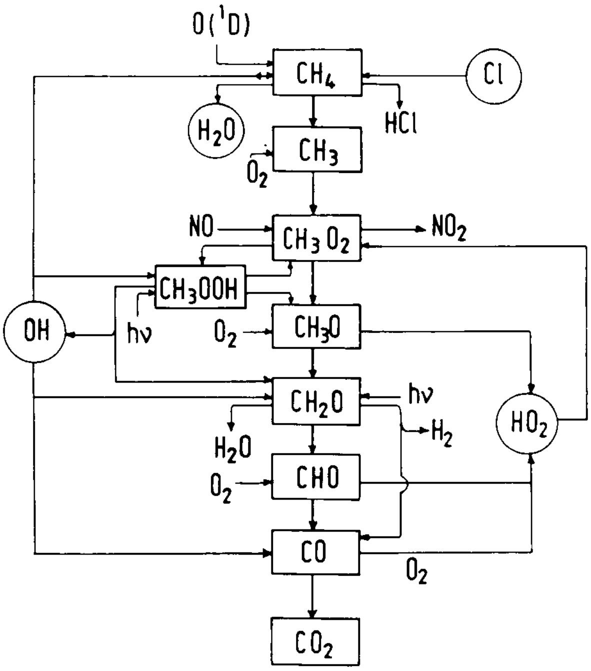
N87-10613

CHAPTER 2

STRATOSPHERIC CHEMISTRY



Panel Members

R.A. Cox, Chairman

W.B. DeMore
E.E. Ferguson
R. Lesclaux
A.R. Ravishankara
S.P. Sander
N.D. Sze
R.Zellner

CHAPTER 2

STRATOSPHERIC CHEMISTRY

TABLE OF CONTENTS

2.0 INTRODUCTION

Ozone is present in the earth's atmosphere at all altitudes from the surface up to at least 100 km. The bulk of the ozone resides in the *stratosphere* with a maximum ozone concentration of 5×10^{12} molecule cm^{-3} at about 25 km. In the *mesosphere* ($>$ 60 km) O_3 densities are quite low and are not discussed in the present report. Although O_3 concentrations in the *troposphere* are also less than in the stratosphere, ozone plays a vital role in the atmospheric chemistry in this region and also affects the thermal radiation balance in the lower atmosphere.

Atmospheric ozone is formed by combination of atomic and molecular oxygen.

$$O + O_2 + M \rightarrow O_3 + M \tag{1}$$

where M is a third body required to carry away the energy released in the combination reaction. At altitudes above approximately 20 km production of O atoms results almost exclusively from photodissociation of molecular O_2 by short wavelength ultraviolet radiation ($\lambda < 243$ nm):

$$O_2 + h\nu \rightarrow O + O \tag{2}$$

At lower altitudes and particularly in the troposphere, O atom formation from the photodissociation of nitrogen dioxide by long wavelength ultraviolet radiation is more important:

$$NO_2 + h\nu \rightarrow NO + O \tag{3}$$

Ozone itself is photodissociated by both UV and visible light:

$$O_3 + h\nu \rightarrow O_2 + O \tag{4}$$

but this reaction together with the combination reaction (1) only serves to partition the 'odd oxygen' species between O and O_3. The production processes (2) and (3) are balanced by chemical and physical loss processes. Until the 1950s, chemical loss of odd oxygen was attributed only to the reaction:

$$O + O_3 \rightarrow O_2 + O_2 \tag{5}$$

originally proposed by S. Chapman (1930). It is now known that ozone in the stratosphere is removed predominantly by catalytic cycles involving homogeneous gas phase reactions of active free radical species in the HO_X, NO_X, ClO_X and BrO_X families:

$$X + O_3 \rightarrow XO + O_2 \tag{6}$$

$$\begin{array}{rl} & XO + O \rightarrow X + O_2 \\ \hline \text{net:} & O + O_3 \rightarrow 2O_2 \end{array} \tag{7}$$

where the catalyst X = H, OH, NO, Cl and Br. Thus these species can, with varying degrees of efficiency, control the abundance and distribution of ozone in the stratosphere. Assignment of the relative importance and the prediction of the future impact of these catalytic species is dependent on a detailed understanding of the chemical reactions which form, remove and interconvert the active components of each family.

This in turn requires knowledge of the atmospheric life cycles of the hydrogen, nitrogen and halogen-containing precursor and sink molecules, which control the overall abundance of HO_x, NO_x and ClO_x species.

Physical loss of ozone from the stratosphere is mainly by dynamical transport to the troposphere where further photochemically driven sources and sinks modify the ozone concentration field. Ozone is destroyed at the surface of the earth and so there is an overall downward flux in the lower part of the atmosphere. Physical removal of ozone and other trace gaseous components can also occur in the precipitation elements and on the surface of atmospheric aerosols. Since most of the precursor and sink molecules for the species catalytically active in ozone removal in the stratosphere are derived from or removed in the troposphere, global tropospheric chemistry is a significant feature of overall atmospheric ozone behavior.

Numerical simulation techniques are used to describe and investigate the behavior of the complex chemical system controlling atmospheric composition, the models having elements of chemistry, radiation and transport. The chemistry in such models may include some 150 elementary chemical reactions and photochemical processes involving some 50 different species. Laboratory measurements of the rates of these reactions have progressed rapidly over the past decade and have given us a basic understanding of the kinetics of these elementary processes and the way they act in controlling ozone. This applies particularly in the upper stratosphere where local chemical composition is predominantly photochemically controlled.

It has proved more difficult to describe adequately both the chemistry and the dynamics in the lower stratosphere. Here the chemistry is complicated by the involvement of temporary reservoir species such as $HOCl$, H_2O_2, HNO_3, HCl, HNO_4, N_2O_5 and $ClONO_2$ which 'store' active radicals and which strongly couple the HO_x, NO_x and ClO_x families. The long photochemical and thermal lifetimes of ozone and the reservoir species in this region give rise to strong interaction between chemistry and dynamics (transport) in the control of the distribution of ozone and other trace gases. Moreover, seasonal variability and natural perturbations due to volcanic injections of gases and aerosol particles add further to complicate the description and interpretation of atmospheric behavior in this region. Most of the changes in the predicted effects of chlorofluoromethanes and other pollutants on ozone column density have resulted from changes in our view of the chemistry in the lower stratosphere. A great deal of importance must therefore be attached to achieving an understanding of the key factors in ozone chemistry in this region of the atmosphere.

Description of atmospheric chemistry in the troposphere is similarly complicated by dynamical influence and additionally by involvement of the precipitation elements (i.e. cloud, rain and snow) in the chemical pathways. The homogeneous chemistry of the troposphere is centered round the role of the hydroxyl radical in promoting oxidation and scavenging of trace gases released from surface terrestrial sources. Tropospheric OH is an important issue for stratospheric ozone since it controls the flux of source gases such as CH_4, halogenated hydrocarbons, and sulfur compounds to the stratosphere. Although the mechanisms are more complex due to the involvement of larger and more varied entities, the overall pattern of relatively rapid photochemical cycles involving a coupled carbon/hydrogen/nitrogen and oxygen chemistry is similar to that in the stratosphere. The photochemical cycles influence both the odd hydrogen budget and also, through coupling of the hydrocarbon oxidation with NO_2 photochemistry, the *in situ* production and removal of tropospheric ozone. The concentration and distribution of tropospheric ozone is important in respect of its significant contribution to the total ozone column, and its radiative properties in the atmospheric heat balance. A detailed description of tropospheric chemistry is given in Chapter 4.

The numerical models employed to investigate atmospheric behavior require the best available input data. Provision of an evaluated photochemical and kinetics data base for modelling atmospheric chemistry and ozone perturbations, has been recognized as an important feature of atmospheric programmes for some years now. With the rapid growth in the amount of information and expertise available in recent years this has become even more important. The evaluated data base produced by the NASA panel for Data Evaluation, updated in February 1985 (NASA, 1985) is provided in Appendix A of this assessment. An updated evaluation, containing more detailed presentation of the available data, has been published by the CODATA Task Group for Chemical Kinetics (Baulch *et al.*, 1984). These ongoing evaluation activities ensure that atmospheric models can benefit promptly from new laboratory data and improvements in the data base.

There have been a number of detailed descriptions of the basic chemical and photochemical processes which occur in the atmosphere and which control ozone and other trace gas budgets (NAS, 1976; NASA, 1979; Brasseur and Solomon, 1984; Wayne, 1985). The present discussion focusses mainly on the current key issues in chemistry relating to atmospheric ozone in the stratosphere and on changes that have occurred in the data base and perception of the problem since the last international report (WMO, 1982). An evaluation of the prospects for improvement in the knowledge in the near future is also given for some key areas. The present discussion does not attempt to assess the state of knowledge of chemistry related to ozone formation in the atmospheric boundary layer.

The first part of the assessment deals with the recent improvements in the data base for the currently identified reactions describing the chemistry of the major families of trace gas species, HO_x, NO_x, ClO_x, hydrocarbons, etc. The important coupling reactions between the families are introduced progressively in the subsections e.g., new data for the reactions which lead to net removal of HO_x but involve NO_x species are considered in the NO_x subsection. Discussion of the chemistry of sulphur and organic species (hydrocarbons and halocarbons) is restricted to those aspects impacting on the stratosphere and the unpolluted troposphere. The fluorine released in the breakdown of fluorocarbons in the stratosphere is converted ultimately to hydrogen fluoride, HF. As a result of the very high stability of HF, it is the predominant form of fluorine at all altitudes. The amounts of other FO_x species, which could become involved in catalytic cycles are too small to have a significant effect on stratospheric ozone. Kinetic data for FO_x species which may be formed in the breakdown of fluorocarbons are included in the evaluation given in Appendix I. The rate data are considerably more uncertain than those for the corresponding Cl and Br reactions, reflecting the fewer experimental measurements available for FO_x reactions.

The second part of the assessment considers a number of special issues relating to stratospheric chemistry. This includes a discussion of chemical aspects such as heterogeneous reactions and reactions of sodium species, the importance of which have not yet been completely established. Recent attempts to reconcile some of the more unexpected kinetic behavior which has emerged from the extensive experimental studies of key reactions with current reaction rate theory are also examined. Finally, a discussion of the uncertainties in the current kinetic and photochemical data base is given. An attempt is made to assess the prospects for improvement of the data for known reactions of atmospheric importance as well as for the identification of gaps in the chemical description of the atmosphere.

2.1 CURRENT STATUS OF DATA BASE FOR TRACE GAS FAMILIES INVOLVED IN OZONE CHEMISTRY

2.1.1 O_x Chemistry

The kinetic data base related to the reactions of O, O_2 and O_3 species appears to be well established. There remains some concern about the possible role of the excited singlet states of molecular oxygen in particular O_2 ($^1\Delta$) which is present at high concentrations in the stratosphere. Possible reactions with free radicals such as H or ClO are of concern and discussed in the following sections. There is also a possible role of $O_2(^1\Delta)$ in providing an additional source of odd oxygen if the photodissociation reaction:

$$O_2(^1\Delta) + h\nu \rightarrow 2\ O\ (^3P) \qquad (8)$$

occurred at a comparable rate to the photodissociation of ground state O_2. A significant effect would require an absorption cross section for $O_2(^1\Delta)$ in the 200 nm region of the order of 10^{-19}cm^{2}molecule^{-1}. However, there is no definite evidence to date that O_2 singlet states have any important effects on the chemistry of the stratosphere.

The quantum yield of $O(^1D)$ atoms in the photolysis of ozone still needs to be considered carefully. Quantum yields in the 'fall-off' region ($\lambda > 300$ nm) have been measured relative to the yields for shorter wavelengths where a value of 0.9 has been selected in the NASA evaluation for $\Phi(O^1D)$. Additional measurements are required to confirm this value and to better establish the temperature dependence of the quantum yields in the 280-330 nm region.

Observed ozone abundance in the upper stratosphere and lower mesosphere is larger than predicted by model calculations (Solomon *et al.*, 1983a, Ko and Sze, 1983). Possible reasons for this discrepancy which are related to O_X chemistry are discussed in the chapter on O_X measurements.

2.1.2 HO_X Chemistry

There have been relatively few changes recently in the kinetics data base for HO_X. The principal catalytic cycle for odd-oxygen destruction within the HO_X family is:

$$\begin{array}{lcr}
\text{(I)} & OH + O_3 \rightarrow HO_2 + O_2 & (9) \\
 & \underline{O + HO_2 \rightarrow OH + O_2} & (10) \\
\text{net:} & O + O_3 \rightarrow 2\ O_2 &
\end{array}$$

Depending on altitude the following cycles may also become important:

$$\begin{array}{lcr}
\text{(II)} & OH + O_3 \rightarrow HO_2 + O_2 & (9) \\
 & \underline{HO_2 + O_3 \rightarrow OH + 2\ O_2} & (11) \\
\text{net:} & 2O_3 \rightarrow 3O_2 & \\
\text{III} & O + OH \rightarrow H + O_2 & (12) \\
 & H + O_2 + M \rightarrow HO_2 + M & (13) \\
 & \underline{O + HO_2 \rightarrow OH + O_2} & (10) \\
\text{net:} & 2\ O \rightarrow O_2 &
\end{array}$$

Most of the reactions involved in these cycles are now reasonably well characterized. An exception is reaction (11) which is the rate controlling step in cycle (II). Previous revisions in the measured temperature dependence of k_{11} have had a significant effect on calculated ozone depletion. There has been only one direct temperature dependence study of reaction (11), the results of which indicate an A-factor for the rate coefficient which is surprisingly low. The temperature dependence of reactions (10) and (12) are also in need of additional study in view of the sensitivity of the upper stratospheric ozone profile to these rate coefficients.

Recent changes in the data base for HO_x reactions have also affected processes involved in the destruction of odd hydrogen. An example is the catalytic cycle which result in the recombination of OH and HO_2 through H_2O_2:

$$\text{(IV)} \qquad HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (14)$$

$$OH + H_2O_2 \rightarrow H_2O + HO_2 \qquad (15)$$

$$\text{net:} \qquad OH + HO_2 \rightarrow H_2O + O_2$$

The complex dependence of the rate coefficient for reaction (14) on pressure, temperature and water vapor has now been examined in detail, and this behavior has been incorporated into atmospheric models. The rate coefficient for reaction (15) is also now reasonably well known.

The direct reaction between OH and HO_2,

$$OH + HO_2 \rightarrow H_2O + O_2 \qquad (16)$$

has received considerable attention recently. DeMore (1982) has shown that the rate coefficient for this reaction increases from a low-pressure limiting value of $7.0 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$ at 298 K to about $1.1 \times 10^{-10} cm^3 molecule^{-1} s^{-1}$ at a total pressure of 1 atm. N_2. Sridharan *et al.* (1984) recently carried out the first temperature dependence study of this reaction, obtaining a value for E/R of $-(416 \pm 86)$ K. While this reaction is now reasonably well characterized, additional temperature and pressure dependence studies would be desirable in view of the important role of this reaction in HO_x destruction.

The branching ratios for the reaction

$$\begin{aligned} H + HO_2 &\rightarrow 2\,OH && (17a) \\ &\rightarrow O + H_2O && (17b) \\ &\rightarrow H_2 + O_2 && (17c) \end{aligned}$$

have recently been measured by Keyser (1985 private communication) with the values $k_{17a}/k_{17} = (0.91 \pm 0.08)$, $k_{17b}/k_{17} = (0.09 \pm 0.04)$ and $k_{17c}/k_{17} < 0.1$ being obtained at 298 K. These results are in reasonably good agreement with the study by Sridharan *et al.* (1982). In the only measurement of the temperature dependence, Keyser (1985) reports a value for k_{17} independent of temperature between 245 and 300 K. The temperature dependences of the individual reaction channels has not yet been determined.

The potential role of HO_x-chemistry arising from species in low lying electronically excited states such as O_2 ($^1\Delta_g$) and $HO_2(\tilde{A}^2A')$ has been a subject of much speculation in the past. Recent laboratory work, however, suggests that neither source nor sink reactions of HO_X are likely to be influenced by these electronically excited states.

For example, the reaction

$$H + O_2\,(^1\Delta) \rightarrow OH + O \qquad (18)$$

is too slow ($k_{18} = 1.8 \times 10^{-13} \exp(-1560/T)$ $cm^3 molecule^{-1}s^{-1}$; Hack, Kurzke, 1985) to be relevant in either HO_X or O_X chemistry in the stratosphere.

The importance of $HO_2(A^2A')$ can be assessed by estimating its steady state concentration relative to the ground state. Using the rate coefficients for the excitation processes (Hack, Kurzke, 1984; Holstein *et al.*, 1983).

$$HO_2(X) + O_2(^1\Delta) \rightarrow HO_2(A) + O_2(^3\Sigma) \qquad (19)$$

$$H + O_2(^3\Sigma) \rightarrow HO_2\,(X) \rightarrow HO_2(A) \qquad (20)$$

and for de-excitation,

$$HO_2(A) + M \rightarrow HO_2(X) + M \qquad (21)$$

the fraction of $HO_2(A)$ relative to ground state $HO_2(X)$ is below 2×10^{-6} throughout the stratosphere. Since this factor is unlikely to be compensated for by an enhanced reactivity of $HO_2(A)$, no influence on stratospheric HO_2 chemistry can be expected.

2.1.3 NO_x Chemistry

Odd nitrogen species are important in the stratosphere because they are involved in catalytic cycles which directly destroy O_3,

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (22)$$

$$NO_2 + O \rightarrow NO + O_2 \qquad (23)$$

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

and

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (22)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (24)$$

$$NO_3 + h\nu \rightarrow NO + O_2 \qquad (25)$$

$$\text{net:} \quad 2\,O_3 \rightarrow 3\,O_2$$

The first of these two cycles is much more important than the second. Even though all the above reactions have been studied in the laboratory, there exist some uncertainties in the values for the rate coefficient for reaction (22) at stratospheric temperatures and the quantum yield for NO in NO_3 photolysis. In addition to their involvement in direct O_3 destruction, NO_X species play crucial roles in the partitioning of odd hydrogen and odd chlorine into various forms. The rates of conversion of HO_2 to OH and ClO to Cl are determined by the reactions involving NO,

$$HO_2 + NO \rightarrow OH + NO_2 \tag{26}$$

$$ClO + NO \rightarrow Cl + NO_2 \tag{27}$$

and those involving $O(^3P)$, i.e., $O + HO_2 \rightarrow OH + O_2$ and $O + ClO \rightarrow Cl + O_2$. Thus, these reactions in conjunction with reactions of OH and Cl with O_3, control the ratios $[HO_2]/[OH]$ and $[ClO]/[Cl]$. Both reactions 26 and 27 are well characterized. NO_X species are also involved in sequestering HO_X species in temporary reservoirs e.g.:

$$OH + NO_2 \xrightarrow{M} HNO_3 \tag{28}$$

$$HO_2 + NO_2 \xrightarrow{M} HO_2NO_2 \tag{29}$$

The above processes have been thoroughly investigated and their rate coefficients are quite well established. The photolysis of NO_2, reaction (3), serves as the major source of odd oxygen in the troposphere. The absorption cross section for NO_2 and the quantum yield for O atom production are still somewhat uncertain, as are their temperature dependences.

In addition to the above mentioned reactions, the majority of reactions involving NO_X that are important in understanding stratospheric chemistry are well characterized. In the following section, we will discuss only the problem areas and areas where significant new data have been recently reported.

N_2O is the major source of NO_X in the stratosphere. The predominant path for N_2O destruction is photolysis. Its reaction with $O(^1D)$ contributes only 2% to N_2O destruction but is currently assumed to be the main NO_X production mechanism. Therefore, the possibility of N_2O photolysis to give NO + N needs to be very carefully assessed. Even if such a pathway constitutes only 1% of the total N_2O photolysis rate, it could be equal to the $O(^1D) + N_2O$ source [for each N_2O photolyzed to give NO + N, one more molecule of NO is produced due to the reaction of N with O_2 or O_3].

The majority of $O(^1D)$ produced by O_3 is physically deactivated to $O(^3P)$. The thermal rate coefficients for the reaction/deactivation of $O(^1D)$ by atmospheric gases N_2, O_2, O_3, CO_2, Ar, N_2O, H_2O and CH_4 are well defined (NASA evaluation). However, the yield of NO due to the $O(^1D) + N_2O$ reaction in the stratosphere is uncertain by as much as 30%. This uncertainty is partly due to the combined errors in the measured values of all the rate coefficients for $O(^1D)$ removal reactions, and is partly due to the possibility that the branching ratio of $O(^1D) + N_2O$ reaction to yield NO (as opposed to N_2 and O_2) changes with the kinetic energy of $O(^1D)$. Since $O(^1D)$ produced by ozone photolysis is translationally hot, and since the $O(^1D) + N_2$ and $O(^1D) + O_2$ quenching rates are temperature dependent, the uncertainty of the atmospheric rate of $O(^1D) + N_2O \rightarrow 2NO$ reaction branch is further enhanced if translationally hot $O(^1D)$ reacts differently than thermal $O(^1D)$. Therefore, experiments designed to measure NO production under stratospheric conditions which do not rely on the accuracy of the individual reaction rates need to be carried out.

Currently, all stratospheric N_2O is assumed to be produced at the ground level and transported into the stratosphere. However, local production of N_2O due to reactions such as $N_2(A^3\Sigma) + O_2$ and $OH(A^2\Pi) + N_2$ cannot be ruled out (Zipf, Prasad 1982). If such reactions occur in the mesosphere they could influence the stratospheric NO_x budget by downward transport of N_2O.

The main known process which removes NO_x from the stratosphere is transport of long lived species such as HNO_3, but a small amount of NO_x loss occurs through the N+NO and $N+NO_2$ reactions in the upper stratosphere. The latter reaction may produce N_2O as a major product. Kinetic data for reaction of N with NO are reasonably well established, but the rate constant for reaction with NO_2 is only reliable to within a factor of 3 at room temperature and its temperature dependence has not been established.

Removal of odd-hydrogen in the lower stratosphere occurs mainly by the reaction of OH with nitric acid and peroxynitric acid:

$$OH + HNO_3 \rightarrow H_2O + NO_3 \qquad (30)$$

$$OH + HO_2NO_2 \rightarrow H_2O + NO_2 + O_2 \qquad (31)$$

Changes in the recommended rate coefficients for these reactions have previously resulted in significant revisions of the calculated ozone column. The existence of a negative temperature dependence for the $OH + HNO_3$ reaction is now well established and confirmation of the small pressure dependence may help explain some of the divergence between results of the kinetics studies in different laboratory systems (NASA, 1985). The equally important $OH + HO_2NO_2$ reaction is not as well characterized, either with regard to the temperature dependence or the reaction products. New data have been reported recently for the temperature and pressure dependence of the HO_2NO_2 formation reaction (Sander and Peterson, 1984):

$$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M \qquad (29)$$

The rate constant for stratospheric conditions is about 40% lower than previously recommended. The products and temperature dependence of the photodissociation of HO_2NO_2 are still not established and the equilibrium constant for HO_2NO_2 formation is not reliably known. These gaps in the data base lead to some uncertainty in the description of peroxynitric acid behavior in the lower stratosphere and the troposphere.

The possibility of formation of an isomer of nitric acid in the recombination reaction of OH with NO_2 reaction (28) has also been considered. Such an isomer, if more reactive than $HONO_2$, would serve to reduce the effective rate of nitric acid formation. To date no firm evidence has been found for a complication of this kind in the kinetics of the $OH + NO_2$ reaction.

Recently, direct determinations of the rate constants for some key NO_3 reactions including those with NO_2 and NO have been made. The reliability of the data base for these reactions is now greatly improved.

$$NO_3 + NO \rightarrow 2NO_2 \qquad (32)$$

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M \qquad (33)$$

The equilibrium constant for the formation in the latter reaction of the important temporary reservoir species N_2O_5 has also been measured directly in several studies, but there remains some uncertainty in this quantity.

Reaction of NO_3 with the stable stratospheric species CO, CH_4 and H_2O_2 has been found to be too slow to be important; reaction with HCl has not been investigated. The recent suggestion (Johnston *et al.*, 1985) that NO_3 can thermally decompose to give NO + O_2 needs to be carefully examined. If this reaction is fast (i.e., $10^{-5}-10^{-4}s^{-1}$ under stratospheric conditions) it could have significant effects on NO_x chemistry. The temporal behavior, the observed absolute concentration and the seasonal variations of atmospheric NO_3 are still unexplained. These field observations point to an incomplete understanding of the atmospheric chemistry of NO_3.

The absorption cross sections of NO_2, NO_3, N_2O_5, HNO_3 and HO_2NO_2 have been measured at 298 K. The temperature dependence of the cross sections have been investigated only in the cases of NO_2 and N_2O_5 (see NASA, 1985 evaluation). Since photolysis can be the major stratospheric removal channel for many of these species, it is imperative that the absorption cross sections of species such as HNO_3 and HO_2NO_2 be measured over the temperature range of 220-298 K. It is unlikely that the discrepancies in the absorption cross sections of NO_3 or its temperature dependence will have any effect on stratospheric chemistry. However, they do affect the accuracy of the field measurement data obtained using long path visible absorption methods. The identity and quantum yield of products in the photolysis of NO_2 and HNO_3 are reasonably well known but not their temperature dependencies. There is still some controversy regarding the quantum yields for various products (i.e., $O(^3P)$, NO, NO_2 and NO_3) in the photolysis of N_2O_5 (Swanson *et al.*, 1984 and Ravishankara *et al.*, 1985). Since NO, NO_2 and NO_3 are rapidly interconverted, the nature of their photochemical pathways has minimal effect on stratospheric chemistry. All indications to date suggest that NO_3 and NO_2 are the major products. The photochemistry of NO_3 is not well understood. The quantum yields for the two channels — NO + O_2 and NO_2 + $O(^3P)$ — are not accurately measured even at 298 K. The dissociation threshold for the second channel has been established to be 620 nm (Nelson *et al.*, 1983, Ishiwata *et al.*, 1983, and A. Torabi, 1985). The quantum yields for NO and NO_2 production could also be pressure and temperature dependent.

2.1.4 ClO_x Chemistry

The principal odd oxygen destruction cycle involving ClO_x is:

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (34)$$

$$\underline{O + ClO \rightarrow Cl + O_2} \qquad (35)$$

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

However, in large parts of the stratosphere, the conversion of ClO to Cl occurs mainly by coupling with NO_x:

$$NO + ClO \rightarrow NO_2 + Cl \qquad (27)$$

In this case the sequence: reaction (34) followed by reaction (27) does not destroy odd oxygen, because NO_2 is rapidly photolyzed, reaction (3).

The main sink of active chlorine species is the reaction

$$Cl + CH_4 \rightarrow HCl + CH_3 \qquad (36)$$

from which Cl-atoms are recycled by

$$OH + HCl \rightarrow H_2O + Cl \qquad (37)$$

ClO_X species also form temporary reservoir species in the following reactions:

$$ClO + NO_2 + M \rightarrow ClONO_2 + M \qquad (38)$$

$$ClO + HO_2 \rightarrow HOCl + O_2 \qquad (39)$$

Of these, the latter is of less importance. The recycling of ClO_X from both reservoirs is by photolysis.

Most of these processes are now well understood, including the issue of formation of isomers of chlorine nitrate in reaction (38). There have been minor changes in the kinetics data base which are discussed in the following paragraphs. In addition remaining problem areas such as the formation of HCl in the reaction of OH with ClO, and the potential role of higher oxides of chlorine is considered.

The four new studies of the O + ClO reaction by Margitan (1984a), Leu (1984), Schwab *et al.* (1984) and Ongstad and Birks (1984) together average about 20% less than previous determinations of the 298 K rate constant. The temperature dependences, which were reported in the recent studies, are consistent with an E/R value of (50 ± 100) K. Ozone depletion calculations are particularly sensitive to this rate constant since the O + ClO reaction is the rate-limiting step in the chlorine-catalyzed destruction of odd oxygen in the upper stratosphere. However, it is unlikely that additional studies of this reaction using techniques thus far employed will significantly reduce the uncertainty in the rate constant.

A number of early studies of the reaction:

$$OH + HCl \rightarrow H_2O + Cl \qquad (37)$$

by direct methods had suggested a consensus value of 6.5×10^{-13} cm^3 $molecule^{-1}$ s^{-1} for k_{37} at 298 K. However, measurements by Molina *et al.* (1984) and Keyser (1984) resulted in values of (7.9 ± 1.2) and (8.5 ± 0.4) x $10^{-13}cm^3molecule^{-1}s^{-1}$, respectively. These studies are considered more reliable than the earlier determinations because of their more careful measurement techniques for HCl. In view of the sensitivity of model calculations of ozone depletion to this rate constant, the increase of 25% implied by the two recent measurements is significant.

There have been no significant changes recently in other reactions of odd-chlorine radicals including Cl + O_3, HO_2, HCHO, and ClO + HO_2, NO_2 and NO. The suggestion by Chang *et al.* (1979) and Molina *et al.* (1980) that the nascent product of the reaction

$$ClO + NO_2 + M \rightarrow ClNO_3 + M \qquad (38)$$

is an isomer of chlorine nitrate is now considered incorrect. This possibility was based on the observation that the value of k_{38} determined from direct studies was several times larger than the value inferred from the equilibrium constant and measurements of the chlorine nitrate thermal decomposition rate. If, as had been assumed, the isomer were to photolyze rapidly in the stratosphere, the effective rate of $ClONO_2$ formation would be 2-4 times slower than the rate suggested by direct studies. Recent work by Margitan

(1983), however, showed that the isomer, if formed, photodecomposes in a manner identical to that of $ClONO_2$. In addition, neither Cox *et al.* (1984) nor Burrows *et al.* (1984) were able to detect an isomer by direct spectroscopic methods.

Relatively little attention has been paid to the kinetics and photochemistry of HOCl in the last few years. Despite the current uncertainties in reaction rates, photolysis pathways and cross-sections, the role of HOCl in stratospheric chemistry appears to be well understood. The $HO_2 + ClO$ reaction is the only known stratospheric HOCl source, and photolysis is sufficiently rapid that HOCl cannot act as a significant reservoir of odd chlorine. Although the reactions of HOCl with other stratospheric radicals such as O, Cl and OH have not been fully investigated, these processes cannot compete with photolysis for HOCl removal.

Because of the possibility of HCl formation as a minor channel, the OH + ClO reaction,

$$OH + ClO \rightarrow HO_2 + Cl \tag{40a}$$

$$\rightarrow HCl + O_2 \tag{40b}$$

has received considerable attention recently. Determination of branching ratio k_{40b}/k_{40} is complicated experimentally by the $Cl + HO_2$ back-reaction which primarily forms $HCl + O_2$. Two recent studies by Hills and Howard (1984) and Burrows *et al.* (1984) agree as to the room-temperature branching ratio for HO_2 formation, obtaining (0.86 ± 0.14) and (0.85 ± 0.07), respectively. On the other hand Poul *et al.* (1985) report a branching ratio of (0.98 ± 0.07). Due to the complexity of the methods involved, the HCl yield for this reaction cannot be considered established. The three studies are in fair agreement as to the overall rate constant. However, Hills and Howard report a temperature dependence of (235 ± 46)/T, and Burrows *et al.*, report no temperature dependence over the range 243 - 298 K. The currently accepted overall rate constant (NASA, 1985) is about 30% larger than the previously accepted values. Additional work focussing on the HCl product channel as a function of temperature is required.

It is generally assumed that Cl and ClO are the only active chlorine species in the stratosphere. The potential importance of higher chlorine oxides, however, also needs some consideration. Prasad (1980) suggested the formation of asymmetric chlorine trioxide by the interaction of ClO with O_2:

$$ClO + O_2\,(^3\Sigma) \rightarrow OClOO \tag{41}$$

this species has not been observed in the laboratory, however its existence in the stratosphere cannot be ruled out *a priori*. The corresponding reaction of ClO with O_2 ($^1\Delta$) would energetically also allow the formulation of symmetric ClO_3:

$$ClO + O_2\,(^1\Delta) \rightarrow \text{sym.}ClO_3 \tag{42}$$

If these reactions proceeded at sufficient rate and extent, and if the resulting trioxides were photolyzed to yield oxygen atoms:

$$OClOO\ (\text{sym } ClO_3) + h\nu \rightarrow OClO + O \tag{43}$$

$$OClO + h\nu \rightarrow ClO + O \tag{44}$$

a chain mechanism could be set up in which O_2 molecules were catalytically photodissociated. Therefore, instead of ClO destroying odd oxygen in the normal ClO_X-catalyzed O_3 destruction chain it could provide a net odd oxygen source.

Moreover, the rates of radical-radical reactions involving ClO (i.e., reactions NO + ClO, O + ClO, OH + ClO), to which the calculated O_3 perturbation due to ClO_X is highly sensitive, could be affected if ClO were complexed with O_2 under stratospheric conditions. None of these reactions has so far been studied under conditions of high O_2 concentration.

Evidence from recent laboratory kinetic studies (Fritz and Zellner 1984; Handwerk and Zellner 1984) suggests the reactions forming the trioxides OClOO and sym ClO_3 are very slow: $k_{41} < 10^{-19} cm^3 molecule^{-1} s^{-1}$ and $k_{42} < 3 \times 10^{-15} cm^3 molecule^{-1} s^{-1}$, both at 298 K. These studies also allowed an estimate of the equilibrium constant for OClOO formation $K^{\ddagger}_{1} < 10^{-20} cm^3 molecule^{-1}$ at 298 K.

The low value of k_{42} precludes an important role for reaction with $O_2(^1\Delta)$. However the upper limit for k_{41} implies competitive rates with other ClO reactions in the lower stratosphere. Furthermore at the low temperatures prevalent in this region, the equilibrium constant $K^{\ddagger}_{1}$ may be considerably higher than the upper limit value obtained at room temperature leading to significant amounts of active ClO_X present as OClOO. Further studies to establish the magnitude of $K^{\ddagger}_{1}$ at low temperatures are needed.

The mutual interaction of two ClO radicals also needs consideration in the situation of a highly Cl_X perturbed stratosphere:

$$ClO + ClO \rightarrow Cl_2 + O_2 \tag{45}$$

$$ClO + ClO + M \rightarrow Cl_2O_2 + M \tag{46}$$

Whereas reaction (45) would not affect the concentration of active ClO_X since Cl atoms are readily regenerated via the photolysis of Cl_2, the formation of Cl_2O_2 in reaction (46) may serve as a temporary ClO_X reservoir. The available kinetic data base (Cox *et al.*, 1979; Cox, Derwent, 1979; Basco, Hunt, 1979; Watson, 1977) suggests that for stratospheric pressures and temperatures reaction (46) is dominant over reaction (45). The subsequent chemistry of Cl_2O_2, however, is not well defined. Its likely fate is photolysis and reaction with Cl, O, or OH. Mutual reactions between ClO are expected to become important at ClO_X levels exceeding 10 ppb.

2.1.5 BrO_X Chemistry

Although stratospheric Br and BrO destroy odd hydrogen in an analogous manner to ClO_X species, bromine chemistry differs from chlorine chemistry in several important respects. Because the H-Br bond strength is about 16 kcal mol^{-1} less than the H-Cl bond strength, hydrogen abstractions tend to be much more rapid for chlorine than for bromine. Indeed, reactions such as $X + CH_4$ and $X + H_2$ are important for $X = Cl$ but are endothermic and can be neglected for $X = Br$. For the corresponding XO radicals, the Cl-O bond strength is about 8 kcal $mole^{-1}$ stronger than the Br-O bond strength with the result that the ClO + ClO reaction is much slower than the BrO + BrO reaction. For this reason, and because BrO is expected to be the dominant form of BrO_X in the stratosphere (Yung *et al.*, 1980), the BrO + BrO reaction takes on particular importance in the stratosphere despite the relatively low BrO_X mixing ratio.

Since the review and modelling study of Yung *et al.* (1980), relatively few changes have occurred in the kinetics data base for BrO reactions. Most of the work on BrO_X has focused on the hydrogen abstraction reactions of Br including Br + HO_2 and Br + H_2CO, and on the OH + HBr reaction. Two recent studies seem to indicate that the reaction

$$Br + HO_2 \rightarrow HBr + O_2 \qquad (47)$$

is much slower than previously thought. While initial estimates based on the Cl + HO_2 reaction (Yung *et al.*, 1980) placed k_{47} at 2 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, studies by Posey *et al.* (1981) and Poulet *et al.* (1984) resulted in values of 2.2 and 7.6 × 10^{-13} cm^3 $molecule^{-1}$ s^{-1}, respectively. Additional work on this reaction is needed. The data base for the reaction

$$Br + HCHO \rightarrow HBr + HCO \qquad (48)$$

is somewhat more consistent, with a value for k_{48} near 1 × 10^{-12} $cm^3 molecule^{-1}$ s^{-1} at 298 K being obtained by both Nava *et al.* (1981) and Poulet *et al.* (1981).

Recent work on the reaction

$$OH + HBr \rightarrow H_2O + Br \qquad (49)$$

has yielded somewhat inconsistent results with values of k_{49} ranging from 6.0 to 11.7 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K being obtained. While some of the variation may be due to imprecise measurement of the excess reagent, HBr, as in the case of the OH + HCl reaction, most of the recent studies seem to lie near the high end of the range. While the results of recent work on reactions 47 - 49 have been at odds with estimates made in early modelling studies, the impact on predictions of ozone depletion has been minor.

The status of the data base for reactions of BrO with O, NO, NO_2, BrO and ClO remains essentially the same with kinetic data still lacking on the BrO + HO_2 and BrO + OH reactions. Of this group, the reactions

$$BrO + ClO \rightarrow Br + Cl + O_2 \qquad (50a)$$

$$\rightarrow Br + OClO \qquad (50b)$$

are still key steps in the odd-oxygen catalytic destruction cycle involving bromine in the lower stratosphere. This is the case despite recent changes in model predictions which have significantly lowered the ClO mixing ratio below 35 km in better agreement with observations. The temperature dependences of the rate coefficient and product distributions for this reaction are still highly uncertain and require additional work. In addition, because the catalytic cycle involving reaction (50) has diminished in importance, the reactions

$$O + BrO \rightarrow Br + O_2 \qquad (51)$$

and

$$BrO + BrO \rightarrow 2Br + O_2 \qquad (52)$$

have assumed a more significant role in the cycling of BrO to Br and should therefore be given added scrutiny. The possible role of a Br_2O_2 adduct in the BrO + BrO reactions at lower stratospheric temperature should also be investigated.

2.1.6 Sulfur Chemistry

Our current understanding of sulfur chemistry suggests that the only sulfur compound that is not completely degraded in the troposphere and hence can be transported into the stratosphere is COS. In addition various sulfur compounds (including SO_2) can be directly injected into the stratosphere during volcanic eruptions. The current data base suggests that the main fate of sulfur in the stratosphere is the conversion to sulfuric acid aerosols. There are possible catalytic cycles involving the HS radical which could affect the ozone concentration (Friedl *et al.*,1985). However, our overall understanding of HS and HSO chemistry is limited and, in addition, there are no proven sources of significance for HS in the stratosphere.

Details of the oxidation of SO_2 to H_2SO_4 in the homogeneous gas phase are not completely understood. However, recent work by Stockwell and Calvert (1983), Margitan (1984b) and Bandow and Howard (1985 private communication) have shown that the reaction of OH with SO_2 followed by the reaction of the adduct with O_2 leads to the formation of SO_3 at 298 K. The possibility of HSO_3 adding to O_2 at low temperatures needs to be assessed. SO_3 is believed to react very rapidly with H_2O to form H_2OSO_3 which in turn isomerizes to H_2SO_4 (Hoffman-Sievert and Castleman (1984)). The rate of SO_3 reaction with H_2O to form H_2SO_4 under stratospheric conditions of temperature, pressure, and H_2O concentrations must be firmly established. If the rate of this gas to particle conversion reaction is too slow under those conditions, the possibility of SO_3 uptake by existing aerosols and the photochemistry of SO_3 need to be studied.

The main fate of COS in the stratosphere is photolysis and reaction with $O(^3P)$, and the rates of these processes are reasonably well known. Recent laboratory studies have shown that CS_2 will be oxidized in the troposphere leading to COS (Jones *et al.* (1982)), Barnes *et al.* (1983), Wine and Ravinshankara (1982) and Wine *et al.* (1985).

Currently, there is a large research effort underway to understand tropospheric sulfur chemistry. This effort will, undoubtedly, provide a great deal more information on stratospheric sulfur chemistry.

2.1.7 Hydrocarbon Oxidation Chemistry

Hydrocarbon oxidation represents a particular sub-set of atmospheric chemistry, which is closely coupled to all other reactive trace gas species (O_X, HO_X, NO_X, ClO_X) and hence to O_3 photochemistry. CH_4 is the dominant hydrocarbon in the stratosphere and its primary role is the production of H_2O from its oxidation and the conversion of active ClO_X to inactive HCl via reaction (36). The role of higher hydrocarbons, i.e., C_2H_6, C_3H_8, C_2H_4, C_2H_2 etc., in the stratosphere is mainly as an additional sink for active chlorine. They can also be used as tracers to test the transport and chemistry used in current atmospheric models. Our present knowledge of CH_4 oxidation chemistry is illustrated in Figure 2-1. The dominant sink for CH_4 is reaction with OH

$$OH + CH_4 \rightarrow CH_3 + H_2O \tag{53}$$

The CH_3 radical product is further oxidized to CO_2 through the intermediate products; CH_3O_2, CH_3O, HCHO and CO.

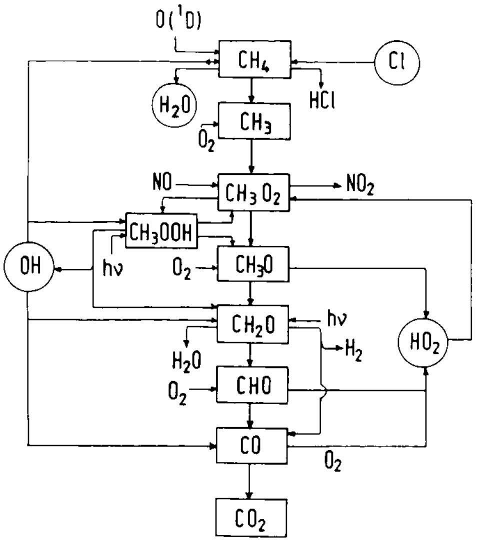


Figure 2-1. Atmospheric Methane Oxidation Scheme

For the stratosphere below 35 km the oxidation scheme is simplified by the presence of sufficient NO for complete conversion of the peroxyradicals by reaction with NO. This makes CH_4 oxidation a net source of O_x through the reactions:

$$CH_2O_2 + NO \rightarrow CH_3O + NO_2 \tag{54}$$

$$NO_2 + h\nu \rightarrow O + NO \tag{3}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{2}$$

This scheme is also a source of HO_x through the photolysis of formaldehyde formed by oxidation of CH_3O:

$$CH_3O + O_2 \rightarrow HO_2 + HCHO \tag{55}$$

$$HCHO + h\nu \rightarrow H + HCO \tag{56}$$

$$HCHO + h\nu \rightarrow H_2 + CO \tag{57}$$

The rate data for these reactions are all reasonably well established, the remaining uncertainties being in the rates of (55) (56) and (57). For the stratosphere the contributions of this source to the total O_3 budget is minor.

The final reaction of the methane oxidation chain, $OH + CO \rightarrow CO_2 + H$, is known to show a complex dependence on pressure and temperature. In view of the importance of this reaction at all altitudes further studies, particularly of the temperature dependence at high and low pressures, are needed.

The higher hydrocarbons are removed by reaction with OH and Cl. The rate coefficients are well established for the saturated hydrocarbons, but are more uncertain for the unsaturated species, due to the complexities of the reactions. No significant effect, however, is to be expected from such uncertainties for stratospheric ozone perturbations. The mechanism of non-methane hydrocarbon oxidation is discussed in detail in Chapter 4.

CH_3CN and HCN have been observed in the atmosphere up to 50 km (Arijs *et al.*, 1982). If they are oxidized instead of being physically removed, these molecules could be minor sources of NO_X (Cicerone and Zellner, 1983). Details of the oxidation pathways are not well known and studies aimed at elucidating the chemistry of these species in the stratosphere are needed.

2.1.8 Halocarbon Oxidation Chemistry

Halocarbons are oxidized in the stratosphere in a sequence of radical reactions initiated by the photolysis of the molecule or by its reaction with $O(^1D)$ atoms. The oxidation mechanism of chlorofluoromethanes has been established by laboratory photooxidation studies and was described in detail in the review by Simonaitis (1980). The kinetics of the elementary reactions involved in the oxidation mechanism were not known until recently and it has been generally assumed in model calculations that all the chlorine atoms of the molecule were released simultaneously in the atmosphere with a negligible delay following the initial photolysis or $O(^1D)$ attack. The new data provide further information on the reaction mechanism prevailing in the stratosphere and reveal the possibility of the formation of reservoir species.

The chlorofluoromethyl radical initially produced by the photolysis of CFMs or by their reactions with $O(^1D)$ atoms, combines rapidly with oxygen to form the peroxy radical CX_3O_2 (X = F or Cl). Under stratospheric conditions this radical reacts principally with NO in the fast reaction (Dognon *et al.*, 1985):

$$CX_3O_2 + NO \rightarrow CX_3O + NO_2 \qquad (58)$$

However, in contrast to the CH_3O_2 radical, the combination of the CX_3O_2 radical with NO_2

$$CX_3O_2 + NO_2 + M \rightarrow CX_3O_2NO_2 + M \qquad (59)$$

is fast enough at the low stratospheric temperatures and pressures (Lesclaux and Caralp, 1984) to form the peroxynitrate to a significant extent. Unlike $CH_3O_2NO_2$, the halogenated peroxynitrates may act as a temporary reservoir for ClO_X and NO_X in the lower stratosphere.

The peroxynitrates are thermally stable in the stratosphere (Simonaitis 1980). Therefore, the photolysis rate is the principal factor which determines their lifetime. Morel *et al.* (1980) have measured the absorption spectra of $CCl_3O_2NO_2$ and $CFCl_2O_2NO_2$ which have similar features to those of HO_2NO_2 and $CH_3O_2NO_2$. However the cross section values at the longest wavelength of measurements (270-280 nm) seem significantly lower for the halogenated compounds. Therefore, the photolysis rates may be low enough to make it possible to consider these compounds as potential reservoirs for ClO_X and NO_X particularly in winter and at high latitudes. An approximate calculation indicates that the ClO_X concentration should not be affected by more than a few percent. However, more accurate cross section measurements are needed in the critical wavelength region 290-320 nm and the temperature dependence of the reaction rate for $CX_3O_2 + NO_2 + M$ should be determined.

The chlorofluoromethoxy radicals CX_2ClO are thought to decompose rapidly into CX_2O + Cl, even at the low stratospheric temperature (Rayez *et al.*, 1983). However, an experimental confirmation is necessary.

The remaining chlorine atoms are released by photolysis of the intermediate products, CFClO and CCl_2O (phosgene) or their reaction with $O(^1D)$. These compounds have fairly low absorption cross sections resulting in low photolysis rates and this should be taken into account in stratospheric modelling. Preliminary calculations have shown that the stratospheric ClO_X concentration is a few percent lower than when the simplified treatment is applied. Moreover, a possible gas phase reaction of phosgene with water may be envisaged since this compound undergoes hydrolysis in the presence of liquid water.

Halogenated hydrocarbons such as CH_3Cl, CH_3CCl_3 etc. can be oxidized in the troposphere by reaction with OH. However, this reaction is relatively slow for most of these compounds and consequently, their input in the stratosphere is important. The oxidation of CH_3Cl, initiated by reaction with OH, results in the formation of CHClO (Sanhueza and Heicklen 1975). The photolysis and the reactions of this compound should be taken into account.

The industrial production of methyl chloroform and CF_3Br is increasing. The oxidation chemistry of these species is not well understood and further studies are required.

2.2 SPECIAL ISSUES IN STRATOSPHERIC CHEMISTRY

2.2.1 Role of Reactions Involving Sodium Species

Meteors are the source of several metallic elements in the upper atmosphere, by far the most important being sodium. The concentration profile of free sodium, which resides mainly in the mesosphere, has been measured. (Megie, Blamont, 1977). However, very little is known about the stratospheric chemistry of sodium. Recent investigations have shown that sodium and sodium compounds are very reactive. Oxides of sodium, unlike many other atmospheric metallic oxides, regenerate atomic sodium and react with many stratospheric constituents. Therefore, the possibility exists for sodium to have a role in chemistry controlling ozone. The current data base is not sufficient to carry out a complete modelling study of the homogeneous gas phase photochemistry of sodium in the stratosphere. However, the total concentration of free sodium in the stratosphere is extremely small. Therefore, it is unlikely that free sodium catalyzed ozone destruction can contribute significantly to the total ozone destruction rate.

One possible role that sodium compounds may play in the stratosphere is to release Cl from HCl augmenting the OH + HCl reaction. Many compounds of sodium (NaOH, NaO_2, and NaO) react rapidly with HCl to form NaCl. (Silver *et al.*, 1984a, 1984b). If NaCl is rapidly photolyzed, a catalytic chain for the conversion of HCl to Cl may be possible. e.g.

$$Na + O_2 \xrightarrow{M} NaO_2 \tag{60}$$

$$Na + O_3 \rightarrow NaO + O_2 \tag{61}$$

$$NaO + H_2O \rightarrow NaOH + OH \tag{62}$$

$$NaO_X + HCl \rightarrow NaCl + HO_X \tag{63}$$

$$NaCl + h\nu \rightarrow Na + Cl \tag{64}$$

The photolysis of NaCl is expected to be rapid in the upper stratosphere but there is some uncertainty in the photolysis rate at longer UV wavelengths, which would be necessary for release of the active species and completion of the catalytic cycle at lower altitudes (Rowland and Rogers, 1982). Further uncertainty arises from the lack of knowledge of the rate of gas to particle conversion of gaseous sodium compounds in the stratosphere.

Clusters containing sodium compounds such as $NaOH$, NaO_2, and NaO can scavenge stratospheric acids and oxides such as HNO_3, HCl, NO_2, and N_2O_5. However, the estimated amount of sodium compounds in the stratosphere is too small for scavenging to be important.

2.2.2 Ion Chemistry

Over the last few decades, considerable effort has been expended in the understanding of mechanisms by which ions can affect the stratospheric ozone budget. As a result it is clear that ion chemistry is not important for the ozone budget. However recent work has shown that useful measurements of neutral species can be made through their interaction with atmospheric ions. With the exception of the rare solar proton events, the ion production rate in the upper stratosphere is relatively small, ranging from 10-50 ion pairs/cm^3/s at 100 km to 0.1 ion pairs/cm^3/s at 50 km. With this small ion input, and the relatively rapid ion recombination rates only the most efficient catalytic processes would be expected to be important. No such catalytic processes involving ions have been identified to date.

Direct ionization processes are now known to produce hydrated ion clusters which are relatively stable. Nascent positive ions, primarily N_2^+ and O_2^+ rapidly form proton hydrates $H_3O^+ (H_2O)n$, with a net input of two odd hydrogen molecules per ion. Similarly, electrons resulting from ionization events form hydrates of the nitrate ion, NO_3^- eventually resulting in nitric acid clusters. Both positive and negative ion clusters are stable towards reaction with most neutral species. However, such clustering processes form a sensitive basis for the stratospheric measurement of species such as NH_3, CH_3OH, HNO_3, H_2SO_4 and gas-phase sodium compounds using *in situ* mass spectrometry. (Arnold, 1984; Arijs *et al.*, 1982). Determination of absolute concentration by this method assumes local equilibrium between the ions and the cluster and requires a knowledge of the equilibrium constant.

Positive and negative ion concentrations in the stratosphere are of the order of $10^3 cm^{-3}$. Their lifetime is determined by mutual recombination and is typically approximately 10^3s. While ions may recombine to form odd nitrogen species (HNO_3) the limiting rate of a few $cm^{-3}s^{-1}$ is negligible. Because these rates are so small, catalytic processes must be invoked for ion chemistry to significantly perturb the stratosphere. It is known that small ions can greatly enhance neutral reactions as, for example,

$$Na^+O_3 + NO \rightarrow NO_2 + O_2 + Na^+ \qquad (65)$$

is four orders of magnitude faster at 250 K than the gas-phase reaction of O_3 with NO, and since the Na^+ is not removed the reaction is catalytic (Rowe *et al.*, 1982). The reaction of N_2O_5 with NO is over nine orders of magnitude faster when N_2O_5 is clustered to Li^+. However, the effect decreases with ion size and there are no small ions in the stratosphere.

A reaction which was examined in great detail because of its potential impact is

$$X\pm(H_2O) + N_2O_5 \rightarrow X\pm HNO_3 + HNO_3 \qquad (66)$$

No reaction was found with any ion $X\pm(H_2O)$ which is present in significant concentrations in the stratosphere (Bohringer *et al.*, 1983).

Some years ago it was proposed (Ruderman *et al.*, 1976) that the reaction

$$NO_3^- + O_3 \rightarrow NO_2^- + 2O_2 \qquad (67)$$

might destroy stratospheric ozone and thus account for a solar cycle variation in ozone, since there is a solar cycle variation in the galactic cosmic ionization rate. However, unsolvated NO_3^- is not a stratospheric ion, and in any case reaction (67) is slow ($k < 10^{-13}$ cm^3 s^{-1}) (Fehsenfeld *et al.*, 1976).

In summary, the stratospheric production rate of HO_X and NO_X from ionic processes is negligible due to the low production rate of ions. Moreover, efficient catalytic cycles for odd oxygen destruction involving ions have not yet been found.

2.2.3 Homogeneous Reactions Between Temporary Reservoir Species

The principal temporary reservoir species involved in stratospheric HO_X, NO_X and ClO_X chemistry are shown in Table 2-1. These species serve to 'tie up' active radicals which would otherwise be involved in catalytic odd oxygen destruction (or production) cycles. Some species act as reservoir for two active types e.g., HNO_3 and $ClONO_2$ act as reservoirs for HO_X and ClO_X respectively as well as NO_X. A common feature of these temporary reservoir species is that they are closed shell molecules and therefore their reactivity towards each other is generally expected to be much less than with atomic or radical species. However, concentrations of reservoir species can exceed those of active species by several orders of magnitude and consequently slow reactions between them may need to be considered because of the important consequences if active species are regenerated or more stable species are formed. For example the reaction of water with N_2O_5 serves to release active NO_X species (NO_2) and also provide a source of OH from H_2O through the reactions

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (68)$$

$$2HNO_3 + h\nu \rightarrow 2OH + 2NO_2 \qquad (69)$$

The source of OH in the lower stratosphere would be comparable in magnitude to the reaction of $O(^1D)$ with water if the bimolecular rate coefficient for reaction of H_2O with N_2O_5 was of the order of 10^{-20}

Table 2-1. Reservoir Species for Active HO_X, NO_X and ClO_X Radicals in the Stratosphere

Family	Reservoir Species
HO_X	H_2O, H_2O_2 HNO_3, HO_2NO_2, HONO
NO_X	N_2O_5 $ClONO_2$
ClO_X	HCl HOCl

cm^3 molecule^{-1} s^{-1}. (Dak Sze, 1984). The upper limit room temperature value of $k_{68} \leq 2 \times 10^{-21}$ is a factor of 5 lower than this, but measurement of such small rate coefficients presents considerable problems and there have been very few systematic studies of the kinetics and temperature dependencies of these slow reactions. Moreover the study of slow reactions in the gas phase is often complicated by heterogeneous reactions which may or may not have atmospheric significance (see Section 2.2.4).

Recently attention has been focussed on the reaction of chlorine nitrate with HCl, which has been known for some time to occur rapidly in laboratory gas and liquid phase reaction systems. Whilst a rationale can be made for a rapid reaction between these two species (Schmeisser and Brandle, 1961), the emerging consensus today is for a very slow bimolecular gas phase reaction (Molina *et al.*, 1985). However, a surface reaction occurs to produce HNO_3 and Cl_2 as products. Any impact of this reaction on stratospheric chemistry would be through the occurrence of the latter process.

The gas phase reactions of ozone with stable molecules has also to be considered in view of the relatively high concentrations of ozone in the mid stratosphere. Of particular interest is the reaction of ozone with water vapor via the exothermic pathway to yield hydrogen peroxide:

$$O_3 + H_2O \rightarrow H_2O_2 + O_2 \qquad (70)$$

Subsequent photolysis of H_2O_2 from this reaction would provide a significant source of OH even with a rate constant as low as 10^{-23} cm^3 molecule^{-1} s^{-1}. There are no data on the kinetics of this reaction.

A summary of the slow reactions involving temporary reservoirs which are potentially important for atmospheric chemistry is given in Table 2-2. The Table shows minimum values for the rate constants of these reactions that would be required to give significant effects on species distribution in the stratosphere, according to calculations with a ID model using current chemistry. (Dak Sze, 1984). These rate constants are mostly approximately equal to or above the upper limit values that have been reported at room temperature.

2.2.4 Heterogeneous Reactions

The possibility that heterogeneous reactions involving trace species on the surface of atmospheric aerosol particles has been a subject of discussion for some time (Cadle *et al.*, 1975).

Aerosol particles are present in the stratosphere and are concentrated mainly in a layer centered at around 25 km altitude. They consist mainly of aqueous sulphuric acid (approximately 75% w/w H_2SO_4) and originate from direct volcanic injection of sulphuric acid and from oxidation of sulphur-containing gases from both volcanic and other sources, e.g., COS. In the troposphere aerosol particles are widely distributed but the composition is very variable and depends on location.

The presence of aerosol particles can potentially impact on stratospheric ozone in several ways through gas surface interactions e.g., production and removal of active radical species, surface catalysis of chemical reactions and surface photochemical effects. The aerosol question now assumes more relevance in view of the 1982 eruption of the El Chichon volcano, which evidently increased the stratospheric aerosol loading by approximately an order of magnitude. There are other conditions in the stratosphere, for example polar high altitude clouds, which may provide potential heterogeneous chemistry effects.

Table 2-2. Minimum Values of Rate Coefficients for Significant Role of Homogeneous and Heterogeneous Reactions Involving Temporary Reservoir Species

Reaction	**k_{bi} (min) $cm^3 molec^{-1} sec^{-1}$**	**γ* min.**
**1. $ClONO_2 + H_2O \rightarrow HOCl + HNO_3$	10^{-19}	5×10^{-3}
2. $N_2O_5 + H_2O \rightarrow 2HNO_3$	10^{-20}	5×10^{-4}
3. $HO_2NO_2 + H_2O \rightarrow HNO_3 + H_2O_2$	10^{-19}	5×10^{-3}
4. $O_3 + H_2O \rightarrow H_2O_2 + O_2$	10^{-23}	1×10^{-6}
**5. $HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$	5×10^{-17}	5×10^{-4}
**6. $ClO + HO_2NO_2 \rightarrow HOCl + NO_2 + O_2$	5×10^{-15}	—
7. $H_2O_2 + HNO_3 \rightarrow HO_2NO_2 + H_2O$	5×10^{-15}	5×10^{-3}

* In deriving γ(min), we assume that an air molecule collides with stratospheric aerosol about once in every 10^4 seconds.

** The required k_{bi}(min) and γ(min) for the chlorine reactions (1), (5) and (6) may be lowered by an order of magnitude if the stratospheric ClX were to exceed 15 ppb.

The rate of removal or reaction of molecular species on the surface of aerosol particles is generally expressed in terms of the effective first order rate constant calculated from the product γZ_S where Z_S is the collision frequency of gas molecules with the surface and γ the fraction of those collisions which lead to reaction. For the surface area corresponding to typical mid stratosphere aerosol Z_S is typically of the order 10^{-4} to 10^{-5} s^{-1}. Most gas phase reactions of active species occur with much greater frequency. Thus even with unit efficiency for reaction at the surface, the heterogeneous reaction cannot be important in determining local partitioning of active species. Experimental studies indicate that γ values are normally in the range 10^{-3} to 10^{-5}, even for such active species as Cl, ClO (Martin *et al.*, 1980) and OH (Baldwin and Golden 1979), on sulphuric acid and other surfaces. It is concluded that for fast reacting radicals like Cl and OH, heterogeneous removal does not provide a significant sink. For slower reacting radicals such as ClO and perhaps HO_2, small perturbations on radical density may result from heterogeneous removal at high aerosol concentrations following volcanic eruptions. This process would compete with the slower processes by which active radicals are converted to reservoir species.

Heterogeneous effects are most likely to be significant for the slow reactions involving temporary reservoir species, particularly in their reactions with water which is present in the aerosol. For example the reaction of N_2O_5 with water can occur on surfaces and if HNO_3 were formed in N_2O_5 and aerosol interactions with $\gamma = 5 \times 10^{-4}$ this would have significant consequences for the HO_x budget in the lower stratosphere. This rate would be equivalent to a homogeneous bimolecular rate constant for the $N_2O_5 + H_2O$ reaction of 1×10^{-20} cm^3 $molecule^{-1}$ s^{-1}.

The experimental data base at the present time does not allow identification of those reactions of stratospheric importance which can be catalyzed in this way and which are not. Moreover little is known about the γ values for the molecular species of interest, N_2O_5, $ClONO_2$, HO_2NO_2 etc. In Table 2-2 are listed the γ values required to give a significant effect on the distribution of stratospheric species involved in the ozone budget, for those reactions between temporary reservoir species which are identified as potentially significant in the stratosphere. In calculating the reaction rates it is assumed that the reaction partner present at higher concentration, is in sufficient excess for the overall removal of the minor reactant to follow pseudo first order kinetics.

The influence of surface adsorption on the visible and ultraviolet spectra of absorbed molecules has been considered in some detail in connection with the photodegradation of chlorofluoromethanes. Since these gases do not absorb at wavelengths above 300 nm they are not removed by direct photodissociation in the troposphere. However there is evidence that the electronic absorption spectra of molecules absorbed on surfaces may be red shifted in a similar way to electronic spectra in the liquid phase. Laboratory experiments have indicated that photodecomposition of these compounds by near UV radiation can occur in the presence of desert sand and other similar materials. (Ausloos *et al.*, 1977). No quantitative estimate of the rate of this process based on laboratory studies can be made at the present time. Due to the small surface area in the atmosphere, the fraction of any particular trace gas that is absorbed on the particles at a given time is extremely small. Thus an extremely large red-shift in the absorption spectrum would be required to give a significant effect. Indeed there is strong evidence from atmospheric measurements of chlorofluoromethanes that this process is of negligible importance as a sink for organochlorine species in the atmosphere.

The effect of light on the surface reaction efficiency parameter, γ has also been considered. Laboratory studies have shown that simulated sunlight has no effect on the heterogeneous reactivities of Cl and ClO (Martin *et al.*, 1980). There is no experimental information relating to this effect in the surface reaction of the temporary reservoir species.

In assessing the current evidence relating to the question whether or not aerosols perturb the homogeneous chemistry related to stratospheric ozone, it can be concluded that the effects are minor and are unlikely to change our overall picture of the chemistry of the stratosphere. Some modification of our detailed formulation of the behavior of temporary reservoir species may result from further characterization of their heterogeneous reactions in the laboratory. Local effects resulting from volcanic injections may be considerably more significant. Detection and understanding these effects is difficult, firstly, because the available baseline information does not allow unambiguous assignment of a given observation to the presence of enhanced aerosol loading and secondly the effects are expected to be subtle and of small magnitude.

2.2.5 Reactions with Complex Temperature and Pressure Functions

One outcome of the intensive research effort in stratospheric chemical kinetics has been the discovery that many radical-radical and radical-molecule reactions do not obey classical pressure and temperature behavior, i.e., positive Arrhenius activation energies and pressure-independent rate coefficients for bimolecular reactions. This departure from classical behavior can be explained by the absence of large (5 kcal mole^{-1} or greater) energy barriers for these reactions and the presence of local minima in the potential energy surface which correspond to metastable reaction intermediates. In general, rate coefficients for reactions of this type decrease with increasing temperature and, over the limited temperature range encountered in the atmosphere, obey Arrhenius-type behavior, i.e.,

$$k(T) = A\exp(-E_a/RT)$$

where E_a, the Arrhenius activation energy, is negative. However, there are now several examples of reactions which show pronounced non-Arrhenius behavior and others which manifest unusual pressure and temperature behavior suggestive of more complex mechanisms. One objective of current research in reaction rate theory is to express such behavior in a general analytical form which is suitable for use in atmospheric models.

There are four reactions of particular interest which show unusual pressure and temperature dependence behavior over atmospheric pressure and temperature conditions. These are:

$$OH + HO_2 \rightarrow H_2O + O_2 \qquad (16)$$

$$OH + CO \rightarrow H + CO_2 \qquad (71)$$

$$OH + HNO_3 \rightarrow \text{products} \qquad (30)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (14)$$

While data on several of these reactions are incomplete, their experimentally observed rate coefficients can be expressed as a sum of pressure-dependent and pressure independent terms,

$$k_{obsd}([M],T) = k_{II}(T) + k_{III}(T)[M]$$

where $k_{II}(T)$ = bimolecular component (zero-pressure intercept), $k_{III}(T)$ = termolecular component and [M] = bath gas density. This empirical expression has a term which is directly proportional to [M] but falloff behavior is expected at higher pressures.

Table 2-3 summarizes the existing measurements of the bimolecular and termolecular components for these reactions. These reactions all have zero or negative values of E/R. For reactions 14, 30 and 71, the A-factors for the bimolecular component are considerably smaller than those expected for simple atom-transfer processes. Both of these observations are strongly suggestive of complex reaction behavior.

Considerable effort has been devoted to the understanding of these reactions and an explanation for their unusual pressure and temperature dependence is emerging (Just and Troe, 1980; Mozurkewich and Benson, 1984; Patrick, *et al.*, 1984; Kircher and Sander, 1984). Reactions such as the ones discussed

Table 2-3. A-factors and temperature dependence for bimolecular and termolecular components of reactions showing unusual behavior

	k_{II}		k_{III}	
Reaction	**A***	**E/R**	**A****	**E/R**
$OH + HO_2$	1.7×10^{-11}	−416	3.0×10^{-31}	−500
$OH + HNO_3$	7.2×10^{-15}	−785	1.9×10^{-33}	−725
$OH + CO$	1.5×10^{-13}	0	3.6×10^{-33}	?
$HO_2 + HO_2$	2.3×10^{-13}	−590	1.7×10^{-33}	−1000

* Units are cm^3 $molecule^{-1}$ s^{-1}

** Units are cm^6 $molecule^{-2}$ s^{-1}, values are for $M = N_2$

+ termolecular parameters are valid for $[M] < 1 \times 10^{18}$ molecules cm^{-3}, $T > 260K$.

above are believed to proceed through a bound intermediate having a sufficiently long lifetime to undergo collisional quenching. The reaction scheme may be written,

$$\begin{tikzcd}
A + B \arrow[r, shift left, "k_{1f}"] & AB^* \arrow[l, shift left, "k_{a1}"] \arrow[r, "k_{a2}"] \arrow[dr, "M", "k_2"'] & C + D \\
 & & AB
\end{tikzcd}$$

The overall rate constant may be divided into bimolecular and termolecular components under conditions where $k_2[M] << k_{a1} + k_{a2}$:

$$k_{obsd} = \frac{k_{1f}k_{a2}}{k_{a1}+k_{a2}} + \frac{k_{1f}k_2}{k_{a1}+k_{a2}}[M] \tag{I}$$

Equation I has the correct functional form to describe the pressure dependence for most of these reactions. However, attempts to apply this theory at a detailed level to reactions of this kind have revealed inconsistencies which may point to a possible incompleteness in the model. Also the pressure dependence of the $OH + HNO_3$ reaction is not consistent with the form of equation I (NASA, 1985). Furthermore there is as yet no way to predict for which reactions we should expect complex k(p,T) behavior for conditions relevant to the atmosphere.

The stability of the complexes involved is not well known but is probably of the order of 10 kcal mol^{-1}, implying that they decompose rather rapidly and do not undergo reactions with other species leading to new chemical pathways. A possible exception is HOCO, which probably reacts with O_2 to give $CO_2 + HO_2$, the same products as for the "low pressure" bimolecular channel in the atmosphere.

Other familiar reactions such as the termolecular association reactions are special cases of this model, having only the collisional deactivation channel open ($k_{a2} = 0$). Familiar "bimolecular" reactions such as NO + XO (X = F, Cl, Br, I), O + OH, N + NO and perhaps HO_2 + NO also proceed via intermediate bound complexes, but show no pressure dependence in the 0-1 atm pressure range because of the relatively short lifetime of the complex ($k_{a1} + k_{a2} >> k_2[M]$). These reactions would nevertheless be expected to exhibit a pressure dependence at sufficiently high pressure.

2.2.6 General Comments on Photodissociation Processes

The solar flux penetrating the stratosphere consists mainly of radiation with wavelength greater than 290 nm with a small amount of radiation in the 200 nm window. This short wavelength radiation is absorbed mainly by the small molecules with large atmospheric abundance such as O_2 and O_3 but is also important for the photolysis of halocarbons. The longer wavelength radiation is important for photolysis of the larger polyatomic species. The features responsible for absorption by polyatomic species in this region and the halocarbons near 200 nm are mainly the tails of absorption bands. Thus the absorption cross sections in this wavelength region may be dependent on temperature. To date, however, the majority of the absorption cross section measurements have been carried out at 298 K. Therefore, it is necessary to measure absorption cross sections at stratospheric temperatures particularly for molecules such as HNO_3, $ClONO_2$ and HO_2NO_2. It is worth nothing that these molecules are hard to manipulate in the laboratory. In general, the cross section measurements have not received the amount of attention commensurate with their importance.

It is assumed that the quantum yield for dissociation of the absorbing molecule is unity if its absorption spectrum is a continuum. It is necessary to confirm this assumption at least for important molecules such as HNO_3 whose primary atmospheric degradation pathway is photolysis. The quantum yield measurements usually are not completely decoupled from the absorption cross section measurements. Consequently, in many instances the product of these two quantities ($\sigma \times \Phi$) is better known than the individual quantities. In general, quantum yields for product formation have not been measured at the appropriate wavelengths, pressures, and temperatures for the atmosphere. In many cases, it is often assumed that the weakest bond breaks, but there are many known exceptions to this assumption; for example $ClONO_2$ photolysis yields $Cl + NO_3$ (Margitan, 1984a) rather than $ClO + NO_2$ as was previously assumed. For the important species, the quantum yield for minor products must also be measured.

2.2.7 Errors and Uncertainties in Kinetic and Photochemical Data

The uncertainties in the chemical and photochemical rate parameters and in the mechanisms involved in the atmospheric chemistry are one of the major factors in limiting the accuracy of model calculations of species concentration and ozone perturbations in the atmosphere. Most of the changes in the predicted ozone depletion due to chlorofluoromethanes that have occurred in recent years have resulted from changes in the values of kinetic parameters used in model calculations.

The uncertainty in the kinetic parameters for the key atmospheric reactions has been reduced greatly over the last 10-15 years due mainly to the rapid development of the techniques used for the direct measurement of radical species in the gas phase and for investigation of their reaction kinetics. Whereas 20 years ago the rates of most radical-molecule reactions were only known to within a factor of 10, today the room temperature rate constants of atmospherically important reactions of this type can be measured within an accuracy of $\pm 10\%$. Moreover the number of reactions for which good kinetic data are available have increased tremendously. The consistency in the experimental measurements gives confidence in the data base. There remain problems in reaction rate theory which is not able to explain some of the observed temperature and pressure dependencies. Although there is improved reliability of the data it should be recognized that the errors in the rate coefficients increase as the temperature diverges from room temperature and that certain reactions e.g., radical + radical reactions are intrinsically more difficult to study and consequently are always likely to carry more uncertainty than straightforward radical + molecule reactions.

Difficulties also arise in the study of very slow reactions between radicals and molecules, due to complications such as those arising from heterogeneous effects.

The uncertainty in the rate coefficients for atmospheric reactions results primarily from systematic errors arising from the chemical systems and the techniques used for their determination rather than measurement error of a statistical nature. Consequently it is not straightforward to assign uncertainties to preferred values given in an evaluation. Errors quoted in the NASA or CODATA evaluations are assessments based on such factors as the number of independent determinations made and the number and reliability of the different techniques employed. Furthermore in most cases, the probability of an error of a given magnitude falls off more slowly than a normal Gaussian function.

The problems of assignment of errors is illustrated by the development of our knowledge of the kinetic parameters for the two key reactions:

$$OH + HNO_3 \rightarrow H_2O + NO_3 \tag{30}$$

$$OH + HCl \rightarrow H_2O + Cl \tag{37}$$

Initial investigations of these reactions apparently provided a sound data base with acceptable uncertainty limits for the k values and their temperature dependence. Subsequent studies have provided data which today gives recommended values for k_{298}, which lie significantly outside the ±20% uncertainty limits proposed originally, and for the $OH + HNO_3$ reaction a very different temperature dependence.

In determining an important atmospheric quantity such as the rate of generation of atmospheric radical species from a source gas, several elementary steps may be involved and cumulative errors in successive steps tend to increase the overall uncertainty for the process to an extent that meaningful interpretation of atmospheric observations cannot be made. The question arises whether it is possible to reduce these uncertainties by experiments or observations relating to the overall process. For example, if the process involved a kinetic competition which could be measured more accurately than the competing processes in isolation, the uncertainty might be reduced by such measurement. Competitive kinetic experiments have been widely used in the past for the determination of relative rate constants, but have now been largely superseded by direct techniques, where the potential for unrecognized systematic errors due to mechanistic and other difficulties is generally lower. For a limited number of simple chemical systems e.g. the production of NO from the $O_3 - N_2O - O_2 - N_2$ photolysis system, some reduction in uncertainty could result from carefully designed measurements of overall reaction rates.

Not many rate coefficients have been measured in the laboratory under atmospheric conditions and extrapolation leads to a further source of uncertainty. Simple well characterized bimolecular and termolecular association reactions present no problem. Errors in extrapolated rate parameters can arise however with reactions exhibiting unexpected pressure and temperature dependence, reactions with more than one reaction channel, and reactions proceeding via complex intermediates which may react with other atmospheric constituents, particularly O_2. Well known examples are the reaction of OH with CO, the $HO_2 + HO_2$ reaction, and the reaction of OH with CS_2. These uncertainties can be eliminated by rigorous experimental study focussed on measurements under conditions appropriate for the atmosphere. In the past, experimental difficulties restricted such kinetic investigations to use of indirect or modulated steady state techniques, but recent improvements in production techniques and detection sensitivity for radical species now allows direct measurements of rate coefficients under simulated atmospheric conditions. Further improvements in the reliability of the data base from this aspect, can be foreseen in the future.

For the key elementary reactions identified as being important for the stratosphere many of which are radical + radical reactions, the prospect of reducing uncertainties in the rate coefficients to less than ± 10% cannot be considered realistic. Some reduction in uncertainty can be expected from further temperature and pressure dependence studies, and a further understanding of product channels and reaction mechanisms can be anticipated in the future.

For the lower stratosphere, the data base for the important temporary reservoir species is slowly but surely improving. There are good prospects for further reduction in uncertainties in the photochemical and kinetic parameters for the gas phase processes involving these species, but formulation and parameterization of the heterogeneous chemistry remains problematical. There is a need for further field measurements to indicate the direction of future emphasis in this area, and further efforts in the development of laboratory techniques for production and study of the labile temporary reservoir species.

The prospects are good for improvement of the data base for homogeneous tropospheric chemistry. There is a need to establish with more reliability the kinetic parameters for certain elementary reactions in the oxidation of CH_4 and C_2 hydrocarbons, particularly those which are important (e.g. reactions forming and removing hydroperoxides) in the low NO_X situation prevailing in the background troposphere.

2.2.8 Identification of Gaps in the Chemical Description of the Atmosphere

The question of the completeness of the current models of stratospheric chemistry has been frequently raised, particularly when disagreement between model calculations and field measurements has appeared. For example at altitudes above 40 km it is believed that ozone is in photochemical equilibrium and its concentration is determined by relatively simple chemistry involving catalytic destruction by HO_x species, as described in Section 2.1. The rate parameters for these reactions are relatively well defined experimentally. Nevertheless comparison of theory and observations shows inconsistencies which cannot be assigned to a particular source of error. The differences may be accommodated within the combined uncertainty of the rate parameters; on the other hand slightly narrower uncertainty limits on the data would constrain the model such that unidentified chemical processes would need to be incorporated to reconcile theory and observation. Another example is the severe problem with the observations of abundance and seasonal variation of atmospheric NO_3, which are incompatible with currently known chemistry of this species.

These examples show that something is wrong with our description of the atmosphere and suggest that chemical processes may be missing. The specific source of the problem is not identified by these comparisons, however. All known reactions that are significant in the atmosphere have been included in the models to date, but there has been no systematic search for the reactions that could be important, but are as yet unidentified.

One possible approach to the identification of new and significant reactions is the application of a matrix technique. The starting point of this approach would be to construct a matrix of all currently proposed atmospheric constituents. The matrix will provide a formulation of all possible interactions between the individual constituents. Reactions of potential atmospheric significance, which have not already been established, can then be identified by application of criteria such as

(1) The rate of the process should be significant when the concentrations of the reacting species in the atmosphere are at their upper limits and the reaction rate coefficient is at its maximum reasonable value.
(2) The occurrence of the reaction should significantly alter the atmospheric trace gas composition.

If these criteria are met, a search for any previously reported information on the reaction should be made and further experimental investigation of the process carried out. If new species are formed as products of reactions identified as potentially important they would then be incorporated into an extended matrix, and their potential significance assessed. Their potential photochemical and thermal decomposition reactions should also be investigated.

Identification of novel aspects of atmospheric chemistry can also come from laboratory experiments. Most of our data base of atmospheric chemistry at the present time arises from laboratory investigations of isolated elementary reactions. This, however, has mainly concentrated on the determination of overall rate coefficients. The area of identification of reaction products has received less attention although this can provide insight into incomplete knowledge of the nature and kinetic behavior of significant atmospheric species.

Elucidation of some important aspects of atmospheric chemical mechanisms and also identification of new species of significance, has in the past resulted from laboratory studies of time dependence of stable reactants and products in more complex chemical systems under pseudo atmospheric conditions. These systems have often been designed to simulate selected components of atmospheric photochemical cycles and can provide a useful check on the completeness of our knowledge of these cycles. For example the discovery of peroxynitric acid as a significant gas phase species resulted from steady state studies designed to investigate the oxidation of NO and NO_2 in the presence of HO_2 (Simonaitis and Heicklen, 1978) and FTIR spectroscopic investigation of this system at atmospheric pressure and room temperature (Niki *et al.*, 1977). Another example is the investigation of the photolysis of the $O_2 - O_3 - H_2O$ system (DeMore, 1973), which helped to clarify the then current issues concerning O_3 decomposition in gas mixtures containing water, through reactions with OH and HO_2. This study also gave strong indication that knowledge of the very important radical loss reaction $OH + HO_2 \rightarrow H_2O + O_2$ was incomplete.

The utility of this type of experiment has clearly been established. Today as a result of dramatic improvements in spectroscopic methods, it will be possible to couple sensitive detection techniques for trace radicals and molecules with experiments on complex reaction systems. This coupling will facilitate a better control of the experimental system, thus providing improved prospects for accurate measurement of rate coefficients and branching ratios and the discovery of new chemistry. However it should be emphasized that true simulation of conditions in the free sunlit atmosphere in the laboratory is not a realistic or useful objective. Furthermore, the potential influence of heterogeneous effects needs to be carefully assessed in the interpretation of this type of laboratory experiment.

2.3. SUMMARY AND CONCLUSIONS

In the last few years, laboratory stratospheric chemistry has been characterized by steady improvements in the data base for reaction rate coefficients, product studies of elementary reactions, absorption cross sections and photodissociation quantum yields. While there have been no discoveries of fundamentally new catalytic cycles, radical or reservoir species, changes in the accepted rate coefficients for several important reactions have led to refinements in predictions of ozone depletion and have, in general, improved the agreement between measured and computed vertical profiles for trace species. With respect to odd oxygen depletion in the stratosphere, the most significant changes in the kinetics data base have concerned the reactions

$$O + ClO \rightarrow Cl + O_2$$

and

$$OH + HCl \rightarrow H_2O + Cl$$

the rates of which are now about 15% slower and 20% faster, respectively, under middle stratospheric conditions. These changes act in opposite directions as far as the chlorine-catalyzed ozone depletion is concerned. Minor changes have been reported in rate constants for the reaction

$$OH + HNO_3 \rightarrow H_2O + NO_3$$

although these revisions are small compared to the major revision of a few years ago which increased the rate constant by a factor of three in the lower stratosphere. Re-evaluation of earlier kinetic data has also resulted in a decrease of about 40% in the rate constant for the reaction

$$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$$

at 30 km.

For the most part, the list of chemical and photochemical processes identified in previous assessments as being the most important in stratospheric chemistry has not changed. In only a few cases are there serious gaps or inconsistencies in the data base, including a few extremely important reactions, e.g.,

$$HO_2 + O_3 \rightarrow OH + 2O_2$$

$$OH + HNO_3 \rightarrow H_2O + NO_3$$

$$OH + HO_2 \rightarrow H_2O + O_2$$

for which the measured rate parameters are difficult to reconcile in terms of reaction rate theory. These and other reactions are examples of systems in which a relatively long-lived intermediate may be involved. The complex pressure and temperature dependence behavior which results has made it difficult to extrapolate rate constants beyond their range of measurement.

Although most of the reactions important in stratospheric chemistry have now been thoroughly studied, there are a number of important and potentially important processes which require attention. In the area of NO_X chemistry, the possible photolysis of N_2O to give NO + N would have a major impact on the odd nitrogen budget. Uncertainties associated with the rates and branching ratios of the reaction

$$\begin{aligned} O(^1D) + N_2O &\rightarrow 2NO \\ &\rightarrow N_2 + O_2 \\ &\rightarrow O(^3P) + N_2O \end{aligned}$$

as well as possible hot atom effects also have important consequences for modelling the NO_X source term.

Considerable progress has been made in understanding the reaction of NO_3 but the reaction of NO_3 with species such as HCl should be investigated. Additional work is required in the area of NO_3 photochemistry focusing on the temperature dependences of primary quantum yields and absorption cross-sections.

In the area of ClO_X chemistry, additional work is necessary to clarify the branching ratio for the OH + ClO reaction and the role, if any, of the higher chlorine oxides. A number of uncertainties remain in the mechanism of BrO_X-catalyzed ozone destruction including the coupling with the ClO_X family through the ClO + BrO reaction and the reactions controlling HBr.

Many of the details of the atmospheric oxidation of methane and of halogenated hydrocarbons under stratospheric conditions have now been investigated and are moderately well understood.

In addition to the specific issues mentioned above, a number of other problem areas of a more speculative nature have been addressed. These include the effects of slow chemical reactions of non-radical reaction partners (e.g., $ClONO_2$, HCl, H_2O, N_2O_5 and HO_2NO_2), possibly occurring homogeneously or heterogeneously on aerosol particles, possible catalytic cycles involving sodium of mesospheric origin, reactions involving excited states of molecular oxygen and reactions of ions. None of these processes have so far been shown to have a significant effect on stratospheric ozone chemistry.

Two related questions of great significance for stratospheric chemistry concern the identification of possible missing reactions or species and the limits that can be placed on the accuracy of chemical and photochemical parameters in the mechanism. The ability of models to predict the response of the atmosphere to perturbations will always depend on both the accuracy of the rate coefficients used as input data and the completeness of the mechanism with regard to the interaction of known and hypothetical species. Although our understanding of the gas-phase chemistry has continued to improve, the prospects are low for further improvement of the accuracy with which the rate constants for certain sensitive reactions can be measured. Moreover, certain key elements of stratospheric models such as the production of NO_x and HO_x are driven by sequences of photochemical and kinetic processes each having a finite uncertainty. The combined effect of these uncertainties can be substantial even if the constituent parameters are well-determined.

One possible approach to this problem is to rely to a greater extent on experimental systems which mimic in a well-controlled fashion the same sequence of reaction steps that takes place in the atmosphere. These ''integrated'' experiments would focus on a narrow aspect of the overall mechanism such as HO_x or NO_x production. Such an approach has the potential for not only reducing the end-to-end uncertainty of a particular process but, with the use of sensitive diagnostic techniques, possibly reveal missing reactions and species.

With regard to omissions of important reactions from current models, the systematic use of the ''matrix'' approach could be useful. In this method, all known atmospheric species are tested, conceptually or experimentally, for reaction with one another. While this approach does not guarantee that important reactions will not be overlooked, it constitutes a systematic procedure for the consideration of all possible reactions, probable or improbable.