependence and a 2.5 times higher rate constant for air as the bath gas.

27. $CH_3O + NO$. New Entry. The recommended values are taken from the results of Frost and Smith (1990b) in argon.

Temperature dependences are from their higher temperature results. The low pressure rate constant is consistent with the measurement of McCaulley et al. (1990) in helium and half the value from Troe type calculations. A bimolecular path also exists, forming $HNO + CH_2O$ (Frost and Smith (1990b)).

28. $CH_3O + NO_2$. New Entry. Recommended values at 298K from the study of Frost and Smith (1990a) in argon. Low pressure results agree with the measurements of McCaulley et al. (1985) in helium. Temperature dependences are estimated.

29 $C_2H_5O + NO$. New Entry. High pressure rate constant at 298K from Frost and Smith (1990b). Low pressure value estimated from a Troe calculation, and temperature dependences from similar reactions.

30. $C_2H_5O + NO_2$. New Entry. High pressure rate constant at 298K from Frost and Smith (1990a). Other values estimated from similar reactions.

31. $CH_3O_2 + NO_2$. Parameters from a reasonable fit to the temperature and pressure-dependent data in Sander and Watson (1980) and Ravishankara et al. (1980a). The former reference reports their room-temperature data in the same form as herein, but they allow F_c to vary. They report:

$$k_0 = 2.33 \times 10^{-30},\ k_\infty = 8 \times 10^{-12},\ F_c = 0.4$$

which is not a qualitatively different fit to the data at 300K. The latter reference reports temperature dependence as:

$$k_0 = 2.2 \times 10^{-30}\,(T/300)^{-2.5},\ k_\infty = 7 \times 10^{-12}\,(T/300)^{-3.5},\ F_c = 0.4$$

These parameters are a better fit at all temperatures than those recommended here. We do not adopt them since they are not much better in stratospheric range, and they would require both a change in our $F_c = 0.6$ format, and the adoption of a quite large negative activation energy for k_∞.

The CODATA recommendation (Baulch et al., 1982) are: $k_0 = 2.3 \times 10^{-30}\,(T/300)^{-4}$, $k_\infty = 8 \times 10^{-12}$ and $F_c = e^{-T/320} + e^{-1280/T}$; yielding $F_c = .41 + 300$ K and .54 at 200 K. These values do not fit the data as well as the current recommendations. It is interesting to note that the data require a negative T-dependence for k_∞, similar to our $HO_2 + NO_2$ recommendation, and that the value of β at 300 K is ~.2.

A recent study of the reverse reaction by Zabel et al. (1989) reports: $k_0/[N_2] = 9.0 \times 10^{-5}\,\exp(-80.6$ kJ $\text{mole}^{-1}/RT)$ cm^3 molecule^{-1} sec^{-1}; $k_\infty = 1.1 \times 10^{16}\,\exp(-87.8$ kJ $\text{mole}^{-1}/RT)$ sec^{-1}

Fc = 0.4.

The values recommended herein taken with the value of the equilibrium constant in Table 3, fit the data in Zabel et al. (1989) very well.

Destriau and Troe (1990) have fit the above data to

$k_o/[N_2] = 2.5 \times 10^{-30}\,(T/298)^{-5.5}$

$k_\infty = 7.5 \times 10^{-12}$ independent of temperature

Fc = 0.36.

32. $OH + SO_2$. Values of the rate constant as a function of pressure at 298 K from Leu (1982), Paraskevopoulos et al. (1983), and Wine et al. (1984). The value of the low pressure limit is from Leu (1982), corrected for fall-off. The high pressure limit is from a fit to all the data.

The value of n comes from the above data combined with calculations such as those of Patrick and Golden (1983), except that the heat of formation of $HOSO_2$ is raised by 4 kcal mol^{-1}, as suggested by the work of Margitan (1984). The value of m is estimated. This is not a radical-radical reaction and is unlikely to have a positive value of m. The limit of m = -2 corresponds to a real activation energy of ~1 kcal mol^{-1}. Earlier data listed in Baulch et al. (1980) and Baulch et al. (1982) are noted. Recent work of Martin et al. (1986), Barnes et al. (1986a), and Lee et al. (1990) confirm the current evaluation.

33. $OH + C_2H_4$. Experimental data of Tully (1983), Davis et al. (1975), Howard (1976), Greiner (1970a), Morris et al. (1971), and Overend and Paraskevopolous (1977b) in helium, Atkinson et al. (1977) in argon, and Lloyd et al. (1976) and Cox (1975) and Klein et al. (1984) in nitrogen/oxygen mixtures, have been considered in the evaluation. This well-studied reaction is considerably more complex than most others in this table. The parameters recommended here fit exactly the same curve proposed by Klein et al. (1984) at 298 K. An error in the k_0 value has been corrected from the previous evaluation. Discrepancies remain and the effect of multiple product channels is not well understood. Kuo and Lee (1991) report very strong temperature dependence for the low pressure limit (n=4). Calculations of the

type in Patrick and Golden (1983) yield the recommended value. The high-pressure limit temperature dependence has been determined by several workers. Almost all obtain negative activation energies, the Zellner and Lorenz (1984) value being equivalent to $m = +0.8$ over the range $(296 < T/K < 524)$ at about 1 atmosphere. Although this could theoretically arise at a result of reversibility, the equilibrium constant is too high for this possibility. If there is a product channel that proceeds with a low barrier via a tight transition state, a complex rate constant may yield the observed behavior. The actual addition process ($OH + C_2H_4$) may even have a small positive barrier. The recommended limits encompass the reported values.

34. $OH + C_2H_2$. The rate constant for this complex process has recently been re-examined by G. P. Smith et al. (1984) in the temperature range from 228 to 1400 K, and in the pressure range 1 to 760 torr. Their analysis, which is cast in similar terms to those used here, is the source of the rate constants and temperature dependences at both limits. The negative value of m reflects the fact that their analysis includes a 1.2 kcal/mole barrier for the addition of OH to C_2H_2. The data analyzed include those of Pastrana and Carr (1974), Perry et al. (1977), Michael et al. (1980), and Perry and Williamson (1982). Other data of Wilson and Westenberg (1967), Breen and Glass (1971), Smith and Zellner (1973), and Davis et al. (1975) were not included. A recent study by Liu et al. (1988) is in general agreement with the recommendation.

    Calculations of k_o via the methods of Patrick and Golden (19830 yield values compatible with those of Smith et al.

35. $CF_3 + O_2$. Caralp et al. (1986) have measured the rate constant in N_2 between 1 and 10 torr. This supplants the value from Caralp and Lesclaux (1983). They recommend different parameters, but the data are well represented by the currently recommended values. Data of Ryan and Plumb (1982) are in agreement.

36. $CF_2Cl + O_2$. New Entry. Values estimated from other reactions in this series.

37. $CFCl_2 + O_2$. Values for both low and high-pressure limits at 300K are from Caralp and Lesclaux (1983). Temperature dependences are rough estimates based on calculations and similar reactions.

38. $CCl_3 + O_2$. Experimental data of Ryan and Plumb (1984) and Danis et al. (1991) have been considered in the evaluation. Ryan and Plumb (1984) report:

    $k_o^{300}(He) = (5.8 \pm 0.6) \times 10^{-31}$, $k_\infty^{300} = 2.5 \times 10^{-12}$ with $F = 0.25$.

    We find a good fit to their data using $F = 0.6$ to yield

    $k_o^{300}(He) = 4 \times 10^{-31}$, keeping $k_\infty^{300} = 2.5 \times 10^{-12}$.

    The recommended value of $k_o^{300}(N_2)$ is 2.5 times the value in He and n=6 is selected to give a good fit to Danis et al.'s (1991) data.

    A Patrick and Golden (1983) type calculation using the thermochemistry of Russell et al. (1990) yields $k_o^{300} = 1.5 \times 10^{-30}$. A value of $k_\infty^{300} = 5 \times 10^{-12}$ has been reported by Cooper et al. (1980).

39. $CFCl_2O_2 + NO_2$. Based on experiments in O_2 of Caralp et al. (1988), who suggest a somewhat different fitting procedure, but the values recommended here fit the data just as well. Destriau and Troe (1990) use yet a different fitting procedure that does not represent the data quite as well as that recommended herein. Reverse rate data are given by Köppenkastrop and Zabel (1991).

40. $CF_2ClO_2 + NO_2$. New Entry. Data are from Moore and Carr (1990).

Their measurements are consistent with others in the series. n and m are same as the other reactions in this family.

41. $CH_3C(O)O_2 + NO_2$. New Entry. Parameters are from Bridier et al. (1990) who report in the format represented here, but using Fc = 0.3. Their values are: $k_0^{300} = (2.7 \pm 1.5) \times 10^{-28}$, $k_\infty^{300} = (12.1 \pm 2.0) \times 10^{-12}$, with $n = 7.1 \pm 1.7$ and $m = 0.9 \pm 0.15$.

42. $CF_3O_2 + NO_2$. Exactly same note as 39.

43. $CCl_3O_2 + NO_2$. Exactly same note as 39.

44. HS + NO. Data and analysis are from the work of Black et al. (1984). The temperature dependence of k_∞ has been estimated.

45. CH_3S + NO. New Entry. The recommended values are from the study by Balla et al. (1986) at 296K in nitrogen. Temperature dependences are derived from the higher temperature results of the same study.

46. $Na + O_2$. A recent study by Plane and Rajasekhar (1989) finds $k_o = (2.9 \pm 0.7) \times 10^{-30}$ at 300 K with $n = 1.30 \pm .04$. They also estimate $k_\infty \approx 6 \times 10^{-10}$ with a slight positive temperature dependence. The k_o value is about 60% higher than that of Silver et al. (1984b). The recommended value is an average of the two studies. It is consistent with the value measured by Marshall et al. (1990) at 600K.

47. $NaO + O_2$. Ager and Howard (1986) have measured the low-pressure limit at room temperature in several bath gases. Their value in N_2 is used in the recommendation. They performed a Troe calculation as per Patrick and Golden (1983) to obtain collision efficiency and temperature dependence. They obtained a high-pressure limit rate constant by use of a simple model. The temperature dependence is estimated.

48. $NaO + CO_2$. Ager and Howard (1986) have measured the rate constant for this process in the "fall-off" regime. Their lowest pressures are very close to the low-pressure limit. The temperature dependence is an estimate. Ager and Howard calculate the high-pressure rate constant from a simple model. The temperature dependence is an estimate.

49. $NaOH + CO_2$. Ager and Howard (1987b) have measured the low-pressure limiting rate constant. The temperature dependence is an estimate. Ager and Howard have calculated the high-pressure limit using a simple model. The temperature dependence is an estimate.

EQUILIBRIUM CONSTANTS

Format

Some of the three-body reactions in Table 2 form products which are thermally unstable at atmospheric temperatures. In such cases the thermal decomposition reaction may compete with other loss processes, such as photodissociation or radical attack. Table 3 lists the equilibrium constants, K(T), for eleven reactions which may fall into this category. The table has three column entries, the first two being the parameters A and B which can be used to express K(T):

$$K(T)/\text{cm}^3 \text{ molecule}^{-1} = A \exp(B/T) \ (200 < T < 300 \text{ K})$$

The third column entry in Table 3 is the calculated value of K at 298 K.

The data sources for K(T) are described in the individual notes to Table 3. When values of the heats of formation and entropies of all species are known at the temperature T, we note that:

$$\log [K(T)/\text{cm}^3 \text{ molecule}^{-1}] = \frac{\Delta S_T^o}{2.303R} - \frac{\Delta H_T^o}{2.303RT} + \log T - 21.87$$

Where the superscript "o" refers to a standard state of one atmosphere. In some cases K values were calculated from this equation, using thermochemical data. In other cases the K values were calculated directly from kinetic data for the forward and reverse reactions. When available, JANAF values were used for the equilibrium constants. The following equations were then used to calculate the parameters A and B:

$$B/°K = 2.303 \ [\log \frac{K_{200}}{K_{300}}] \ (\frac{300 \times 200}{300 - 200})$$

$$= 1382 \log(K_{200}/K_{300})$$

$$\log A = \log K(T) - B/2.303\ T$$

TABLE 3. EQUILIBRIUM CONSTANTS

Reaction	A/cm^3 molecule^{-1}	B±ΔB/°K	K_{eq}(298 K)	f(298 K)^a	Note
$HO_2 + NO_2 \rightarrow HO_2NO_2$	2.1×10^{-27}	10900±1000	1.6×10^{-11}	5	1
$NO + NO_2 \rightarrow N_2O_3$	3.0×10^{-27}	4700±100	2.1×10^{-20}	2	2
$NO_2 + NO_2 \rightarrow N_2O_4$	5.9×10^{-29}	6600±250	2.5×10^{-19}	2	3
* $NO_2 + NO_3 \rightarrow N_2O_5$	4.0×10^{-27}	10930±500	3.4×10^{-11}	1.3	4
$CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2$	1.3×10^{-28}	11200±1000	2.7×10^{-12}	2	5
& $Cl + O_2 \rightarrow ClOO$	5.7×10^{-25}	2500±750	2.5×10^{-21}	2	6
* $ClO + O_2 \rightarrow ClO{\cdot}O_2$	2.9×10^{-26}	<3700	$<7.2\times10^{-21}$	-	7
$Cl + CO \rightarrow ClCO$	1.6×10^{-25}	4000±500	1.1×10^{-19}	5	8
& $ClO + ClO \rightarrow Cl_2O_2$	3.0×10^{-27}	8450±850	6.2×10^{-15}	2	9
$ClO + OClO \rightarrow Cl_2O_3$	1.6×10^{-27}	7200±1400	5.0×10^{-17}	10	10
$F + O_2 \rightarrow FOO$	3.2×10^{-25}	6100±1200	2.5×10^{-16}	10	11
# $OH + CS_2 \rightarrow CS_2OH$	4.5×10^{-25}	5140±500	1.4×10^{-17}	1.4	12

K/cm^3 molecule^{-1} = A exp (B/T) [200 < T/K < 300]

[a] f(298) is the uncertainty factor at 298 K. To calculate the uncertainty at other temperatures, use the expression:

$$f(T) = f(298\ K) \exp\left(\Delta B \left| \frac{1}{T} - \frac{1}{298} \right|\right).$$

* Indicates a change from the previous Panel evaluation (JPL 90-1).

& Indicates a change in the Note.

# Indicates a new entry that was not in the previous evaluation.

NOTES TO TABLE 3

1. $HO_2 + NO_2$. The value was obtained by combining the data of Sander and Peterson (1984) for the rate constant of the reaction as written and that of Graham et al. (1977) for the reverse reaction. From the equilibrium constant, it may be inferred that the thermal decomposition of HO_2NO_2 is unimportant in the stratosphere, but it is important in the troposphere.

2. $NO + NO_2$. The data are from JANAF. This process is included because a recent measurement of the rate constant by Smith and Yarwood (1986) shows that it is too slow to be an important rate process but there will be some equilibrium concentration present.

3. $NO_2 + NO_2$. The data are from JANAF. Recent rate data for this process are reported by Brunning et al. (1988), Borrell et al. (1988) and Gozel et al. (1984).

4. $NO_2 + NO_3$. The recommendation is an average of the temperature dependence data of Burrows et al. (1985c) and Cantrell et al. (1988), and the room temperature data of Tuazon et al. (1983), Perner et al. (1985) and Hjorth et al. (1992). The entry in Table 3 is not exactly equivalent to the ratio of the forward rate constant from Table 2 and the reverse rate constant from the data of Connell and Johnston (1979) and Viggiano et al. (1981). However, there is agreement within experimental error over the range of mutual measurement.

5. $CH_3O_2 + NO_2$. Thermochemical values at 300 K for $CH_3O_2NO_2$ and CH_3O_2 are from Baldwin (1982). In the absence of data, $\Delta H°$ and $\Delta S°$ were assumed to be independent of temperature. Bahta et al. (1982) have measured k(dissociation) at 263 K. Using the values of k(recombination) suggested in this evaluation, they compute $K(263) = (2.68 \pm 0.26) \times 10^{-10}$ cm^3. Our values predict 3.94×10^{-10} cm^3, in good agreement.

   Zabel et al. (1989) have measured k(dissociation) as a function of pressure and temperature. (See Note 25, Table 2). Their values are in good agreement with Bahta et al. (1982) and taken together with k(recombination) would lead to $A = 5.2 \times 10^{-28}$ and $B = 10,766$. This is sufficiently close to the value in Table 3 to forgo any change in parameters, but the uncertainty has been reduced.

6. $Cl + O_2$. Baer et al. (1991) determined K in the temperature range 180 to 300K. Their value at 185.4 K ($5.23 \times 10^{-19} cm^3$ $molecule^{-1}$) compares well with the Nicovich et al. (1991) measurement $K = 4.77 \times 10^{-19}$ cm^3 $molecule^{-1}$, and within error with the Mauldin et al. (1992) value of 2.55×10^{-19} cm^3 $molecule^{-1}$. A different expression for K by Avallone et al. (1991) gives S^o_{298} (ClOO) = 61.8 cal K^{-1} mol^{-1} and $\Delta H^o_{f,298}$ (ClOO) = 23.3 kcal mol^{-1}. Using known thermochemistry for Cl and O_2 and computed entropy values for ClOO, $\Delta H_{f,298}$ (ClOO) = 23.3 ±0.6 kcal $mole^{-1}$ is obtained from the Nicovich et al. (1991) data. The value of S^o_{298} (ClOO) = 64.3 cal $mole^{-1}$ K^{-1} used is computed from a structure with a 105° bond angle and Cl-O and O-O bond lengths of 1.73 and 1.30 Å respectively. Frequencies of 1441, 407 and 373 cm^{-1} are from Arkell and Schwager (1967). Symmetry number is 1 and degeneracy is 2.

7. $ClO + O_2$. DeMore (1990) reports $K < 4 \times 10^{-18}$ cm^3 $molecule^{-1}$ at 197K. His temperature dependence of the equilibrium constant is estimated using S^o_{298} $(ClO \cdot O_2)$ = 73 cal $mol^{-1}K^{-1}$ and $\Delta H^o_{298} < 7.7$ kcal mol^{-1}. A higher value of K has been proposed by Prasad (1980), but it requires $S°(ClO \cdot O_2)$ to be about 83 cal mol^{-1} K^{-1}, which seems unreasonably high. Carter and Andrews (1981) found no experimental evidence for $ClO \cdot O_2$ in matrix experiments.

8. $Cl + CO$. From Nicovich et al. (1990a) who measured both k and K between 185 and 260K in N_2. They report $\Delta H_{f,298}$ (ClCO) = -5.2 ± 0.7 kcal $mole^{-1}$.

9. $ClO + ClO$. The value is from Cox & Hayman (1988). The corresponding second law entropy of the dimer is 74 cal mol^{-1} K^{-1} and ΔH_f = 31.5 kcal mol^{-1}. Previous work of Cox and Derwent (1979) and

Hayman et al. (1986) is noted. The ab initio frequencies of McGrath et al. (1990) give a lower entropy; the resulting parameters for K(T) are indistinguishable from those in the Table.

10. ClO + OClO. Data is taken from Hayman and Cox (1989). They deduce $\Delta H_f (Cl_2O_3) = 34 \pm 3$ kcal $mole^{-1}$ and $S°(Cl_2O_3) = 80 \pm 12$ cal $mole^{-1}$ $°K^{-1}$.

11. F + O_2. Calculated from JANAF thermochemical values except for $\Delta H_{f.298}(FO_2) = 6.24 \pm 0.5$ kcal $mole^{-1}$. The latter was taken from Pagsberg et al. (1987). This direct measurement, which falls between the earlier disputed values, would seem to settle that controversy, but (see Note 21 of Table 2) the calculated value of k_o is not in good agreement with the experiment.

12. OH + CS_2. New Entry. Average of the concordant recent measurements of Murrells et al. (1990) and Diau and Lee (1991) between 249 and 298K. The measurements of Hynes et al. (1988) indicate a less stable adduct, but agree within combined experimental error.

PHOTOCHEMICAL DATA

Discussion of Format and Error Estimates

In Table 4 we present a list of photochemical reactions considered to be of stratospheric interest. The absorption cross sections of O_2 and O_3 largely determine the extent of penetration of solar radiation into the stratosphere and troposphere. Some comments and references to these cross sections are presented in the text, but only a sample of the data is listed here. (See, for example, WMO Report #11, 1982; WMO-NASA, 1985.) The photodissociation of NO in the O_2 Schumann-Runge band spectral range is another important process requiring special treatment and is not discussed in this evaluation (see, for example, Frederick and Hudson, 1979; Allen and Frederick, 1982; and WMO Report #11, 1982).

For some other species having highly structured spectra, such as CS_2 and SO_2, some comments are given in the text, but the photochemical data are not presented. The species CH_2O, NO_2, NO_3, ClO, BrO, and OClO also have complicated spectra, but in view of their importance for atmospheric chemistry a sample of the data is presented in the evaluation; for more detailed information on their high-resolution spectra and temperature dependence, the reader is referred to the original literature.

Table 5 gives recommended reliability factors for some of the more important photochemical reactions. These factors represent the combined uncertainty in cross sections and quantum yields, taking into consideration the atmospherically important wavelength regions, and they refer to the total dissociation rate regardless of product identity (except in the case of $O(^1D)$ production from photolysis of O_3).

The error estimates are not rigorous numbers resulting from a detailed error propagation analysis of statistical manipulations of the different sets of literature values; they merely represent a consensus among the panel members as to the reliability of the data for atmospheric photodissociation calculations, taking into account the difficulty of the measurements, the agreement among the results reported by various groups, etc.

The absorption cross sections are defined by the following expression of Beer's Law:

$$I = I_0 \exp(-\sigma n l),$$

where I_0 and I are the incident and transmitted light intensity, respectively; σ is the absorption cross section in cm^2 $molecule^{-1}$; n is the concentration in molecule cm^{-3}, and l is the pathlength in cm. The cross sections are room temperature values at the specific wavelengths listed in the table, and the expected photodissociation quantum yields are unity, unless otherwise stated.

Table 4. Photochemical Reactions

*	$O_2 + h\nu \rightarrow O + O$	
&	$O_3 + h\nu \rightarrow O_2 + O$	
*	$O_3 + h\nu \rightarrow O_2 + O(^1D)$	
*	$HO_2 + h\nu \rightarrow$ products	
#	$H_2O + h\nu \rightarrow H + OH$	
	$H_2O_2 + h\nu \rightarrow OH + OH$	
	$NO + h\nu \rightarrow N + O$	
	$NO_2 + h\nu \rightarrow NO + O$	
	$NO_3 + h\nu \rightarrow$ products	
&	$N_2O + h\nu \rightarrow N_2 + O(^1D)$	
	$N_2O_5 + h\nu \rightarrow$ products	
	$NH_3 + h\nu \rightarrow NH_2 + H$	
*	$HONO + h\nu \rightarrow OH + NO$	
&	$HNO_3 + h\nu \rightarrow OH + NO_2$	
	$HO_2NO_2 + h\nu \rightarrow$ products	
	$Cl_2 + h\nu \rightarrow Cl + Cl$	
&	$ClO + h\nu \rightarrow Cl + O$	
*	$ClOO + h\nu \rightarrow$ products	
&	$OClO + h\nu \rightarrow O + ClO$	
*	$ClO_3 + h\nu \rightarrow$ products	
#	$Cl_2O + h\nu \rightarrow$ products	
&	$Cl_2O_2 + h\nu \rightarrow$ products	
#	$Cl_2O_3 + h\nu \rightarrow$ products	
#	$Cl_2O_4 + h\nu \rightarrow$ products	
#	$Cl_2O_6 + h\nu \rightarrow$ products	
	$HCl + + h\nu \rightarrow H + Cl$	
	$HOCl + h\nu \rightarrow OH + Cl$	
	$ClNO + h\nu \rightarrow Cl + NO$	
	$ClNO_2 + h\nu \rightarrow$ products	
	$ClONO + h\nu \rightarrow$ products	
&	$ClONO_2 + h\nu \rightarrow$ products	
	$CCl_4 + h\nu \rightarrow$ products	
	$CCl_3F + h\nu \rightarrow$ products	
	$CCl_2F_2 + h\nu \rightarrow$ products	
*	$CHClF_2 + h\nu \rightarrow$ products	
	$CH_3Cl + h\nu \rightarrow$ products	
#	$CF_2ClCFCl_2 + h\nu \rightarrow$ products	
#	$CF_2ClCF_2Cl + h\nu \rightarrow$ products	
#	$CF_3CF_2Cl + h\nu \rightarrow$ products	
	$CH_3CF_2Cl + h\nu \rightarrow$ products	
*	$CF_3CHCl_2 + h\nu \rightarrow$ products	
	$CF_3CHFCl + h\nu \rightarrow$ products	
*	$CH_3CFCl_2 + h\nu \rightarrow$ products	
	$CH_3CCl_3 + h\nu \rightarrow$ products	
#	$CF_3CF_2CHCl_2 + h\nu \rightarrow$ products	
#	$CF_2ClCF_2CHFCl + h\nu \rightarrow$ products	
*	$CF_3Br + h\nu \rightarrow$ products	
*	$CF_2Br_2 + h\nu \rightarrow$ products	
*	$CF_2ClBr + h\nu \rightarrow$ products	
*	$CF_2BrCF_2Br + h\nu \rightarrow$ products	
#	$CH_3Br + h\nu \rightarrow$ products	
#	$CHBr_3 + h\nu \rightarrow$ products	
	$CF_4 + h\nu \rightarrow$ products	
	$C_2F_6 + h\nu \rightarrow$ products	
	$SF_6 + h\nu \rightarrow$ products	
	$CCl_2O + h\nu \rightarrow$ products	
	$CClFO + h\nu \rightarrow$ products	
	$CF_2O + h\nu \rightarrow$ products	
	$BrO + h\nu \rightarrow$ products	
	$BrONO_2 + h\nu \rightarrow$ products	
	$HF + h\nu \rightarrow H + F$	
	$CO + h\nu \rightarrow C + O$	(1)
	$CO_2 + h\nu \rightarrow CO + O$	(1)
	$CH_4 + h\nu \rightarrow$ products	(2)
*	$CH_2O \rightarrow$ products	
	$CH_3OOH + h\nu \rightarrow$ products	
	$HCN + h\nu \rightarrow$ products	
	$CH_3CN + h\nu \rightarrow$ products	
	$SO_2 + h\nu \rightarrow SO + O$	
	$OCS + h\nu \rightarrow CO + S$	
	$H_2S + h\nu \rightarrow HS + H$	
	$CS_2 + h\nu \rightarrow$ products	
	$NaCl + h\nu \rightarrow Na + Cl$	
	$NaOH + h\nu \rightarrow Na + OH$	

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(1) Hudson and Kieffer (1975).

(2) Turco (1975).

\# New Entry.

* Indicates a change in the recommendation from the previous evaluation.

& Indicates a change in the note.

Table 5. Combined Uncertainties for Cross Sections and Quantum Yields

Species	Uncertainty
O_2 (Schumann-Runge bands)	1.2
O_2 (Continua)	1.2
O_3 (Cross Sections Only)	1.1
$O_3 \rightarrow O(^1D)$	1.2
NO_2	1.2
NO_3	2.0
N_2O	1.2
N_2O_5	2.0
H_2O_2	1.3
HNO_3	1.3
HO_2NO_2	2.0
CH_2O	1.4
HCl	1.1
HOCl	1.4
$ClONO_2$	1.3
CCl_4	1.1
CCl_3F	1.1
CCl_2F_2	1.1
CH_3Cl	1.1
CF_2O	2.0
CH_3OOH	1.5
$BrONO_2$	1.4
CF_3Br	1.3
CF_2ClBr	2.0
CF_2Br_2	2.0
$C_2F_4Br_2$	2.0

$O_2 + h\nu \rightarrow O + O$

The photodissociation of molecular oxygen in the stratosphere is due primarily to absorption of solar radiation in the 200-220 nm wavelength region, i.e., within the Herzberg continuum. The 185-200 nm region--the O_2 Schumann-Runge band spectral range--is also very important, since solar radiation penetrates efficiently into the stratosphere at those wavelengths.

Frederick and Mentall (1982), Herman and Mentall (1982) and Anderson and Hall (1983, 1986) estimated O_2 absorption cross sections from balloon measurements of solar irradiance in the stratosphere. These authors find the cross sections in the 200-210 nm range to be ~35% smaller than the smallest of the older laboratory results, which are those of Shardanand and Prasad Rao (1977). The more recent laboratory studies (Johnston et al., 1984; Cheung et al., 1984, 1986; Jenovrier et al., 1986) confirm the lower values obtained from solar irradiance measurements. The recommended absorption cross section values between 205 and 240 nm are listed in Table 6; they are taken from Yoshino et al. (1988b), and are based on the recent laboratory measurements.

Table 6. Absorption Cross Sections of O_2 Between 205 and 240 nm

λ (nm)	$10^{24}\sigma$ (cm^2)	λ (nm)	$10^{24}\sigma$ (cm^2)
205	7.35	223	3.89
206	7.13	224	3.67
207	7.05	225	3.45
208	6.86	226	3.21
209	6.68	227	2.98
210	6.51	228	2.77
211	6.24	229	2.63
212	6.05	230	2.43
213	5.89	231	2.25
214	5.72	232	2.10
215	5.59	233	1.94
216	5.35	234	1.78
217	5.13	235	1.63
218	4.88	236	1.48
219	4.64	237	1.34
220	4.46	238	1.22
221	4.26	239	1.10
222	4.09	240	1.01

The studies of the penetration of solar radiation in the atmosphere in the Schumann-Runge wavelength region were based originally on laboratory measurements of cross sections which were affected by instrumental parameters due to insufficient spectral resolution. Yoshino et al. (1983) reported high resolution O_2 cross section measurements at 300 K, between 179 and 202 nm, obtaining the first set of results which is independent of the instrument width. Additional studies at other temperatures, wavelengths and isotopic compositions have been carried out by Yoshino et al. (1984; 1987; 1988a; 1989; 1990), Lewis et al. (1986a,b), Cheung et al. (1990) and Chiu et al. (1990). Minschwaner et al. (1992) have fit temperature dependent O_2 cross sections between 175 and 204 nm with polynomial expressions, providing accurate means of determining the Schumann-Runge band cross sections with a model that incorporates the most recent laboratory data. Coquart et al. (1990) have reported Herzberg continuum absorption cross sections in the wavelength region 196-205 nm of the Schumann-Runge bands.

For parameterizations of the O_2 absorption in the Schumann-Runge bands used in atmospheric modeling calculations see, e.g., the review in WMO (1985). More recent work by Murtagh (1988), Nicolet and Kennes (1989) and Minschwaner and Salawitch (private communication, 1992) incorporates results of the later laboratory measurements into efficient schemes for computing broad-band transmission and photolysis rates. Transmission values obtained by Murtagh (1988) agree well with the WMO (1986) recommendations, although the high resolution calculations of Minschwaner and Salawitch differ with the WMO values by as much as 10 - 20% at some wavelengths.

In view of the quality of the high resolution laboratory measurements, the primary source of uncertainty in modeling O_2 photolysis in the Schumann-Runge bands (other than the issue of absolute solar irradiance) has shifted to the choice of broadband parameterization.

$O_3 + h\nu \rightarrow O + O_2$

The O_3 absorption cross sections and their temperature dependence have been measured by several groups. For a review see WMO-NASA, 1985; this reference should be consulted to obtain data for atmospheric modeling calculations. Table 7 lists merely a sample of the data taken from this review, namely the 273 K cross section values averaged over the wavelength intervals commonly employed in modeling calculations, except for the wavelength range 185 to 225 nm, where the present recommendation incorporates the averaged values from the recent work of Molina and Molina (1986); the older values were based on the work of Inn and Tanaka (1953). The temperature effect is negligible for wavelengths shorter than ~260 nm. Recent work by Mauersberger et al. (1986, 1987) yields a value of 1137×10^{-20} cm^2 for the cross section at 253.7 nm, the mercury line wavelength; it is about 1% smaller than the commonly accepted value of 1147×10^{-20} cm^2 reported by Hearn (1961), and about 2% smaller than the value obtained by Molina and Molina (1986), 1157×10^{-20} cm^2; see also Barnes and Mauersberger (1987). The reason for the small discrepancy, which appears to be beyond experimental precision, is unclear. Cacciani et al. (1989) reported measurements of the ozone cross sections in the wavelength range from 339 to 355 nm, in reasonable agreement with the present recommendation; the same group has measured recently the cross sections in the 590-610 nm region, at 230 K and at 299 K (Amoruso et al., 1990).

Table 7. Absorption Cross Sections of O_3 at 273 K

λ (nm)	10^{20} σ(cm^2) average	λ (nm)	10^{20} σ(cm^2) average
175.439 - 176.991	81.1	238.095 - 240.964	797
176.991 - 178.571	79.9	240.964 - 243.902	900
178.571 - 180.180	78.6	243.902 - 246.914	1000
180.180 - 181.818	76.3	246.914 - 250.000	1080
181.818 - 183.486	72.9	250.000 - 253.165	1130
183.486 - 185.185	68.8	253.165 - 256.410	1150
185.185 - 186.916	62.2	256.410 - 259.740	1120
186.916 - 188.679	57.6	259.740 - 263.158	1060
188.679 - 190.476	52.6	263.158 - 266.667	965
190.476 - 192.308	47.6	266.667 - 270.270	834
192.308 - 194.175	42.8	270.270 - 273.973	692
194.175 - 196.078	38.3	273.973 - 277.778	542
196.078 - 298.020	34.7	277.778 - 281.690	402
198.020 - 200.000	32.3	281.690 - 285.714	277
200.000 - 202.020	31.4	285.714 - 289.855	179
202.020 - 204.082	32.6	289.855 - 294.118	109
204.082 - 206.186	36.4	294.118 - 298.507	62.4
206.186 - 208.333	43.4	298.507 - 303.030	34.3
208.333 - 210.526	54.2	303.030 - 307.692	18.5
210.526 - 212.766	69.9	307.692 - 312.5	9.80
212.766 - 215.054	92.1	312.5 - 317.5	5.01
215.054 - 217.391	119	317.5 - 322.5	2.49
217.391 - 219.780	155	322.5 - 327.5	1.20
219.780 - 222.222	199	327.5 - 332.5	0.617
222.222 - 224.719	256	332.5 - 337.5	0.274
224.719 - 227.273	323	337.5 - 342.5	0.117
227.273 - 229.885	400	342.5 - 347.5	0.0588
229.885 - 232.558	483	347.5 - 352.5	0.0266
232.558 - 235.294	579	352.5 - 357.5	0.0109
235.294 - 238.095	686	357.5 - 362.5	0.00549

The quantum yields for O(^{1}D) production, $\Phi(O^1D)$ for wavelengths near 310 nm, i.e., the energetic threshold or fall-off region, have been measured mostly relative to quantum yields for wavelengths shorter than 300 nm, which were assumed to be unity. There are several studies which indicate that this assumption is not correct: Fairchild et al. (1978) observed approximately 10% of the primary photolysis products in the ground state channel, that is $\Phi(O^3P) \sim 0.1$, at 274 nm: Sparks et al. (1980) also report $\Phi(O^3P) \sim 0.1$, at 266 nm; according to Brock and Watson (1980b) $\Phi(O^1D) = 0.88$ at 266 nm; Amimoto et al. (1980) report $\Phi(O^1D) = 0.85$ at 248 nm, and Wine and Ravishankara (1982) measured directly $\Phi(O^1D) = 0.9$ at 248 nm. There are also some indications that (O^{1}D) decreases slightly between 304 and 275 nm (see Brock and Watson, 1980a,b). Turnipseed et al. (1991b) report $\Phi(O^1D) = 0.87 \pm 0.04$ at 222 nm and 0.46 ± 0.29 at 193 nm. The photochemistry of ozone has been reviewed by Wayne (1987) and by Steinfeld et al. (1987). Table 8 presents a polynomial expression for the (O^{1}D) quantum yield as a function of wavelength and temperature in the fall-off range, 305 to 320 nm. The upper limiting value of $\Phi(O^1D)$ at 305 nm is taken as 0.95, in view of the above-mentioned evidence for a less than unit value, but with a slight maximum near 305 nm.

The recommendations of Table 8 are based on the high resolution laser data of Arnold et al. (1977), Brock and Watson (1980b), and Trolier and Wiesenfeld (1988). An exception is that the "tail" sometimes seen in the laser experiments at longer wavelengths has been eliminated, on the grounds that it is not reproduced in the monochromator experiments and may be an artifact. Temperature dependence in the present recommendation is based on the monochromator experiments of Moortgat and Kudzus (1978).

The uncertainty in the quantum yield values for atmospheric modeling purposes is estimated in Table 5 as 1.2. However, considering the importance of the process additional high resolution measurements should be carried out in the fall-off region (the Huggins bands) for cross sections, quantum yields and their temperature dependency.

Table 8. Mathematical Expression for O(^{1}D) Quantum Yields, Φ, in the Photolysis of O_3 in the Wavelength Region 305 to 320 nm.

$$\Phi(\lambda, T) = a_0(\tau) + a_1(\tau)x + a_2(\tau)x^2 + a_3(\tau)x^3 + a_4(\tau)x^4 + a_5(\tau)x^5 + a_6(\tau)x^6$$

where $x = (\lambda - 305)$ and $\tau = (298 - T(K))$ and

$$a_0 = .94932 - 1.7039 \cdot 10^{-4}\,\tau + 1.4072 \cdot 10^{-6}\,\tau^2$$

$$a_1 = -2.4052 \cdot 10^{-2} + 1.0479 \cdot 10^{-3}\,\tau - 1.0655 \cdot 10^{-5}\,\tau^2$$

$$a_2 = 1.8771 \cdot 10^{-2} - 3.6401 \cdot 10^{-4}\,\tau - 1.8587 \cdot 10^{-5}\,\tau^2$$

$$a_3 = 1.454 \cdot 10^{-2} - 4.7787 \cdot 10^{-5}\,\tau + 8.1277 \cdot 10^{-6}\,\tau^2$$

$$a_4 = 2.3287 \cdot 10^{-3} + 1.9891 \cdot 10^{-5}\,\tau - 1.1801 \cdot 10^{-6}\,\tau^2$$

$$a_5 = -1.4471 \cdot 10^{-4} - 1.7188 \cdot 10^{-6}\,\tau + 7.2661 \cdot 10^{-8}\,\tau^2$$

$$a_6 = 3.183 \cdot 10^{-6} + 4.6209 \cdot 10^{-8}\,\tau - 1.6266 \cdot 10^{-9}\,\tau^2$$

If $\phi(\lambda,T) < 0.02$ then let $\phi(\lambda,T) = 0$. For $\lambda > 320$ nm, $\phi(\lambda,T) = 0$.
Expression is valid for the temperature range 220-300 K.

$H_2O + h\nu \rightarrow H + OH$

Water vapor has a continuum absorption spectrum at wavelengths longer than 145 nm, with a maximum around 165 nm, the cross sections falling off rapidly toward longer wavelengths; the photodissociation threshold occurs at 246 nm. Below 69 nm the spectrum is also a continuum, and between 69 and 145 nm it consists of diffuse bands. In the atmosphere water vapor is photodissociated mainly by the solar Lyman alpha line (121.6 nm).

The absorption cross sections and the photochemistry of water vapor have been reviewed, for example, by Hudson (1971; 1974), by Hudson and Kiefer (1975); by Calvert and Pitts (1966c); and by Okabe (1978).

The recommended absorption cross sections are taken from the review by Hudson and Kiefer (1975), and are listed in Table 9 between 175 and 190 nm. At these wavelengths the quantum yield for production of H and OH is unity. At shorter wavelengths H_2 and O are also formed as primary products; Stief et al. (1975) report a quantum yield of 0.11 for this process between 105 and 145 nm.

Table 9. Absorption Cross Sections of H_2O Vapor

λ(nm)	$10^{20}\sigma(\text{cm}^2)$
175.5	262.8
177.5	185.4
180.0	78.1
182.5	23.0
185.0	5.5
186.0	3.1
187.5	1.6
189.3	0.7

$HO_2 + h\nu \rightarrow OH + O$

The absorption cross sections of the hydroperoxyl radical, HO_2, in the 200-250 nm region have been measured at room temperature by Paukert and Johnston (1972), Hochanadel et al. (1972; 1980), Cox and Burrows (1979), McAdam et al. (1987), Kurylo et al. (1987a), Moortgat et al. (1989), Dagaut and Kurylo (1990), by Lightfoot and Jemi-Alade (1991), who measured the cross sections up to 777 K, and by Crowley et al. (1991); and by Sander et al. (1982) at 227.5 nm. There are significant discrepancies in the cross section values, particularly around 200 nm; no definitive explanation of the differences can be offered at present.

Table 10 lists the recommended cross sections, which are taken from the review by Wallington et al. (1992). Photolysis of HO_2 in the stratosphere and troposphere is slow and can be neglected, but the UV absorption cross sections are important in laboratory studies of reaction kinetics.

Lee (1982) has detected $O(^1D)$ as a primary photodissociation product at 193 and at 248 nm, with a quantum yield which is about 15 times larger at the longer wavelength. The absolute quantum yield for $O(^1D)$ production has not been reported yet.

Table 10. Absorption Cross Sections of HO_2

λ(nm)	$10^{20}\sigma(cm^2)$
190	387
200	458
210	454
220	373
230	245
240	135
250	60

$H_2O_2 + h\nu \rightarrow OH + OH$

The recommended 298 K absorption cross section values, listed in Table 11, are the mean of the data of Lin et al. (1978b), Molina and Molina (1981), Nicovich and Wine (1988), and Vaghjiani and Ravishankara (1989b). Molina and Molina (1981) supersedes the earlier results of Molina et al. (1977a). Nicovich and Wine measured the cross sections at $\lambda \geq 230$ relative to the values at 202.6, $\sigma = 4.32 \times 10^{-19}$ cm^2, and at 228.8 nm, $\sigma = 1.86 \times 10^{-19}$ cm^2. The values are within 2% of the recommended value.

Table 11. Absorption Cross Sections of H_2O_2 Vapor

λ(nm)	$10^{20}\sigma(cm^2)$		λ(nm)	$10^{20}\sigma(cm^2)$	
	298 K	355 K		298 K	355 K
190	67.2		270	3.3	3.5
195	56.4		275	2.6	2.8
200	47.5		280	2.0	2.2
205	40.8		285	1.5	1.6
210	35.7		290	1.2	1.3
215	30.7		295	0.90	1.0
220	25.8		300	0.68	0.79
225	21.7		305	0.51	0.58
230	18.2	18.4	310	0.39	0.46
235	15.0	15.2	315	0.29	0.36
240	12.4	12.6	320	0.22	0.27
245	10.2	10.8	325	0.16	0.21
250	8.3	8.5	330	0.13	0.17
255	6.7	6.9	335	0.10	0.13
260	5.3	5.5	340	0.07	0.10
265	4.2	4.4	345	0.05	0.06
			350	0.04	0.05

Nicovich and Wine have measured the temperature dependence of these cross sections. They expressed the measured cross sections as the sum of two components; σ_1, due to absorption from H_2O_2 which has the O-O stretch excited and the other σ_0, due to absorption by ground state molecules. For atmospheric calculations the expression given in Table 12 may be used. The photodissociation quantum yield is believed to be unity. At and above 248 nm, the major photodissociation process is that leading to OH, i.e., the quantum yield for OH production is 2 (Vaghjiani and Ravishankara, 1990 and Vaghjiani et al., 1992).

Table 12. Mathematical Expression for Absorption Cross Sections of H_2O_2 as a Function of Temperature

$$10^{21}\,\sigma(\lambda,T) = \chi \sum_{n=0}^{7} A_n \lambda^n + (1-\chi) \sum_{n=0}^{4} B_n \lambda^n$$

Where T: temperature Kelvin; λ: nm; $\chi = [1 + \exp(-1265/T)]^{-1}$

$A_0 = 6.4761 \times 10^4$ $B_0 = 6.8123 \times 10^3$

$A_1 = -9.2170972 \times 10^2$ $B_1 = -5.1351 \times 10^1$

$A_2 = 4.535649$ $B_2 = 1.1522 \times 10^{-1}$

$A_3 = -4.4589016 \times 10^{-3}$ $B_3 = -3.0493 \times 10^{-5}$

$A_4 = -4.035101 \times 10^{-5}$ $B_4 = -1.0924 \times 10^{-7}$

$A_5 = 1.6878206 \times 10^{-7}$

$A_6 = -2.652014 \times 10^{-10}$

$A_7 = 1.5534675 \times 10^{-13}$

Range 260-350 nm; 200-400 K

$NO_2 + h\nu \rightarrow NO + O$

Earlier recommendations for the absorption cross sections of nitrogen dioxide were taken from the work of Bass et al. (1976). More recent measurements have been reported by Schneider et al. (1987), at 298 K, for the wavelength range from 200 to 700 nm; and by Davidson et al. (1988), from 270 to 420 nm, in the 232-397 K temperature range. At room temperature the agreement between these three sets of measurements is good; within 5 % between 305 and 345 nm, and within 10% at the longer wavelengths. The agreement is poor below room temperature, as well as at the shorter wavelengths. A possible cause for the discrepancies is the presence of N_2O_4. The corrections needed to account for the presence of this species are largest around 200 nm, where it absorbs strongly. The corrections are also large at the lowest temperatures, because a significant fraction of the NO_2 forms N_2O_4. On the other hand, there is no error apparent in the corrections carried out by Bass et al., so that the reason for the discrepancy is not clear.

Table 13 lists the recommended absorption cross sections, averaged over the wavelength intervals used for atmospheric photodissociation calculations. For the wavelength range from 200 to 274 nm the values are taken from Schneider et al. (1987); in this range the temperature effect is negligible. For the 274 to 420 nm region the temperature-dependent values are taken from Davidson et al. (1988).

Table 13. Absorption Cross Sections of NO_2

λ (nm)	10^{20} σ, average at 25°C cm^2 molecule^{-1}	λ (nm)	10^{20} σ, average at 0°C (cm^2 molecule^{-1})	10^{22} a* (cm^2 molecule^{-1} degree^{-1})
202.02 - 204.08	41.45	273.97 - 277.78	5.03	0.075
204.08 - 206.19	44.78	277.78 - 281.69	5.88	0.082
206.19 - 208.33	44.54	281.69 - 285.71	7.00	-0.053
208.33 - 210.53	46.41	285.71 - 289.85	8.15	-0.043
210.53 - 212.77	48.66	289.85 - 294.12	9.72	-0.031
212.77 - 215.06	48.18	294.12 - 298.51	11.54	-0.162
215.06 - 217.39	50.22	298.51 - 303.03	13.44	-0.284
217.39 - 219.78	44.41	303.03 - 307.69	15.89	-0.357
217.78 - 222.22	47.13	307.69 - 312.50	18.67	-0.536
222.22 - 224.72	37.72	312.5 - 317.5	21.53	-0.686
224.72 - 227.27	39.29	317.5 - 322.5	24.77	-0.786
227.27 - 229.89	27.40	322.5 - 327.5	28.07	-1.105
229.89 - 232.56	27.78	327.5 - 332.5	31.33	-1.355
232.56 - 235.29	16.89	332.5 - 337.5	34.25	-1.277
235.29 - 238.09	16.18	337.5 - 342.5	37.98	-1.612
238.09 - 240.96	8.812	342.5 - 347.5	40.65	-1.890
240.96 - 243.90	7.472	347.5 - 352.5	43.13	-1.219
243.90 - 246.91	3.909	352.5 - 357.5	47.17	-1.921
246.91 - 250.00	2.753	357.5 - 362.5	48.33	-1.095
250.00 - 253.17	2.007	262.5 - 367.5	51.66	-1.322
253.17 - 256.41	1.973	367.5 - 372.5	53.15	-1.102
256.41 - 259.74	2.111	372.5 - 377.5	55.08	-0.806
259.74 - 263.16	2.357	377.5 - 382.5	56.44	-0.867
263.16 - 266.67	2.698	382.5 - 387.5	57.57	-0.945
266.67 - 270.27	3.247	387.5 - 392.5	59.27	-0.923
270.27 - 273.97	3.785	392.5 - 397.5	58.45	-0.738
		397.5 - 402.5	60.21	-0.599
		402.5 - 407.5	57.81	-0.545
		407.5 - 412.5	59.99	-1.129
		412.5 - 417.5	56.51	0.001
		417.5 - 422.5	58.12	-1.208

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* The quantity a is the temperature coefficient of σ as defined in the equation $\sigma(t) = \sigma(0°) + a \times t$ where t is in degrees Celsius.

The earlier recommendation for quantum yields was based on the work of Harker et al. (1977) and of Davenport (1978) for the atmospherically important 375-470 nm region. The work by Gardner et al. (1987) yields values which are in much better agreement with the values reported earlier by Jones and Bayes (1973). The recommended quantum yield values, listed in Table 14, are in agreement with the recommendation of Gardner et al. (1987); they are based on a smooth fit to the data of Gardner et al. (1987) for the wavelength range from 334 to 404 nm; Harker et al. (1977) for 397-420 nm (corrected for cross sections); Davenport (1978) for 400-420 nm; and Jones and Bayes (1973) for 297-412 nm. Direct measurements of the solar photodissociation rate of NO_2 in the troposphere by Parrish et al. (1988) and by Shetter et al. (1988) agree better with theoretical estimates based on this recommendation than with the earlier one.

Table 14. Quantum Yields for NO_2 Photolysis

λ, nm	Φ	λ, nm	Φ
< 285	1.000	393	0.953
290	0.999	394	0.950
295	0.998	395	0.942
300	0.997	396	0.922
305	0.996	397	0.870
310	0.995	398	0.820
315	0.994	399	0.760
320	0.993	400	0.695
325	0.992	401	0.635
330	0.991	402	0.560
335	0.990	403	0.485
340	0.989	404	0.425
345	0.988	405	0.350
350	0.987	406	0.290
355	0.986	407	0.225
360	0.984	408	0.185
365	0.983	409	0.153
370	0.981	410	0.130
375	0.979	411	0.110
380	0.975	412	0.094
381	0.974	413	0.083
382	0.973	414	0.070
383	0.972	415	0.059
384	0.971	416	0.048
385	0.969	417	0.039
386	0.967	418	0.030
387	0.966	419	0.023
388	0.964	420	0.018
389	0.962	421	0.012
390	0.960	422	0.008
391	0.959	423	0.004
392	0.957	424	0.000

$NO_3 + h\nu \rightarrow NO + O_2$ (Φ_1)

$\rightarrow NO_2 + O$ (Φ_2)

The absorption cross sections of the nitrate free radical, NO_3, have been studied by (1) Johnston and Graham (1974); (2) Graham and Johnston (1978); (3) Mitchell et al. (1980); (4) Marinelli et al. (1982); (5) Ravishankara and Wine (1983); (6) Cox et al. (1984a); (7) Burrows et al. (1985b); (8) Ravishankara and Mauldin (1986); (9) Sander (1986); (10) Cantrell et al. (1987a); and (11) Canosa-Mas et al. (1987). The 1st and 4th studies required calculation of the NO_3 concentration by modeling a complex kinetic system. The other studies are more direct and the results in terms of integrated absorption coefficients are in good agreement. The recommended value at 298 K and 662 nm, $(2.00 \pm 0.25) \times 10^{-17}$ cm^2, is the average of the results of studies (4), (5) and (7) through (11). The values in the wavelength range 600-670 nm, shown in Figure 2 and listed in Table 15, were calculated using the spectra measured in studies (8), (9) and (11), and normalizing the 662 nm value to the above average. The spectra obtained in other studies are consulted for a more extended wavelength range. The temperature dependence of the 662 nm band has been studied by Ravishankara and Mauldin (1986), Sander (1986) and Cantrell et al. (1987a), while the first two investigators observe the cross section at 662 nm to increase with decreasing temperature, Cantrell et al. (1987a) found no measurable temperature dependence. The reason for this discrepancy is not clear.

The quantum yields Φ_1 and Φ_2 have been measured by Graham and Johnston (1978), and under higher resolution by Magnotta and Johnston (1980), who report the product of the cross section times the quantum yield in the 400 to 630 nm range. The total quantum yield value, $\Phi_1 + \Phi_2$, computed from the results of this latter study and the cross sections of Graham and Johnston (1978), is above unity for $\lambda < 610$ nm, which is, of course, impossible. Hence, there is some systematic error and it is most likely in the primary quantum yield measurements. Magnotta and Johnston (1980) and Marinelli et al. (1982) have discussed the probable sources of this error, but the question remains to be resolved and further studies are in order. At present, the recommendation remains unchanged, namely, to use the following photodissociation rates estimated by Magnotta and Johnston (1980) for overhead sun at the earth's surface.

$$J_1(NO + O_2) = 0.022\ s^{-1}$$

$$J_2(NO_2 + O) = 0.18\ s^{-1}.$$

The spectroscopy of NO_3 has been reviewed recently by Wayne et al. (1991). The reader is referred to this work for a more detailed discussion of the cross section and quantum yield data, and for estimates of the photodissociation rates as a function of zenith angle.

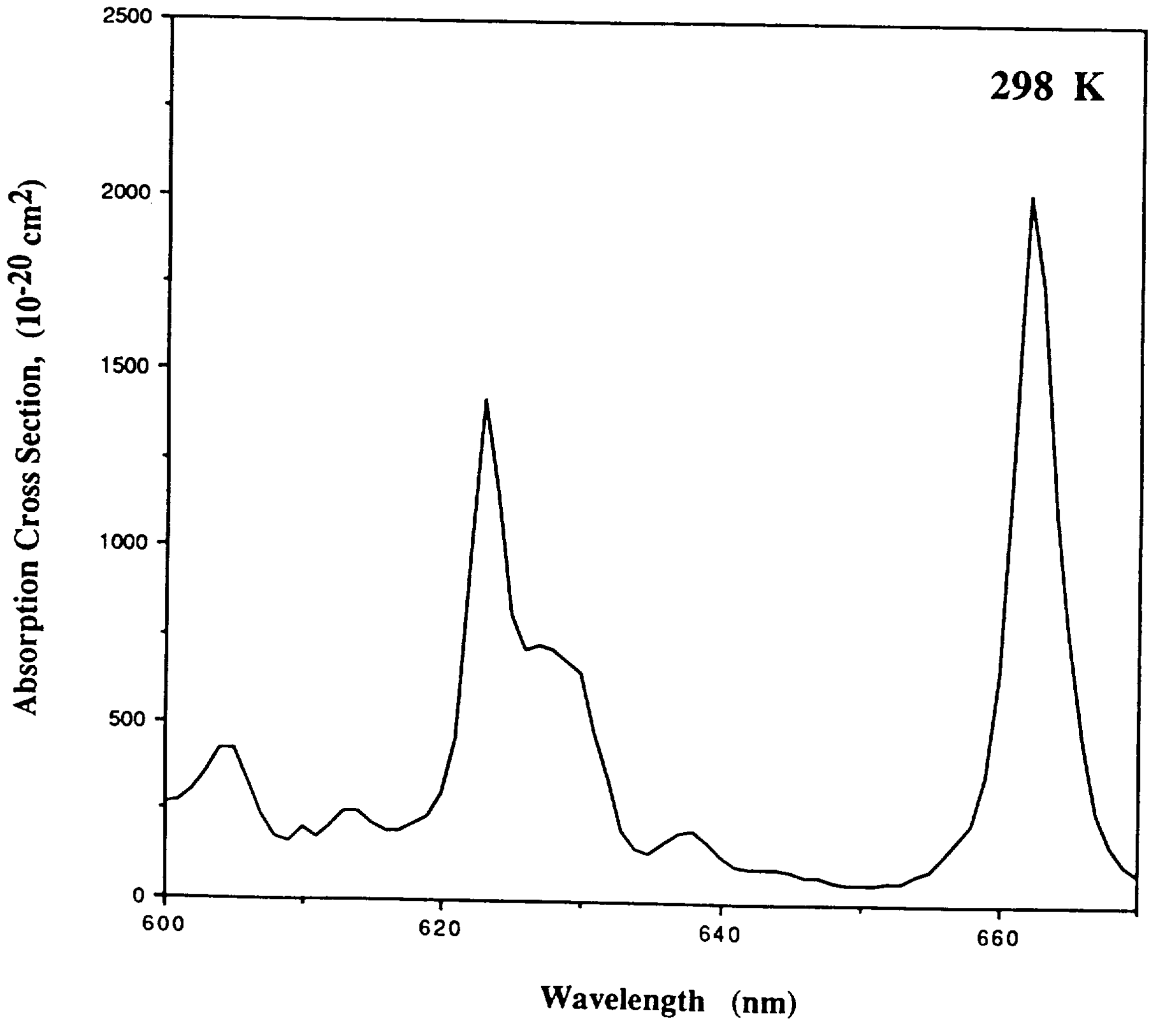

Figure 2. Absorption Spectrum of NO_3

Table 15. Absorption Cross Sections of NO_3 at 298 K

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
600	258	625	796	648	60
601	263	626	703	649	51
602	302	627	715	650	49
603	351	628	702	651	52
604	413	629	672	652	55
605	415	630	638	653	61
606	322	631	470	654	76
607	225	632	344	655	93
608	170	633	194	656	131
609	153	634	142	657	172
610	192	635	128	658	222
611	171	636	159	659	356
612	202	637	191	660	658
613	241	638	193	661	1308
614	242	639	162	662	2000
615	210	640	121	663	1742
616	190	641	99	664	1110
617	189	642	91	665	752
618	208	643	93	666	463
619	229	644	92	667	254
620	292	645	85	668	163
621	450	646	72	669	113
622	941	647	69	670	85
623	1407				
624	1139				

$N_2O + h\nu \rightarrow N_2 + O(^1D)$

The recommended values are taken from the work of Selwyn et al. (1977), who measured the temperature dependence of the absorption cross sections in the atmospherically relevant wavelength region. They have fitted their data with the expression shown in Table 16; Table 17 presents the room temperature data. Hubrich and Stuhl (1980) remeasured the N_2O cross sections at 298 K and 208 K and Merienne et al. (1990) in the range from 220 K to 296 K. The results of these two sets of measurements are in very good agreement with those of Selwyn et al. The quantum yield for photodissociation is unity and the products are N_2 and $O(^1D)$ (Zelikoff and Aschenbrand, 1954; Paraskevopoulos and Cvetanovic, 1969; Preston and Barr, 1971; Simonaitis et al., 1972). The yield of $N(^4s)$ and $NO(^2\Pi)$ is less than 1% (Greenblatt and Ravishankara, 1990).

Table 16. Mathematical Expression for Absorption Cross Sections of N_2O as a Function of Temperature

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$$\ln \sigma(\lambda,T) = \sum_{n=0}^{4} A_n \lambda^n + (T-300) \exp\left(\sum_{n=0}^{3} B_n \lambda^n\right)$$

Where T: temperature Kelvin; λ: nm;

$A_0 = 68.21023$	$B_0 = 123.4014$
$A_1 = -4.071805$	$B_1 = -2.116255$
$A_2 = 4.301146 \times 10^{-2}$	$B_2 = 1.111572 \times 10^{-2}$
$A_3 = -1.777846 \times 10^{-4}$	$B_3 = -1.881058 \times 10^{-5}$
$A_4 = 2.520672 \times 10^{-7}$	

Range 173 to 240 nm; 194 to 320 K

Table 17. Absorption Cross Sections of N_2O at 298 K

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
173	11.3	196	6.82	219	0.115
174	11.9	197	6.10	220	0.0922
175	12.6	198	5.35	221	0.0739
176	13.4	199	4.70	222	0.0588
177	14.0	200	4.09	223	0.0474
178	13.9	201	3.58	224	0.0375
179	14.4	202	3.09	225	0.0303
180	14.6	203	2.67	226	0.0239
181	14.6	204	2.30	227	0.0190
182	14.7	205	1.95	228	0.0151
183	14.6	206	1.65	229	0.0120
184	14.4	207	1.38	230	0.00955
185	14.3	208	1.16	231	0.00760
186	13.6	209	0.980	232	0.00605
187	13.1	210	0.755	233	0.00478
188	12.5	211	0.619	234	0.00360
189	11.7	212	0.518	235	0.00301
190	11.1	213	0.421	236	0.00240
191	10.4	214	0.342	237	0.00191
192	9.75	215	0.276	238	0.00152
193	8.95	216	0.223	239	0.00123
194	8.11	217	0.179	240	0.00101
195	7.57	218	0.142		

$N_2O_5 + h\nu \rightarrow$ Products

The absorption cross sections of dinitrogen pentoxide, N_2O_5, have been measured at room temperature by Jones and Wulf (1937) between 285 and 380 nm, by Johnston and Graham (1974) between 210 and 290 nm, by Graham (1975) between 205 and 380 nm; and for temperatures in the 223 to 300 K range by Yao et al. (1982), between 200 and 380 nm. The agreement is good, particularly considering the difficulties in handling N_2O_5. The recommended cross section values, listed in Table 18, are taken from Yao et al. (1982); for wavelengths shorter than 280 nm there is little or no temperature dependence, and between 285 and 380 nm the temperature effect is best computed with the expression listed at the bottom of Table 18.

There are several studies on the primary photolysis products of N_2O_5: Swanson et al. (1984) have measured the quantum yield for NO_3 production at 249 and at 350 nm, obtaining a value close to unity, which is consistent with the observations of Burrows et al. (1984b) for photolysis at 254 nm. Barker et al. (1985) report a quantum yield for $O(^3P)$ production at 290 nm of less than 0.1, and near unity for NO_3. For O-atom production Margitan (private communication, 1985) measured a quantum yield value of 0.35 at 266 nm, and Ravishankara et al. (1986) report values of 0.72, 0.38, 0.21 and 0.15 at 248, 266, 287 and 289 nm, respectively, with a quantum yield near unity for NO_3 production at all these wavelengths. It appears, then, that NO_3 is produced with unit quantum yield while the O-atom and hence the NO yield increases at shorter wavelengths with a consequent decrease in the NO_2 yield. The study of Oh et al. (1986) indicates that, besides NO_3, the primary photolysis products are a wavelength dependent mixture of NO_2, NO_2^* and NO + O, where NO_2^* represents one or more excited electronic states, most likely the $^2B_1$ state.

Table 18. Absorption Cross Sections of N_2O_5

λ (nm)	$10^{20}\sigma(cm^2)$	λ (nm)	$10^{20}\sigma(cm^2)$
200	920	245	52
205	820	250	40
210	560	255	32
215	370	260	26
220	220	265	20
225	144	270	16.1
230	99	275	13.0
235	77	280	11.7
240	62		

For 285 nm < λ < 380 nm; 300 K > T > 225 K:

$10^{20}\,\sigma = \exp[2.735 + ((4728.5 - 17.127\,\lambda)/T)]$

where σ is in cm^2/molecule; λ in nm; and T in Kelvin.

HONO + hv → HO + NO

The ultraviolet spectrum of HONO between 300 and 400 nm has been studied by Stockwell and Calvert (1978) by examination of its equilibrium mixtures with NO, NO_2, H_2O, N_2O_3 and N_2O_4; the possible interferences by these compounds were taken into account. More recently, Vasudev (1990) measured relative cross sections by monitoring the OH photodissociation product with laser-induced fluorescence; and Bongartz et al. (1991) determined absolute cross section values at 0.1 nm resolution in a system containing a highly diluted mixture of NO, NO_2, H_2O and HONO, by measuring total NO_x, NO and NO_2. There are some discrepancies between these two recent sets of results in terms of relative peak heights; however, both yield essentially the same photodissociation rate provided Vasudev's relative data are normalized to match the cross section value reported by Bongartz et al. at 354 nm; at this wavelength the value reported earlier by Stockwell and Calvert is about 20% smaller. The recommended values, listed in Table 19, are taken from Bongartz et al.

Table 19. Absorption Cross Sections of HONO

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
310	1.3	339	18.8	368	52.0
311	1.9	340	10.0	369	38.8
312	2.8	341	17.0	370	17.8
313	2.2	342	38.6	371	11.3
314	3.6	343	14.9	372	10.0
315	3.0	344	9.7	373	7.7
316	1.4	345	10.9	374	6.2
317	3.1	346	12.3	375	5.3
318	5.6	347	10.4	376	5.3
319	3.6	348	9.1	377	5.0
320	4.9	349	7.9	387	5.8
321	7.8	350	11.2	379	8.0
322	4.9	351	21.2	380	9.6
323	5.1	352	15.5	381	11.3
324	7.1	353	19.1	382	15.9
325	5.0	354	58.1	383	21.0
326	2.9	355	36.4	384	24.1
327	6.6	356	14.1	385	20.3
328	11.7	357	11.7	386	13.4
329	6.1	358	12.0	387	9.0
330	11.1	359	10.4	388	5.6
331	17.9	360	9.0	389	3.4
332	8.7	361	8.3	390	2.7
333	7.6	362	8.0	391	2.0
334	9.6	363	9.6	392	1.5
335	9.6	364	14.6	393	1.1
336	7.2	365	16.8	394	0.6
337	5.3	366	18.3	395	1.0
338	10.0	367	30.2	396	0.4

HNO_3 + hν → OH + NO_2

The recommended absorption cross sections, listed in Table 20, are taken from the work of Molina and Molina (1981). These data are in good agreement throughout the 190-330 nm range with the values reported by Biaume (1973). They are also in very good agreement with the data of Johnston and Graham (1973) except towards both ends of the wavelength range. Okabe (1980) has measured the cross sections in the 110-190 nm range; his results are 20-30% lower than those of Biaume and of Johnston and Graham around 185-190 nm.

Johnston et al. (1974) measured a quantum yield value of ~1 for the OH + NO_2 channel in the 200-315 nm range, using end product analysis. The quantum yield for O-atom production at 266 nm has been measured to be 0.03, and that for H-atom production less than 0.002, by Margitan and Watson (1982), who looked directly for these products using atomic resonance fluorescence. Jolly et al. (1986) measured a quantum yield for OH production of 0.89 ± 0.08 at 222 nm. Turnipseed et al. (1992) have measured a quantum yield near unity for OH production at 248 and 222 nm. However, at 193 nm they report this quantum yield to be only ~0.33, and the quantum yield for production of O-atoms to be about 0.8. Thus, it appears that HONO is a major photolysis product at 193 nm.

There are some indications that the temperature dependency of the cross sections in the 300-350 nm range is significant (R. A. Cox, private communication, 1991). Additional measurements are required of this temperature effect as well as of the cross sections at λ's longer than 330 nm, particularly in connection with polar stratospheric chemistry calculations.

Table 20. Absorption Cross Sections of HNO_3 Vapor at 298 K

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
190	1560	260	1.88
195	1150	265	1.71
200	661	270	1.59
205	293	275	1.35
210	105	280	1.10
215	35.6	285	0.848
220	15.1	290	0.607
225	8.62	295	0.409
230	5.65	300	0.241
235	3.72	305	0.146
240	2.57	310	0.071
245	2.10	315	0.032
250	1.91	320	0.012
255	1.90	325	0.005
		330	0.002

$HO_2NO_2 + h\nu \rightarrow$ Products

There are five studies of the UV spectrum of HO_2NO_2 vapor: Cox and Patrick (1979), Morel et al. (1980), Graham et al. (1978b), Molina and Molina (1981), and Singer et al. (1989). The latter three studies are the only ones covering the gas phase spectrum in the critical wavelength range for atmospheric photodissociation, that is, wavelengths longer than 290 nm. The recommended values, listed in Table 21, are an average of the work of Molina and Molina (1981) and of Singer et al. (1989), which are the more direct studies. The cross sections appear to be temperature-independent between 298 and 253 K (Singer et al. 1989). MacLeod et al. (1988) report that photolysis at 248 nm yields one third OH and NO_3 and two thirds $HO_2 + NO_2$.

Table 21. Absorption Cross Sections of HO_2NO_2 Vapor

λ (nm)	$10^{20}\,\sigma$ (cm^2)	λ (nm)	$10^{20}\,\sigma$ (cm^2)
190	1010	260	28.5
195	816	265	23.0
200	563	270	18.1
205	367	275	13.4
210	239	280	9.3
215	161	285	6.2
220	118	290	3.9
225	93.5	295	2.4
230	79.2	300	1.4
235	68.2	305	0.9
240	58.1	310	0.5
245	48.9	315	0.3
250	41.2	320	0.2
255	35.0	325	0.1

$Cl_2 + h\nu \rightarrow Cl + Cl$

The absorption cross sections of Cl_2, listed in Table 22, are taken from the work of Seery and Britton (1964). These results are in good agreement with those reported by Gibson and Bayliss (1933), Fergusson et al. (1936), and Burkholder and Bair (1983).

Table 22. Absorption Cross Sections of Cl_2

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
240	0.08	350	18.9
250	0.12	360	13.1
260	0.23	370	8.3
270	0.88	380	4.9
280	2.7	390	3.3
290	6.5	400	1.9
300	12.0	410	1.3
310	18.5	420	0.99
320	23.6	430	0.73
330	25.6	440	0.53
340	23.6	450	0.34

$ClO + h\nu \rightarrow Cl + O$

The absorption cross sections of chlorine monoxide, ClO, have been reviewed by Watson (1977). There are more recent measurements yielding results in reasonable agreement with the earlier ones, (1) by Mandelman and Nicholls (1977) in the 250-310 nm region; (2) by Wine et al. (1977) around 283 nm; (3) by Rigaud et al. (1977), (4) Jourdain et al. (1978a), (5) Sander and Friedl (1989), (6) Trolier et al. (1990) in the 270-310 nm region, and (7) Simon et al. (1990a) between 240 and 310 nm. The peak cross section at the top of the continuum is 5.2×10^{-18}, based on the average of studies (4) - (7), and Johnston et al. (1969). Figure 3 shows a spectrum of ClO. It should be noted that the cross sections on the structured part are extremely dependent on instrument resolution, and the figure is only a guide to the line positions and approximate shapes. The cross sections of the continuum are independent of temperature (Trolier et al. (1990), while the structured part is extremely temperature dependent. The bands sharpen and grow with a decrease in temperature.

The calculations of Coxon et al. (1976) and Langhoff et al. (1977) indicate that photodecomposition of ClO accounts for at most 2 to 3 percent of the total destruction rate of ClO in the stratosphere, which occurs predominantly by reaction with oxygen atoms and nitric oxide.

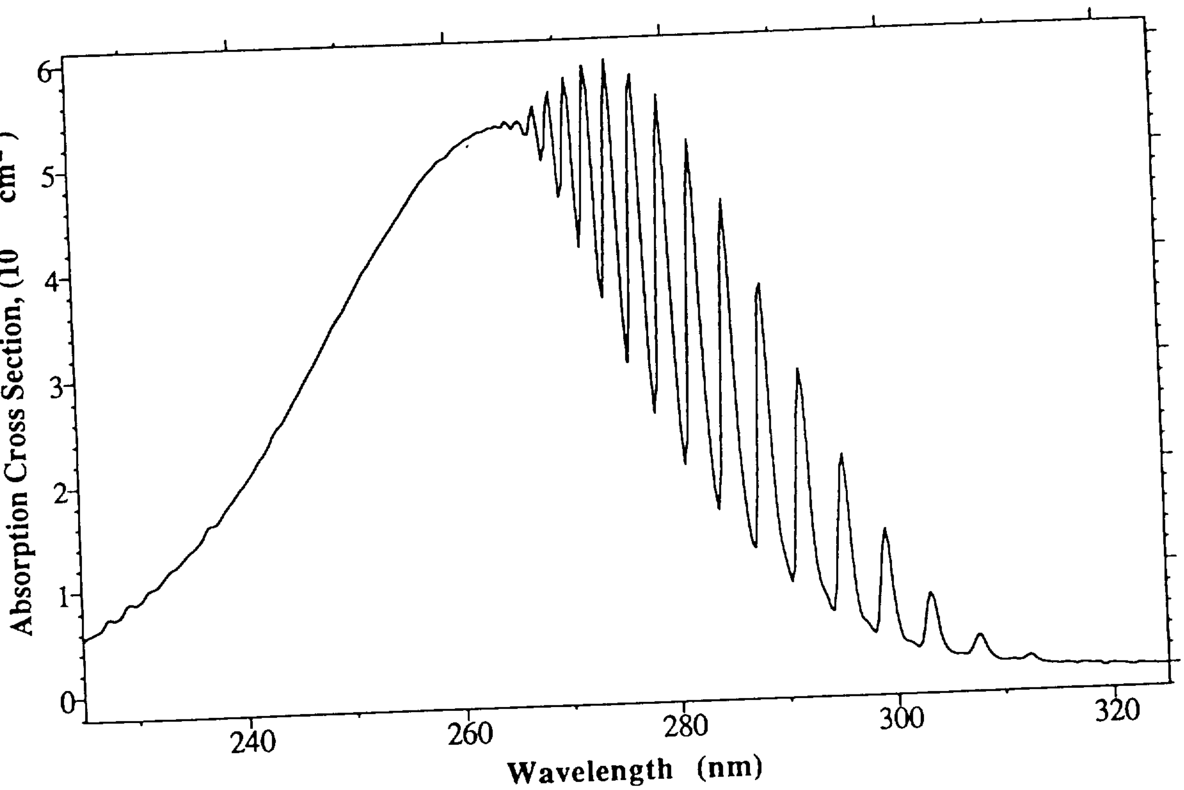


Figure 3. Absorption Spectrum of ClO

$ClOO + h\nu \rightarrow ClO + O$

Johnston et al. (1969) measured the absorption cross sections of the ClOO radical using a molecular modulation technique which required interpretation of a complex kinetic scheme. More recently, Mauldin et al. (1992) reported cross section measurements in the range from 220 to 280 nm, and Baer et al. (1992) from 240 to 300 nm. These two studies are in very good agreement, yielding cross section values which are more than twice as large as the older Johnston et al. values. The recommended cross sections are listed in Table 23, and are taken from the work of Mauldin et al.

Table 23. Absorption Cross Sections of ClOO

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
220	611	252	2630
222	670	254	2370
224	747	256	2120
226	951	258	1890
228	1100	260	1610
230	1400	262	1370
232	1650	264	1120
234	1960	266	905
236	2240	268	725
238	2520	270	596
240	2730	272	435
242	2910	274	344
244	2960	276	282
246	2980	278	210
248	2950	280	200
250	2800		

$OClO + h\nu \rightarrow O + ClO$

The spectrum of OClO is characterized by a series of well developed progressions of bands extending from ~280 to 480 nm. The spectroscopy of this molecule has been studied extensively, and the quantum yield for photodissociation appears to be unity throughout the above wavelength range. See for example, the review by Watson (1977). Birks et al. (1977) have estimated a half-life against atmospheric photodissociation of OClO of a few seconds.

The recommended absorption cross section values are those reported by Wahner et al. (1987), who measured the spectra with a resolution of 0.25 nm at 204, 296 and 378 K, in the wavelength range 240 to 480 nm. Table 24 lists the cross section values at the peak of the bands [a(0) to a(26)]. Figure 4, from Wahner et al., shows the OClO spectrum at 204 K and at room temperature.

Colussi (1990) measured the quantum yield for chlorine atom production to be less than 0.01, and for oxygen atom production to be unity (within experimental error), both at 308 nm. Vaida et al. (1989) and Ruhl et al. (1990) reported chlorine atom production at 362 nm; and Bishenden et al.

(1991) measured the quantum yield for this process to be 0.15 ± 0.10 around that same wavelength; in contrast, Lawrence et al. (1990) report a quantum yield for Cl-atom production in the 359-368 nm region of less than $5\text{x}10^{-4}$. This conclusion is supported by photofragment studies of Davis and Lee (1992), who report Cl yields <0.2% below 370 nm, rising to a maximum of 4% near 404 nm. The recommended values are based on the work of Colussi (1990), namely unit quantum yield for O-atom production.

Table 24. Absorption Cross Sections of OClO at the Band Peaks

	$10^{20}\,\sigma(\text{cm}^2)$		
λ(nm)	204 K	296 K	378 K
475.53	-	13	-
461.15	17	17	16
446.41	94	69	57
432.81	220	166	134
420.58	393	304	250
408.83	578	479	378
397.76	821	670	547
387.37	1046	844	698
377.44	1212	992	808
368.30	1365	1136	920
359.73	1454	1219	984
351.30	1531	1275	989
343.44	1507	1230	938
336.08	1441	1139	864
329.22	1243	974	746
322.78	1009	791	628
317.21	771	618	516
311.53	542	435	390
305.99	393	312	291
300.87	256	219	216
296.42	190	160	167
291.77	138	114	130
287.80	105	86	105
283.51	089	72	90
279.64	073	60	79
275.74	059	46	-
272.93	053	33	-

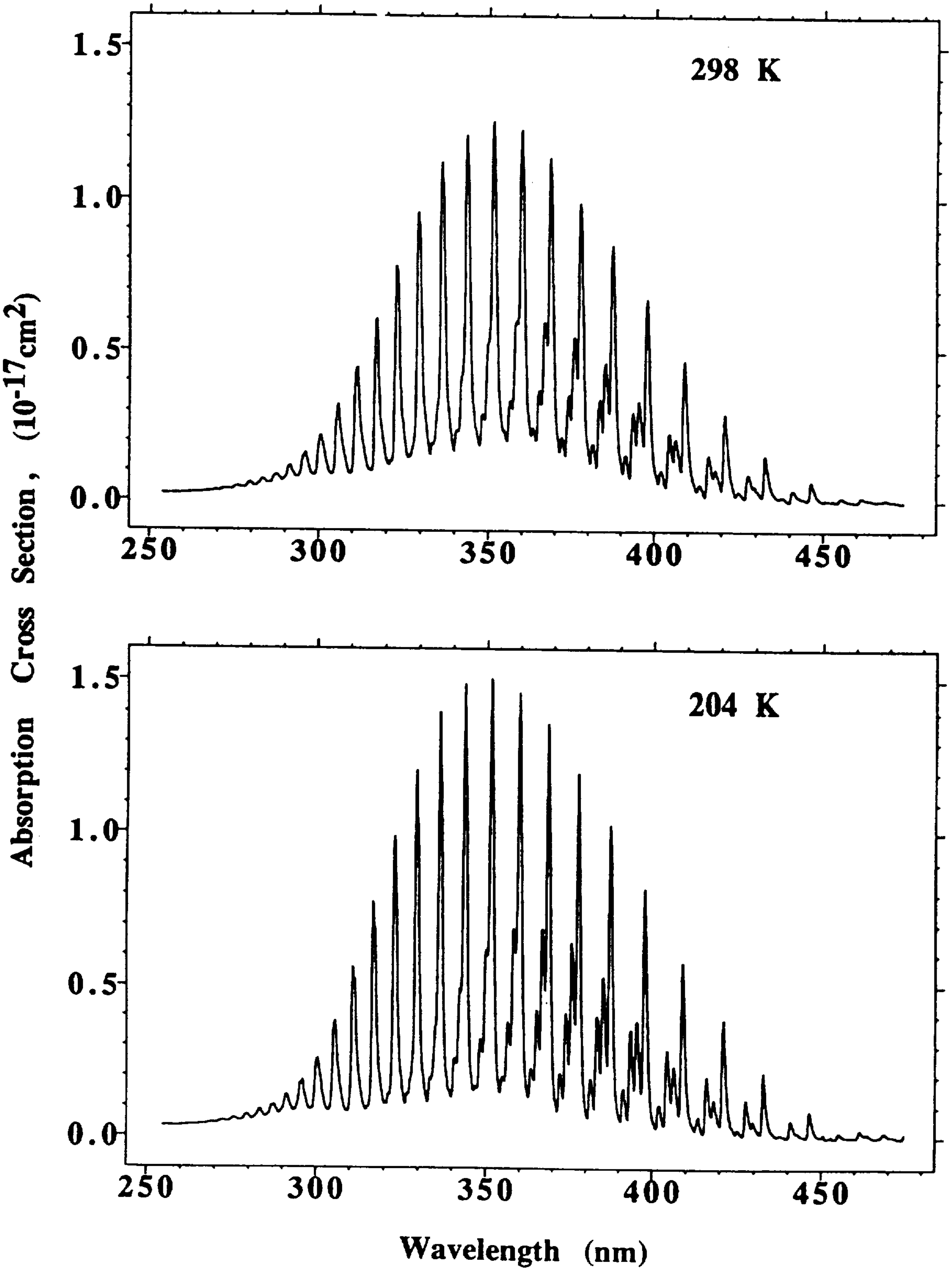


Figure 4. Absorption Spectrum of OClO

ClO_3 + hv → Products

The previous recommendation for absorption cross sections was based on the work of Goodeve and Richardson (1937). Lopez and Sicre (1990) have shown that the spectrum reported by Goodeve and Richardson is most likely that of Cl_2O_6. Thermochemical estimates by Colussi et al. (1991) further corroborate this assignment. No recommendation is given at present for the ClO_3 cross sections.

Cl_2O + hv → Products

The preferred absorption cross sections, listed in Table 25, are those reported by Knauth et al. (1979) at 298 K. They are in very good agreement with the cross sections measured by Lin (1976) and by Molina and Molina (1978); the discrepancy is largest at the longest wavelengths. Nee (1991) has recently reported cross section measurements in the 150-200 nm wavelength region.

Sander and Friedl (1989) have measured the quantum yield for production of O-atoms to be 0.25 ± 0.05, using a broadband photolysis source extending from 180 nm to beyond 400 nm. The main photolysis products are Cl and ClO.

Table 25. Absorption Cross Sections of Cl_2O

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
200	71.0	330	8.40
210	23.8	340	3.58
220	8.6	350	1.54
230	28.1	360	0.73
240	103	370	0.40
250	191	380	0.36
260	195	390	0.51
270	151	400	0.79
280	126	420	1.26
290	103	440	1.11
300	71.0	460	0.63
310	40.3	480	0.32
320	19.5	500	0.22

Cl_2O_2 + hv → Cl + ClOO

The recommended absorption cross sections for dichlorine peroxide (the ClO dimer), ClOOCl, are listed in Table 26. The values are the smoothed average of the results reported by Cox and Hayman (1988), DeMore and Tschuikow-Roux (1990), Permien et al. (1988), and Burkholder et al. (1990). These measurements were carried out in the 200-250 K temperature range; thermal decomposition of the dimer occurs very fast at higher temperatures. There is general agreement among these workers on the shape of the spectrum, and the cross section values at the maximum at about 245 nm are within 10%. There are, however, significant discrepancies, i.e., around 280 nm. The results of Burkholder et al. (1989) are about 35% larger than those of the other three data sets. More accurate measurements are needed, particularly beyond 290 nm, in order to better estimate atmospheric photodissociation rates. These studies also indicate that only one stable species is produced in the recombination reaction of ClO with itself, and that this species is dichlorine peroxide, ClOOCl, rather than ClOClO. Using submillimeter wave spectroscopy, Birk et al. (1989) have further established the structure of the recombination product to be ClOOCl. These observations are in agreement with the results of quantum mechanical calculations (McGrath et al., 1988; 1990; Jensen and Odershede, 1990; Stanton et al., 1991).

The experiments of Cox and Hayman (1988) indicate that the main photodissociation products at 253.7 nm are Cl and ClOO. Molina et al. (1990) measured the quantum yield ϕ for this channel to be unity at 308 nm, with no ClO detectable as a product, with an experimental uncertainty in ϕ of about ± 25%. These results are also supported by quantum mechanical calculations (Stanton et al., 1990). In contrast, Eberstein (1990) suggested a quantum yield of unity for the production of two ClO radicals, based merely on an analogy with the photolysis of H_2O_2 at shorter wavelengths. For atmospheric photodissociation calculations the recommended quantum yield value is based on the work of Molina et al. (1990), i.e. a quantum yield of unity for the Cl + ClOO channel.

Table 26. Absorption Cross Sections of ClOOCl around 200-250 K

λ (nm)	σ 10^{20}(cm^2)	λ (nm)	σ 10^{20}(cm^2)	λ (nm)	σ 10^{20}(cm^2)	λ (nm)	σ 10^{20}(cm^2)
200	383.5	240	600.3	280	172.5	320	25.6
202	352.9	242	625.7	282	159.6	322	23.4
204	325.3	244	639.4	284	147.3	324	21.4
206	298.6	246	642.6	286	136.1	326	19.2
208	274.6	248	631.5	288	125.2	328	17.8
210	251.3	250	609.3	290	114.6	330	16.7
212	231.7	252	580.1	292	104.6	332	15.6
214	217.0	254	544.5	294	95.4	334	14.4
216	207.6	256	505.4	296	87.1	336	13.3
218	206.1	258	463.1	298	79.0	338	13.1
220	212.1	260	422.0	300	72.2	340	12.1
222	227.1	262	381.4	302	65.8	342	11.5
224	249.4	264	344.6	304	59.9	344	10.9
226	280.2	266	311.6	306	54.1	346	10.1
228	319.5	268	283.3	308	48.6	348	9.0
230	365.0	270	258.4	310	43.3	350	8.2
232	415.4	272	237.3	312	38.5	352	7.9
234	467.5	274	218.3	314	34.6	354	6.8
236	517.5	276	201.6	316	30.7	356	6.1
238	563.0	278	186.4	318	28.0	358	5.8
						360	5.5

Cl_2O_3 + hν → Products

The absorption cross sections of Cl_2O_3 have been measured by Hayman and Cox (1989) and by Burkholder et al. (1992). The agreement on the shape of the spectrum is very good, but the cross section values reported by Hayman and Cox are 30 - 50% larger. Table 27 lists the recommended values; these are taken from the work of Burkholder et al., which is the more direct study.

Table 27. Absorption Cross Sections of Cl_2O_3

λ (nm)	10^{20} σ (cm^2)	λ (nm)	10^{20} σ (cm^2)
220	968	275	1376
225	930	280	1136
230	908	285	890
235	883	290	642
240	904	295	435
245	989	300	288
250	1154	305	176
255	1352	310	107
260	1512	315	56
265	1594	320	16
270	1544		

Cl_2O_4 + hν → Products

The absorption cross sections of Cl_2O_4 have been measured by Lopez and Sicre (1988); their results are given in Table 28.

Table 28. Absorption Cross Sections of Cl_2O_4

λ (nm)	10^{20} σ (cm^2)	λ (nm)	10^{20} σ (cm^2)
200	161	255	42
205	97	260	31
210	72	265	22
215	64	270	14
220	71	275	8.8
225	75	280	5.5
230	95	285	4.0
235	95	290	2.7
240	87	295	2.2
245	72	300	1.7
250	56	305	1.2
		310	0.7

Cl_2O_6 + hν → Products

The absorption cross sections for Cl_2O_6 are listed in Table 29, and are taken from the work of Lopez and Sicre (1990). These authors show that the spectrum originally attributed to ClO_3 by Goodeve and Richardson (1937) was most likely that of Cl_2O_6. The cross section values measured by Lopez and Sicre are several times larger than those reported by Goodeve and Richardson, but the shape of the spectrum is similar.

Table 29. Absorption Cross Sections of Cl_2O_6

λ (nm)	10^{20} σ (cm^2)	λ (nm)	10^{20} σ (cm^2)
200	1230	300	980
210	1290	310	715
220	1230	320	450
230	1080	330	285
240	1010	340	180
250	1010	350	112
260	1290	360	59
270	1440	370	28
280	1440	380	12
290	1290		

HCl + hν → H + Cl

The absorption cross sections of HCl, listed in Table 30, are taken from the work of Inn (1975).

Table 30. Absorption Cross Sections of HCl Vapor

λ (nm)	10^{20} σ (cm^2)	λ (nm)	10^{20} σ (cm^2)
140	211	185	31.3
145	281	190	14.5
150	345	195	6.18
155	382	200	2.56
160	332	205	0.983
165	248	210	0.395
170	163	215	0.137
175	109	220	0.048
180	58.8		

$HOCl + h\nu \rightarrow OH + Cl$

The absorption cross sections of HOCl vapor have been measured by several groups. Molina and Molina (1978) and Knauth et al. (1979) produced this species using equilibrium mixtures with Cl_2O and H_2O; their results provided the basis for the earlier recommendation. More recently, Mishalanie et al. (1986) and Permien et al. (1988) used a dynamic source to generate the HOCl vapor. The cross section values reported by Molina and Molina (1978), Mishalanie et al. (1986), and Permien et al. (1988) are in reasonable agreement between 250 and 330 nm. In this wavelength range, the values reported by Knauth et al. (1977) are significantly smaller, e.g., a factor of four at 280 nm. Beyond 340 nm, the cross sections of Mishalanie et al. are much smaller than those obtained by the other three groups: at 365 nm, the discrepancy is about an order of magnitude.

The recommended values are taken from the work of Permien et al.; they are listed in Table 31. These authors were able to produce HOCl vapor in the absence of significant amounts of other absorbing gases such as Cl_2 and Cl_2O. The corrections due to the presence of these impurities are the most likely source of error in most of the investigations.

Molina et al. (1980b) observed production of OH radicals in the laser photolysis of HOCl around 310 nm, and Butler and Phillips (1983) found no evidence for O-atom production at 308 nm, placing an upper limit of ~0.02 for the primary quantum yield for the HCl + O channel.

Table 31. Absorption Cross Sections of HOCl

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
215	8.71	295	16.12
220	13.26	300	14.55
225	18.95	305	12.30
230	25.33	310	10.43
235	31.48	315	8.60
240	36.48	320	6.95
245	38.89	325	5.54
250	40.49	330	4.35
255	38.54	335	3.32
260	34.11	340	2.48
265	28.34	345	1.83
270	23.61	350	1.34
275	20.63	355	0.92
280	19.18	360	0.61
285	18.26	365	0.42
290	17.38	370	0.27
		375	0.15

$\mathrm{ClNO} + h\nu \rightarrow \mathrm{Cl} + \mathrm{NO}$

Nitrosyl chloride has a continuous absorption extending beyond 650 nm. There is good agreement between the work of Martin and Gareis (1956) for the 240 to 420 nm wavelength region, of Ballash and Armstrong (1974) for the 185 to 540 nm region, of Illies and Takacs (1976) for the 190 to 400 nm region, and of Tyndall et al. (1987) for the 190 to 350 region except around 230 nm, where the values of Ballash and Armstrong are larger by almost a factor of two. The recommended absorption cross sections, listed in Table 32, are taken from the recent work of Tyndall et al. (1987).

The quantum yield for the primary photolytic process has been reviewed by Calvert and Pitts (1966a); it is unity over the entire visible and near-ultraviolet bands.

Table 32. Absorption Cross Sections of ClNO

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
190	4320	230	266	270	12.9	310	11.5
192	5340	232	212	272	12.3	312	11.9
194	6150	234	164	274	11.8	314	12.2
196	6480	236	120	276	11.3	316	12.5
198	6310	238	101	278	10.7	318	13.0
200	5860	240	82.5	280	10.6	320	13.4
202	5250	242	67.2	282	10.2	322	13.6
204	4540	244	55.2	284	9.99	324	14.0
206	3840	246	45.2	286	9.84	326	14.3
208	3210	248	37.7	288	9.71	328	14.6
210	2630	250	31.7	290	9.64	330	14.7
212	2180	252	27.4	292	9.63	332	14.9
214	1760	254	23.7	294	9.69	334	15.1
216	1400	256	21.3	296	9.71	336	15.3
218	1110	258	19.0	298	9.89	338	15.3
220	896	260	17.5	300	10.0	340	15.2
222	707	262	16.5	302	10.3	342	15.3
224	552	264	15.3	304	10.5	344	15.1
226	436	266	14.4	306	10.8	346	15.1
228	339	268	13.6	308	11.1	348	14.9
						350	14.5

$ClNO_2 + h\nu \rightarrow$ Products

The absorption cross sections of nitryl chloride, $ClNO_2$, have been measured between 230 and 330 nm by Martin and Gareis (1956), between 185 and 400 nm by Illies and Takacs (1976), and between 270 and 370 nm by Nelson and Johnston (1981). The results are in good agreement below 300 nm. Table 33 lists the recommended values, which are taken from Illies and Takacs (1976) between 190 and 270 nm, and from Nelson and Johnston (1981) between 270 and 370 nm. These latter authors showed that an approximate 6% Cl_2 impurity in the samples used by Illies and Takacs could explain the discrepancy in the results above 300 nm. Nelson and Johnston (1981) report a value of one (within experimental error) for the quantum yield for production of chlorine atoms; they also report a negligible quantum yield for the production of oxygen atoms.

Table 33. Absorption Cross Sections of $ClNO_2$

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
190	2690	290	18.1
200	455	300	15.5
210	339	310	12.5
220	342	320	8.70
230	236	330	5.58
240	140	340	3.33
250	98.5	350	1.78
260	63.7	360	1.14
270	37.2	370	0.72
280	22.3		

ClONO + hv → Products

Measurements in the near-ultraviolet of the cross sections of chlorine nitrite (ClONO) have been made by Molina and Molina (1977). Their results are listed in Table 34. The characteristics of the spectrum and the instability of ClONO strongly suggest that the quantum yield for decomposition is unity. The Cl-O bond strength is only about 20 kilocalories, so that chlorine atoms are likely photolysis products.

Table 34. Absorption Cross Sections of ClONO at 231 K

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
235	215.0	320	80.3
240	176.0	325	75.4
245	137.0	330	58.7
250	106.0	335	57.7
255	65.0	340	43.7
260	64.6	345	35.7
265	69.3	350	26.9
270	90.3	355	22.9
275	110.0	360	16.1
280	132.0	365	11.3
285	144.0	370	9.0
290	144.0	375	6.9
295	142.0	380	4.1
300	129.0	385	3.3
305	114.0	390	2.2
310	105.0	395	1.5
315	98.1	400	0.6

$ClONO_2$ + hv → Products

The recommended cross section values, listed in Table 35, are taken from the work of Molina and Molina (1979), which supersedes the earlier work of Rowland, Spencer and Molina (1976).

The identity of the primary photolytic fragments has been investigated by several groups. Smith et al. (1977) report O + ClONO as the most likely products, using end product analysis and steady-state photolysis. The results of Chang et al. (1979b), who employed the "Very Low Pressure Photolysis" (VLPPh) technique, indicate that the products are Cl + NO_3. Adler-Golden and Wiesenfeld (1981), using a flash photolysis atomic absorption technique, find O-atoms to be the predominant photolysis product, and report a quantum yield for Cl-atom production of less than 4%. Marinelli and Johnston (1982b) report a quantum yield for NO_3 production at 249 nm between 0.45 and 0.85 with a most likely value of 0.55; they monitored NO_3 by tunable dye-laser absorption at 662 nm. Margitan (1983a) used atomic resonance fluorescence detection of O- and Cl-atoms and found the quantum yield at 266 and at 355 nm to be 0.9 ± 0.1 for Cl-atom production, and ~0.1 for O-atom production, with no discernible difference at the two wavelengths. These results were confirmed by Knauth and Schindler (1983), who used end-product analysis to infer the quantum yields. Burrows et al. (1988) report also Cl and NO_3 as the photolysis products at 254 nm, with a quantum yield of unity within experimental error.

The preferred quantum yield values are 0.9 for the Cl + NO_3 channel, and a complementary value of 0.1 for the O + ClONO channel. The recommendation is based on Margitan (1983a), whose direct study is the only one with results at a wavelength longer than 290 nm, which is where atmospheric photodissociation will predominantly occur. The reason for the discrepancy with the studies by Adler-Golden and Wiesenfeld (1981) and by Marinelli and Johnston (1982b) is almost surely that the rate constant for Cl + $ClNO_3$ is much faster (two orders of magnitude) than previously thought (Margitan, 1983a; Kurylo et al., 1983a).

Table 35. Absorption Cross Sections of $ClONO_2$

	10^{20} σ(cm^2)		
λ(nm)	227 K	243 K	296 K
190	555	-	589
195	358	-	381
200	293	-	307
205	293	-	299
210	330	-	329
215	362	-	360
220	348	-	344
225	282	-	286
230	206	-	210
235	141	-	149
240	98.5	-	106
245	70.6	-	77.0
250	52.6	50.9	57.7
255	39.8	39.1	44.7
260	30.7	30.1	34.6
265	23.3	23.1	26.9
270	18.3	18.0	21.5
275	13.9	13.5	16.1
280	10.4	9.98	11.9
285	7.50	7.33	8.80
290	5.45	5.36	6.36
295	3.74	3.83	4.56
300	2.51	2.61	3.30
305	1.80	1.89	2.38
310	1.28	1.35	1.69
315	0.892	0.954	1.23
320	0.630	0.681	0.895
325	0.463	0.502	0.655
330	0.353	0.381	0.514
335	0.283	0.307	0.397
340	0.246	0.255	0.323
345	0.214	0.223	0.285
350	0.198	0.205	0.246
355	0.182	0.183	0.218
360	0.170	0.173	0.208
365	0.155	0.159	0.178
370	0.142	0.140	0.162
375	0.128	0.130	0.139
380	0.113	0.114	0.122
385	0.098	0.100	0.108
390	0.090	0.083	0.090
395	0.069	0.070	0.077
400	0.056	0.058	0.064
405	-	-	0.055
410	-	-	0.044
415	-	-	0.035
420	-	-	0.027
425	-	-	0.020
430	-	-	0.016
435	-	-	0.013
440	-	-	0.009
445	-	-	0.007
450	-	-	0.005

Halocarbon Absorption Cross Sections and Quantum Yields

The primary process in the photodissociation of chlorinated hydrocarbons is well established: absorption of ultraviolet radiation in the lowest frequency band is interpreted as an n-σ^* transition involving excitation to a repulsive electronic state (antibonding in C-Cl), which dissociates by breaking the carbon chlorine bond (Majer and Simons, 1964). As expected, the chlorofluoromethanes, which are a particular type of chlorinated hydrocarbons, behave in this fashion (Sandorfy, 1976). Hence, the quantum yield for photodissociation is expected to be unity for these compounds. There are several studies which show specifically that this is the case for CF_2Cl_2, $CFCl_3$ and CCl_4. These studies, which have been reviewed in CODATA (1982), also indicate that at shorter wavelengths two halogen atoms can be released simultaneously in the primary process.

The absorption cross sections for various other halocarbons not listed in this evaluation have also been investigated: $CHCl_2F$ by Hubrich et al. (1977); $CClF_3$, $CHCl_3$, CH_2Cl_2, CH_2ClF, CF_3CH_2Cl and CH_3CH_2Cl by Hubrich and Stuhl (1980); $CHCl_3$, $CHFCl_2$, C_2HCl_3 and $C_2H_3Cl_3$ by Robbins (1977); CH_2Cl_2 and $CHCl_3$ by Vanlaethem-Meuree et al. (1978a); $CHCl_2F$, $CClF_2CH_2Cl$ and CF_3CH_2Cl by Green and Wayne (1976-1977); and CH_2Br_2 and $CBrF_2CF_3$ by Molina et al. (1982). Simon and co-workers have reported absorption cross section measurements over the temperature range 295-210 K for various other halocarbons not listed here. These include the following: $CHCl_3$, CH_2Cl_2, $CHFCl_2$ and CF_3Cl by Simon et al. (1988a).

As before, the recommendation for the photodissociation quantum yield value is unity for all these species.

CF_4 and C_2F_6 do not have any absorptions at wavelengths longer than 105 and 120 nm, respectively (Sauvageau et al., 2973, 1974; Inn, 1980); therefore, they are not expected to photodissociate until they reach the mesosphere. SF_6 does not absorb at wavelengths longer than 130 nm.

CCl_4 + hv → Products

CCl_3F (CFC-11) + hv → Products

CCl_2F_2 (CFC-12) + hv → Products

Tables 36, 37 and 38 list the present recommendations for the cross sections of CCl_4, CCl_3F and CCl_2F_2, respectively. These data are given by the mean of the values reported by various groups, i.e., Hubrich et al. (1977), Hubrich and Stuhl (1980), Vanlaethem-Meuree et al. (1978a,b), and Green and Wayne (1976, 1977), as well as those referred to in earlier evaluations (CODATA, 1982). Absorption cross sections for these species over the temperature range 295-210 K have also been reported by Simon et al. (1988a). These results are in generally good agreement with the present recommendations. Expressions for the temperature dependence of the CCl_3F and CCl_2F_2 cross sections are given at the bottom of Tables 37 and 38, respectively. These expressions are valid in the wavelength range of maximum solar photodissociation, i.e., about 190-210 nm, but may not exactly reproduce the experimental temperature dependences outside this wavelength range. However, J-value calculations should not be affected.

Table 36. Absorption Cross Sections of CCl_4

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
174	995	218	21.8
176	1007	220	17.0
178	976	222	13.0
180	772	224	9.61
182	589	226	7.19
184	450	228	5.49
186	318	230	4.07
188	218	232	3.01
190	144	234	2.16
192	98.9	236	1.51
194	74.4	238	1.13
196	68.2	240	0.784
198	66.0	242	0.579
200	64.8	244	0.414
202	62.2	246	0.314
204	60.4	248	0.240
206	56.5	250	0.183
208	52.0	255	0.0661
210	46.6	260	0.0253
212	39.7	265	0.0126
214	33.3	270	0.0061
216	27.2	275	0.0024

Table 37. Absorption Cross Sections of CCl_3F

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
170	316	208	21.2
172	319	210	15.4
174	315	212	10.9
176	311	214	7.52
178	304	216	5.28
180	308	218	3.56
182	285	220	2.42
184	260	222	1.60
186	233	224	1.10
188	208	226	0.80
190	178	228	0.55
192	149	230	0.35
194	123	235	0.126
196	99	240	0.0464
198	80.1	245	0.0173
200	64.7	250	0.00661
202	50.8	255	0.00337
204	38.8	260	0.00147
206	29.3		

$\sigma_T = \sigma_{298} \exp[1.0\mathrm{x}10^{-4}(\lambda-184.9)(T-298)]$

Where σ_{298} = cross section at 298 K

λ : nm

T : temperature, Kelvin

Table 38. Absorption Cross Sections of CCl_2F_2

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
170	124	200	8.84
172	151	202	5.60
174	171	204	3.47
176	183	206	2.16
178	189	208	1.52
180	173	210	0.80
182	157	212	0.48
184	137	214	0.29
186	104	216	0.18
188	84.1	218	0.12
190	62.8	220	0.068
192	44.5	225	0.022
194	30.6	230	0.0055
196	20.8	235	0.0016
198	13.2	240	0.00029

$\sigma_T = \sigma_{298} \exp[4.1\mathrm{x}10^{-4}(\lambda-184.9)(T-298)]$

Where σ_{298} = cross section at 298 K

λ : nm

T : temperature, Kelvin

$CHClF_2$ (HCFC-22) + hν → Products

The absorption cross sections of $CHClF_2$ (HCFC-22) have been measured at room temperature by Robbins and Stolarski (1976) and by Chou et al. (1976), at 208 K and 218 K by Hubrich et al. (1977), and between 210 and 295 K by Simon et al. (1988a). The agreement between these groups is reasonable. The preferred absorption cross sections, listed in Table 39, are taken from work of Simon et al.

Photolysis of $CHClF_2$ is rather unimportant throughout the atmosphere: reaction with OH radicals is the dominant destruction process.

Table 39. Absorption Cross Sections of $CHClF_2$

	$10^{20}\sigma$ (cm^2)				
λ (nm)	295 K	270 K	250 K	230 K	210 K
174	5.72	5.72	5.72	5.72	5.72
176	4.04	4.04	4.04	4.04	4.04
178	2.76	2.76	2.76	2.76	2.76
180	1.91	1.91	1.91	1.91	1.91
182	1.28	1.28	1.28	1.28	1.28
184	0.842	0.842	0.842	0.842	0.842
186	0.576	0.576	0.576	0.576	0.576
188	0.372	0.372	0.372	0.372	0.372
190	0.245	0.245	0.245	0.245	0.242
192	0.156	0.156	0.156	0.152	0.148
194	0.103	0.102	0.099	0.096	0.093
196	0.072	0.069	0.067	0.064	0.062
298	0.048	0.045	0.043	0.041	0.039
200	0.032	0.029	0.029	0.0259	0.0159
202	0.0220	0.0192	0.0184	0.0169	0.0159
204	0.0142	0.0121	0.0114	0.0104	0.0096

CH_3Cl + hν → Products

The preferred absorption cross sections, listed in Table 40, are those given by Vanlaethem-Meuree et al. (1978b). These values are in very good agreement with those reported by Robbins (1976) at 298 K, as well as with those given by Hubrich et al. (1977) at 298 K and 208 K, if the temperature trend is taken into consideration. The results recently reported by Simon et al. (1988a) over the temperature range 295-210 K are in excellent agreement with the present recommendation.

Table 40. Absorption Cross Sections of CH_3Cl

λ (nm)	10^{20} σ(cm^2) 296 K	279 K	255 K
186	24.7	24.7	24.7
188	17.5	17.5	17.5
190	12.7	12.7	12.7
192	8.86	8.86	8.86
194	6.03	6.03	6.03
196	4.01	4.01	4.01
198	2.66	2.66	2.66
200	1.76	1.76	1.76
202	1.09	1.09	1.09
204	0.691	0.691	0.691
206	0.483	0.475	0.469
208	0.321	0.301	0.286
210	0.206	0.189	0.172
212	0.132	0.121	0.102
214	0.088	0.074	0.059
216	0.060	0.048	0.033

$CF_2ClCFCl_2$ (CFC-113) + hν → Products

CF_2ClCF_2Cl (CFC-114) + hν → Products

CF_3CF_2Cl (CFC-115) + hν → Products

The recommended absorption cross section values for these species at 295 K and at 210 K are presented in Table 41, and are taken from Simon et al. (1988b). These values are in good agreement with those reported by Hubrich and Stuhl (1980), who also carried out measurements at lower temperatures. They are also in good agreement with the data of Chou et al. (1978), except that these authors report cross section values for CF_3CF_2Cl that are about 50% higher. Also, for this species the temperature dependency is unimportant in the wavelength range of interest.

Table 41. Absorption Cross Sections for $CF_2ClCFCl_2$, CF_2ClCF_2Cl and CF_3CF_2Cl

λ (nm)	10^{20} σ(cm^2) $CF_2ClCFCl_2$ 295 K	$CF_2ClCFCl_2$ 210 K	CF_2ClCF_2Cl 295 K	CF_2ClCF_2Cl 210 K	CF_3CF_2Cl 295 K
172			69	69	5.65
174			55	55	4.05
176			43	43	2.85
178			34	34	2.05
180			26	26	1.45
182			19.8	19.8	1.05
184	118	118	15.0	15.0	0.75
186	104	104	11.0	11.0	0.53
188	83.5	83.5	7.80	7.72	0.38
190	64.5	64.5	5.35	5.03	0.27
192	48.8	48.8	3.70	3.28	0.19
194	36.0	36.0	2.56	2.13	0.13
196	26.0	24.3	1.75	1.39	0.090
198	18.3	15.9	1.20	0.88	0.063
200	12.5	10.1	0.80	0.55	0.044
202	8.60	6.54	0.54	0.34	0.031
204	5.80	4.09	0.37	0.22	0.021
206	4.00	2.66	0.24	0.13	
208	2.65	1.68	0.16	0.084	
210	1.8	1.12	0.104	0.051	
212	1.15	0.696	0.068	0.031	
214	0.760	0.452	0.044	0.020	
216	0.505	0.298	0.029	0.012	
218	0.318	0.184	0.019	0.007	
220	0.220	0.125	0.012	0.004	
222	0.145	0.081			
224	0.095	0.053			
226	0.063	0.034			
228	0.041	0.022			
230	0.027	0.014			

CH_3CF_2Cl (HCFC-142b) + hv → Products

The preferred absorption cross sections at 298 K, listed in Table 42, are the mean of the values reported by Gillotay et al. (1989a) and Orlando et al. (1991a) over the wavelength range where the agreement is better than a factor of two. At lower wavelengths the agreement is much better; e.g., at 200 nm the agreement is within 5%. Green and Wayne (1976/77) and Hubrich and Stuhl (1980) have also measured the cross sections in the ranges 185-200 nm and 160-230 nm, respectively. The results of Green and Wayne are very different from the recommended value and were not considered for this evaluation. The results of Hubrich and Stuhl (reported at 5 nm intervals) are in reasonable agreement with the more recent studies of Gillotay et al. and Orlando et al. The temperature dependence of the cross sections has been measured by Orlando et al. and by Gillotay and Simon (1991); it has not been included in this evaluation.

CF_3CHCl_2 (HCFC-123) + hv → Products

The preferred absorption cross sections at 298 K, listed in Table 42, are the mean of the values reported by Gillotay and Simon (1991) and Orlando et al. (1991a). The agreement is quite good over the entire wavelength range. The measurements by Green and Wayne (1976/77) over the range 185-205 nm are in reasonable agreement with the recommended values. The temperature dependence of the cross sections has been measured by Orlando et al. and by Gillotay and Simon; it is not included here.

CF_3CHFCl (HCFC-124) + hv → Products

The preferred values are those reported by Orlando et al. (1991a), this being the only available set of measurements between 190 and 230 nm. The data are listed in Table 42. The temperature dependence of the cross section has been measured by Orlando et al. but has not been evaluated here. The quantum yield for the dissociation to give Cl atoms is expected to be unity.

CH_3CFCl_2 (HCFC-141b) + hv → Products

The preferred absorption cross sections listed in Table 42 are the mean of the 298 K values reported by Talkudar et al. (1991a) and Gillotay and Simon (1991). The agreement between these two sets of measurements is not very good. Both groups also report the temperature dependence of the cross sections down to 210 K.

Table 42. Absorption Cross Sections of Hydrochlorofluoroethanes at 298 K

λ (nm)	10^{20} σ(cm^2) at 298 K			
	CH_3CFCl_2	CH_3CF_2Cl	CF_3CHCl_2	CF_3CHFCl
190	75.3	0.94	59.0	0.73
192	58.8	0.66	44.5	0.53
194	44.3	0.46	32.9	0.38
196	32.2	0.31	23.6	0.26
198	22.8	0.21	16.9	0.18
200	15.8	0.14	11.9	0.13
202	10.8	0.09	8.3	0.086
204	7.3	0.061	5.7	0.059
206	4.9	0.039	4.0	0.040
208	3.2	0.026	2.7	0.026
210	2.2	0.017	1.8	0.018
212	1.4	0.010	1.3	0.012
214	0.94	0.007	0.87	0.008
216	0.61	0.004	0.61	0.006
218	0.41	0.003	0.40	0.004
220	0.27	0.002	0.28	0.003

CH_3CCl_3 + hν → Products

The absorption cross sections have been measured by Robbins (1977), by Vanlaethem-Meuree et al. (1979) and by Hubrich and Stuhl (1980). These latter authors corrected the results to account for the presence of a UV-absorbing stabilizer in their samples, a correction which might account for the rather large discrepancy with the other measurements. The results of Robbins (1977) and of Vanlaethem-Meuree et al. (1979) are in good agreement. The recommended values are taken from this latter work (which reports values at 210 K, 230 K, 250 K, 270 K and 295 K, every 2 nm, and in a separate table at wavelengths corresponding to the wavenumber intervals generally used in stratospheric photodissociation calculations). Table 43 lists the values at 210 K, 250 K and 295 K, every 5 nm; the odd wavelength values were computed by linear interpolation.

Table 43. Absorption Cross Sections of CH_3CCl_3

λ (nm)	10^{20} σ(cm^2) 295 K	250 K	210 K
185	265	265	265
190	192	192	192
200	81.0	81.0	81.0
205	46.0	44.0	42.3
210	24.0	21.6	19.8
215	10.3	8.67	7.47
220	4.15	3.42	2.90
225	1.76	1.28	0.97
230	0.700	0.470	0.330
235	0.282	0.152	0.088
240	0.102	0.048	0.024

$CF_3CF_2CHCl_2$ (HCFC-225 ca) + hν → Products

CF_2ClCF_2CHFCl (HCFC-225 cb) + hν → Products

Table 44 lists the absorption cross sections for these molecules at 298 K, taken from the work of Braun et al. (1991). These values have been fitted with a mathematical expression for the wavelength range from 170 to 250 nm, for each of the two molecules; the expressions are listed in the original publication. The authors also measured the cross sections in the liquid phase.

Table 44. Absorption Cross Sections of $CF_3CF_2CHCl_2$ and CF_2ClCF_2CHFCl

λ (nm)	10^{20} σ(cm^2)	
	$CF_3CF_2CHCl_2$	CF_2ClCF_2CHFCl
160	269	188
165	197	145
170	183	91
175	191	47
180	177	21
185	129	9.1
190	74	3.5
195	37	1.4
200	16	0.63
205	6.9	0.33
210	2.9	0.25
215	1.2	
220	0.46	
225	0.17	
230	0.065	
235	0.025	
239	0.011	

CF_3Br (Halon-1301) + hv → Products

The preferred absorption cross sections at 298 K, listed in Table 45, are the mean of the values reported by Gillotay and Simon (1989) at 2 nm intervals and Burkholder et al. (1991) at 1 nm intervals over the wavelength range where the agreement is acceptable, i.e., better than 70%. At longer wavelengths Burkholder et al. (1991) measure larger values than those reported by Gillotay and Simon. Molina et al. (1982) have also measured these cross sections which agree better with Gillotay and Simon. However, the agreement in the wavelength range 190-230 nm among the three studies is excellent. The temperature dependence of the cross sections has been measured by Gillotay and Simon as well as Burkholder et al. (1991). The agreement between these two studies is poor. We have not evaluated the temperature dependence of the cross section and the readers are referred to the original publications for this information. For all the bromofluoromethanes, photolysis is expected to cleave the C-Br bond with unit quantum efficiency.

CF_2Br_2 (Halon-1202) + hv → Products

The preferred absorption cross sections at 298 K, listed in Table 45, are the mean of the values reported by Gillotay and Simon (1989) at 2 nm intervals and Burkholder et al. (1991) at 1 nm intervals over the wavelength range where the agreement is no more than a factor of two. At wavelengths longer than ~250 nm, Burkholder et al. (1991) measured cross sections larger than those reported by Gillotay and Simon (1989) and Molina et al. (1982). The discrepancy increases with wavelength and is more than a factor of two beyond 280 nm. However, the agreement between all three measurements is acceptable below 250 nm. The values of Molina et al. agree with those of Gillotay and Simon over the entire range of wavelengths. The temperature dependence of the cross sections has been measured by Gillotay and Simon as well as Burkholder et al. (1991). The agreement between these two studies is poor.

The quantum yield for the dissociation of CF_2Br_2 has been measured to be unity at 206, 248 and 308 nm by Molina and Molina (1983), independent of pressure, in contrast to an earlier report by Walton (1972) that the quantum yield at 265 nm decreases from unity when the system pressure is raised to 50 torr of CO_2.

CF_2BrCl (Halon-1211) + hv → Products

The preferred absorption cross sections at 298 K, listed in Table 45, are the mean of the values reported by Gillotay and Simon (1989) at 2 nm intervals and Burkholder et al. (1991) at 1 nm intervals. Molina et al. (1982) and Giolando et al. (1980) have also measured the cross sections at 5 nm and 10 nm intervals, respectively. The agreement between the four studies is quite good.

The temperature dependence of the cross sections has been measured by Gillotay and Simon as well as Burkholder et al. (1991). The agreement between the two studies is poor. We have not evaluated the temperature dependence of the cross section and the readers are referred to the original publications for this information.

CF_2BrCF_2Br (Halon-2402) + hv → Products

The preferred absorption cross sections at 298 K, listed in Table 45, are the mean of the values reported by Gillotay et al. (1988) at 2 nm intervals and Burkholder et al. (1991) at 1 nm intervals over the wavelength range where the agreement is acceptable, i.e., ~70%. At longer wavelengths, Burkholder et al. (1991) measured larger cross sections than those measured by Gillotay et al. Molina et al. (1982) have also measured these cross sections and they agree with the results of Gillotay et al. at longer wavelengths. The agreement between the three studies at wavelengths shorter than 250 nm is good. The results of Robbins (1977) are in good agreement with the recommended values.

The temperature dependence of the cross sections has been measured by Gillotay et al. (1988) and Burkholder et al. (1991). The agreement between the two studies is poor at longer wavelengths. We have not evaluated the temperature dependence of the cross section and the readers are referred to the investigators for the information.

Table 45. Absorption Cross Sections of CF_2ClBr, CF_2Br_2, CF_3Br, and CF_2BrCF_2Br at 298 K

λ	10^{20} σ(cm^2)			
(nm)	CF_2ClBr	CF_2Br_2	CF_3Br	CF_2BrCF_2Br
190	47	114	6.4	109
192	58	109	7.5	114
194	70	100	8.5	119
196	83	91	9.5	122
198	96	82	10.4	124
200	112	75	11.2	124
202	118	72	11.8	124
204	121	74	12.2	120
206	122	81	12.4	117
208	121	93	12.4	112
210	117	110	12.0	106
212	112	136	11.4	100
214	106	155	10.7	92
216	98	180	9.8	85
218	90	203	8.8	77
220	81	224	7.7	69
222	72	242	6.7	61
224	64	251	5.7	54
226	56	253	4.7	47
228	49	250	3.8	40
230	42	241	3.1	35
232	36	227	2.4	29
234	31	209	1.9	24
236	26	189	1.4	20
238	22	168	1.1	16
240	18	147	0.81	13
242	15	126	0.59	11
244	12	106	0.43	8.4
246	10	88	0.31	6.7
248	8.0	73	0.22	5.2
250	6.5	59	0.16	4.1
252	5.1	47	0.11	3.1
254	4.0	37	0.076	2.3
256	3.2	29	0.053	1.8
258	2.4	23	0.037	1.3
260	1.9	18	0.026	0.95

Continued on next page. . .

Table 45. (Continued)

λ (nm)	10^{20} σ(cm^2)			
	CF_2ClBr	CF_2Br_2	CF_3Br	CF_2BrCF_2Br
262	1.4	13	0.018	0.71
264	1.1	10	0.012	0.53
266	0.84	7.6	0.009	0.39
268	0.63	5.7	0.006	0.28
270	0.48	4.2		0.21
272	0.36	3.1		0.16
274	0.27	2.2		0.11
276	0.20	1.6		0.082
278	0.15	1.2		0.060
280	0.1	0.89		0.044
282	0.079	0.65		
284	0.058	0.48		
286	0.043	0.34		
288	0.031	0.24		
290		0.18		
292		0.13		
294		0.096		
296		0.068		
298		0.050		
300		0.036		

CH_3Br + hν → Products

Table 46 lists the recommended absorption cross sections at 298 K, taken from Gillotay and Simon (1988). These authors measured the cross sections down to 210 K; for < 210 nm the temperature effect is negligible. Molina et al. (1982) and Robbins (1976) have also measured the absorption cross sections for this molecule at room temperature; the agreement among the three studies is very good.

Table 46. Absorption Cross Sections of CH_3Br

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
190	44	230	15
192	53	232	12
194	62	234	9.9
196	69	236	7.6
198	76	238	5.9
200	79	240	4.5
202	80	242	3.3
204	79	244	2.5
206	77	246	1.8
208	73	248	1.3
210	67	250	0.96
212	61	252	0.69
214	56	254	0.49
216	49	256	0.34
218	44	258	0.23
220	38	260	0.16
222	32		
224	28		
226	23		
228	19		

$CHBr_3 + h\nu \rightarrow$ Products

The only published absorption cross section values are those of Gillotay et al. (1989), who report measurements at temperatures down to 240 K. Table 47 lists the values at 298 K taken from this work.

Table 47. Absorption Cross Sections of $CHBr_3$

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
190	399	250	174
192	360	252	158
194	351	254	136
196	366	256	116
198	393	258	99
200	416	260	83
202	433	262	69
204	440	264	57
206	445	266	47
208	451	268	38
210	468	270	31
212	493	272	25
214	524	274	20
216	553	276	16
218	574	278	12
220	582	280	9.9
222	578	282	7.8
224	558	284	6.1
226	527	286	4.8
228	487	288	3.7
230	441	290	2.9
232	397	292	2.2
234	362	294	1.7
236	324	296	1.3
238	295	298	0.96
240	273	300	0.72
242	253	302	0.54
244	234	304	0.40
246	214	306	0.30
248	194	308	0.22
		310	0.16

CCl_2O + hv → Products, CClFO + hv → Products, and CF_2O + hv → Products

Table 48 shows the absorption cross sections of CCl_2O (phosgene) and CFClO given by Chou et al. (1977), and of CF_2O taken from the work of Molina and Molina (1982). The spectrum of CF_2O shows considerable structure; the values listed in Table 48 are averages over each 50 wavenumber interval. The spectrum of CFClO shows less structure, and the CCl_2O spectrum is a continuum; its photodissociation quantum yield is unity (Calvert and Pitts, 1966a).

The quantum yield for the photodissociation of CF_2O at 206 nm appears to be ~0.25 (Molina and Molina, 1982); additional studies of the quantum yield in the 200 nm region are required in order to establish the atmospheric photodissociation rate.

Table 48. Absorption Cross Sections of CCl_2O, CClFO and CF_2O

λ (nm)	10^{20} σ(cm^2)		
	CCl_2O	CClFO	CF_2O
184.9	204.0	-	-
186.0	189.0	15.6	5.5
187.8	137.0	14.0	4.8
189.6	117.0	13.4	4.2
191.4	93.7	12.9	3.7
193.2	69.7	12.7	3.1
195.1	52.5	12.5	2.6
197.0	41.0	12.4	2.1
199.0	31.8	12.3	1.6
201.0	25.0	12.0	1.3
103.0	20.4	11.7	0.95
205.1	16.9	11.2	0.69
207.3	15.1	10.5	0.50
209.4	13.4	9.7	0.34
211.6	12.2	9.0	0.23
213.9	11.7	7.9	0.15
216.2	11.6	6.9	0.10
218.6	11.9	5.8	0.06
221.0	12.3	4.8	0.04
223.5	12.8	4.0	0.03
226.0	13.2	3.1	-

BrO + hv → Br + O

The BrO radical has a banded spectrum in the 290-380 nm range. The strongest absorption feature is around 338 nm. The measured cross sections are both temperature and resolution dependent. As an example, the spectrum measured by Wahner et al. (1988) is shown in Figure 5. The bands are due to a vibrational progression in the A ← X system, and the location of the bands, along with the assignments and cross sections measured using 0.4 nm resolution, are shown in Table 49. BrO is expected to dissociate upon light absorption. As a guide, the cross sections averaged over 5 nm wavelength intervals are taken from the work of Cox et al. (1982), and are listed in Table 50. These authors estimate a BrO lifetime against atmospheric photodissociation of ~20 seconds at the earth's surface, for a solar zenith angle of 30°.

The earlier BrO cross section measurements were carried out mostly around 338 nm, and have been reviewed by CODATA (1980; 1982).

Table 49. Absorption Cross Sections at the Peak of Various Bands in the A ← X Spectrum of BrO

v', v"	λ (nm)	10^{20} σ(cm^2) 298 K	223 K
13,0	313.5	712	938
12,0	317.0	1010	1360
11,0	320.8	1180	1570
10,0	325.0	1130	1430
9,0	329.1	1130	1390
8,0	333.5	1210	1470
7,0	338.3	1550	1950
6,0	343.7	935	1110
5,0	348.8	703	896
4,0	354.7	722	1050
3,0	360.4	264	344
2,0	367.7	145	154
1,0	374.5	90	96

Spectral resolution is 0.4 nm, fwhm.

Table 50. Absorption Cross Sections of BrO

λ (nm)	10^{20} σ(cm^2) average
300 - 305	200
305 - 310	259
310 - 315	454
315 - 320	391
320 - 325	600
325 - 330	753
330 - 335	628
335 - 340	589
340 - 345	515
345 - 350	399
350 - 355	228
355 - 360	172
360 - 365	161
365 - 370	92
370 - 375	51

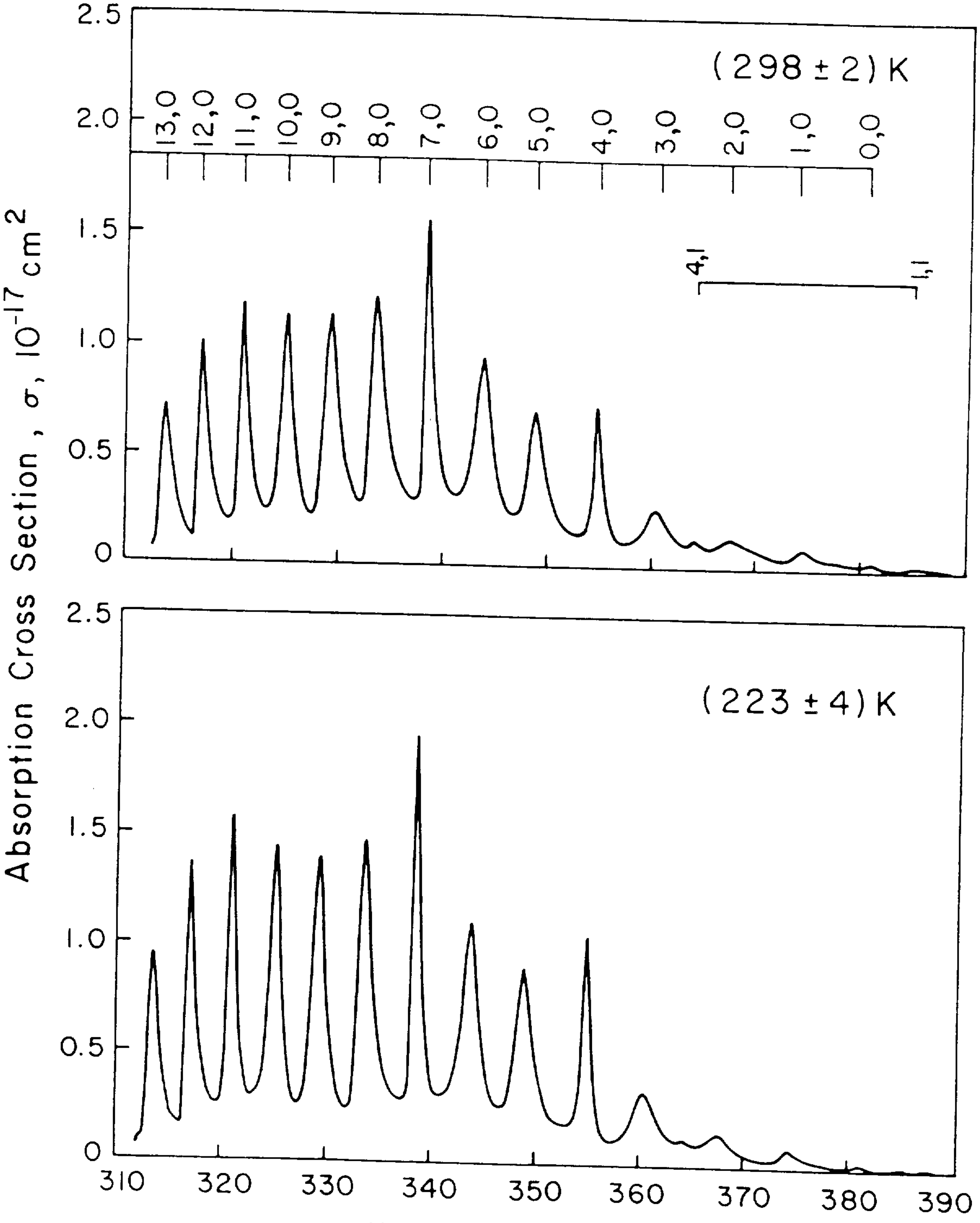


Figure 5. Absorption Spectrum of BrO

$BrONO_2$ + hv → Products

The bromine nitrate cross sections have been measured at room temperature by Spencer and Rowland (1978) in the wavelength region 186-390 nm; their results are given in Table 51. The photolysis products are not known.

Table 51. Absorption Cross Sections of $BrONO_2$

λ (nm)	10^{20} σ (cm^2)	λ (nm)	10^{20} σ (cm^2)
186	1500	280	29
190	1300	285	27
195	1000	290	24
200	720	295	22
205	430	300	19
210	320	305	18
215	270	310	15
220	240	315	14
225	210	320	12
230	190	325	11
235	170	330	10
240	130	335	9.5
245	100	340	8.7
250	78	345	8.5
255	61	350	7.7
260	48	360	6.2
265	39	370	4.9
270	34	380	4.0
275	31	390	2.9

$HF + h\nu \rightarrow H + F$

The ultraviolet absorption spectrum of HF has been studied by Safary et al. (1951). The onset of absorption occurs at $\lambda < 170$ nm, so that photodissociation of HF should be unimportant in the stratosphere.

$H_2CO + h\nu \rightarrow H + HCO \quad (\Phi_1)$

$\rightarrow H_2 + CO \quad (\Phi_2)$

The earlier recommendation for the formaldehyde absorption cross sections was based on the work carried out by Bass et al. (1980) with a resolution of 0.05 nm at 296 K and 223 K, and by Moortgat et al. (1980; 1983) with a resolution of 0.5 nm in the 210-360 K temperature range. More recently, Cantrell et al. (1990b) measured the cross sections in the 300-360 nm range between 223 K and 293 K, and Rogers (1990) measured the cross sections in the 235-365 nm range at 296 K, both groups using Fourier transform spectrometry at a resolution of up to 0.011 nm (1 cm^{-1}). The agreement between these two reports is very good. The recommended values are those given by Cantrell et al. as a function of temperature; the reader is referred to the original article to obtain the high resolution data. Table 52 lists the low resolution cross sections taken from that work, which are suitable for atmospheric photodissociation calculations.

The quantum yields have been reported with good agreement by Horowitz and Calvert (1978), Clark et al. (1979a), Tang et al. (1979), Moortgat and Warneck (1979), and Moortgat et al. (1980; 1983). The recommended values listed in Table 52 are based on the results of these investigators, as evaluated by S. Madronich (private communication, 1991). The quantum yield for the production of H_2 and CO is pressure and temperature dependent for wavelengths longer than about 330 nm (Moortgat et al., 1983). Table 52 gives the values at atmospheric pressure and room temperature; the reader is referred to the Moortgat et al. publication for information on values at lower pressures and temperatures.

Table 52. Absorption Cross Sections and Quantum Yields for Photolysis of CH_2O

λ (nm)	10^{20} σ(cm^2) 223 K	293 K	T-Parameters* A	B	Φ_1 (H + HCO)	Φ_2 (H_2 + CO)
301.25	1.38	1.36	1.37	-0.21	0.749	0.251
303.75	4.67	4.33	4.43	-4.73	0.753	0.247
306.25	3.32	3.25	3.27	-1.06	0.753	0.247
308.75	2.27	2.22	2.24	-0.724	0.748	0.252
311.25	0.758	0.931	0.882	2.48	0.739	0.261
313.75	3.65	3.40	3.47	-3.64	0.724	0.276
316.25	4.05	3.89	3.94	-2.30	0.684	0.316
318.75	1.66	1.70	1.69	0.659	0.623	0.368
321.25	1.24	1.13	1.16	-1.52	0.559	0.423
323.75	0.465	0.473	0.471	0.118	0.492	0.480
326.25	5.06	4.44	4.61	-8.86	0.420	0.550
328.75	2.44	2.29	2.34	-2.15	0.343	0.634
331.25	1.39	1.28	1.31	-1.53	0.259	0.697
333.75	0.093	0.123	0.114	0.432	0.168	0.739
336.25	0.127	0.131	0.130	0.050	0.093	0.728
338.75	3.98	3.36	3.54	-8.96	0.033	0.667
341.25	0.805	0.936	0.898	1.86	0.003	0.602
343.75	1.44	1.26	1.31	-2.64	0.001	0.535
346.25	0.004	0.071	0.052	0.957	0	0.469
348.75	0.009	0.040	0.031	0.438	0	0.405
351.25	0.169	0.235	0.216	0.948	0	0.337
353.75	1.83	1.55	1.63	-4.05	0	0.265
356.25	0.035	0.125	0.099	1.27	0	0.197

Note: The values are averaged for 2.5 nm intervals centered on the indicated wavelength.

* Cross section for -50°C < T < 20°C calculated as $\sigma(T) = A + B\times10^{-3}\ T$; T in °C, and σ in 10^{-20} cm^2.

CH_3OOH + hν → Products

Vaghjiani and Ravishankara (1989b) have measured the cross sections of CH_3OOH by measuring the CH_3OOH concentration via trapping and titration. These results are recommended and are listed in Table 53. The earlier results of Molina and Arguello (1979) are consistently 40% higher than the values shown in Table 53; this difference is believed to be due to difficulty in trapping CH_3OOH and measuring its concentration. CH_3OOH dissociates upon light absorption to give CH_3O with unit quantum yield (Vaghjiani and Ravishankara, 1990). At shorter wavelength (i.e. 193 nm) production of H and O atoms is also seen.

Table 53. Absorption Cross Sections of CH_3OOH

λ (nm)	$10^{20} \sigma$ (cm^2)	λ (nm)	$10^{20} \sigma$ (cm^2)
210	31.2	290	0.69
220	15.4	300	0.41
230	9.62	310	0.24
240	6.05	320	0.14
250	3.98	330	0.079
260	2.56	340	0.047
270	1.70	350	0.027
280	1.09	360	0.016

HCN + hν → Products

Herzberg and Innes (1957) have studied the spectroscopy of hydrogen cyanide, HCN, which starts absorbing weakly at $\lambda < 190$ nm.

The solar photodissociation rate for this molecule is rather small, even in the upper stratosphere; estimates of this rate would require additional studies of the absorption cross sections and quantum yields in the 200 nm region.

CH_3CN + hν → Products

McElcheran et al. (1958) have reported the spectrum of acetonitrile or methyl cyanide, CH_3CN; the first absorption band appears at $\lambda < 220$ nm. More recently, Suto and Lee (1985) and Zetzsch (1989) have measured the cross sections around 200 nm; solar photodissociation is unimportant compared to reaction with OH radicals.

SO_2 + hν → Products

The UV absorption spectrum of SO_2 is highly structured, with a very weak absorption in the 340-390 nm region, a weak absorption in the 260-340 nm region, and a strong absorption extending from 180 to 235 nm; the threshold wavelength for photodissociation is ~220 nm. The atmospheric photochemistry of SO_2 has been reviewed by Heicklen et al. (1980) and by Calvert and Stockwell

(1983). Direct photo-oxidation at wavelengths longer than ~300 nm by way of the electronically excited states of SO_2 appears to be relatively unimportant.

The absorption cross sections have been measured recently by McGee and Burris (1987) at 295 and 210 K, between 300 and 324 nm, which is the wavelength region commonly used for atmospheric monitoring of SO_2.

$OCS + h\nu \rightarrow CO + S$

The absorption cross sections of OCS have been measured by Breckenridge and Taube (1970), who presented their 298 K results in graphical form, between 200 and 260 nm; by Rudolph and Inn (1981) between 200 and ~300 nm (see also Turco et al., 1981), at 297 and 195 K; by Leroy et al. (1981) at 294 K, between 210 and 260 nm, using photographic plates; by Molina et al. (1981) between 195 and 260 nm, in the 195 K to 403 K temperature range. The results are in good agreement in the regions of overlap, except for $\lambda > 280$ nm, where the cross section values reported by Rudolph and Inn (1981) are significantly larger than those reported by Molina et al. (1981). The latter authors concluded that solar photodissociation of OCS in the troposphere occurs only to a negligible extent.

The recommended cross sections, given in Table 54, are taken from Molina et al. (1981). (The original publication also lists a table with cross section values averaged over 1 nm intervals, between 185 and 300 nm.)

The recommended quantum yield for photodissociation is 0.72. This value is taken from the work of Rudolph and Inn (1981), who measured the quantum yield for CO production in the 220-254 nm range.

$CS_2 + h\nu \rightarrow CS + S$

The CS_2 absorption spectrum is rather complex. Its photochemistry has been reviewed by Okabe (1978). There are two distinct regions in the near UV spectrum: a strong absorption extending from 185 to 230 nm, and a weaker one in the 290-380 nm range. The threshold wavelength for photodissociation is ~280 nm.

The photo-oxidation of CS_2 in the atmosphere has been discussed by Wine et al. (1981d), who report that electronically excited CS_2 may react with O_2 to yield eventually OCS.

Table 54. Absorption Cross Sections of OCS

λ (nm)	$10^{20}\sigma(\mathrm{cm}^2)$		λ (nm)	$10^{20}\sigma(\mathrm{cm}^2)$	
	295 K	225 K		295 K	225 K
186.1	18.9	13.0	228.6	26.8	23.7
187.8	8.33	5.63	231.2	22.1	18.8
189.6	3.75	2.50	233.9	17.1	14.0
191.4	2.21	1.61	236.7	12.5	9.72
193.2	1.79	1.53	239.5	8.54	6.24
195.1	1.94	1.84	242.5	5.61	3.89
197.0	2.48	2.44	245.4	3.51	2.29
199.0	3.30	3.30	248.5	2.11	1.29
201.0	4.48	4.50	251.6	1.21	0.679
203.1	6.12	6.17	254.6	0.674	0.353
205.1	8.19	8.27	258.1	0.361	0.178
207.3	10.8	10.9	261.4	0.193	0.0900
209.4	14.1	14.2	264.9	0.0941	0.0419
211.6	17.6	17.6	268.5	0.0486	0.0199
213.9	21.8	21.8	272.1	0.0248	0.0101
216.2	25.5	25.3	275.9	0.0119	0.0048
218.6	28.2	27.7	279.7	0.0584	0.0021
221.5	30.5	29.4	283.7	0.0264	0.0009
223.5	31.9	29.5	287.8	0.0012	0.0005
226.0	30.2	27.4	292.0	0.0005	0.0002
			296.3	0.0002	-

$NaCl + h\nu \rightarrow Na + Cl$

There are several studies of the UV absorption spectra of NaCl vapor. For a review of the earlier work, which was carried out at high temperatures, see Rowland and Rogers (1982). The recommended cross sections, listed in Table 55, are taken from the work of Silver et al. (1986), who measured spectra of gas phase NaCl at room temperature in the range from ~190 to 360 nm, by directly monitoring the product Na atoms.

Table 55. Absorption Cross Sections of NaCl Vapor at 300 K

λ(nm)	$10^{20}\sigma(cm^2)$
189.7	612
193.4	556
203.1	148
205.3	90.6
205.9	89.6
210.3	73.6
216.3	151
218.7	46.3
225.2	146
230.4	512
231.2	947
234.0	1300
237.6	638
241.4	674
248.4	129
251.6	251
254.8	424
260.2	433
268.3	174
277.0	40
291.8	0.8

$NaOH + h\nu \rightarrow Na + OH$

The spectrum of NaOH vapor is poorly characterized. Rowland and Makide (1982) inferred the absorption cross section values and the average solar photodissociation rate from the flame measurements of Daidoji (1979). Additional measurements are required.

HETEROGENEOUS CHEMISTRY

We have evaluated and tabulated the currently available information on heterogeneous stratospheric processes. However, this is a relatively new and rapidly developing field and further results can be expected to change our quantitative, and even qualitative, understanding on a regular basis. The topic's complexity is compounded by the difficulty of characterizing the chemical and physical properties of stratospheric heterogeneous surfaces and then reproducing suitable simulations in the laboratory.

Surface Types

To a first approximation there are three major types of surfaces believed to be present at significant levels in the stratosphere. They are: 1) Type I - polar stratospheric clouds (PSCs) nominally composed of nitric acid trihydrate ($HNO_3 \bullet 3H_2O$); 2) crystals of relatively pure water ice, designated as Type II PSCs because they form at lower temperatures than Type I and are believed to be nucleated by Type I (similar surfaces may form as contrails behind high altitude aircraft under some stratospheric conditions); and 3) sulfuric acid aerosol, which is nominally a liquid phase surface generally composed of 60 - 80 weight percent H_2SO_4 and concomitantly, 40-20 weight percent H_2O. While PSCs, as their name suggests, are formed primarily in the cold winter stratosphere at high latitudes, sulfuric acid aerosol is present year round at all latitudes and may influence stratospheric chemistry on a global basis, particularly after large injections of volcanic sulfur periodically increase their abundance and surface area.

The detailed composition and morphology of each surface type are uncertain and probably subject to a significant range of natural variability. Certain chemical and physical properties of these surfaces, such as their ability to absorb and/or solvate HCl and HNO_3, are known to be strongly dependent on their detailed chemical composition. Moreover, most heterogeneous processes studied under laboratory conditions (and in some cases proceeding under stratospheric conditions) can change the chemical composition of the surface in ways which significantly affect the kinetic or thermodynamic processes of interest. Thus, a careful analysis of the time-dependent nature of the active surface is required in the evaluation of measured uptake kinetics experiments. Experimental techniques which allow the measurement of mass accommodation or surface reaction kinetics with high time resolution and/or with low trace gas fluxes are often more credible in establishing that measured kinetic parameters are not seriously compromised by surface saturation or changing surface chemical composition.

The measured kinetic uptake parameters, mass accommodation coefficients and surface reaction probabilities are separately documented for relevant atmospheric trace gas species for the three stratospheric surfaces noted above. Since these parameters can vary significantly with surface composition (e.g., the H_2SO_4/H_2O ratio for sulfate aerosol or the HNO_3/H_2O ratio for Type I PSC) the dependence of these parameters on surface composition is reviewed where sufficient data are available. Furthermore, data are also compiled for liquid water for several reasons. This surface is one asymptote of the H_2SO_4/H_2O aerosol continuum; the interactions of some trace species with liquid water and water ice (Type II PSC) surfaces are often similar; and the uptake of some trace species by water surfaces in the troposphere can play a key role in understanding their tropospheric chemical lifetimes and thus, the fraction which may be transported into the stratosphere. Finally, a few processes measured on solid inorganic salt surfaces, which may be relevant to the stratosphere perturbed by volcanic eruptions or solid rocket exhaust particles are also included. Heterogeneous processes on soot produced by high altitude aircraft or rockets using hydrocarbon propellants are not addressed in this tabulation but may be addressed in the future.

Temperature Dependence

A number of laboratory studies have shown that mass accommodation coefficients and, to some extent, surface reaction probabilities can be temperature dependent. While these dependencies have not been characterized for many systems of interest, temperature effects on kinetic data are noted where available. More work which fully separates heterogeneous kinetic temperature effects from temperature controlled surface composition is obviously needed.

Solubility Limitations

Experimental data on the uptake of some trace gases by various stratospherically relevant surfaces can be shown to be governed by solubility limitations rather than kinetic processes. In these cases properly analyzed data can yield measurements of trace gas solubility parameters relevant to stratospheric conditions. In general, such parameters can be strongly dependent on both condensed phase composition and temperature. Such parameters may be very important in stratospheric models since they can govern the availability of a reactant for a bimolecular heterogeneous process (e.g., the concentration of HCl available for the HCl + $ClONO_2$ reaction on sulfuric acid aerosols) or the gas/condensed phase partitioning of a heterogeneous reaction product (e.g., the HNO_3 formed by the reaction of N_2O_5 on sulfuric acid aerosols).

Data Organization

Data for trace gas heterogenous interactions with relevant condensed phase surfaces are tabulated in Tables 56, 57 and 58. These are organized into:

Table 56 - Mass Accommodation (Sticking) Coefficients
Table 57 - Surface Reaction Probabilities
Table 58 - Solubility Data

Mass accommodation coefficients (α), often called sticking coefficients, represent the probability of reversible uptake of a gaseous species colliding with the condensed surface of interest. For liquid surfaces this process is generally followed by bulk solvation. Examples include: simple surface absorption, absorption followed by ionic dissociation and solvation (e.g., $HCl + H_2O \leftrightarrow H^+(aq) + Cl^- (aq)$ and absorption followed by a reversible chemical reaction with a condensed phase substituent (e.g., $SO_2 + H_2O \leftrightarrow H^+ + HSO_3^-$). Processes involving liquid surfaces are subject to Henry's law which limits the fractional uptake of a gas phase species into a liquid. If the gas phase species is simply solvated a physical Henry's law restraint holds; if the gas phase species reacts with a condensed phase substituent, as in the sulfur dioxide/liquid water case noted above, a "chemically modified" or "effective" Henry's law constraint holds. It is presently unclear whether "surface solubility" effects govern the uptake on nominally solid water ice or HNO_3/H_2O ice surfaces in a manner analogous to bulk solubility effects for liquid substrates.

For some trace species on some surfaces experimental data suggest that mass accommodation coefficients untainted by experimental saturation limitations have been obtained. These are tabulated in Table 56. In other cases experimental data can be shown to be subject to Henry's law constraints, and Henry's law constants, or at least their upper limits, can be determined. These are tabulated for liquid surfaces in Table 58. Some experimental data sets are insufficient to determine if measured "uptake" coefficients are true accommodation coefficients or if the measurement values are lower limits compromised by saturation effects. These are currently tabulated, with suitable caveats, in Table 56.

Surface reaction probabilities (γ) are kinetic values for generally irreversible reactive uptake of trace gas species on condensed surfaces. Such processes are not subject to Henry's law constraints; however, the fate of the uptake reaction products may be subject to saturation limitations. For example, N_2O_5 has been shown to react with sulfuric acid aerosol surfaces. However, if the H_2SO_4/H_2O ratio is too high, the product HNO_3 will be insoluble and a large fraction will be expelled back into the gas phase. Surface reaction probabilities for substantially irreversible processes are presented in 57. Reaction products are identified where known.

The data in Tables 56 and 57 are organized by trace gas species, since some systematic variation may be expected for surface accommodation or reaction as the surface composition and/or phase is varied. Data presented for one surface may be judged for "reasonableness" by comparing with data for a "similar" surface. In some cases it is not yet clear if surface uptake is truly reversible (accommodation) or irreversibly reactive in nature. In such cases the available uptake coefficients are generally tabulated in Table 56 as accommodation coefficients, a judgement which will be subject to change if more definitive data become available.

Where a specific evaluated value for an accommodation coefficient or reaction probability has been obtained, an estimated uncertainty factor is also tabulated. However, when the data evaluation yielded only a lower or upper limit, no uncertainty factor can be reliably estimated and none are presented.

Table 56. Mass Accommodation Coefficients (α)

Gaseous Species	Surface Type	Composition	T(K)	α	Uncertainty Factor	Notes
HCl	Water Ice	$H_2O(s)$	191-211	0.3	3	1
	Liquid Water	$H_2O(l)$	274	0.2*	2	2
	Nitric Acid Ice	$HNO_3 \bullet 3H_2O(s)$	191-211	0.3	See note	3
	Sulfuric Acid	$H_2SO_4 \bullet nH_2O(l)$				4
		($n \geq 8$, ≤ 40 wt.% H_2SO_4)	283	0.15*	2	
			218	>0.05*		
		($n < 8$, >40 wt.% H_2SO_4)	(No data - all measurements limited by HCl solubility)			
HNO_3	Water Ice	$H_2O(s)$	200	0.03	3	5
	Liquid Water	$H_2O(l)$	268	0.2*	2	6
	Sulfuric Acid	$H_2SO_4 \bullet nH_2O(l)$				7
		(73 wt.% H_2SO_4)	283	0.1	2	
		(75 wt.% H_2SO_4)	230	$> 2 \times 10^{-3}$		
		(96.5 wt.% H_2SO_4)	295	$< 4 \times 10^{-3}$		
O_3	Water Ice	$H_2O(s)$	195-262	$< 1 \times 10^{-6}$‡		8
	Liquid Water	$H_2O(l)$	292	$> 2 \times 10^{-3}$‡		9
	Nitric Acid Ice	$HNO_3 \bullet 3H_2O(s)$	195	2.5×10^{-4}‡	3	8
	Sulfuric Acid	$H_2SO_4 \bullet nH_2O(l)$				10
		(50 wt.% H_2SO_4)	195	$< 1 \times 10^{-6}$‡		
		(97 wt.% H_2SO_4)	196	$< 1 \times 10^{-6}$‡		
H_2O_2	Liquid Water	$H_2O(l)$	273	0.18*	2	11
	Sulfuric Acid	$H_2SO_4 \bullet nH_2O(l)$				
		(96 wt.% H_2SO_4)	298	$> 8 \times 10^{-4}$‡		12
NO_2	Water Ice	$H_2O(s)$	195	$< 1 \times 10^{-4}$‡		13
	Liquid Water	$H_2O(l)$	273	$> 6 \times 10^{-4}$‡		14
	Sulfuric Acid	$H_2SO_4 \bullet nH_2O(l)$				
		(96 wt.% H_2SO_4)	298	$< 1 \times 10^{-6}$‡		12
NO	Water Ice	$H_2O(s)$	195	$< 1 \times 10^{-4}$‡		15
	Sulfuric Acid	$H_2SO_4 \bullet nH_2O$				
		(96 wt.% H_2SO_4)	298	$< 1 \times 10^{-6}$‡		16
SO_2	Liquid Water	$H_2O(l)$	260-292	0.11	2	17
	Sulfuric Acid	$H_2SO_4 \bullet nH_2O(l)$				
		(96 wt.% H_2SO_4)	298	$< 1 \times 10^{-6}$‡		18
HO_2	Liquid Water	$H_2O(l)$	275	> 0.02		19
	Aqueous Salts	$NH_4HSO_4(aq)$	293	> 0.2		19
		and $LiNO_3(aq)$				
	Sulfuric Acid	$H_2SO_4 \bullet nH_2O(l)$	275	>0.07		20
		(28 wt.% H_2SO_4)				

Table 56. (Continued)

Gaseous Species	Surface Type	Composition	T(K)	α	Uncertainty Factor	Notes
OH	Liquid Water	$H_2O(l)$	275	$> 4 \times 10^{-3}$		21
	Sulfuric Acid	$H_2SO_4 \bullet nH_2O(l)$				22
		(28 wt.% H_2SO_4)	275	> 0.07		
		(96 wt.% H_2SO_4)	298	$> 5 \times 10^{-4}$‡		
O	Sulfuric Acid	$H_2SO_4 \bullet nH_2O(l)$				23
		(96 wt.% H_2SO_4)	298	$< 1 \times 10^{-6}$‡		
HO_2NO_2	Sulfuric Acid	$H_2SO_4 \bullet nH_2O(l)$				24
		(96 wt.% H_2SO_4)	298	$< 2.7 \times 10^{-5}$‡		
H_2O	Water Ice	$H_2O(s)$	200	0.5	2	25
	Sulfuric Acid	$H_2SO_4 \bullet nH_2O$				26
		(96 wt.% H_2SO_4)	298	$> 2 \times 10^{-3}$‡		
CF_2O	Water Ice	$H_2O(s)$	192	$< 3 \times 10^{-6}$‡		27
	Liquid Water	$H_2O(l)$	260-290	$< 1 \times 10^{-3}$‡		28
	Nitric Acid Ice	$HNO_3 \bullet 3H_2O(s)$	192	$< 3 \times 10^{-6}$‡		27
	Sulfuric Acid	$H_2SO_4 \bullet nH_2O(l)$	215-230			27
		(60 wt.% H_2SO_4)		3×10^{-6}‡	3	
		(40 wt.% H_2SO_4)		6×10^{-5}‡	2	
CCl_2O	Liquid Water	$H_2O(l)$	260-290	$< 1 \times 10^{-3}$‡		28
CF_3CClO	Liquid Water	$H_2O(l)$	260-290	$< 1 \times 10^{-3}$‡		28
CF_3CFO	Liquid Water	$H_2O(l)$	260-290	$< 1 \times 10^{-3}$‡		28
Cl_2	Water Ice	$H_2O(s)$	200	$< 1 \times 10^{-4}$‡		29

* Varies with T, see Notes.

‡ Measurement likely affected by saturation.

NOTES FOR TABLE 56

1. HCl on $H_2O(s)$ - Leu, 1988a (0.4; +0.6, -0.2) and Hanson and Ravishankara, 1991b ($\alpha \geq 0.3$) are in reasonable agreement at stratospheric ice temperatures.

2. HCl on $H_2O(1)$ - Recommendation is based on Van Doren et al., 1990. Measured α's decrease from 0.18 ± 0.02 at 274 K to 0.064 ± 0.01 at 294 K, demonstrating a strong negative temperature dependence. Tang and Munkelwitz (1989) have measured a larger (0.45 ± 0.4) HCl evaporation coefficient for an aqueous NH_4Cl droplet at 299 K.

3. HCl on $HNO_3 \bullet nH_2O$ - There is severe disagreement between Hanson and Ravishankara (1991b) ($\alpha \geq 0.3$) for NAT (54 wt. % HNO_3), and Leu et al., (1991) ($\alpha = 8 \times 10^{-3}$ to $< 9 \times 10^{-7}$ over weight % range of 44-57). Variation with HNO_3 wt. % in Leu et al. seems unreasonable unless a solubility limitation is operating. Data plotted in Moore et al. (1990) suggest uptake coefficients measured by Leu et al. (1991) may be surface solubility limited and hence may not represent α. However, further work is needed to reconcile the measurements of Hanson and Ravishankara with those of Leu et al. The measurements of Hanson and Ravishankara (1991) are consistent with $\alpha = 1$.

4. HCl on $H_2SO_4 \bullet nH_2O$ - Measurements by Watson et al. (1990) at 284 K show $\alpha = 0.15 \pm 0.01$ independent of n for $n \geq 8$. Experimental uptake and, therefore, apparent α falls off for $n \leq 8$ (≥ 40 wt. % H_2SO_4). This behavior is also observed at stratospheric temperature (218 K) by Hanson and Ravishankara (1991d). Solubility constraints also controlled earlier low temperature uptake measurements of Tolbert et al. (1988b).

5. HNO_3 on $H_2O(s)$ - Leu (1988a) reports 0.3 (+0.7, -0.1). Some additional uncertainty is introduced by effective ice surface area in fast flow measurement (see Keyser et al., 1991).

6. HNO_3 on $H_2O(l)$ - Measured α has a strong negative temperature dependence varying from 0.19 ± 0.02 at 268 K to 0.07 ± 0.02 at 293 K (Van Doren et al., 1991).

7. HNO_3 on $H_2SO_4 \bullet nH_2O$ - Initial uptake at 73 wt. % H_2SO_4 allows a measurement of $\alpha = 0.11 \pm 0.01$ at 283 K (Van Doren et al., 1991). This value is expected to increase at lower temperatures, similar to $H_2O(1)$ uptake (Van Doren et al., 1990). Total HNO_3 uptake is subject to Henry's law solubility constraints, even at stratospheric temperatures (Reihs et al., 1990). Solubility limitations also affected the earlier "sticking coefficient" measurements of Tolbert et al. (1988b).

8. O_3 on $H_2O(s)$ - Undoped ice surfaces saturate too quickly for reliable measurements. When ice is doped with Na_2SO_3 to chemically remove absorbed O_3, the apparent α increases to 1×10^{-2} (0.1M) or up to 4×10^{-2} (1M) (Dlugokencky and Ravishankara, 1992). Limit of $\alpha = 10^{-6}$ or undoped ice is consistent with earlier measurement by Leu (1988b) of $\leq 1 \times 10^{-4}$. Dlugokencky and Ravishankara also measured the tabulated value of an uptake coefficient for O_3 on an NAT "like" surface but the data were difficult to reproduce and the surfaces were not well characterized.

9. O_3 on $H_2O(l)$ - Utter et al. (1992) used a wetted wall flow tube technique with various chemical scavengers to measure a lower limit for α of 2×10^{-3}. The stopped flow measurement technique using an $SO_3{}^{=}$ scavenger (Tang and Lee, 1987) is subject to saturation effects, so their quoted α of 5.3×10^{-4} is also taken as a lower limit.

10. O_3 on $H_2SO_4 \bullet nH_2O$ - Recent flow tube measurements (Dlugokencky and Ravishankara, 1992) of $\alpha < 10^{-6}$ on solid H_2SO_4 surfaces are consistent with earlier, but probably less

quantitative, static systems measurements of Olszyna et al. (1979) and aerosol chamber measurements of Harker and Ho (1979) who report α's of the order 10^{-8} or less for a variety of sulfuric acid concentrations and temperatures. In these earlier experiments doping the H_2SO_4 with Ni^{2+}, Cr^{2+}, Al^{3+}, Fe^{3+} and NH_4^+ (Olszyna et al., 1979) or Al_2O_3 or Fe_2O_3 (Harker and Ho, 1979) did not significantly increase measured O_3 loss. Ozone uptake is probably limited by saturation effects.

11. H_2O_2 on $H_2O(l)$ - Measured accommodation coefficient (Worsnop et al., 1989) has a strong negative temperature dependence over the measured range of 260-272 K, with $\alpha = 0.3$ at 260K decreasing to 0.1 at 292 K.

12. H_2O_2 on $H_2SO_4 \bullet nH_2O$ - Knudsen cell uptake measurement is subject to surface saturation, thus value quoted by Baldwin and Golden (1979) is almost certainly a lower limit. This is probably also responsible for the lack of measured uptake for NO, NO_2, SO_2 and other species reported in this reference and Baldwin and Golden (1980).

13. NO_2 on $H_2O(s)$ - In the absence of a chemical sink, Leu (1988b) measured no sustained uptake of NO_2 on ice yielding an apparent $\alpha \leq 1 \times 10^{-4}$. This value is probably influenced by surface saturation.

14. NO_2 on $H_2O(1)$ - Measured α of $(6.3 \pm 0.7) \times 10^{-4}$ (Tang and Lee, 1988) was achieved by chemical consumption of NO_2 by $SO_3^{=}$. Stopped flow measurement was probably still affected by surface saturation, lending to the measurement of a lower limit.

15. NO on $H_2O(s)$ - See note 13; NO subject to same concerns as NO_2.

16. NO on $H_2SO_4 \bullet nH_2O$. See Note 12.

17. SO_2 on $H_2O(1)$ - Measured α of 0.11 ± 0.02 has no significant temperature variation over temperature range of 260 - 292 K (Worsnop et al., 1989).

18. SO_2 on $H_2SO_4 \bullet nH_2O$. See Note 12.

19. HO_2 on $H_2O(l)$ - Determination of α in liquid wall flow tube (Hanson et al., 1992) is dependent on diffusion corrections; measured limit ($\alpha > 0.02$) is consistent with $\alpha = 1$. In the aqueous salt aerosol measurements of Mozurkewich et al. (1987), HO_2 was chemically scavenged by Cu^{++} from added $CuSO_4$ to avoid Henry's law constraints; this measurement is also consistent with $\alpha = 1$.

20. HO2 on $H_2SO_4 \bullet nH_2O$ - Liquid wall flow tube technique used by Hanson et al. (1992) is subject to a large gas phase diffusion correction; measured lower limit is consistent with $\alpha = 1$.

21. OH on $H_2O(l)$ - see Note 20, OH and HO_2 measurements of Hanson et al. (1992) are subject to same analysis issues.

22. OH on $H_2SO_4 \bullet nH_2O$ - See Note 20 for measurement by Hanson et al. (1992) and Note 12 for measurement by Baldwin and Golden (1980).

23. O on $H_2SO_4 \bullet nH_2O$ - See Note 12.

24. HO_2NO_2 on $H_2SO_4 \bullet nH_2O$ - See Note 12.

25. H_2O on $H_2O(s)$ - Measurements are available from Leu (1988a) giving 0.3 (+0.7, -0.1) at 200 K and Haynes et al. (1991) (1.1 ± 0.1 to 0.71 ± 0.2) from 20 to 185 K.

26. H_2O on $H_2SO_4 \bullet nH_2O$ - See Note 12.

27. CF_2O coefficient uptake measurements by Hanson and Ravishankara (1991c) on stratospheric surfaces are probably subject to surface and/or bulk saturation effects and may not represent accommodation coefficient measurements.

28. Halocarbonyls on $H_2O(l)$ - Uptake may be solubility limited, thus limits on accommodation coefficients measured by Worsnop and Davidovits (1991) could be too large.

29. See Note 13, Cl_2 subject to same concern as NO_2.

Table 57. Gas/Surface Reaction Probabilities (γ)

Gaseous Species	Surface Type	Composition	T(K)	γ	Uncertainty Factor	Notes
ClO + Surface → Products						
ClO	Water Ice	$H_2O(s)$	190	> 0.01		1
	Sulfuric Acid	$H_2SO_4 \cdot nH_2O(l)$ (72 to 95 wt.% H_2SO_4)	221-296	8×10^{-5}	10	2
Cl + Surface → Products						
Cl	Sulfuric Acid	$H_2SO_4 \cdot nH_2O(l)$ (72 to 95 wt.% H_2SO_4)	221-296	2×10^{-4}	10	3
$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$						
$ClONO_2$	Water Ice	$H_2O(s)$	200-202	0.3	3	4
	Nitric Acid Ice	$HNO_3 \cdot 3H_2O(s)$	200-202	0.006	See note	5
	Sulfuric Acid	$H_2SO_4 \cdot nH_2O(l)$				
		(40 wt.% H_2SO_4)	218	6.4×10^{-1}	2	6
		(60 wt.% H_2SO_4)	215	3.1×10^{-3}	2	
		(65 wt.% H_2SO_4)	215	1.2×10^{-3}	2	
		(70 wt.% H_2SO_4)	220	3.9×10^{-4}	2	
		(75 wt.% H_2SO_4)	230	1.9×10^{-4}	2	
		(96 wt.% H_2SO_4)	295	3.2×10^{-4}	2	
$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$						
$ClONO_2/HCl$	Water Ice	$H_2O(s)$	200-202	0.3	3	7
	Nitric Acid Ice Doped with HCl	$HNO_3 \cdot 3H_2O \cdot HCl$	200-202	0.3	3	8
	Sulfuric Acid	$H_2SO_4 \cdot nH_2O(l)$ (H_2SO_4 wt.% > 60))		See note		9
$ClONO_2 + NaCl(s) \rightarrow Cl_2 + NaNO_3$						
$ClONO_2$	Sodium Chloride	$NaCl(s)$	300	See note		10
$ClONO_2 + NaBr(s) \rightarrow BrCl + NaNO_3$						
$ClONO_2$	Sodium Bromide	$NaBr(s)$	300	See note		10
$N_2O_5 + H_2O \rightarrow 2HNO_3$						
N_2O_5	Water Ice	$H_2O(s)$	195-200	0.03	1.5	11
	Liquid Water	$H_2O(l)$	270-275	0.08*	2	12
	Nitric Acid Ice	$HNO_3 \cdot 3H_2O(s)$	200	6×10^{-4}	3	13
	Sulfuric Acid	$H_2SO_4 \cdot nH_2O(l)$	210-230	0.1	2	14

Table 57. (Continued)

Gaseous Species	Surface Type	Composition	T(K)	γ	Uncertainty Factor	Notes
$N_2O_5 + HCl \rightarrow ClNO_2 + HNO_3$						
N_2O_5	Water Ice	$H_2O(s)$	190-220	0.03	See note	15
	Nitric Acid Ice	$HNO_3 \cdot 3H_2O(s)$	200	0.003	2	16
$N_2O_5 + NaCl(s) \rightarrow ClNO_2 + NaNO_3(s)$						
N_2O_5	Sodium Chloride	NaCl(s)	298	$> 2.5 \times 10^{-3}$		17
$N_2O_5 + NaBr(s) \rightarrow BrNO_2 + NaNO_3(s)$						
N_2O_5	Sodium Bromide	NaBr(s)	298		See note	17
$HOCl + HCl(s) \rightarrow Cl_2 + H_2O$						
HOCl/HCl	Water Ice	$H_2O(s)$	195-200	0.3	3	18
	Nitric Acid Ice	$HNO_3 \cdot 3H_2O(s)$	195-200	0.1	3	18

* γ is temperature dependent

NOTES FOR TABLE 57

1. ClO on $H_2O(s)$ - Proposed reaction (Leu et al., 1988b) is $2\ ClO \rightarrow Cl_2 + O_2$; reactive uptake may depend on ClO surface coverage, which in turn, may depend on gas phase ClO concentrations.

2. ClO on $H_2SO_4 \bullet nH_2O$ - Measured reaction probability (Martin et al., 1980) varies between 2×10^{-5} and 2×10^{-4} as H_2O content is varied by changing wall temperature. Reaction product is claimed to be HCl, not Cl_2.

3. Cl on $H_2SO_4 \bullet nH_2O$ - Measured reaction probability (Martin et al., 1980) varies between 3×10^{-5} and 7×10^{-4} as H_2O and T co-vary as stated in Note 2. Reaction product is claimed to be HCl.

4. $ClONO_2$ on $H_2O(s)$ - Measurement of $\gamma = 0.3\ (+0.7, -0.1)$ (Hanson and Ravishankara, 1991a) significantly exceeds previous measurements of Molina et al. (1987), Tolbert et al. (1987), Leu (1988a) and Moore et al. (1990). Previous measurements were probably impeded by NAT formation on surface. Lower levels of $ClONO_2(g)$ used by Hanson and Ravishankara (1991a) minimized this surface saturation problem. Reaction products are HNO_3 and HOCl. All of the HNO_3 and much of the HOCl is retained on the surface under polar stratospheric conditions (Hanson and Ravishankara, 1991b).

5. $ClONO_2$ and $HNO_3 \bullet nH_2O$ - Hanson and Ravishankara (1991a, b) report a value of 0.006 for $ClONO_2$ reaction with the water in NAT ($HNO_3 \bullet 3H_2O$). Similar experiments (Moore et al., 1990; Leu et al., 1991) report a larger value 0.02 ± 0.01 which falls very rapidly as slight excesses of H_2O above the 3/1 H_2O/HNO_3 ratio for NAT are removed. They measure γ of less than 10^{-6} for slightly water poor "NAT" surfaces. The inconsistency between Hanson and Ravishankara (1991a,b) and the JPL group (Moore et al., 1990; Leu et al., 1990) has not been resolved. Hanson and Ravishankara (1991b) report that γ for this reaction increases by a factor of 4 as the surface temperature increases from 191 to 211 K.

6. $ClONO_2$ for $H_2SO_4 \bullet nH_2O$ - Quoted results are from Hanson and Ravishankara (1991d) and Rossi et al. (1987). The former agree within a factor of two at 65 and 75 wt.% H_2SO_4 with measurements by Tolbert et al. (1988b), further results which are consistent with those in Table 57 have been obtained by Reihs et al. (1991). Results of Hanson and Ravishankara (1991d) and Reihs et al. (1991) can be expressed as $\log^{10} (\gamma) = 1.87 - 0.0747\ W$, for $40 < W < 75$ where W is H_2SO_4 wt.%.

7. $ClONO_2/HCl$ on $H_2O(s)$ - Reaction probabilities of 0.27 (+0.73, -0.13) (Leu, 1988a) and 0.05 to 0.1 (Molina et al., 1987) have been reported near 200 K. Abbatt et al. (1991), Abbatt and Molina (1992), and Hanson and Ravishankara (1991b) report that a portion of the reaction may be due to $HOCl + HCl \rightarrow Cl_2 + H_2O$, with HOCl formed from $ClONO_2 + H_2O(s) \rightarrow HOCl + HNO_3(s)$. Hanson and Ravishankara (1991b) see no enhancement of the $ClONO_2$ reaction probability when $H_2O(s)$ is doped with HCl. Their preferred value is $\gamma = 0.3$, but is consistent with $\gamma = 1$.

8. $ClONO_2 + HCl$ on $HNO_3 \bullet 3H_2O$ - Measurements by Hanson and Ravishankara (1991a,b) and Leu and co-workers (Moore et al., 1990; Leu et al., 1991) both confirm a very high γ, relatively independent of the HNO_3/H_2O ratio.

9. $ClONO_2 + HCl$ on $H_2SO_4 \bullet nH_2O$ - Hanson and Ravishankara (1991d) have determined that low temperature solubility limits for HCl in $H_2SO_4 \bullet nH_2O$ (> 60 wt.% H_2SO_4) will restrict the $ClONO_2 + HCl$ reaction by demonstrating that HCl vapor has a minimal effect on $ClONO_2$ uptake on 60-75 wt.% H_2SO_4 surfaces, confirming the conclusion of Watson et al.

(1990) that HCl solubility will restrict $ClONO_2$ + HCl on normal stratospheric sulfuric acid aerosols. Tolbert et al. (1988b) also noted no measurable enhancement of $ClONO_2$ loss on a 65 wt.% H_2SO_4 surface at 210 K when the surface is exposed to HCl; however the reaction products do change to include Cl_2. Sulfuric acid surfaces with less than ~60 wt.% H_2SO_4 have sufficient water to absorb significant levels of HCl. Wolff and Mulvaney (1991) have suggested that such water rich H_2SO_4 aerosols may form under polar stratospheric conditions.

10. $ClONO_2$ on NaCl(s), NaBr(s) - Finlayson-Pitts and co-workers have shown that $ClONO_2$ reacts with crystalline NaCl (Finlayson-Pitts et al., 1989) and NaBr (Berko et al., 1991) to produce Cl_2 and BrCl respectively. No rate data for these reactions have been reported.

11. N_2O_5 on H_2O(s) - Leu (1988b) and Hanson and Ravishankara (1991a) have measured nearly identical values of 0.28 (±0.11) and 0.24 (±30%) near 200 K. Quinlan et al. (1990) have measured a lower limit for γ on fresh ice surfaces of 0.03 at 188 K.

12. N_2O_5 on H_2O(l) - Reaction on liquid water has a negative temperature dependence. Van Doren et al. (1990) measured γ's of 0.057 ±0.003 at 271 K and 0.036 ±0.004 at 282 K. Mozurkewich and Calvert (1988) studied γ on $NH_3/H_2SO_4/H_2O$ aerosols. For their most water rich aerosols (RH = 76%) they measured γ's of 0.10 ±0.02 at 274 and 0.039 ±0.012 at 293 K.

13. N_2O_5 on $HNO_3 \bullet 3H_2O$(s) - Hanson and Ravishankara (1991a) have measured $\gamma = 0.0006$ (±30%) at 200 K. This is in very poor agreement with $\gamma = 0.015$ (±0.006) reported by Quinlan et al. (1990). This latter measurement may have been biased by a supercooled nitric acid surface rather than NAT.

14. N_2O_5 on $H_2SO_4 \bullet nH_2O$(s) - Recent measurements by Hanson and Ravishankara (1991d) yielded γ(215 K) = 0.14 (±0.08) for 60 wt.% H_2SO_4, γ(220) = 0.10 (±0.02) for 70% H_2SO_4 and γ (230) = 0.10 (±0.02) for 75% H_2SO_4. This is in good agreement with γ(283) = 0.055 (±0.006) for 70% H_2SO_4 measured by Van Doren et al. (1991), since higher temperatures can be expected to yield lower γ's. Reihs et al. (1991) measured values near 0.055 over the temperature range 220-295 K, for 75-90 wt.% H_2SO_4. Their data show little dependence on either temperature or H_2SO_4 content. Their values are significantly smaller than Hanson and Ravishankara (1991d). Both Reihs et al. (1991) and Van Doren et al. (1990) measured significant levels of product HNO_3 in the gas phase, indicating that HNO_3 solubility limitations will limit gas phase denitrification due to reaction on normal stratospheric sulfuric acid aerosols. NH_3/H_2SO_4 aerosol studies at 274 and 294 K by Mozurkewich and Calvert (1988) are also consistent with the recommended lower temperature γ for $SO_4^=$ concentrations consistent with stratospheric aerosols.

15. N_2O_5 + HCl on H_2O(s) - Leu (1988b) measured $\gamma = 0.028$ (±0.011) at 195 K, while Tolbert et al. (1988a) measured a lower limit of 1 x 10^{-3} at 185 K. These experiments were done at high HCl levels probably leading to a liquid water/acid surface solution (Abbott et al., 1991). The reaction probability may be much smaller on HCl/H_2O ice surfaces characteristic of the stratosphere.

16. N_2O_5 + HCl on $HNO_3 \bullet 3H_2O$ - Hanson and Ravishankara (1991a) measured $\gamma = 0.0032$ (±30%) near 200 K.

17. N_2O_5 on NaCl, NaBr - Finlayson-Pitts and co-workers (Finlayson-Pitts et al., 1989; Livingston and Finlayson-Pitts, 1991) have demonstrated the N_2O_5 reacts with crystalline NaCl and NaBr to form $NaNO_3$(s) plus $ClNO_2$ and $BrNO_2$, respectively. A lower limit of γ

for the NaCl reaction of 2.5×10^{-3} has been reported by Livingston and Finlayson-Pitts (1991).

18. HOCl + HCl on $H_2O(s)$ and $HNO_3 \bullet 3H_2O(s)$ - Hanson and Ravishankara (1991b) and Abbatt and Molina (1992) have investigated the HOCl + HCl reaction on water ice and NAT like surfaces. The high reaction probabilities measured indicate that this reaction may play a significant role in release of reactive chlorine from the HCl reservoir. The reaction probability on "NAT-like" surfaces falls off dramatically (a factor of 10) on water-poor (HNO_3-rich) surfaces (Abbatt and Molina, 1992). The measured yield of product Cl_2 is 0.87±0.20 (Abbatt and Molina, 1992).

Table 58. Henry's Law Constants for Gas-Liquid Solubilities

T	wt. % H_2SO_4	A (M/atm)	H(T) (M/atm)	B(K)	Notes
HNO_3 in $H_2SO_4 \cdot nH_2O$					
			H = A exp(B/T)		
188-240	58	7.47×10^{-8}		7.16×10^{3}	1
	66	0.202		3.19×10^{3}	
	74	8.54×10^{-3}		3.55×10^{3}	
	87	3.56×10^{-3}		3.32×10^{3}	
283	73		4×10^{3}		2
HCl in $H_2SO_4 \cdot nH_2O$					
203	60		$> 8.6 \times 10^{3}$		3
283	40		$> 1.0 \times 10^{4}$		4
283	50		$> 1.0 \times 10^{3}$		4
283	60		$> 1.0 \times 10^{2}$		4
283	70		$> 1.0 \times 10^{1}$		4
F_2CO in $H_2SO_4 \cdot nH_2O$					
215-230	60		> 5		5

NOTES FOR TABLE 58

1. These parameters are from measurements of Reihs et al. (1990) in the temperature range 188-240 K. Extrapolation to higher temperatures shows good agreement with other studies (Van Doren et al., 1991).

2. High temperature value from Van Doren et al. (1991). Estimated from decrease in HNO_3 uptake and gaseous evolution of HNO_3 from N_2O_5 uptake.

3. From Tolbert (1989, private communication); see Watson et al. (1990).

4. From Watson et al. (1990). Estimated by assuming HCl uptake is solubility limited as calculated from a Hammett-type acidity function (H_0) of aqueous sulfuric acid. Effective solubility given by:

$$H^* = HK_a/10^{-H_0}$$

where

$$HK_a = 10^7\ M^2/\text{atm at } 283\ K$$

$$H_0 = -3 \text{ at } 40\ \text{wt\%}$$

$$H_0 = -6 \text{ at } 70\ \text{wt\%}$$

See discussion in Watson et al. (1990), Clegg and Brimblecombe (1986), and Schwartz (1988).

5. Hanson and Ravishankara (1991c) calculate an upper limit for H of F_2CO based on assumed solubility limit resulting in lack of measurable uptake into 60 wt% H_2SO_4.

APPENDIX 1

GAS PHASE ENTHALPY DATA

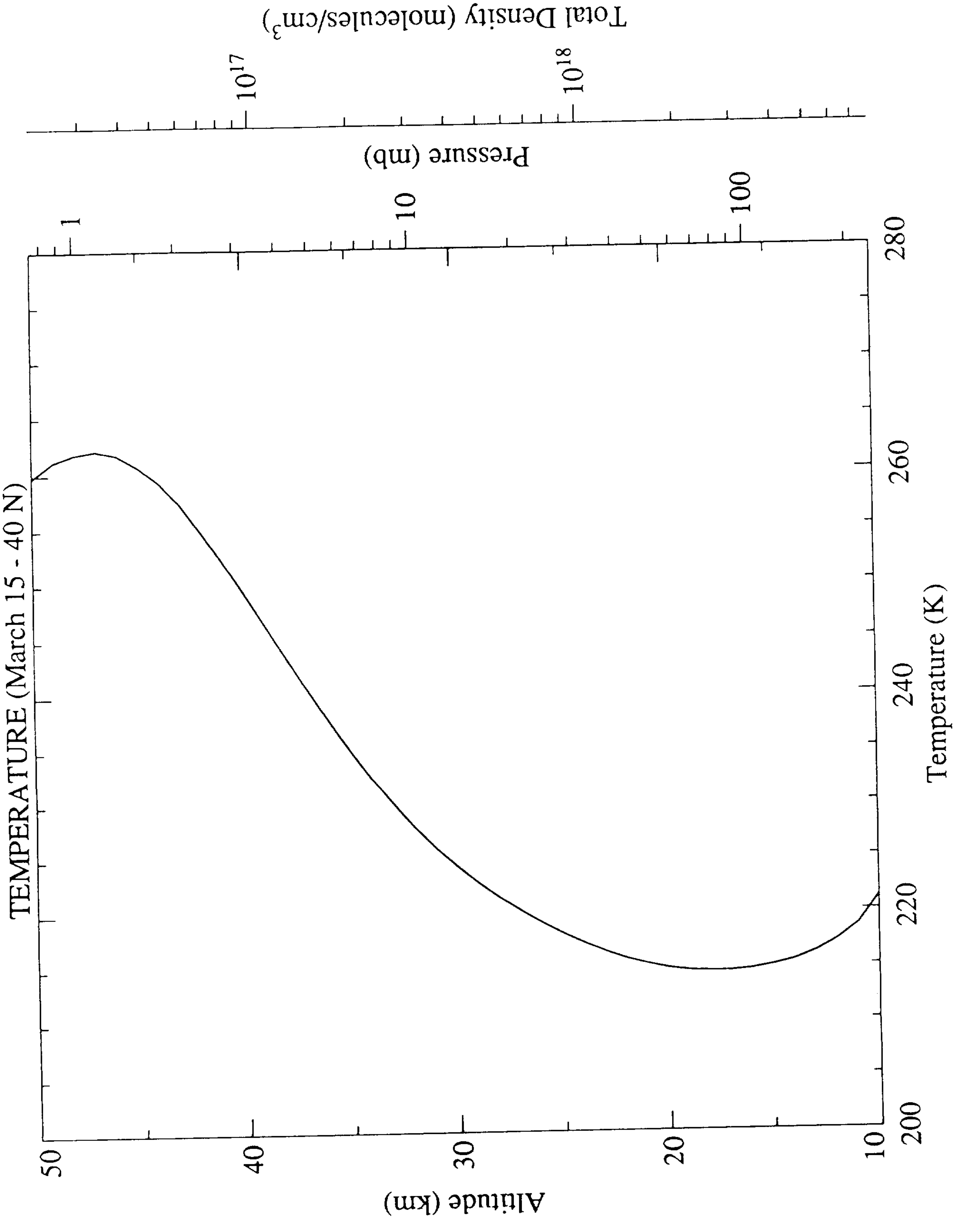
SPECIES	ΔH_f(298) (Kcal/mol)	SPECIES	ΔH_f(298) (Kcal/mol)	SPECIES	ΔH_f(298) (Kcal/mol)	SPECIES	ΔH_f(298) (Kcal/mol)
H	52.1	C_2H	133±2	FO	26±5	CF_3Cl	-169.2
H_2	0.00	C_2H_2	54.35	F_2O	5.9±.4	$CHFCl_2$	-68.1
O	59.57	C_2H_2OH	30±3	FO_2	6±1	CHF_2Cl	-115.6
$O(^1D)$	104.9	C_2H_3	72±3	F_2O_2	5±2	COFCl	-102±2
O_2	0.00	C_2H_4	12.45	FONO	-15±7	CH_3CH_2F	-63±2
$O_2(^1\Delta)$	22.5	C_2H_5	28.4	FNO	-16±2	CH_3CHF	-17±2
$O_2(^1\Sigma)$	37.5	C_2H_6	-20.0	FNO_2	-26±2	CH_2CF_3	-124±2
O_3	34.1	CH_2CN	57±2	$FONO_2$	2.5±7	CH_3CHF_2	-120±1
HO	9.3	CH_3CN	15.6	CF_2	-44±2	CH_3CF_2	-71±2
HO_2	3±1	CH_2CO	-11±3	CF_3	-112±1	CH_3CF_3	-179±2
H_2O	-57.81	CH_3CO	-5.8	CF_4	-223.0	CF_2CF_3	-213±2
H_2O_2	-32.60	CH_3CHO	-39.7	CHF_3	-166.8	CHF_2CF_3	-264±2
N	113.00	C_2H_5O	-4.1	CHF_2	-58±2	CH_3CF2Cl	-127±2
N_2	0.00	CH_2CH_2OH	-10±3	CH_2F_2	-107.2	CH_2CF_2Cl	-75±2
NH	85.3	C_2H_5OH	-56.2	CH_2F	-8±2	C_2Cl_4	-3.0
NH_2	45.3	CH_3CO_2	-49.6	CH_3F	-55.9±1	C_2HCl_3	-1.9
NH_3	-10.98	$C_2H_5O_2$	-6±2	FCO	-41±14	CH_2CCl_3	17±2
NO	21.57	CH_3COO_2	-41±5	COF_2	-153±2	CH_3CCl_3	-34.0
NO_2	7.9	CH_3OOCH_3	-30.0	Cl	28.9	CH_3CH_2Cl	-26.8
NO_3	17±2	C_3H_5	39.4	Cl_2	0.00	CH_2CH_2Cl	22±2
N_2O	19.61	C_3H_6	4.8	HCl	-22.06	CH_3CHCl	17.6±1
N_2O_3	19.8	n-C_3H_7	22.6±2	ClO	24.4	Br	26.7
N_2O_4	2.2	i-C_3H_7	19±2	ClOO	23±1	Br_2	7.39
N_2O_5	2.7±2	C_3H_8	-24.8	OClO	23±2	HBr	-8.67
HNO	23.8	C_2H_5CHO	-44.8	$ClOO_2$	16.7	HOBr	-19±2
HONO	-19.0	CH_3COCH_3	-51.9	ClO_3	52±4	BrO	30
HNO_3	-32.3	$CH_3COO_2NO_2$	-62±5	Cl_2O	19.5	BrNO	19.7
HO_2NO_2	-11±2	S	66.22	Cl_2O_2	31±3	BrONO	25±7
C	170.9	S_2	30.72	Cl_2O_3	34±3	$BrNO_2$	17±2
CH	142.0	HS	34±1	HOCl	-18±3	$BrONO_2$	12±5
CH_2	93±1	H_2S	-4.9	ClNO	12.4	BrCl	3.5
CH_3	35±.2	SO	1.3	$ClNO_2$	3.0	CH_2Br	40±2
CH_4	-17.88	SO_2	-70.96	ClONO	13	$CHBr_3$	6±2
CN	104±3	SO_3	-94.6	$ClONO_2$	5.5	$CHBr_2$	45±2
HCN	32.3	HSO	-1±3	FCl	-12.1	CBr_3	48±2
CH_3NH_2	-5.5	HSO_3	-92±2	CCl_2	57±5	CH_2Br_2	-2.6±2
NCO	38	H_2SO_4	-176	CCl_3	18±1	CH_3Br	-8.5
CO	-26.42	CS	67±2	CCl_4	-22.9	CH_3CH_2Br	-14.8
CO_2	-94.07	CS_2	28.0	$CHCl_3$	-24.6	CH_2CH_2Br	32±2
HCO	10±1	CS_2OH	26.4	$CHCl_2$	23±2	CH_3CHBr	30±2
CH_2O	-26.0	CH_3S	33±2	CH_2Cl	29±2	I	25.52
COOH	-53±2	CH_3SO_2	-57	CH_2Cl_2	-22.8	I_2	14.92
HCOOH	-90.5	CH_3SH	-5.5	CH_3Cl	-19.6	HI	6.3
CH_3O	4±1	CH_2SCH_3	36±3	ClCO	-5±1	CH_3I	3.5
CH_3O_2	4±2	CH_3SCH_3	-8.9	$COCl_2$	-52.6	CH_2I	52±2
CH_2OH	-6.2	CH_3SSCH_3	-5.8	CHFCl	-15±2	IO	41.1
CH_3OH	-48.2	OCS	-34	CH_2FCl	-63±2	INO	29.0
CH_3OOH	-31.3	F	18.98	CFCl	7±6	INO_2	14.4
CH_3ONO	-15.6	F_2	0.00	$CFCl_2$	-22±2		
CH_3ONO_2	-28.6	HF	-65.34	$CFCl_3$	-68.1		
$CH_3O_2NO_2$	-10.6±2	HOF	-23.4±1	CF_2Cl	-64±3		
				CF_2Cl_2	-117.9		

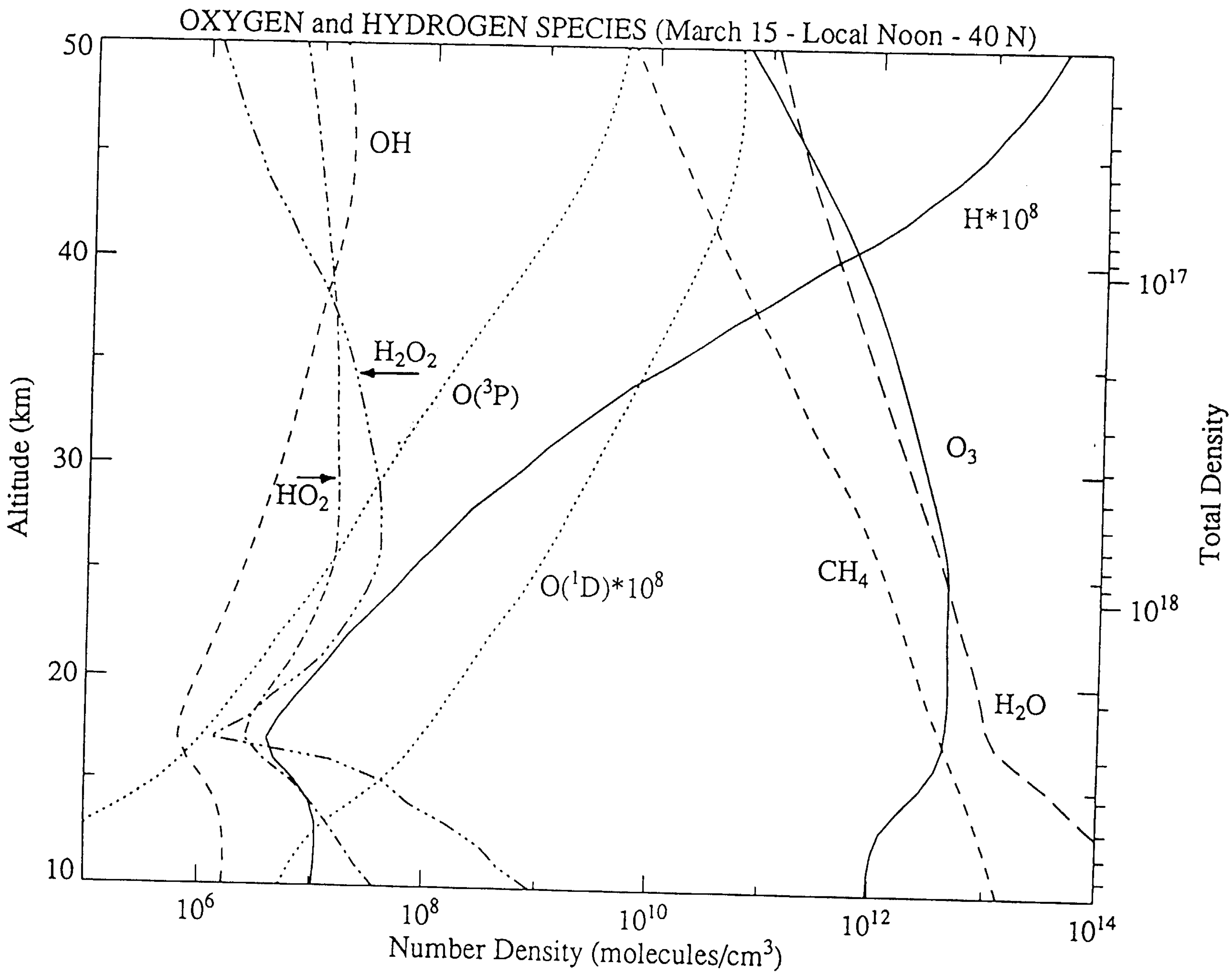
APPENDIX 2

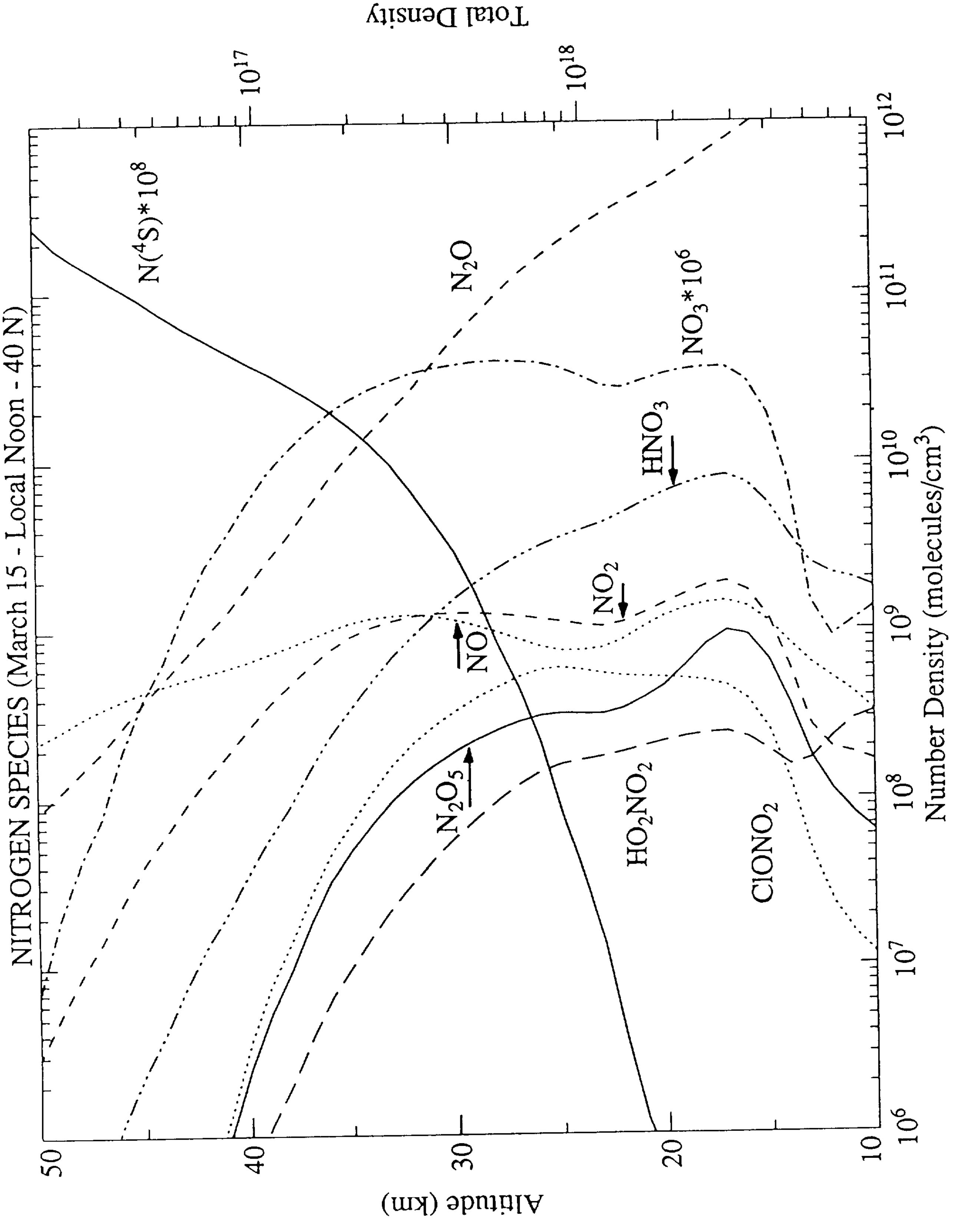
PROFILES

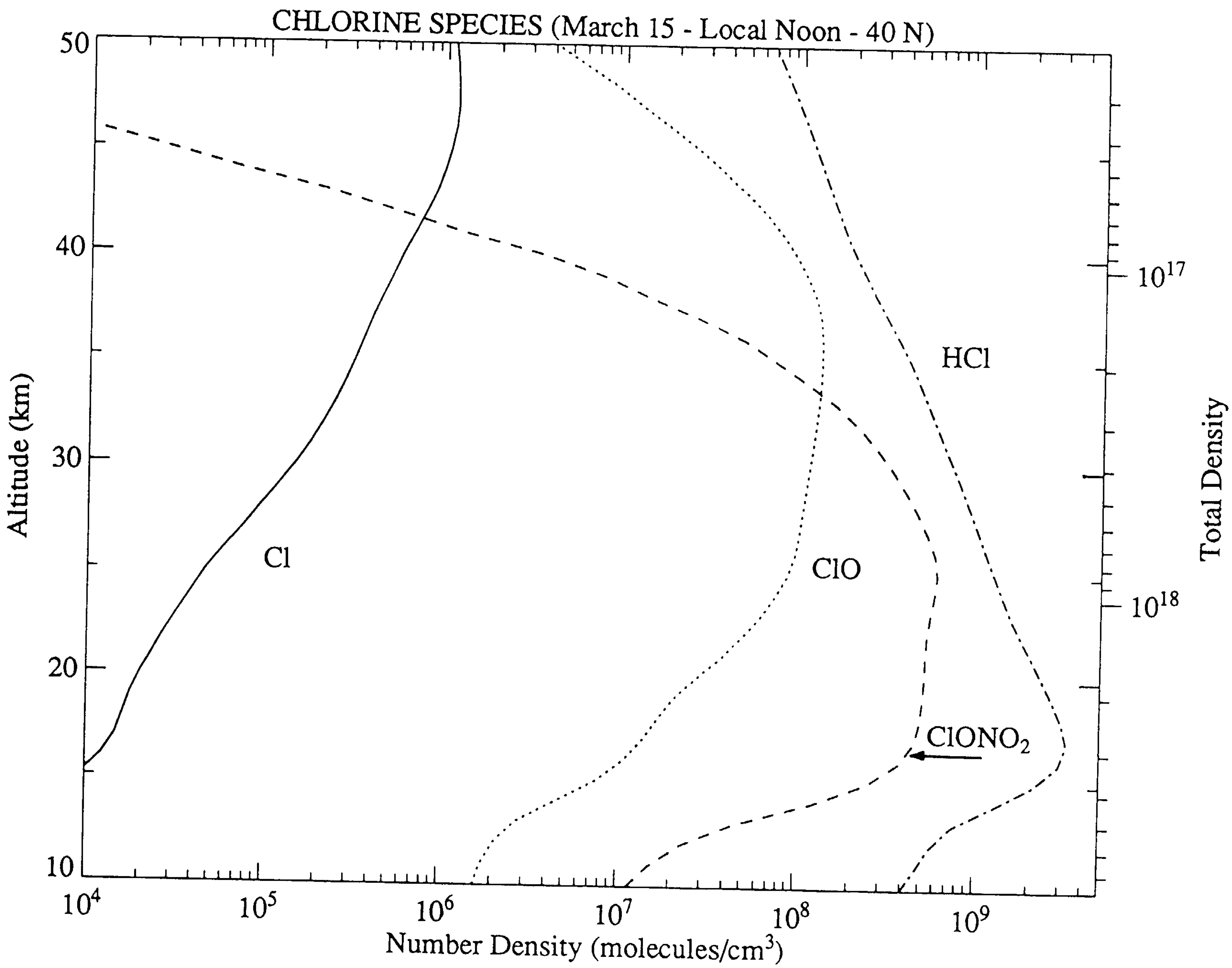
The species profiles presented in these figures were generated by the LLNL 2-D model of the troposphere and stratosphere. The tropopause mixing ratios of key trace gases are as follows: total chlorine 3.4 ppb, methane 1.69 ppm, nitrous oxide 307 ppb, carbon dioxide 350 ppm, and total bromine 0. The kinetic parameters used were consistent, where possible, with the Evaluation Number 9 recommendations of the NASA Panel for Data Evaluation (JPL 90-1). The model was constrained by observational fields for temperature, ozone, methane, nitrous oxide, and water vapor. These fields of satellite data were obtained from the UARS program (Robert Seals, Jr., private communication, 1990) and incorporated into the model to produce distributions for other infrequently observed species. This version of the model did not incorporate the heterogeneous reaction of N_2O_5 with H_2O to form nitric acid, and the predicted nitric acid profiles are smaller than the available satellite distributions indicate.

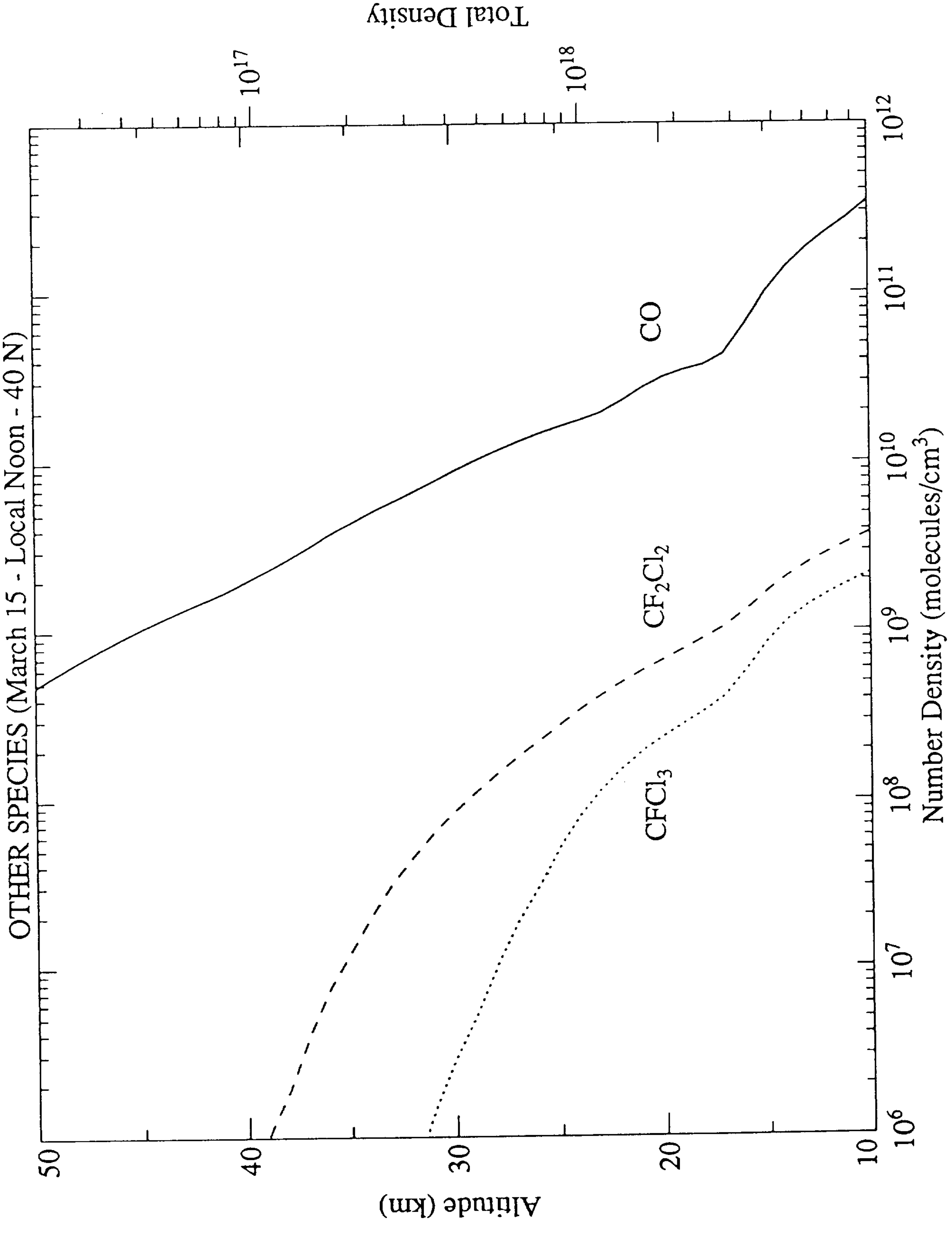
The rate constants shown for various photolytic processes are derived from a version of the LLNL 2-D model developed for the 91/92 UNEP report and incorporated the temperature dependence of the absorption cross sections for all appropriate species in the calculation of both atmospheric transmission and absorption. This version of the model represents a 1990 ambient atmosphere. Further details on this model will appear in the UNEP report.


TEMPERATURE (March 15 - 40 N)
Altitude (km)
50
40
30
20
10
Temperature (K)
200
220
240
260
280
Pressure (mb)
1
10
100
Total Density (molecules/cm^3)
10^{17}
10^{18}

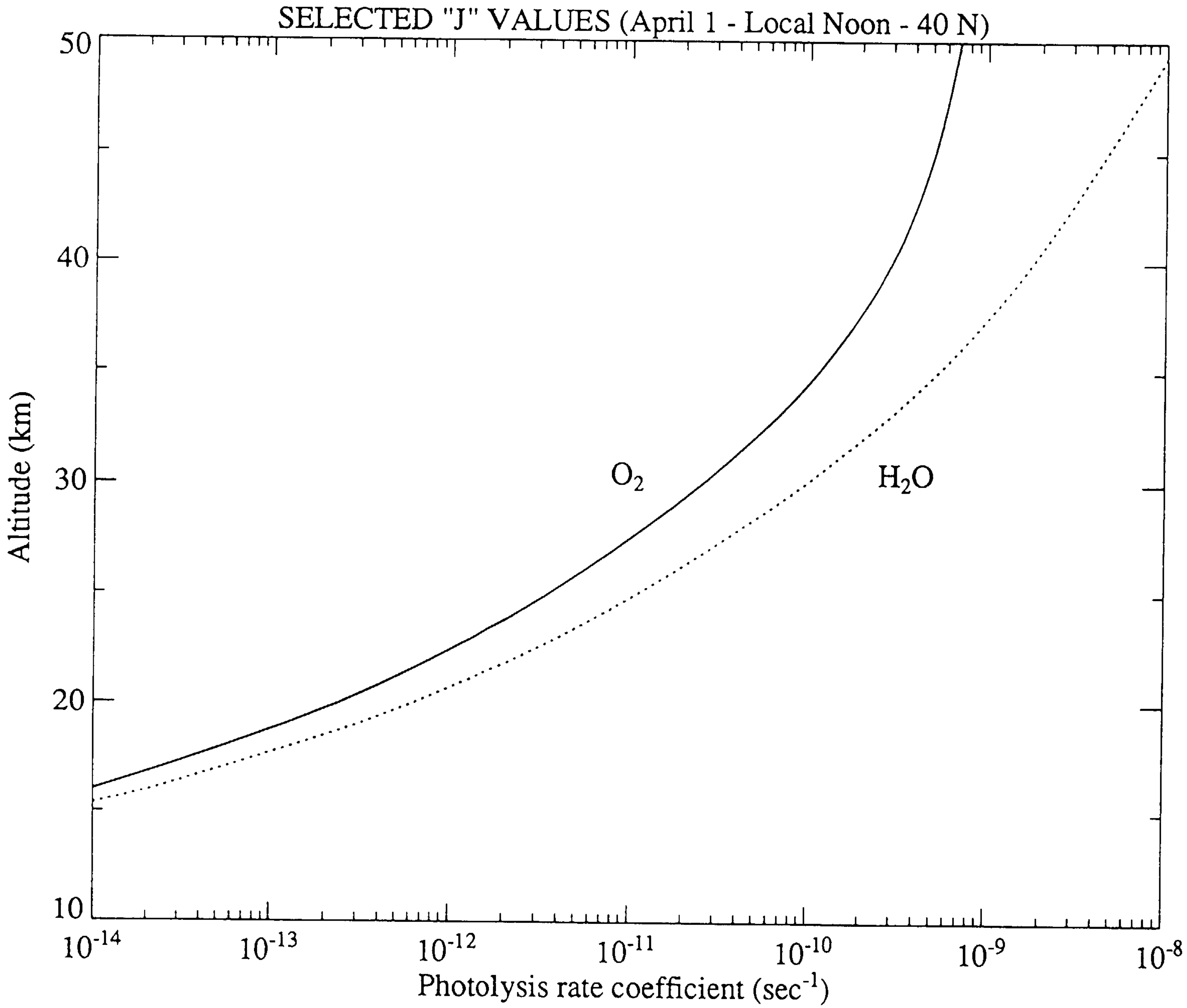

OXYGEN and HYDROGEN SPECIES (March 15 - Local Noon - 40 N)
Altitude (km)
50
40
30
20
10
OH
H_2O_2
$O(^3P)$
HO_2
$H*10^8$
O_3
CH_4
$O(^1D)*10^8$
H_2O
10^6
10^8
10^{10}
10^{12}
10^{14}
Number Density (molecules/cm^3)
10^{17}
10^{18}
Total Density


NITROGEN SPECIES (March 15 - Local Noon - 40 N)
Altitude (km)
50
40
30
20
10
Number Density (molecules/cm^3)
10^6
10^7
10^8
10^9
10^{10}
10^{11}
10^{12}
Total Density
10^{17}
10^{18}
N(^{4}S)*10^8
N$_2$O
NO$_3$*10^6
HNO$_3$
NO$_2$
NO
N$_2$O$_5$
HO$_2$NO$_2$
ClONO$_2$

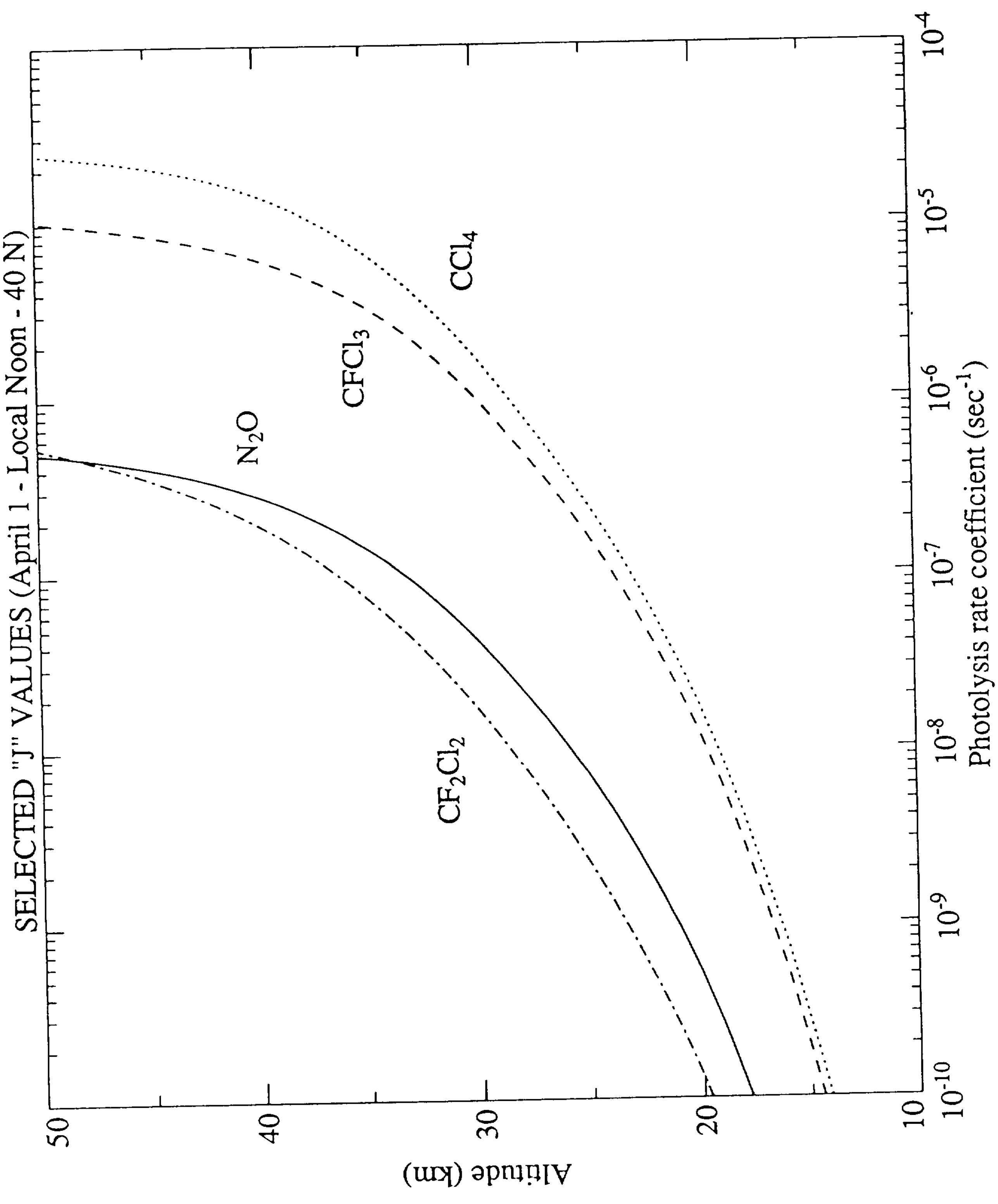

CHLORINE SPECIES (March 15 - Local Noon - 40 N)
Altitude (km)
50
40
30
20
10
Number Density (molecules/cm^3)
10^4
10^5
10^6
10^7
10^8
10^9
Total Density
10^{17}
10^{18}
Cl
ClO
HCl
ClONO$_2$

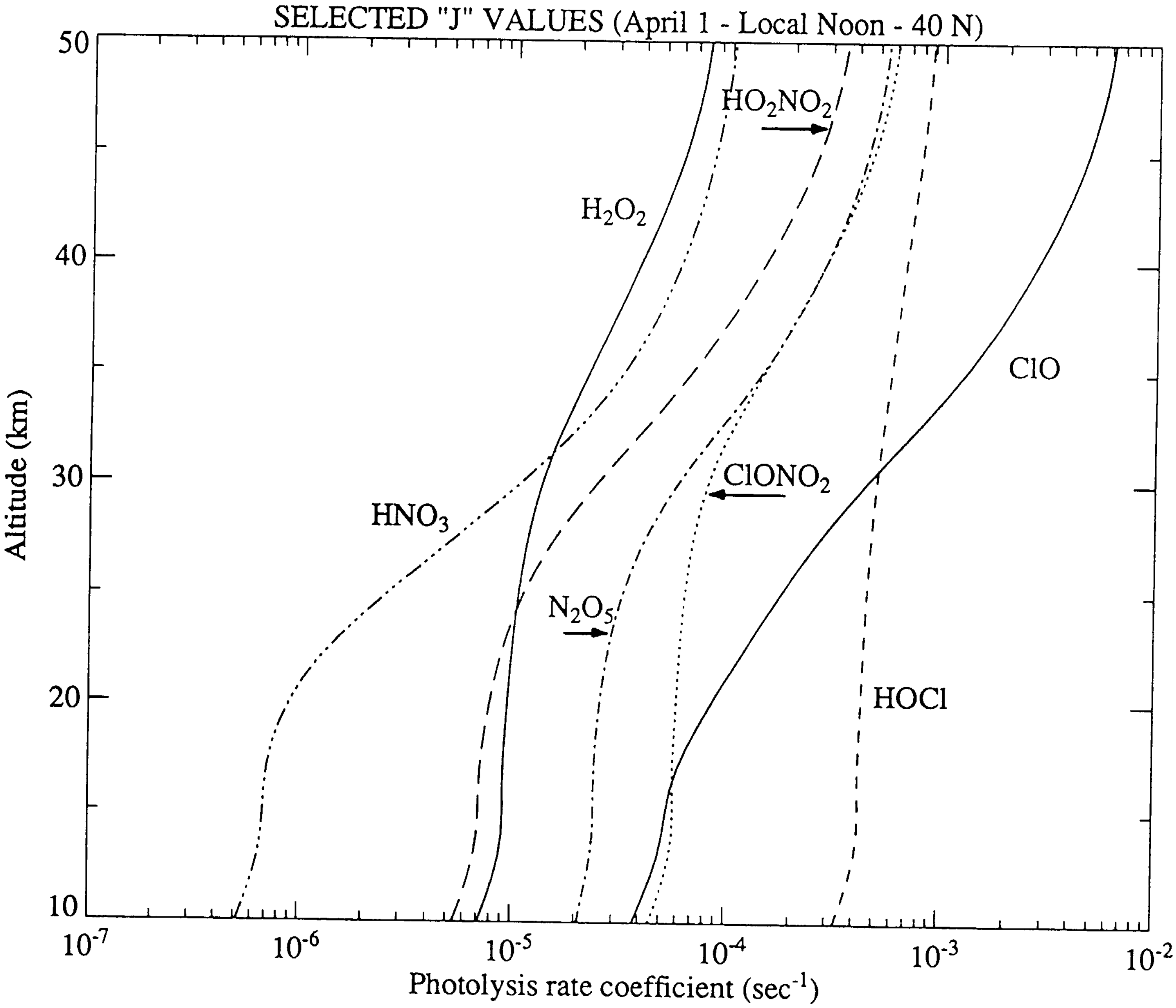


OTHER SPECIES (March 15 - Local Noon - 40 N)

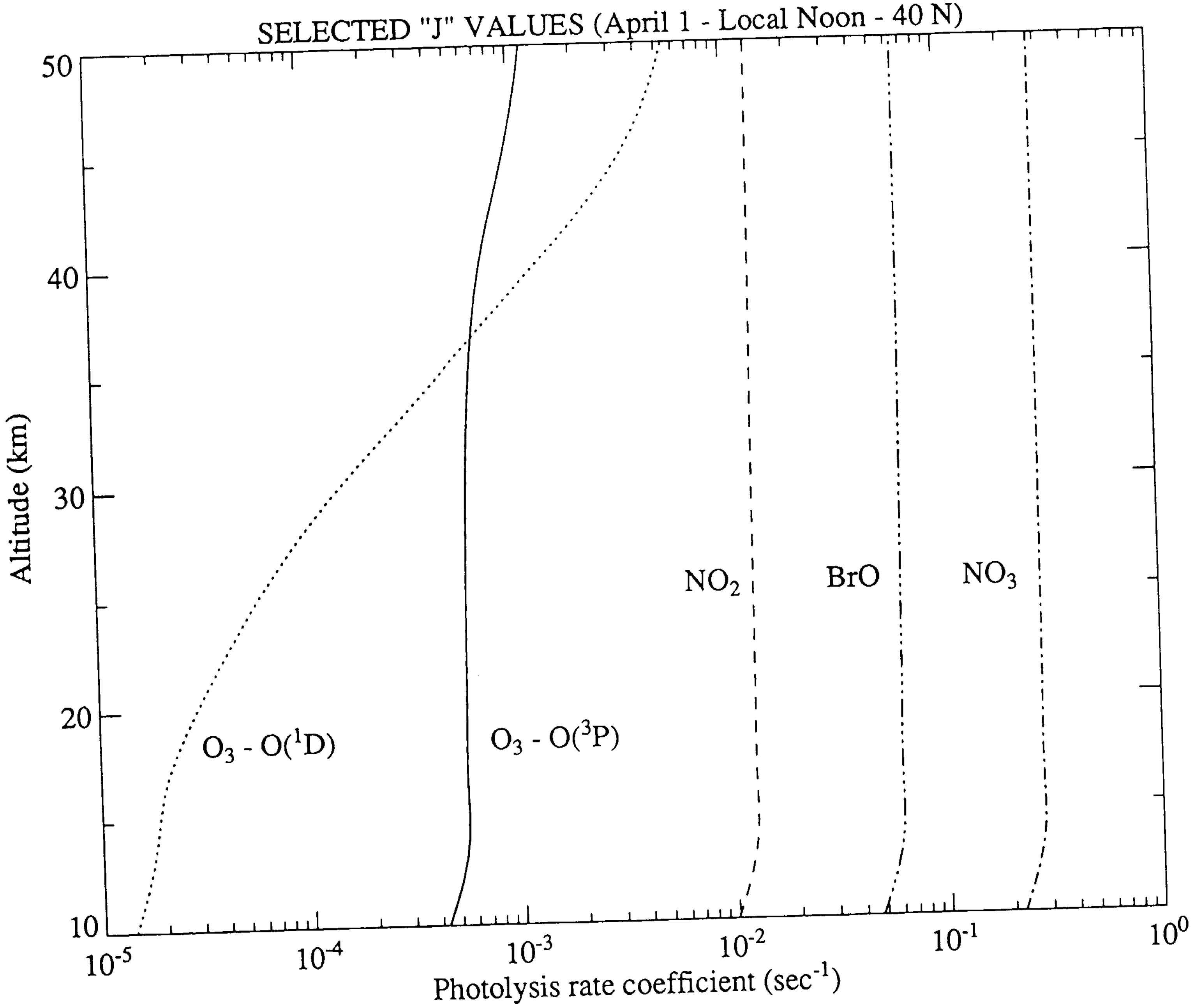


SELECTED "J" VALUES (April 1 - Local Noon - 40 N)


SELECTED "J" VALUES (April 1 - Local Noon - 40 N)
Altitude (km)
50
40
30
20
10
Photolysis rate coefficient (sec^{-1})
10^{-10}
10^{-9}
10^{-8}
10^{-7}
10^{-6}
10^{-5}
10^{-4}
CF_2Cl_2
N_2O
$CFCl_3$
CCl_4



SELECTED "J" VALUES (April 1 - Local Noon - 40 N)


SELECTED "J" VALUES (April 1 - Local Noon - 40 N)
Altitude (km)
50
40
30
20
10
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
Photolysis rate coefficient (sec^{-1})
O_3 - O(^{1}D)
O_3 - O(^{3}P)
NO_2
BrO
NO_3

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This is the tenth 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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