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Laboratory Studies of Atmospheric Reactions at Low Temperatures

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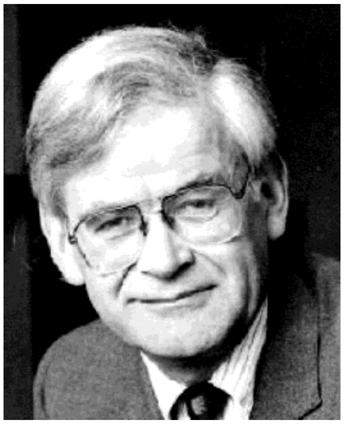

Ian Smith obtained his B.A. and Ph.D. degrees from the University of Cambridge. He was on the staff of the Department of Physical Chemistry in Cambridge until 1985 when he moved to the University of Birmingham as Professor of Physical Chemistry. He became Mason Professor of Chemistry in Birmingham in 1991, a post he now holds in an Emeritus capacity, following his formal retirement in 2002. Ian Smith has wide-ranging interests in the fundamentals and applications of gas phase processes. He was elected a Fellow of the Royal Society in 1995. With his collaborators, he was awarded one of the first Descartes Prizes (EU, Brussels). He gave the RSC's Liversidge Lectures in 2001–2002, and in 2003, he will deliver the Wilhelm Jost Memorial Lectures in Germany. He is current President of the Faraday Division of the RSC.

1. Introduction

The need to attain a thorough understanding of the chemistry of the Earth's atmosphere has served as a huge stimulus in the experimental study of elementary reactions for at least 30 years. Despite increased awareness of the role played by processes occurring in and on aerosol particles, the role of homogeneous gas phase reactions remains central to this understanding, and the experimental determination of rate constants for important atmospheric reactions and how these rate constants vary with temperature remain a crucially important part of atmospheric science.[1,2]

The temperature in the Earth's atmosphere varies with latitude and longitude and with altitude above the Earth's surface, as well as with the season and the time of day.[3] Nevertheless, such variations are sufficiently small that it is possible, and common, to represent the variation with altitude of temperatures in the atmosphere by the kind of graph shown in Figure 1. It can be seen that the mean atmospheric temperatures for latitude 40° N during June pass through two minima: one at the tropopause, which occurs at an altitude of ca. 15 km, where the temperature is ca. 220 K and the pressure is ca. 100 mbar, and a second at the mesopause, which occurs at an altitude of ca. 85 km, where the temperature is ca. 170 K and the pressure is ca. 10^{-2} mbar. However, in reality, the temperature at the tropopause can reach values much lower than 220 K, down to 180 K above the Antarctic in winter.[4]

If one widens one's focus to include both the atmospheres of other planets in the solar system and those of their satellites, one finds good reasons for examining the kinetics of selected gas phase reactions to still lower temperatures. Table 1 lists the lowest temperatures found in the atmospheres of some of the heavier planets and their moons. Finally, in this brief survey of the different environments in which an earth-bound kineticist can take an interest, we reach interstellar space.[5,6] About 120 molecules have now been observed in the interstellar medium. The majority have been identified by matching mmwave emission lines from space with laboratory spectra, although infrared observations, made by instruments lifted above the Earth's atmosphere,[7] are playing an increasing role in identifying which molecules are present and in what abundance.

The great majority of interstellar molecules have been found in dark, dense, giant "molecular clouds". From the relative intensity of different lines from the same molecular emitter, it is possible to estimate that

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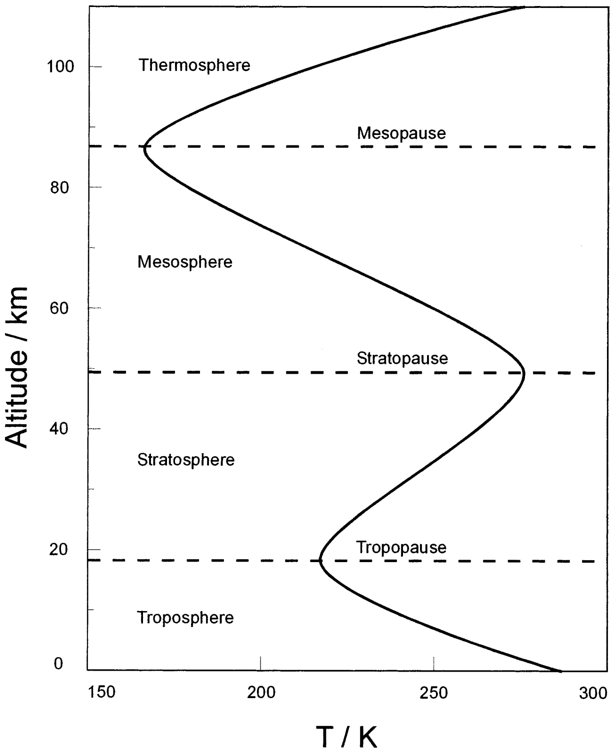

Figure 1. Variation of temperature in the Earth's atmosphere showing minima reached at the stratopause and the mesopause. The curve represents the mean temperature variation for latitude 40° N during June. (Adapted from Figure 2.13 in Wayne, R. P. *Chemistry of Atmospheres*, 2nd ed.; Oxford University Press: Oxford, 1991.)

Table 1. Low Temperatures in Planetary Atmospheres and the Interstellar Medium[3]

environment	T (K)
Earth (tropopause)	220
Earth (mesopause)	170
Jupiter (tropopause)	115
Saturn (tropopause)	85
Titan (tropopause)	70
Neptune (tropopause)	55
Uranus (tropopause)	55
dense, dark, molecular clouds	10−50

the temperature of the regions where molecules are most abundant is typically between 10 and 50 K. Moreover, the evidence strongly suggests that despite these extremely low temperatures, there is a rich chemistry occurring in these regions, with molecules being continuously formed and destroyed in chemical reactions. These observations provide another strong stimulus to laboratory studies of reaction kinetics at very low temperatures.

The need to provide information that can be used directly in atmospheric models, without recourse to uncertain extrapolation, is one stimulus to low temperature measurements of reaction rate constants. In assessing this need, it is valuable to remember that even at its warmest, the Earth's atmosphere is quite cool. As a result, even reactions with quite modest activation energies, i.e., $E_{act} > 20$ kJ mol^{-1} (i.e., ca. $8RT$ at 298 K), are too slow to play a significant role in atmospheric chemistry. It also means that extrapolation of data obtained over a limited temperature range using the Arrhenius expression, $k = A \exp(-E_{act}/RT)$, may not give satisfactory estimates of rate constants far outside the range of temperatures that was covered in the experiments. We shall see several examples later. This takes us to a second reason for studying atmospherically important reactions over a wide range of temperatures, especially down to low temperatures: such data can assist us in gaining a full understanding of reaction mechanisms. Again, a number of examples are given later in this paper.

In the next section of this paper, I review the experimental methods that have been used to study elementary reactions directly, with an emphasis on low temperature experiments. I also seek to identify the strengths and limitations of the techniques with respect to their use at low temperatures. Following that, in the main body of the paper, I give examples of a number of reactions whose kinetics have been studied at low temperatures. (I consider here a relatively small number of important, well-studied reactions. I place the emphasis on those studies in which measurements have been performed at low temperatures. I make no effort to reference all of the numerous studies that have been carried out on each of these reactions.) Here, the reactions are divided into different categories, both with respect to the chemical nature of the reagents and by whether the dynamics are thought to be direct or to proceed via a collision complex. Reactions between two free radicals, which are difficult to study experimentally, comprise an important class of atmospheric reaction. Their minimum reaction path often passes through one or more significant energy minima, and commonly, they yield more than one set of products. For these reactions, it is imperative to study the kinetics and product branching ratios over as wide a range of temperatures and pressures as possible, to gain a full understanding of the process.

2. Experimental Methods

Essentially, all direct methods for measuring the rates of elementary gas phase reactions are based either (i) on pulsed photolysis and the subsequent observation of transient species in real time or (ii) on the flow method, in which transient concentrations are measured in steady state at different distances from the point at which the reagents are mixed and the reaction starts. In both cases, it is possible to cool the apparatus cryogenically and thereby reach low temperatures, but a number of conditions need to be satisfied if such an arrangement is to lead to successful kinetic experiments on any particular reaction. Experiments in which continuous photolysis has been combined with product analysis have provided valuable information about the relative rates of reactions and the mechanisms by which species undergo oxidation in the atmosphere, but they have not been applied at low temperatures and will not be considered further in this review.

2.1. Cryogenic Cooling: Pulsed Photolysis Methods

Pulsed photolysis methods were first applied to the kinetics of reactions in the form of flash photolysis.

Table 2. Low Temperature Pulsed Photolysis Experiments on Reactions of the OH Radical

co-reagent (T_{bp}; K)	source of OH (photolysis wavelength)	T_{min} (K) (vp(T_{min}); mbar)	$k(T_{min})$ (cm^3 molecule^{-1} s^{-1})	ref
CH_4 (111.6)	HNO_3 (266 nm)	216	1.9×10^{-15}	10
		178 (>1000)	$<3 \times 10^{-16}$	10
	H_2O (flash)			
	N_2O/H2O (193 nm)	195	3.5×10^{-16}	12
	N_2O/CH_4 (flash)			
C_2H_6 (184.5)	HNO_3 (266 nm)	138 (31)	1.3×10^{-14}	10
	H_2O (flash)			
	O_3/H_2O (193 nm)	231	8.4×10^{-14}	13
	H_2O_2 (248 and 266 nm)			
HCl (188)	HNO_3 (266 nm)	138 (14.8)	5.2×10^{-13}	10
	HONO (355 nm)			
	HNO_3 (248 nm)	200	5.4×10^{-13}	14
	H_2O_2 (248 nm)			
CO (81.6)	HNO_3 (266 nm)	82 (ca. 1000)	1.0×10^{-13}	11
	H_2O (flash)	250	1.2×10^{-13}	15
N (not known)	HNO_3 (266 nm)	103	8.0×10^{-11}	17
O (not known)	HNO_3 (266 nm)	158	6.1×10^{-11}	17

The development and application of this technique led to Norrish and Porter being awarded a share of the Nobel Prize in Chemistry in 1967. Since that time, the development of short pulsed lasers, which can be used both to initiate photochemical reactions and to observe changes in the concentration of transients, has led to an improvement in time resolution of more than six orders of magnitude (and to the award of the 1999 Nobel Prize to Zewail).

Atmospheric scientists are almost exclusively concerned with bimolecular reactions,[1-3] and in laboratory experiments, their rates can be adjusted by selecting appropriate concentrations of the reagents. Most measurements are made in the pseudo-first-order regime, where the initial concentration, $[\mathrm{Rad}]_0$, of the transient species that is observed, usually a free radical, is much less than that of the co-reagent, $[\mathrm{Reag}]_0$. In this case, $[\mathrm{Reag}]_0$ must be chosen to bring the first-order rate constant within the time response of the experimental method and the detection of the radical must be sufficiently sensitive to ensure that $[\mathrm{Rad}]_0 \ll [\mathrm{Reag}]_0$.[8]

Most of the modern rate measurements of interest to atmospheric chemists, which employ pulsed photolysis to generate radicals, have been made using commercial laser systems. In most cases, pulses of ca. 10 ns duration from a fixed frequency laser photolyze a suitable precursor to provide the radical of interest, and a pulsed or continuous tuneable laser is used to observe how the concentration of this radical changes with time following its production. For example, OH radicals can be created by pulsed photolysis of HNO_3 or H_2O_2 at 248 nm, using a KrF excimer laser, or at 266 nm, using the frequency-quadrupled output from a Nd:YAG laser. Changes in the concentration of the OH radicals can then be followed by laser-induced fluorescence (LIF), that is, by observing changes in the intensity of fluorescence induced by a dye laser, which is tuned to lines in either the (1,0) or (0,0) bands of the $A^2\Sigma^+-X^2\Pi$ electronic band system of OH. The probe laser can be pulsed, and signals recorded as the time delay between the pulses from the photolysis and probe lasers are systematically varied, or a cw laser can be used with the fluorescence intensity observed continuously. To prevent problems associated with the depletion of the reagents and the accumulation of products, experiments of this kind are generally performed in a slow flow mode, so that the mixture in the reaction cell is replenished each time the photolysis laser is fired. In general, the reaction cell can be heated or cooled but one must guard against pyrolysis or condensation of constituents of the reaction mixture.

However, because kinetic experiments are performed under pseudo-first-order conditions, with $[\mathrm{Rad}]_0 \ll [\mathrm{Reag}]_0$, it is not necessary to know the absolute concentrations of the radical. This has important implications for experiments performed in cryogenically cooled reaction cells. To extract second-order rate constants, one needs to know accurately the concentration of the co-reagent, i.e., $[\mathrm{Reag}]_0$, since the measured first-order rate constant is assumed to vary linearly with $[\mathrm{Reag}]_0$. Consequently, it is necessary to ensure that no loss of this co-reagent is suffered by it condensing on the cooled walls of the reactor. On the other hand, some loss of the photochemical precursor of the radical can be tolerated, as long as a sufficient amount remains to yield observable concentrations of the radical. This objective can be achieved by a suitable choice of the gas flow: slow enough to ensure cooling of the gas in the region where the observations are made but rapid enough to ensure that not all of the radical precursor in the gas mixture diffuses to the cold walls of the reactor and is lost there. The method has some features in common with the collisional cooling method of De Lucia and co-workers,[9] in which a gas such as NO or CO is cooled to very low temperatures by injection into a large excess of ultracold He gas, and its spectrum is recorded before the molecular gas diffuses to the walls of the container and condenses.

The present author and co-workers have made a number of studies of elementary reactions of the OH radical using cryogenic cooling methods.[10,11] Table 2 summarizes some features of these experiments and compares them with similar measurements made by Ravishankara and co-workers.[12-15] When the co-reagent is a stable molecule, the lowest temperatures achieved reflect two connected and conflicting constraints: first, the necessity to keep the partial pressure of the co-reagent below the value of its saturated vapor pressure at the temperature of the cooled walls of the reactor, and thus prevent condensation, and second the need to add enough co-reagent to achieve a first-order removal rate by reaction, which exceeds the rate of loss by other processes, such as diffusion from the region where the radicals are formed and observed. The latter requirement can be especially limiting for reactions, such as that between OH and CH_4, which have appreciable activation energies and therefore slow rates at low temperatures. In Table 2, I list both the boiling points of the co-reagents and the saturated vapor pressures of the co-reagents at the lowest temperatures of the experiments on the various reactions that are listed.

Pulsed photolysis methods can also be used to find the rate constants of reactions between free radicals. For example, Smith and co-workers[16,17] have combined pulsed photolysis methods with those of discharge flow (see below) to measure rate constants for the reactions of OH radicals with oxygen and nitrogen atoms. The O and N atoms were generated in a measured excess concentration by a microwave discharge, and then, OH radicals were produced by pulsed photolysis of HNO_3. In these experiments, the lowest temperatures at which rate measurements could be made were determined by two factors: first, the possibility of rapid and complete loss of HNO_3 by condensation at the low total pressure (ca. 2−5 Torr) of a conventional flow−discharge system, and second, the significant loss of atoms at the cold walls of the flow tube reactor as the temperature was lowered.

Reactions between free radicals can also be studied using pulsed photolysis to generate both radicals. However, it is necessary both to prepare one radical in excess and to measure the absolute concentration of this species, if reaction rate constants are to be extracted by kinetic measurements on the other radical. These requirements are difficult to satisfy even in room temperature experiments. At low temperatures, it is additionally necessary that the precursors for both radicals do not condense at the cold walls. As a result, experiments of this kind have only been carried out on a limited number of reactions and only at moderately low temperatures.

2.2. Cryogenic Cooling: Flow Tube Methods

In the flow tube method, unstable radicals are generally produced, directly or indirectly, by passing a microwave discharge through a flow of gas that contains a molecular constituent. Thus, H, O, N, or halogen atoms can be generated by application of a discharge through gas containing H_2, O_2, N_2, or a diatomic halogen. Molecular radicals, such as OH or ClO, can then be created by addition of a gas that undergoes rapid reaction with the atoms that have been produced in the discharge. Thus, OH can be generated from the reactions $H + NO_2 \rightarrow OH + NO$ and $F + H_2O \rightarrow OH + HF$, and ClO can be generated from $Cl + O_3 \rightarrow ClO + O_2$ and $Cl + ClO_2 \rightarrow 2ClO$.

The conventional flow tube method is applied under laminar flow conditions at low total pressure, normally below ca. 5 Torr.[18] Observations of radical concentrations are made at a fixed observation station near the downstream end of the tubular reactor, and the co-reagent is introduced either at fixed inlets upstream or, more commonly, through a moveable injector. The reaction times can be calculated knowing the linear flow velocity of the gas mixture along the reactor. As compared with pulsed photolysis experiments, measurements of radical concentrations in flow tubes can be made with a wider range of techniques, not only the forms of optical spectroscopy that can be employed in pulsed photolysis experiments but also various forms of mass spectrometry. In most modern experiments, the flow tube has two jackets. The outer one is evacuated to provide thermal insulation, and heated or cooled fluid is passed through the inner jacket to change the temperature of the gas mixture in the main tube.

In conventional experiments, the total pressure and gas flow are chosen so that radial diffusion is rapid and axial diffusion is slow relative to the flow of the gas mixture down the tube. Generally, the atomic or molecular radicals can be removed at the wall of the reactor at an appreciable rate, and much effort has gone into finding coatings that minimize this loss so that the dominant removal of the radicals is by the reaction that is being studied. In flow tube experiments, as in pulsed photolysis experiments, the maximum concentration of the co-reagent that can be introduced at low temperatures is determined by the requirement not to exceed the vapor pressure of this species at the temperature of the cooled reactor. In addition, however, it is essential that the removal of the radicals at the walls is not too rapid.

There is some evidence that the removal of some radicals at untreated flow tube walls might increase at low temperatures.[18c] However, it is not clear that this is so for walls that have been coated appropriately to reduce heterogeneous removal. For example, Beach et al.[19] have shown that the rate of removal of Cl atoms on walls that had been coated with halocarbon wax actually decreased slightly as the temperature was lowered from 298 to 210 K, and the rate of the $Cl + O_3$ reaction was measured down to 184 K.

In recent years, the range of experimental conditions that can be employed in flow tube experiments has been expanded considerably. To a large extent, these methods have been devised in order to extend the use of the flow tube method to much higher total pressures. However, they have, in addition, reduced the problems arising from loss of radicals at the walls of the reactor. Anderson's group has constructed a very large, generally recirculating flow tube in which concentrations of radicals are measured as a function of both axial and radial position.[20] They have reported measurements at total pressures up to 600 Torr.[21] Moreover, using an ingenious form of cryogenic cooling, they have succeeded in performing experiments at temperatures down to 180 K.[22] In a similar vein, Molina and co-workers have reported the results of kinetic measurements in turbulent flow reactors.[23−25] Again, these can be operated at much higher pressures than is customary in the conventional, laminar flow reactors. Measurements at pressures up to 300 Torr have been reported. Another significant advantage is that the pattern of flow is such that the effective wall removal rate is appreciably reduced. They have reported measurements on the Cl + CH_4 reaction at temperatures down to 181 K.[23]

2.3. Cooling by Supersonic Expansion: Laval Nozzles and the CRESU Technique

If gas is expanded through a small orifice from a region of high pressure to one of high vacuum, it is drastically cooled, typically to temperatures of ca. 1 K. Such expansions have been widely used to generate concentrations of weakly bound complexes for spectroscopic studies of their structure. However, the resultant medium is inhomogeneous with respect to both temperature and density, making it difficult, but not entirely impossible,[26] to perform kinetics experiments.

On the other hand, expansion of a gas through an appropriately designed, axisymmetric, converging−diverging, Laval nozzle provides a supersonic flow of cold and relatively dense (ca. $10^{16}-10^{17}$ cm^{-3}) gas that remains uniform for about a meter downstream of the exit of the nozzle. Such nozzles are the central feature of the CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus. To avoid clustering, helium is chosen as the carrier gas for the lowest temperatures. The integrity of the flow will be maintained for additions of $\leq 1-2\%$ of other gases, and high levels of supersaturation can be maintained for these added gases, because the gas encounters no walls and because homogeneous dimerization and subsequent condensation into higher aggregates are generally quite slow.

The CRESU method was devised in 1984, by Rowe and co-workers, to study ion−molecule reactions.[27] Then, and for subsequent studies of ion−molecule reactions, it has been operated in a flow tube mode, with kinetic information being determined by comparing changes in the concentrations of the ions by mass spectrometry, either as the distance between the points at which ions were produced and sampled or as the concentration of the molecular reagent was varied. For the past decade, kinetic measurements have been performed on neutral−neutral reactions, using the two independent continuous flow CRESU apparatuses that exist in Rennes and in Birmingham.[28,29] In these experiments, relative concentrations of radicals have been observed in real time, usually by LIF, following their creation by pulsed laser photolysis.

Like any other technique, the CRESU method has its limitations. Among these is the fact that it can only be used to measure the rates of fast processes. The supersonic flow remains uniform for some tens of centimeters, which corresponds to 100−500 μs. Any change in concentration of an observed species must occur on this time scale. Given the limit placed on the introduction of an added gas, second-order rate constants for any process other than those involving the carrier must exceed ca. 10^{-12} cm^3 $molecule^{-1}$ s^{-1} if they are to be measured. In addition, the large flows of the added co-reagent that are needed mean that it is difficult to introduce sufficient concentration of any species with a low vapor pressure or one that is not readily available. This makes it very difficult to study radical−radical reactions, although, in very recent experiments, rate constants have been determined for the reaction $O(^3P) + OH \rightarrow O_2 + H$.[30] In this instance, both radicals are created by pulsed photolysis of O_2 and H_2O at 157 nm. The concentration of $O(^3P)$ atoms is estimated from a knowledge of the absorption cross-section for O_2 at this wavelength and the measured fluence of the photolysis laser.

The continuous flow CRESU apparatus does consume large amounts of gas when it is running, and it requires pumps that are unusually large. These features have led to the development and use of pulsed Laval nozzles[31] in experiments that consume less gas and therefore allow kinetic measurements to be performed on reactions with co-reagents that are expensive and/or difficult to synthesize. Although measurements using both the continuous flow and the pulsed techniques are in good agreement,[32] the pulsed Laval nozzle method has not yet provided rate constants at the very low temperatures achieved in the continuous flow CRESU method.[33]

The unique strength of the CRESU apparatus, especially the continuous flow CRESU apparatus, is the ability to reach very low temperatures indeed. The lowest temperature achieved so far is 7 K,[29] but this required the reservoir, where gases are mixed before passing through the Laval nozzle, to be cooled in liquid N_2, imposing a constraint on which gases can be included in the mixture. The lowest temperature achieved so far, without such precooling, is 13 K. Such temperatures are, of course, well below those encountered in the Earth's, and other planetary, atmospheres, and a main focus of the measurements made in the CRESU apparatuses has been to determine rate constants at temperatures found in dense interstellar clouds. Partly for this reason, the measurements have emphasized the reactions of $C(^3P)$ and $Si(^3P)$ atoms and of the small carbon-based radicals (CH, C_2H, and CN).[6] Some measurements have been made, at temperatures down to 23 K, on the following reactions of the OH radical: $OH + HBr \rightarrow H_2O + Br$,[34−36] $OH + NO (+ M) \rightarrow HONO (+ M)$,[37] and OH + butanes.[38]

3. Low Temperature Rate Constants for Atmospheric Reactions

In this section, I consider the kinetic data available for a selection of reactions that are important in the Earth's atmosphere. The reactions are characterized according to the broad chemical nature of the reagents.

3.1. Reactions between Free Radicals and Saturated Molecules

Exothermic reactions between radicals and saturated molecules, that is, molecules containing only single bonds, generally occur by transfer of an atom from the molecule to the radical. They are usually characterized by direct dynamics. (Direct bimolecular

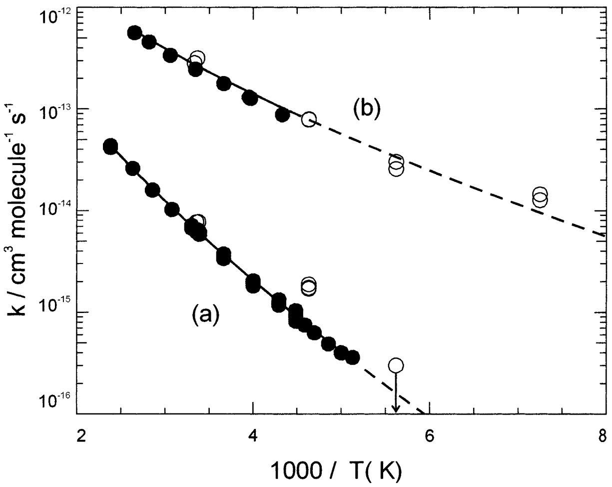

Figure 2. Arrhenius plots of the rate constants for the reactions of OH radicals with (a) CH_4 and (b) C_2H_6. The closed circles (●) show the data of (a) Vaghjiani and Ravishnakara[12a] and Gierczak et al.,[12b] and (b) Talukdar et al.;[13] the open circles (○) show the data of Sharkey et al.[10] The full lines represent the functional forms suggested by Gierczak et al.[12b] and Talukdar et al.[13] to represent the rate constants between (a) 196 and 420 K and (b) 231 and 371 K. The dashed lines represent these formulas extended to lower temperatures.

reactions occur without the formation of a collision complex that lasts for, at least, a fraction of a molecular rotation. Such behavior is likely when there is no significant potential energy minimum or "well" along the reaction path of minimum energy.) The reactions between OH and alkanes and those between OH and substituted alkanes are apparently of this type, and they initiate the oxidative breakdown of such compounds in the troposphere. The simplest, most studied, and arguably most important of these reactions is

$$OH + CH_4 \rightarrow H_2O + CH_3 \quad (1)$$

where $\Delta H_{298}°$ (kJ mol^{-1}) = −57.8. Figure 2 shows the values of the rate constants, k_1, obtained in three recent studies at temperatures between approximately 500 and 200 K. In the restricted range from 240 to 300 K, the rate constants can be expressed in terms of the Arrhenius expression k (cm^3 molecule^{-1} s^{-1}) = $2.3 \times 10^{-12} \exp(-1765\ K/T)$,[1,2] but over a wider temperature range, as Figure 2 shows, the Arrhenius plot of ln k against $(1/RT)$ shows curvature.

Despite its appreciable activation energy (E_{act} = 14. 7 kJ mol^{-1}), reaction 1 is very important in atmospheric chemistry. About 30% of the OH radicals formed in the atmosphere are removed by reaction 1 with CH_4, nearly all of the other 70% being removed by reaction with CO (see below). These two reactions are the first and last elementary steps in the atmospheric oxidation of CH_4. In addition, reaction 1 largely determines the lifetime of CH_4 in the atmosphere.[39] Using the rate constant k_1 at 290 K and an estimate[3] of the globally averaged concentration of OH (9×10^5 molecule cm^{-3}) suggests that the CH_4 has an atmospheric lifetime (= $1/k_1$[OH]) of ca. 6−7 years, although other processes do shorten this estimate. Nevertheless, this relatively long lifetime (at least 100 times greater than that of any other alkane) means that it is especially important to define the temperature dependence of k_1 accurately, since a significant fraction of the methane released at the Earth's surface will reach altitudes in the atmosphere where the temperatures are appreciably lower than those at the surface.

Liquid CH_4 boils at 111.6 K, so its condensation in low temperature experiments causes no problems. However, the low rate of reaction 1 does, especially as methane efficiently quenches OH($A^2\Sigma^+$),[38] making the observation of OH concentrations by resonance or LIF difficult, at the CH_4 concentrations that are needed if reaction 1 is to occur at a rate comparable to other loss processes. Despite these difficulties, Gierczak et al.[10] have succeeded in measuring values of k_1 down to 196 K. Their rate constants, for temperatures between 196 and 420 K, fit the modified Arrhenius expression k_1 (cm^3 molecule^{-1} s^{-1}) = $1.76 \times 10^{-13} (T/298)^{2.82} \exp(-(987 \pm 100)K/T)$. Between 240 and 300 K, this expression yields rate constants that are no more than 4−5% higher than those obtained from the Arrhenius expression recommended by the IUPAC Evaluation Panel.[2]

Sharkey and Smith[10] have also made low temperature measurements of k_1. At 178 K, they were only able to determine an upper limit, k_1 (cm^3 molecule^{-1} s^{-1}) < 3×10^{-16}, which is consistent with the value predicted by the modified Arrhenius expression for k_1 derived by Gierczak et al.[12b] However, at 216 K, the lowest temperature at which Sharkey and Smith[10] actually measured k_1 (see Table 2), their value was approximately twice that given by the expression of Gierczak et al.[12b] (see Figure 2).

Given the low boiling point of CH_4, it should, in fact, be possible to measure rate constants for this reaction down to still lower temperatures. Thus, at 150 K, 1 bar pressure of CH_4 corresponds to 4.83×10^{19} molecule cm^{-3}. Using the modified Arrhenius expression to estimate k_1 at 150 K suggests that in the presence of 1 bar of CH_4, OH would be removed with a pseudo-first-order rate constant of ca. 1.7×10^3 s^{-1} at 150 K. It should be possible to measure this rate, although it might be better to use an absorption technique to follow changes in the OH concentration, because rapid quenching of OH($A^2\Sigma^+$) will render fluorescence methods quite difficult.

Because their reactions with OH radicals are approximately 100 times faster than reaction 1, the atmospheric lifetimes of higher alkanes are much shorter than that of CH_4 and much less of them reach the high altitudes of the Earth's atmosphere where the temperatures are much lower. Again, Sharkey and Smith[10] and Ravishankara's group[13] have made low temperature kinetics measurements on the reaction

$$OH + C_2H_6 \rightarrow H_2O + C_2H_5 \quad (2)$$

where $\Delta H_{298}°$ (kJ mol^{-1}) = −74.1, using the pulsed laser photolysis LIF method. Their results are both recorded on the Arrhenius plot in Figure 2. For this reaction, Talukdar et al.[13] have determined rate constants only down to 231 K, whereas Sharkey and Smith[10] have measured k_2 down to 138 K. Their results are consistent with one another, and Sharkey and Smith's data are quite well-fit by the modified Arrhenius expression k_2 (cm^3 molecule^{-1} s^{-1}) = 1.26 × 10^{-12} $(T/298)^2$ exp($-461K/T$) that was proposed in 1992[41] to fit the rate constants then available for temperatures between 226 and 800 K. In addition, Clarke et al.[22] have measured values of k_2 at temperatures down to 180 K in the Harvard high pressure flow tube. Their results are in excellent agreement with those of Sharkey and Smith[10] and Talukdar et al.[13] and with other previously published measurements.

In recent years, both kinetic and mechanistic studies have been carried out on the reactions of the OH radical with fluorinated hydrocarbons; that is, with the so-called hydrofluorocarbons or HFCs. These compounds have emerged as suitable replacements for the chlorofluorocarbons (CFCs) in many of their applications. As compared with the CFCs, the HFCs are more rapidly oxidized because their breakdown can be initiated by abstraction of an H-atom by the OH radical. Moreover, the only halogen that they contain, fluorine, is not destructive of stratospheric ozone in the same way as the other halogens.[3] Consequently, their ozone destruction potentials are much lower than those of the CFCs that they are designed to replace.

The reactions of OH with those HFCs that have been adopted for technological uses have similar rate constants and activation energies to those for reaction 1. As an example, I cite the reaction of OH with CF_3-CFH_2 (HFC134a), which has been widely adopted as a replacement for CF_2Cl_2 (CFC-12) in refrigeration and air conditioning systems.

$$OH + CF_3CFH_2 \rightarrow H_2O + CF_3CFH \qquad (3)$$

where $\Delta H_{298}°$ (kJ mol^{-1}) = -66. The kinetics of this reaction have been studied down to 220 K,[42] and the JPL Evaluation Panel[1] recommends the expression k_3 (cm^3 molecule^{-1} s^{-1}) = 1.5 × 10^{-12} exp($-(1750 \pm 200)K/T$) for its rate constant. This expression yields a rate constant at 290 K that is about two-thirds of that for reaction 1; therefore, the atmospheric lifetime of HFC134a is ca. 50% longer than that of CH_4. This estimate demonstrates that HFC134a will disperse widely in the Earth's atmosphere and that further low temperature measurements on the kinetics of reaction 3 would assist in establishing the atmospheric lifetime of CF_3CFH_2 and the fraction of this compound that will reach the stratosphere.

As a second family of important atmospheric reactions that involve radicals and saturated molecules, I consider the reactions between OH and the hydrogen halides HCl and HBr:

$$OH + HCl \rightarrow H_2O + Cl \qquad (4)$$

where $\Delta H_{298}°$ (kJ mol^{-1}) = -65.4, and

$$OH + HBr \rightarrow H_2O + Br \qquad (5)$$

where $\Delta H_{298}°$ (kJ mol^{-1}) = -130.9. The molecules HCl and HBr, unlike CH_4, do not reach the low temperature regions of the atmosphere around the tropopause as a result of release at the Earth's surface and a long lifetime in the troposphere. Rather, they can be created in situ in the stratosphere and act as reservoir compounds. Reactions 4 and 5 can convert these relatively inactive forms of chlorine and bromine to active forms, i.e., Cl and Br atoms.

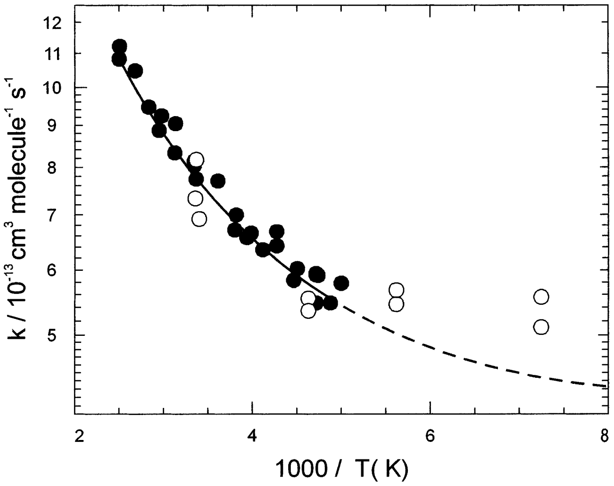

Figure 3. Arrhenius plots of the rate constants for the reaction of OH radicals with HCl at temperatures below 500 K. The closed circles (●) show the data of Battin-Leclerc et al.,[14] and the open circles (○) show the data of Sharkey et al.[10] The full line represents the functional form suggested by Battin-Leclerc et al.[14] to represent the rate constants between 200 and 400 K. The dashed line represents this formula extended to lower temperatures.

The kinetics of reaction 4 have been studied in cryogenically cooled, pulsed photolysis experiments by Sharkey and Smith[10] and by Battin-Leclerc et al.[14] Their results are shown in Figure 3. Sharkey and Smith's measurements[10] were carried out at 216, 178, and 138 K, as well as at 298 K. Their values of k_4 at the three low temperatures were the same, within experimental error, but lower than the value at 298 K. The experiments by Battin-Leclerc et al. covered the range 400−200 K. Over the low temperature range common to both sets of experiments, the results of Sharkey and Smith and Battin-Leclerc et al. are in good agreement. However, the low temperature results of Sharkey and Smith are significantly higher than predictions based on the Arrhenius expressions recommended by both the IUPAC and the JPL Evaluation Panels.[1,2] Thus, at 180 K, the lowest temperature reached in the stratosphere,[4] the result of Sharkey and Smith, exceeds both of these recommendations by ca. 50%.

At 298 K, reaction 5 is 14 times faster than reaction 4, and its rate constant apparently does not depend on the temperature between 249 and 416 K.[43] The fast rate of this reaction and its lack of activation energy have allowed it to be studied to very low temperatures in experiments utilizing a continuous flow CRESU apparatus[34,36] and a pulsed Laval nozzle.[35,36] These measurements, which are shown in Figure 4, demonstrate that k_5 increases as the temperature is lowered below 180 K, but the form of that decrease was disputed[34,35] until some recent experiments[36] appeared to have cleared up the earlier differences. As these differences referred to temper-

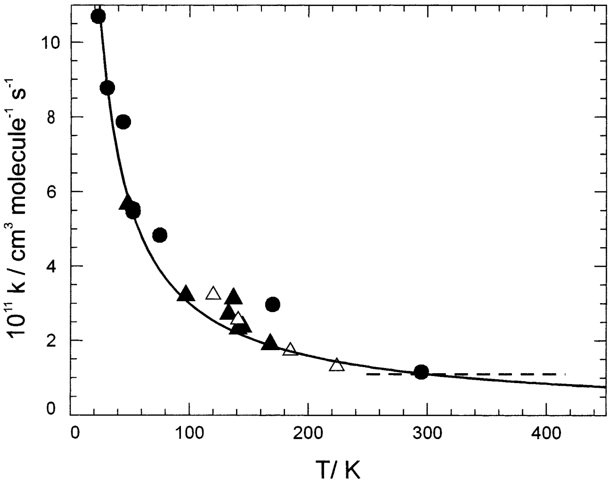

Figure 4. Plot showing the variation with temperature of the rate constants for the reaction of OH radicals with HBr at temperatures below 500 K. The dashed line (- - -) represent the temperature-independent data of Ravishankara et al.[43] at temperatures between 249 and 416 K; the filled circles (●) show the data obtained by Sims et al.[34] from experiments performed in a continuous flow CRESU apparatus, and the triangles show the rate constants reported by Jaramillo et al.[36] from measurements in a continuous flow CRESU apparatus (▲) and in a pulsed Laval nozzle apparatus (▽). The full line represents the functional form suggested by Jaramillo et al.[36] to represent the rate constants between 20 and 350 K.

atures below those encountered in the Earth's atmosphere, they were irrelevant to atmospheric chemistry but not to the question of how an apparently direct atom transfer reaction of this kind could exhibit such a strong negative temperature dependence at low temperatures. A possible explanation is that the rate constant for reaction is dependent on the rotational states of the reagents; therefore, the thermally averaged rate constant is affected as the rotational populations of OH and HBr change with temperature.[34] In addition, Smith and Ravishankara[44] have discussed the possible effects on the dynamics of reactions 4 and 5 of the formation of hydrogen bonds between the reagents.

3.2. Reactions between Free Radicals and Unsaturated Molecules

The initial stage of reactions of free radicals with unsaturated molecules, that is species with double or triple bonds, is addition or association. The fate of this internally energized addition complex depends first and foremost on energetics; in particular, whether the lowest energy pathway for dissociation of the addition complex leads back to the reagents from which it was formed. If so, then the only reaction pathway will be collision-assisted association and the reaction rate will depend on total pressure, as well as temperature. In general, kinetics experiments will seek to define the rate constants at the limit of low and high pressure, $k°$ and k^∞, respectively, and the behavior in the falloff region between these two limits. Because $k°$ and k^∞ depend differently on temperature, the range of pressure that covers the falloff region also depends on temperature, and the temperature dependence of the rates of such reactions can therefore be quite complex. If, on the other hand, the energized addition complex can dissociate by a pathway that is energetically more favorable than redissociation to reagents, then that channel for reaction is likely to be favored and the rate of reaction will be largely determined by the rate of formation of the complex, although in some interesting cases (see below) collisional stabilization and decomposition to products can occur at comparable rates, leading to quite a complex relationship between the overall rate constant and the total pressure.

As a first example of the first type of reaction, I take the addition of OH to unsaturated hydrocarbons, reactions that initiate the oxidation of such compounds in the atmosphere. This process is followed by the addition of O_2 to the hydroxy-substituted radical to form a peroxy radical, and the subsequent chemistry parallels that for the oxidation of alkanes.[3] The most extensively studied examples are the reactions of OH with ethene and ethyne:

$$OH + C_2H_4\,(+ M) \rightarrow C_2H_4OH\,(+ M) \qquad (6)$$

where $\Delta H_{298}°$ (kJ mol^{-1}) = -123.4, and

$$OH + C_2H_2\,(+ M) \rightarrow C_2H_2OH\,(+ M) \qquad (7)$$

where $\Delta H_{298}°$ (kJ mol^{-1}) = -147. In these cases, the addition complexes are small enough that the kinetic falloff region covers the range of pressures found in the atmosphere.

The only low temperature study of reaction 6, down to 210 K, appears to be the 1973 study of Smith and Zellner.[45] Under the conditions of their experiments ($10 \leq p$ (Torr) ≤ 200), they found the reaction to have a small but significant activation energy and it is generally believed that the addition has a small barrier, although the JPL Evaluation[1] recommends a temperature-independent high pressure rate constant. At room temperature, the rate constant for reaction 7 in the limit of high pressure, i.e., k_7^∞, is about 1/10 of k_6^∞ and shows a positive temperature dependence, again suggesting a barrier in the entrance channel to formation of the addition complex.

Again, there has been rather little work on reaction 7 at low temperatures. However, the results of Michael et al.,[46] at temperatures down to 238 K, are in good agreement with those of Smith and Zellner,[45] at temperatures down to 210 K. Given the uncertainties about these complex reactions, experiments to still lower temperatures would be rewarding. In particular, measurements using the continuous CRESU or pulsed Laval nozzle apparatuses might help to define the presence and size of the energy barriers to addition of OH to C_2H_4 and C_2H_2.

Continuous flow CRESU experiments have been performed on the reactions of OH with three butenes: but-1-ene, (*E*)-but-2-ene, and (*Z*)-but-2-ene.[47] These reactions were chosen because they would clearly be in their high pressure limit, even at the low pressures used in the CRESU flows, and because from measurements at room temperature and above, it appeared that the addition of OH to these alkenes is not inhibited by the presence of potential energy barriers. The absence of barriers in all three cases was confirmed by these ultralow temperature measurements. For all three butenes, the rate constants for reaction rose as the temperature was lowered from 298 to 23 K reaching values of 3.9×10^{-10} ((*Z*)-but-2-ene), 4.3×10^{-10} (but-1-ene), and 4.5×10^{-10} ((*E*)-but-2-ene) cm^3 $molecule^{-1}$ s^{-1} at 23 K.[47]

The reactions of OH with alkenes and alkynes apparently proceed predominantly by addition to form the hydroxy-alkyl and hydroxy-vinyl radicals, as shown in eqs 6 and 7 for ethene and ethyne. The reaction of OH with CO is different. It has been studied many times, partly because of its importance as the only reaction that converts CO to CO_2 in the atmosphere and in combustion, and partly because of its intriguing mechanism. Its rate constant shows a rather complex dependence on temperature and pressure.

The primary step in the reaction is the association of OH and CO to form an energized HOCO radical. This species can then undergo three competitive processes, which have comparable rates under atmospheric conditions: redissociation to OH + CO, collisional stabilization to HOCO, and decomposition to $H + CO_2$.[48] In practice, in the atmosphere, the second two channels lead to the same overall result, as HOCO reacts with O_2 to form $HO_2 + CO_2$, and any H-atoms produced in the atmosphere rapidly combine with O_2 to yield HO_2.

$$
\begin{aligned}
&\mathrm{OH} + \mathrm{CO} \underset{k_{-\mathrm{a}}}{\overset{k_{\mathrm{a}}}{\rightleftharpoons}} \\
&\qquad (\mathrm{HOCO})^{*} \rightarrow \mathrm{CO_2} + \mathrm{H}\ (+\ \mathrm{O_2} \rightarrow \mathrm{HO_2}) \\
&\qquad +\ \mathrm{M} \downarrow k_{\mathrm{M}}[\mathrm{M}] \\
&\qquad \mathrm{HOCO}\ (+\ \mathrm{O_2}) \rightarrow \mathrm{CO_2} \rightarrow \mathrm{HO_2}
\end{aligned}
$$

It is now clear, both from quantum chemical calculations[49-51] and from semiempirical calculations[11,52-54] designed to match the extensive experimental data on the kinetics of the reaction, that the barriers between OH + CO and HOCO and between HOCO and CO_2 + H have comparable heights. Despite the large number of attempts to fit the temperature and pressure dependences, there is as yet no consensus on some features of the reaction: in particular, the height of the two barriers and whether quantum mechanical tunneling through the second barrier is important.

The kinetics of reaction between OH and CO have been studied down to 80 K by Frost et al.[11] They found that the rate constant at 80 K is only about 30% lower than that at 298 K. This result, which sets a limit to the height of the entrance channel barrier, is particularly hard to reproduce in the calculations. Nevertheless, the feeling persists that there must be a small entrance channel barrier because both the absolute value of the rate constant and its dependence on temperature between 80 and 400 K are small. Further measurements at low, indeed even lower, temperatures would be valuable, both to confirm the low temperature results of Frost et al.[11] and to see whether the rate constant starts to decrease sharply as the entrance barrier becomes appreciable relative to k_BT.[55] Unfortunately, the absolute value of the second-order rate constant is too small for CRESU experiments on the rate to be feasible.

The reaction between OH and HNO_3 does not fit easily into the classification that I have used to discuss reactions in the present paper. Although HNO_3 is arguably an unsaturated molecule, this character plays little part in the detailed mechanism of the reaction of HNO_3 with OH, a reaction which plays an important role in the chemistry of NO_x in the atmosphere. In particular, this reaction, the photodissociation of HNO_3, and the association of OH radicals with NO_2 (see below, reaction 10) combine to determine the balance between NO_x and NO_y in the upper troposphere and lower stratosphere,[56] where the temperatures are quite low (see Figure 1). Recent experiments[57] have demonstrated conclusively that the reaction produces $H_2O + NO_3$ exclusively:

$$\mathrm{OH} + \mathrm{HNO_3} \rightarrow \mathrm{H_2O} + \mathrm{NO_3} \tag{8}$$

where $\Delta H_{298}°$ (kJ mol^{-1}) = −70.2, deceptively suggesting that the reaction is a simple H-atom abstraction. However, like the reaction between OH + CO, the rate constant shows a complex dependence on temperature and pressure,[57,58] and the kinetic isotope effects do not accord with simple ideas of changes in zero-point energies in the reagents and at the transition state.[8]

This intriguing reaction has been extensively studied over the past quarter of a century.[1,2] The most thorough investigations, including measurements on the OH + HNO_3 reaction down to 200 K, have been undertaken by Ravishankara's group.[57-59] The experiments (i) confirmed the unit yield of NO_3 from the OH + HNO_3 and OD + DNO_3 reactions at all temperatures (240−330 K; 296 K) and pressures (at 296 K for OH + HNO_3, p = 23−770 Torr; and at 296 K for OD + DNO_3, p = 74−360 Torr) at which experiments were performed[57] and (ii) examined how the rate constants for all isotopic variants of this reaction, OH + HNO_3,[58] OD + HNO_3,[57] OH + DNO_3,[57] and OD + DNO_3,[57] depend on temperature and pressure. The results of the measurements on the OH + HNO_3 and OD + HNO_3 reactions are summarized in Figure 5. Especially notable is the strong negative temperature dependence of the rate coefficients and their dependence on total pressure. Moreover, we note that the dependence on total pressure of the rate constants for OH + HNO_3 and for OD + HNO_3 (no such dependence is found for the reactions of OH and OD with DNO_3)[57] only becomes significant at temperatures below 298 K, becoming stronger the lower the temperature.

Brown et al.[57] have discussed the experimental results on reaction 8 and its isotopic variants in terms of a mechanism that involves the initial formation of an OH·HNO_3 complex, which is held together by two hydrogen bonds (see Figure 6), yielding an overall binding energy of ca. 25 kJ mol^{-1}. The role of such a complex was first proposed by Margitan and Watson[60] and is supported by recent quantum chemical calculations.[61,62] According to this proposed mecha-

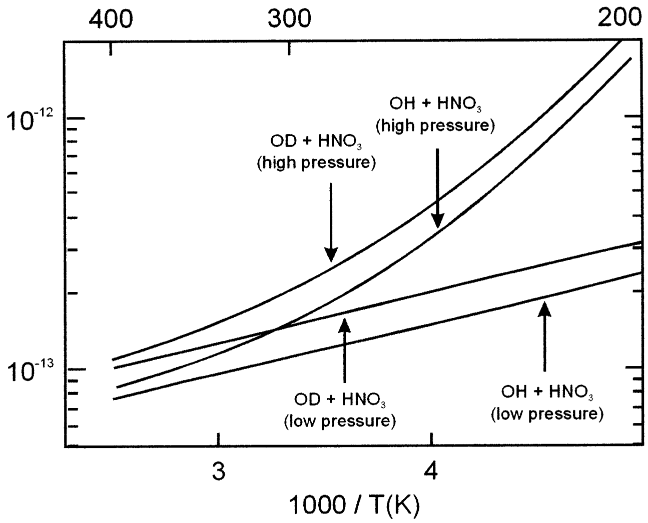

Figure 5. Arrhenius plots of the rate constants for the reactions of OH and OD radicals with HNO_3 at temperatures below 500 K. Curves are shown for conditions of high and low total pressure. (Adapted with permission from ref 58. Copyright 1999 American Chemical Society.)

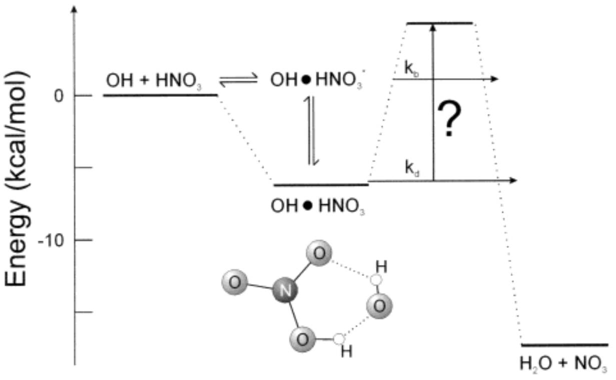

Figure 6. Diagram showing how the potential energy is proposed to vary along the minimum energy path for the reaction between OH radicals and HNO_3. (Adapted with permission from refs 57 and 58. Copyright 1999, 2001 American Chemical Society.)

nism, which is illustrated in Figure 6, the complex can then redissociate, be collisionally stabilized, at least temporarily, or undergo internal H-atom transfer and subsequent dissociation to yield $H_2O + NO_3$. The proposed mechanism is similar to that now generally accepted for reaction between OH and CO, but in the case of OH + HNO_3, redissociation is assumed to be the fastest decay channel for the energized adduct OH·HNO_3*, because of its relatively small binding energy and the assumed large barrier between the OH·HNO_3 complex and the $H_2O + NO_3$ products. At present, the height of this barrier on the minimum energy path is uncertain. Brown et al.[57] have assumed that it is significantly higher than the OH + HNO_3 asymptote. Then, a simplified kinetic model of the mechanistic scheme can fit all of the experimental findings, at least semiquantitatively, if it is assumed that transfer of the H/D atom from HNO_3/DNO_3 to OH/OD within the hydrogen-bonded complex must occur by tunneling through the barrier.

To investigate further certain aspects of the kinetic model for the OH + HNO_3 reaction proposed by Brown et al.,[57,58] McCabe et al.[59] have recently measured the rate constants for removal of OH ($v = 1$) and OD ($v = 1$) by HNO_3 and DNO_3 at temperatures between 253 and 383 K. In all cases, the rate constants are much larger (ca. 100 times) than those for reaction 8; for example, at 298 K and low pressure, k_8 (cm^3 $molecule^{-1}$ s^{-1}) = 1.2×10^{-13}, whereas at the same temperature the rate constant for removal of OH ($v = 1$) by HNO_3 is k (cm^3 $molecule^{-1}$ s^{-1}) = 2.5×10^{-11}. The high value of the latter rate constant is a strong indication of rapid vibrational relaxation. McCabe et al.[59] argue that this occurs through the facile formation of the hydrogen-bonded complexes, such as OH ($v = 1$)·HNO_3 and intramolecular vibrational relaxation within these complexes at rates that are comparable with the rate of redissociation of the complex.

Experiments on the OH + HNO_3 reaction provide a very good example of how kinetic measurements over a range of conditions, especially ones down to low temperature, can reveal unexpected complexities in the mechanism of an apparently simple reaction and with the aid of kinetic modeling provide acceptable descriptions of how the reaction occurs.

3.3. Reactions between Pairs of Free Radicals

Interactions between pairs of free radicals are characterized, inter alia, by the existence of multiple potential energy surfaces.[8] Normally, the potential energy on the lowest of these surfaces falls monotonically as the radicals approach and unpaired electrons on each of the radicals pair up to form a chemical bond. Consequently, the first stage of radical−radical reactions is often the formation of an internally energized addition complex. As discussed earlier for reactions of radicals with unsaturated molecules, the fate of these complexes will depend on the energetics of the molecular system, as well as on the total pressure and the temperature. In this section, I consider examples of three types of radical−radical reactions: (i) association reactions, exemplified by the reactions of OH with NO and NO_2; (ii) atom transfer reactions between atomic and diatomic radicals, especially O + OH; and (iii) reactions in which different product channels are produced at comparable rates, where I shall discuss the reactions of ClO with OH and with HO_2. These examples are chosen because of their atmospheric relevance, and given the context of this paper, I attempt to show the value of low temperature studies of these reactions.

In general, radical−radical reactions are difficult to study, especially when the two radicals are not the same species, since, to determine a rate constant, it is necessary to produce one radical and observe changes in its concentration in the presence of a second radical, which is present in a known, greater concentration. This problem is, of course, ameliorated in the situation where the second radical is one of those that is relatively stable; that is, O_2, NO, or NO_2.

The association reactions

$$OH + NO (+ M) \rightarrow HONO (+ M) \qquad (9)$$

where $\Delta H_{298}°$ (kJ mol^{-1}) = −207.0, and

$$OH + NO_2 (+ M) \rightarrow HONO_2 (+ M) \qquad (10)$$

where $\Delta H_{298}°$ (kJ mol^{-1}) = −207.6, are both important in the atmosphere, especially the latter. It removes the reactive species OH and NO_2 converting them to the "reservoir compound", $HONO_2$. Reactions 9 and 10 are both of a size such that their kinetics are in the falloff regime under atmospheric conditions. Consequently, it is important to study the dependence of their kinetics on both pressure and temperature. Both reactions have been the subject of many studies, using both pulsed photolysis and flow tube techniques.

Low temperature studies of reaction 10 are somewhat constrained by the fact that NO_2 increasingly dimerizes to N_2O_4 at low temperatures. In principle, this is less of a constraint in discharge flow experiments, since smaller pseudo-first-order rate constants can generally be measured than in pulsed photolysis experiments. Up to 1997, when the extensive evaluations of the IUPAC and JPL panels were published,[1,2] the two lowest temperature studies of these reactions were those by Erler et al. (down to 213 K),[63] using a discharge flow technique, and that of Anastasi and Smith (down to 220 K),[64] who generated OH by flash photolysis of HNO_3 and observed the decay of radical concentrations using resonance absorption. One advantage of using resonance absorption is that although pressure broadening slightly reduces the sensitivity of OH detection at high total pressures, the method does not suffer from the efficient quenching of fluorescence by N_2 and O_2, the main two atmospheric constituents.

Since 1997, there has been a further burst of papers dealing with reaction 10 from both experimental[21,65−68] and theoretical[69−72] viewpoints. These have had two main, and connected, purposes: (i) to define further the rate constants for the reaction between OH and NO_2 in the presence of N_2 and O_2 at the temperatures and pressures found in the Earth's atmosphere and (ii) to establish the branching ratio for association to nitric acid, $HONO_2$, and to peroxynitrous acid, HOONO

$$OH + NO_2 (+ M) \rightarrow HOONO (+ M) \qquad (10')$$

and how this branching ratio depends on conditions. The importance of reaction 10, in conjunction with the reaction of OH with HNO_3 (i.e., reaction 8 discussed above) and the photodissociation of HNO_3, in determining the ratio of NO_x to NO_y in the upper troposphere and lower stratosphere, have been mentioned earlier in this review and have been discussed at length by Perkins et al.[56]

In practice, although the latest experimental studies[65−68] improve the definition of the rate constant at high pressures, up to 130 bar,[65] and hence decrease any uncertainty in the limiting high pressure rate constant, k^∞, they have not extended the experiments to lower temperatures than previously. Brown et al.[67] have reported rate constants from pulsed photolysis experiments, over a temperature and pressure range similar to the measurements of Anastasi and Smith.[64] Likewise, Dransfield et al.[66a] have performed kinetic measurements at temperatures down to 220 K in the Harvard high pressure flow tube, extending previous room temperature experiments[21] at total pressures up to 600 Torr. In most of these experiments, N_2 was the diluent gas but Brown et al.[67] and D'Ottone et al.[68] also performed some measurements in O_2. Consequently, the results can be transferred directly to atmospheric conditions without correction for different third body efficiencies. Troe,[72] in analyzing the available kinetic data in terms of unimolecular rate theory, has also cited work down to 50 K,[73] performed in the continuous flow CRESU apparatus in Rennes, but this work has not yet been published.

The agreement between the rate constants obtained in the most recent experiments and those obtained by Anastasi and Smith[64] is, on the whole, quite satisfactory (at least, to the present author!). Two problems have emerged. First, the raw experimental data obtained in the atmospheric ranges of temperature and pressure do not fit as well as they might to the simplified expressions used to represent the falloff behavior in the most comprehensive sets of data evaluation.[1,2] At least in part, it appears that this is the result of trying to fit all of the available kinetic data, including that obtained at very high pressures,[65] to fairly simple analytical expressions. This problem is accentuated at the low temperature (ca. 220 K) characteristic of the upper troposphere and lower stratosphere, where the latest results[66a,67] yield rate constants about 20% higher than those reported by Anastasi and Smith,[64] although within the combined experimental errors of both sets of measurements.

The role of the association reaction (10′) to HOONO, both in the atmosphere and in laboratory experiments, remains unclear. Quantum chemical calculations[69,71] indicate that the binding energy of HOONO relative to OH + NO_2 is only about a quarter of that of $HONO_2$. This difference means that the limiting low pressure rate constant, $k_{10'}$, will be much less than k_{10}, so that production of $HONO_2$ will be strongly favored at low pressures. On the other hand, at high pressures, the rates of the two reactions are likely to be comparable. From his analysis, Troe[72] suggests that reaction 10′ would account for no more than 2.5% of the total rate at pressure below 1 bar at 298 K. At low temperatures, because the limiting low pressure rate constants increase more steeply than the high pressure rate constants, reaction 10′ might become significant at lower total pressure. Hippler et al.[65b] advance some kinetic evidence for the importance of reaction 10′, in that they observe double exponential decays in the OH concentration in experiments performed at high total pressures and temperatures between 430 and 480 K. They attribute this to the onset of the reverse of reaction 10′ and estimate the HO−ONO bond energy to be 83 ± 1 kJ mol^{-1}, which is in very fair agreement with the theoretical estimates.[69,71]

Spectroscopic evidence for the formation of HOONO via reaction 10′ has proved hard to come by. Thus, Dransfield et al.[66b] were unable to detect the formation of HOONO by FTIR spectroscopy at 230 K. However, ingenious experiments by Nizkorodov and Wennberg have yielded part of the IR spectrum of a species assigned as HOONO. They mixed OH radicals and an excess of NO_2 in a discharge flow apparatus and detected OH created when they irradiated the gas mixture downstream with tuneable infrared radiation in the region of the O−H vibrational overtone. They attributed the bands observed in this "action spectrum" to overtones of different conformers of HOONO and estimated that the yield of peroxynitrous acid was 0.05 ± 0.03 under the conditions of their experiment: $T = 253$ K and a total pressure of 20 Torr, with the carrier gas being a mixture of N_2 and helium. In addition, a paper by Okumura et al.[75] described the detection of peroxynitrous acid by cavity ring-down spectroscopy, performed in the region of the O−H stretch fundamental band. It is likely that more studies of this reaction will be reported soon, with the emphasis on the relative rates of reactions 10 and 10′ and how the branching ratio depends on temperature and total pressure.

Reaction 9 is of less importance in the Earth's atmosphere than reaction 10. Moreover, its kinetics are subject to fewer uncertainties, as there is only one possible channel and kinetic experiments at low temperatures are not complicated by dimerization of the co-reagent. Forster et al.[76] have studied the pressure dependence of this association reaction at room temperature and pressures from 1 to 150 bar, enabling the limiting high pressure rate constant for the reaction to be derived with only a short extrapolation: k_9^∞ (cm^3 molecule^{-1} s^{-1}) = 3.3×10^{-11}. A comprehensive study of the temperature dependence of this reaction has been reported by Sharkey et al.[77] They performed pulsed photolysis experiments between 298 and 80 K in cryogenically cooled cells and similar experiments down to 23 K in a continuous flow CRESU apparatus. At 53 K, they determined rate constants at five carrier gas densities, varying over a 16-fold change of density. These results, spanning a wide range of conditions, enabled them to derive a consistent picture of the kinetics with derived values of the rate constants in the limits of high and low pressure: k_9^∞ (cm^3 molecule^{-1} s^{-1}) ≈ 5.4×10^{-11} $(T/298\ \text{K})^{-0.1}$ and k_9° (cm^6 molecule^{-2} s^{-1}) = 8.9×10^{-31} $(T/298\ \text{K})^{-2.1}$. Of course, Sharkey's experiments were conducted at much lower total pressures than those of Forster et al.,[76] so their derived value of k_9^∞ is subject to much greater error.

In some senses, the simplest radical−radical reactions are those in which an atom is transferred from a diatomic radical to an atomic radical. Two important examples are

$$O(^3P) + OH \rightarrow O_2 + H \qquad (11)$$

where ΔH_{298}° (kJ mol^{-1}) = −68.4, and

$$N(^4S) + OH \rightarrow NO + H \qquad (12)$$

where ΔH_{298}° (kJ mol^{-1}) = −201.6. Reaction 11 is particularly important in the upper reaches of the Earth's atmosphere and in dense interstellar clouds, and the reverse reaction is very important in combustion.

Despite their molecular simplicity, reactions 11 and 12 are not easy to study experimentally, since they require the generation of two unstable radicals, with one in an excess, and known, concentration. In the few kinetic measurements that have been performed, O or N atoms were created in excess concentration and the decay of OH radicals was observed. In 1980, Howard and Smith[16] reported the results of experiments that combined the use of discharge flow techniques to create atomic oxygen or nitrogen with pulsed photolysis to produce OH radicals. The decay of the OH concentration was then observed in real time using the technique of resonance fluorescence. Their experiments covered the range $250 \le T$ (K) ≤ 515. (It is stressed that the experiments performed by Howard and Smith[16] and the later experiments of Smith and Stewart[17] both observed kinetic decays of [OH] in real time following the pulsed photolytic production of OH. Discharge flow methods were used only to generate the excess concentrations of the radical atoms. These experiments seem to have been misunderstood in the kinetics database maintained by NIST (http://kinetics.nist.gov).)

The rate constants measured by Howard and Smith[16] both showed a mild negative dependence on temperature. The values were in quite good agreement with those obtained at about the same time in two "traditional" flow tube studies, one providing rate constants for reaction 11 between 221 and 499 K[78] and the other only reporting room temperature values of the rate constants for both reactions.[79] These measurements strongly suggested that both reactions proceed across a potential energy surface without a barrier along the minimum reaction path. The relatively small values of the rate constants, k_{11} (cm^3 molecule^{-1} s^{-1}) = 3.8×10^{-11} and k_{12} (cm^3 molecule^{-1} s^{-1}) = 5.0×10^{-11} at 298 K, were attributed,[16] at least in part, to the multiple potential energy surfaces that arise and the likelihood that reaction occurs only over the lowest surface or surfaces.

Using essentially the same method as Howard and Smith, Smith and Stewart[17] have extended the temperature range over which rate constants have been measured for reactions 11 and 12. Once again, known atomic concentrations were generated by discharge flow methods and OH radicals were produced by pulsed laser photolysis of HNO_3 but now OH radicals were observed by LIF. Results were reported for temperatures down to 158 K for reaction 11 and 103 K for reaction 12. The low temperature limit in these experiments was set by the rate of loss of the radical atoms on the wall of the flow tube. The rate constants for both reactions increased monotonically to the lowest temperatures achieved in the experiments. Smith and Stewart[17] assumed that in part, the observed temperature dependence arose because of changes in a factor, $F_{el}(T)$, which represents the ratio of the electronic degeneracy of the surface over which reaction occurs (assumed to be 2 for O + OH and 4 for N + OH) and the product of the electronic partition functions for the reagents. According to this assumption, and including Howard and Smith's results[16] in the analysis, the temperature dependence of the rate constants could be expressed as:

$$k_{11}\,(\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = F_{\text{el}}(T)\ 3.7 \times 10^{-10}\ (T/298\ \text{K})^{-0.24}$$

and

$$k_{12}\,(\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = F_{\text{el}}(T)\ 2.0 \times 10^{-10}\ (T/298\ \text{K})^{-0.17}$$

At the present time, Carty et al.[30] are measuring rate constants for reaction 11 at temperatures down to 38 K in the continuous flow CRESU apparatus in Birmingham, partly because of the possible importance of this reaction in forming O_2 in the cold environment of dark, dense, interstellar clouds. These are challenging experiments, since they require the creation of large concentrations of $O(^3P)$ atoms ($\geq 5 \times 10^{14}$ molecule cm^{-3}) in the supersonic flow of the CRESU apparatus. This is being done by photolyzing O_2 at 157 nm using the output from an F_2 laser. N_2 is used as the carrier gas to ensure that the $O(^1D)$ atoms that are formed in this photodissociation are rapidly quenched to the ground state. Preliminary results from these experiments yield rate constants that are somewhat lower than those of Stewart and Smith and which show little dependence on temperature down to 38 K.

The reaction between O atoms and OH, and its reverse, has also been the subject of numerous theoretical studies. Among the most recent and comprehensive are those by Troe and co-workers.[80] The lowest potential energy surface leading from reagents to products has been characterized by high quality ab initio calculations. Then, a combination of classical trajectories, to determine the capture rate to form the HO_2 complex, and statistical adiabatic channel model calculations, to determine the subsequent decomposition of this short-lived complex, was employed to calculate rate coefficients.[80a] For temperatures below 300 K, the calculations indicate that reaction occurs only on the lowest potential energy surface and that redissociation of the energized HO_2 complexes to O + OH is unimportant. Given the complexity of these ab initio calculations, the agreement between the rate constants that they yield and those found experimentally is extraordinarily good, the calculated values of k_{11} being ca. 25% below their experimental counterparts at the lowest temperatures covered by the experiments. Below the lowest temperature covered by the experiments, the calculations suggest that k_{11} will start to decrease as the temperature is lowered further.

One advantage of experiments where the atomic radical reagent is the one in excess is that their rate of loss by termolecular gas phase recombination is quite slow. The same is not true when the radical acting as coreagent is molecular, even if it is only a diatomic species. To illustrate this point, I consider next the reaction between OH and ClO. The major reaction is

$$\text{OH} + \text{ClO} \rightarrow \text{HO}_2 + \text{Cl} \qquad (13)$$

where $\Delta H_{298}°$ (kJ mol^{-1}) = − 2.9, but there is also a minor channel, which is much more exothermic

$$\text{OH} + \text{ClO} \rightarrow \text{HCl} + \text{O}_2 \qquad (13')$$

where $\Delta H_{298}°$ (kJ mol^{-1}) = −231.1. These reactions could play a significant role in the partitioning of chlorine in the upper stratosphere. Clearly, they will have different effects. By converting ClO to Cl, reaction 13 propagates O_3 destruction, since Cl atoms react rapidly with O_3. On the other hand, reaction 13′ converts active chlorine to the reservoir species HCl.

Kegley-Owen et al.[81] have measured rate constants for the overall reaction between OH and ClO at temperatures from 234 to 356 K. Their experiments were similar to those devised by Howard and Smith,[16] in that excess concentrations of ClO were created using discharge flow techniques from the Cl + O_3 reaction and measured using ultraviolet absorption, and then, much smaller concentrations of OH were generated by pulsed laser photolysis and observed by LIF. Measurements were carried out with ClO concentrations between 10^{13} and 10^{14} molecule cm^{-3}, which were large enough to ensure pseudo-first-order conditions but small enough for the mutual reaction of two ClO radicals (k_{298} (cm^3 molecule^{-1} s^{-1}) = 1.6×10^{-14}) to be unimportant.

For the overall reaction between OH and ClO, Kegley-Owen et al.[81] fitted their rate constants to the Arrhenius form, $k_{13} + k_{13'}$ (cm^3 molecule^{-1} s^{-1}) = $(8.9 \pm 2.7) \times 10^{-12} \exp[(295 \pm 95)K/T]$, but their experiments did not yield information about the branching ratio. The negative temperature dependence of the rate constant is consistent with reaction via a transient peroxide complex, HOOCl, which can then decompose to the products of reaction 13 by the rupture of the O−Cl bond.

Lipson et al.[82] have also studied the reaction between OH and ClO, in their case, in a turbulent flow reactor coupled to a high pressure chemical ionization mass spectrometer. OH radicals were produced from H + NO_2 and ClO radicals from the reaction between Cl atoms and O_3. At temperatures between 207 and 298 K, they found values of the overall rate constant in fair agreement with those determined by Kegley-Owen at al., yielding $k_{13} + k_{13'}$ (cm^3 molecule^{-1} s^{-1}) = $(5.5 \pm 1.6) \times 10^{-12} \exp[(292 \pm 72)K/T]$. However, Lipson et al. placed most emphasis on obtaining the branching ratio for producing HCl + O_2 from reaction 13′ and HO_2 + Cl from reaction 13. They found $k_{13'}/(k_{13} + k_{13'})$ to be equal to 0.07 ± 0.03 and to be independent of pressure and temperature throughout the ranges investigated. Although quite extensive modeling had to be employed to extract it, this value should replace earlier efforts to establish the branching ratio[1,2] and it demonstrates that a small, but significant, fraction of the reaction between OH and ClO produces HCl + O_2.

Table 3. Kinetic Data for Atmospheric Reactions Studied at Low Temperature

reaction	range of T	exptl method	A (cm^3 molecule^{-1} s^{-1})	n	θ/T	ref
$OH + CH_4 \rightarrow H_2O + CH_3$	196−420	PLP-LIF	1.76×10^{-13}	2.82	987 ± 100	10
$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	231−371	PLP-LIF	1.26×10^{-12}	2	461	11
	138	PLP-LIF	$k_{138} = 1.3 \times 10^{-14}$			10
$OH + HCl \rightarrow H_2O + Cl$	200−400	PLP-LIF	4.2×10^{-13}	1.66	−184	14
	138	PLP-LIF	$k_{138} = 5.4 \times 10^{-13}$			10
$OH + HBr \rightarrow H_2O + Br$	20−350	CRESU/PLP-LIF	1.11×10^{-11}	−0.91	0	36
			1.06×10^{-11}	−1.09	10.5	
$OH + CO \rightarrow H + CO_2$	90−3000	PLP-LIF	the pressure and temperature dependences of these rate constants are complex and are discussed in detail in the refs given			53, 54
$OH + CO \rightarrow$ products	90−3000	PLP-LIF				
$OH + HNO_3 \rightarrow H_2O + NO_3$	200−375	PLP-LIF	$k = k_0 + (k_\Delta/\{1 + k_\Delta/\beta_M k_c[M]\})$; $\beta_M(N_2) = 1.0$ $k_0 = 2.4 \times 10^{-14} \exp(460/T)$ $k_\Delta = 2.7 \times 10^{-17} \exp(2200/T)$ $k_c[N_2] = 6.5 \times 10^{-34} \exp(1335/T)\,[N_2]$			57
$OH + NO \rightarrow HO\ NO$	23−301	PLP-LIF and CRESU/PLP-LIF	$A[N_2] = 8.9 \times 10^{-31}[N_2]$	−2.1	0	77
			$A^\infty = 5.4 \times 10^{-11}$	−0.1	0	
$OH + NO_2 \rightarrow HO\ NO_2$	220−400	PLP-LIF	$A[N_2] = 3.0 \times 10^{-30}\,[N_2]$	−3.0	0	72
			$A^\infty = 3.6 \times 10^{-11}$	0	0	
$OH + O \rightarrow O_2 + H$	103−294	PLP-LIF (D-F for O)	$F_{el}(T)\ 3.7 \times 10^{-10}$	−0.24	0	17
$OH + N \rightarrow NO + H$	158−294	PLP-LIF (D-F for N)	$F_{el}(T)\ 2.0 \times 10^{-10}$	−0.17	0	17
$OH + ClO \rightarrow$ products	234−456	PLP-LIF (D-F for ClO)	$(8.9 \pm 2.7) \times 10^{-12}$	0	295 ± 95	81
$OH + ClO \rightarrow HCl + O_2$	207−298	TFT-CIMS	$(3.2 \pm 0.8) \times 10^{-13}$	0	325 ± 60	82

The kinetic behavior of the OH + ClO reaction prompts some interesting dynamical questions. The relatively high value of the rate constant k_{13} and its small negative dependence on temperature strongly suggest that "capture" on a potential energy surface that is monotonically attractive at long-range is rate determining. The exothermicity of reaction 13 is, however, so slight that redissociation of this energized peroxide complex, (HOOCl)*, to the reagents OH + ClO cannot be ruled out.

The interesting question is whether the minor channel (13′) also proceeds via the same complex. Certainly a direct four center reaction can be excluded, given the negative dependence of $k_{13'}$. An intriguing possibility is that on some occasions as the (HOOCl)* complex fragments to HO_2 + Cl, the departing Cl atom comes close enough to the H-atom to abstract it. Such a mechanism would be consistent with the fact that the rate constants k_{13} and $k_{13'}$ exhibit an identical temperature dependence.

Because of its close relationship to the OH + ClO reaction system, the last reaction that I review is that between Cl atoms and HO_2 radicals, that is, between the products of reaction 13. Of course, by using the principle of detailed balance,[6] one could calculate an expression for the rate constant of the reverse reaction to reaction 13, i.e.,

$$Cl + HO_2 \rightarrow ClO + OH \qquad (-13)$$

where $\Delta H_{298}°$ (kJ mol^{-1}) = +2.9. However, it is from direct measurements of k_{13} and k_{-13} and the principle of detailed balance that the enthalpy for this reaction, and hence $\Delta_f H_{298}°$ for HO_2, has been determined. The products of the other channel for this reaction are HCl + O_2:

$$Cl + HO_2 \rightarrow HCl + O_2 \qquad (14)$$

where $\Delta H_{298}°$ (kJ mol^{-1}) = −228.2.

The most thorough study of the reaction between Cl and HO_2 is that carried out in 1982 by Lee and Howard.[83] They used a conventional flow discharge system with observation of radicals by laser magnetic resonance. They found the overall rate constant to be independent of temperature between 250 and 420 K, $k_{14} + k_{-13}$ (cm^3 molecule^{-1} s^{-1}) = $(4.2 \pm 0.7) \times 10^{-11}$. The large value of this rate constant and its temperature independence show that the endothermic reaction −13 cannot be other than a relatively minor channel. Lee and Howard's measurements showed the branching ratio, $k_{-13}/(k_{14} + k_{-13})$, to be 0.22 at 298 K and, as expected, to depend quite strongly on temperature. It seems that the positive temperature dependence of k_{-13} is probably compensated for by a negative temperature dependence of k_{14}. The rapid rate of reaction 14 provides support for the suggestion that reaction 13′ may proceed via breakdown of the (HOOCl)* complex with the Cl atom abstracting the H-atom as it departs.

4. Summary and Conclusions

In this paper, I have reviewed laboratory measurements on atmospherically important reactions at low temperatures. In the body of the text, I first reviewed the major laboratory methods that have been used to study the kinetics of elementary reactions at low and very low (< ca. 80 K) temperatures, laying some emphasis on the limitations of each method. Then in section III, I reviewed the present state of knowledge, with respect to low temperature behavior, for a selection of important reactions of different types. In Table 3, I have gathered together the kinetic information that is available for these selected reactions. Earlier in the text, I made some suggestions as to what new low temperature measurements might be made to improve our understanding of these reactions.

As Table 3 demonstrates, reactions of the OH radical have figured prominently in this paper for two reasons. Of course, the first reason is their overwhelming importance in the chemistry of the Earth's atmosphere, especially, although not only, in the troposphere. Consequently, many laboratory experiments have been performed on these reactions.

Somewhat connected to the fact that there is a large database for these reactions is the relative simplicity of such kinetic experiments. Good sources for OH radicals exist for use in both pulsed photolysis and discharge flow experiments. In addition, the radicals can be observed with high sensitivity by absorption and fluorescence techniques in the $A^2\Sigma^+ - X2\Pi$ band system at wavelengths around 300 nm that are easy to generate using dye lasers.

This paper has emphasized the measurement of rate constants for reactions between OH and different co-reagents. In the great majority of the experiments that have been cited, these rate constants have been determined by measuring how the pseudo-first-order rate constant, defined by $-\mathrm{d}\ \ln[\mathrm{OH}]/\mathrm{d}t$, changes as the excess concentration of the co-reagent is systematically varied in a series of experiments. Of course, such experiments provide no direct information about the products of the reaction. As we have seen with respect to some of the reactions used as examples in this article, multiple sets of reaction products may be accessible, especially in reactions between radicals and unsaturated species or between pairs of free radicals, which proceed via intermediate collision complexes. In these cases, it is important to determine the branching ratios into different channels and how they vary with temperature, both for use in atmospheric modeling and to understand properly the mechanism of the reaction. In this respect, the deployment of flow methods can be advantageous since these experiments can be coupled to a wider range of detection techniques including mass spectrometry, as illustrated by the work of Lipson et al.[82] on the OH + ClO reaction. The optical spectroscopic techniques, such as LIF, which are so powerful in measuring kinetic decays of OH in pulsed photolysis experiments, are not easily adapted to measuring branching ratios. In such experiments, time-resolved absorption using tuneable infrared lasers shows promise for the measurement of branching ratios but has not, as yet, been widely used on atmospherically important reactions.[84]

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