J. Chem. Soc., Faraday Trans. 2, 1981, 77, 997-1008

Direct Rate Measurements on the Reactions $N+OH \rightarrow NO+H$ and $O+OH \rightarrow O_2+H$ from 250 to 515 K

BY MARK J. HOWARD AND IAN W. M. SMITH*

Department of Physical Chemistry, University Chemical Laboratories, Cambridge CB2 1EP

Received 10th September, 1980

Rate coefficients for the reactions

$$N + OH \rightarrow NO + H$$
 (1)

and

$$O + OH \rightarrow O_2 + H$$
 (2)

have been determined, in direct experiments, from 250 to 515 K. A discharge-flow system is used to generate measured concentrations of N or O; then OH radicals are formed by flash photolysis of H_2O and monitored by resonance fluoresence as they are removed by reaction (1) or (2) under pseudo-first-order conditions. The results are fitted to the rate expressions:

$$k_1 = (2.21 \pm 0.18) \times 10^{-10} T^{-0.25 \pm 0.17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

 $k_2 = (6.65 \pm 0.23) \times 10^{-10} T^{-0.50 \pm 0.12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

where the errors represent 95% confidence intervals within the range of temperature covered in the experiments. The rate coefficient k_2 is compared with a calculation assuming that the reaction proceeds *via* a bound state HO₂ collision complex.

Current interest in stratospheric chemistry has stimulated a number of recent studies of fast bimolecular reactions where both reacting species are atomic or molecular free radicals. The most reliable data have been obtained by direct observation of both reactants in simple kinetic systems, with one radical in excess concentration to ensure pseudo-first-order kinetics with respect to the other. Consequently, only relative concentrations of the minor species need to be measured and the effects of side and secondary reactions are reduced.¹ Experiments of this kind have been made possible by using sensitive detection techniques such as laser magnetic resonance,²⁻⁶ mass spectrometry⁷⁻¹⁰ and resonance fluorescence.¹¹⁻¹³ These conditions have been fulfilled in flow-tube experiments on the reactions: O + OH,¹¹ $O + HO_2$,² $H + HO_2$,⁶ $OH + HO_2$,³ $NO + HO_2$,^{5.13} CIO + NO,^{9,10} $CIO + HO_2$,^{4.7} $BrO + NO^8$ and $SO + NO_2$,¹⁰ and in time-resolved flash-photolysis experiments on: $O + OH^{12}$ and BrO + NO.¹⁴ Other flow-tube studies include direct measurements on $HO_2 + HO_2^{15}$ and $OH + HO_2^{16}$ in a second-order regime and indirect experiments on: O + CIO,¹⁷ CIO + NO,¹⁷ $CI + HO_2$,^{18,19} $OH + HO_2^{18}$ and $NO + HO_2^{18}$ in which steady-state radical concentrations or concentration ratios were determined, yielding relative rate coefficients. Finally, a few indirect studies by molecular modulation spectrometry ($CI + CIOO^{20}$) and pulsed electron irradiation ($OH + HO_2$,²¹ $O + HO_2$,²² $HO_2 + HO_2^{23}$) have been reported.

998 RATE COEFFICIENTS FOR $N+OH \rightarrow NO+H$ and $O+OH \rightarrow O_2+H$

A limited number of these radical-radical reactions have been studied over a range of temperature $(O + OH, {}^{11}HO_2 + NO, {}^{5,13}BrO + NO, {}^{8,14}ClO + NO, {}^{9,17}ClO + HO_2, {}^4O + ClO^{17})$ and most of the rate coefficients have a shallow negative temperature dependence. In some cases, it has been suggested 4,9,11,14 that this decrease in reaction rate with temperature results from the formation of a collision complex which can either dissociate to products or redissociate to reactants at approximately equal rates. If the latter process is accelerated more rapidly with temperature and the rate of formation of complexes is only mildly temperature dependent, the rate of the overall reaction will fall as the temperature is raised. An alternative explanation 5,17 is that the rate of complex formation falls at higher temperatures because the transition state becomes "tighter". This effect has also been proposed 24,25 to explain the similar temperature dependence of the rates of certain radical recombination reactions in the limit of high pressure.

This paper describes a direct method for measuring the rate coefficients of fast radical-radical reactions, over a range of temperatures. A relatively large steady-state concentration of one radical is created in a conventional discharge-flow system, which can be heated or cooled. The second radical species, OH in these experiments, is formed directly in the flow tube at much lower concentrations by flash photolysis and it is continuously monitored by resonance fluorescence. The flash lamp is pulsed repetitively and the fluorescent signals accumulated in a signal averager. The conditions are chosen to ensure a pseudo-first-order reaction that is complete before the reaction mixture has moved a significant distance. Wolfrum and coworkers have employed a similar technique to study the reaction of O atoms with CN radicals using kinetic absorption spectroscopy to detect CN or c.w. laser absorption or gain to monitor the CO product.²⁶

We have measured the rate coefficients of the reactions:

$$N + OH \rightarrow NO + H; \quad \Delta H^{\circ}_{298} = -203.8 \text{ kJ mol}^{-1}$$
(1)

$$O + OH \rightarrow O_2 + H; \quad \Delta H^\circ_{298} = -70.7 \text{ kJ mol}^{-1}$$
(2)

from 250 to 500 K; preliminary room-temperature results have already been reported.¹² All other determinations of k_1 and k_2 are from indirect flow-tube experiments²⁷⁻³² with the single exception of Lewis and Watson's recent work on reaction (2).¹¹

The reaction of O atoms with OH is of interest because of its important role in deciding the ratios of odd hydrogen species in the upper stratosphere and mesosphere and the subsequent effect on the ozone concentration.³³ Reaction (1) is involved in most mechanisms for forming NO in fuel-rich hydrocarbon flames.³⁴

EXPERIMENTAL

Fig. 1 shows a schematic diagram of the central part of the apparatus that was used for experiments above and below room temperature. The brass block (HB) surrounding the flow tube was heated by eight cartridge elements to above 500 K or cooled to 250 K by circulating cold methanol. The temperature at various points inside the flow tube was measured by the retractable thermocouples T1, T2 and T3, and found to be constant across and along the flow tube to within 5 K. The larger, but otherwise similar vessel used in the earlier room-temperature experiments has already been described.¹²

DISCHARGE-FLOW SYSTEM

A dilute mixture of N₂ in Ar (*ca.* 1%) was pumped through the flow system at *ca.* 4 dm³ s⁻¹. The total pressure was measured at point P by an oil manometer (± 10 Pa,

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FIG. 1.—Schematic diagram of the apparatus. The symbols are identified in the text.

0.08 Torr) and found to be *ca*. 530 Pa (4 Torr); pressure gradients along the flow tube are expected to be <1.3 Pa (10 mTorr). The mass flows of Ar and N₂, measured with floating-ball rotameters ("MeTeRate", Glass Precision Engineering; $\pm 2\%$ accuracy), were typically $800 \ \mu \text{mol s}^{-1}$ and $1-30 \ \mu \text{mol s}^{-1}$, respectively. The resulting linear-flow velocities varied from 3.1 m s⁻¹ at 250 K to 6.2 m s⁻¹ at 500 K. Both N₂ and Ar were taken directly from Air Products high purity cylinders [Ar, 99.998%; N₂, 99.9% (O₂ free)].

Approximately 5% of the N₂ molecules were dissociated as they passed through the microwave cavity (MC, 2450 MHz, *ca.* 50 W) resulting in a continuous flow of N atoms through the reaction vessel. The atom flow, and hence concentration, was determined by titrating with a flow of NO in Ar, measured from the pressure drop in a known volume. The rapid titration reaction:³⁵

$$N + NO \rightarrow N_2 + O(^3P) \tag{3}$$

was followed by observing the NO or N₂ chemiluminescent emissions up to the end point and the NO₂ emission beyond, using a photomultiplier (PM2, EM1 9781 B) with suitable filters. At the end point, all three emissions are extinguished. Therefore, known steady-state concentrations of $N({}^{4}S)$ or $O({}^{3}P)$ could be generated in the flow tube.

Depletion of atom concentration down the flow tube owing to homogeneous recombination was < 1.5%, providing the excess NO concentration³⁶ was $< 1 \times 10^{13}$ molecule cm⁻³. Heterogeneous losses of N(⁴S) atoms on the Pyrex walls were estimated by comparing titration end points from two injectors, upstream and downstream of the reaction vessel. The atom loss between injectors was negligible, < 3%, in the room-temperature apparatus and small, *ca.* 4%, in the narrower variable-temperature flow tube. The depletion of O(³P) atoms was estimated by comparing the NO₂ emission intensities when an excess of NO was added at either injector. This varied according to the temperature of the walls (and from day to day) from *ca.* 5% at 250 K to *ca.* 16% at 500 K. These figures gave values for the fraction of reactive collisions at the walls of $\gamma = 5 - 7 \times 10^{-5}$ for N and $\gamma = 6 - 30 \times 10^{-5}$ for O over the experimental temperature range. The atom losses up to the observation region in the centre of the flow tube were estimated at each temperature, assuming an exponential decay, and the atom concentration measurements corrected accordingly. Bearing in mind the precision of the end-point determination and the variability of the wall losses, an overall accuracy of *ca.* 5% is assigned to the atom concentrations.

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FLASH-PHOTOLYSIS SYSTEM

A small flow of thoroughly degassed H₂O was injected into the gas flow to give a partial pressure between 5 and 16 Pa (40–120 mTorr). Any metastable N₂($A^{3}\Sigma_{u}^{+}$) molecules formed in the microwave cavity were rapidly quenched by N(⁴S) atoms³⁷ and subsequent steady-state concentrations, due to N atom recombination, were negligible. Therefore, processes such as:

$$N_2(A^{3}\Sigma_{u}^{+}) + H_2O \rightarrow N_2 + H + OH$$
(4)

were not significant.

A very small fraction (ca. 0.05%) of the H₂O molecules were photolysed by an intense pulse of u.v. light ($\lambda > 120$ nm) from the flash lamp, FL. The lamp has three tungsten electrodes: an e.h.t., ground and trigger. The e.h.t. pin is charged to between 8 and 11 kV in common with one plate of a 3 μ F capacitor. The discharge, through flowing nitrogen at atmospheric pressure, is initiated by a 10 kV pulse across the trigger and ground electrodes.

A typical pulse dissipates between 100 and 200 J of electrical energy and has a full width at half maximum of $ca. 3 \mu s$. Unfortunately, the flash, and the various emissions it excites, have a long tail which is scattered into the photomultiplier, PM1. This restricts data collection to ca. 0.5 ms and onwards after the flash. Light from the spark gap is roughly collimated by CaF₂ optics through the filter vessel F and along the axis of the flow tube. The filter vessel could be filled with Cl₂ to filter out the flash in the region of OH resonance fluorescence; however, much of the flash is observed *via* fluorescence in the flow tube and the Cl₂ appeared to attenuate the deep u.v. photolysis of H₂O, so the filter vessel was normally evacuated.

Photolysis of H₂O in its first absorption continuum, from 186 to 140 nm, yields OH radicals in their ² Π electronic ground state with a near thermal rovibrational distribution.³⁸ Below the 136 nm threshold, photolysis produces small fractions (<10%) of OH($A^{2}\Sigma^{+}$) having excited rovibrational populations.³⁹ The mean radiative lifetime of this species is $ca. 1 \mu s;^{39}$ any OH($X^{2}\Pi$) radicals in vibrational levels above v = 0, produced by the decay of OH($A^{2}\Sigma^{+}$), are rapidly quenched by H₂O⁴⁰ [OH(v = 1)+H₂O \rightarrow OH(v = 0)+H₂O; $k = (1.35 \pm 0.5) \times 10^{11}$ cm³ molecule⁻¹ s⁻¹] so an internal distribution that is indistinguishable from thermal can be expected within 100 μ s of the flash.

RESONANCE FLUORESCENCE OF OH

The OH radicals produced by photolysis were continuously monitored by resonance fluorescence. The resonance lamp (RL) consists of a flow of H₂O in He (*ca.* 2%), at *ca.* 100 Pa (0.75 Torr), through a microwave cavity (2450 MHz, 150 W). Fluorescence from excited OH radicals produced in the cavity⁴¹ is directed along an aluminised light pipe, through a quartz window and into the observation zone where it excites the fluorescence of ground-state OH radicals. This is observed at right angles to the incident light by a gated photomultiplier (PM1, RCA 1P28) through a series of baffles and an interference filter (IF; centre wavelength, 308.3 nm; half-bandwidth, 3.2 nm; maximum transmission, 12%) centred on the low rotational lines of the OH($A^{2}\Sigma^{+}$, v = 0)-OH($X^{2}\Pi$, v = 0) band. This transition is a weak oscillator ($f \approx 7 \times 10^{-4}$). Consequently, the fluorescent intensity should increase linearly with the radical concentration up to *ca.* 5×10^{14} molecule cm⁻³:⁴² this has been experimentally confirmed up to 2×10^{12} molecule cm⁻³.⁴²

Although an absolute determination of [OH] is not required to calculate the rate coefficients k_1 and k_2 , it is necessary to know the initial OH concentration in order to justify the assumption of pseudo-first-order kinetics. To this end, H_2O was photolysed in an excess of N atoms and an OH fluorescent signal recorded in the usual way. The initial OH radicals were quantitatively converted to O atoms via reactions (1) and (3), and the total yield of O atoms estimated by integrating the NO emission as the photolysed gas was swept past photomultiplier PM2. The initial distribution of OH in the flow tube is uncertain so an even distribution was checked in the room-temperature reaction vessel by generating OH radicals in the discharge-flow system. Hydrogen atoms, produced by discharging H_2 in Ar, were titrated with NO₂

from a moveable injector assembly replacing the flash lamp and filter vessel. The titration reaction

$$H + NO_2 \rightarrow NO + OH$$
 (5)

was followed by observing the HNO emission⁴³ with a red-sensitive photomultiplier (RCA, C 7164R) replacing PM2. Analysis of the OH fluorescent intensity against time profiles, by comparison with a computer model, gave a sensitivity in reasonable agreement with the flash-photolysis calibration. Under typical experimental conditions these experiments indicate a detection limit better than 2×10^{10} molecule cm⁻³ (S/N = 1) when monitoring slow decays ($k_{1st} \approx 500 \text{ s}^{-1}$) and better than 7×10^{10} molecule cm⁻³ for the fastest decays ($k_{1st} > 2 \times 10^3 \text{ s}^{-1}$).

DATA ACCUMULATION AND ANALYSIS

Having established a known concentration of N or O atoms in the presence of H_2O , the flash lamp was pulsed repetitively at 0.2 Hz. Each fluorescent signal was observed at PM1 and recorded by a transient recorder (Data Laboratories, DL 905); the digitised signals were accumulated in a signal averager (Data Laboratories, DL 4000) and output onto punched tape. After summing 128 signals in the averager, the resonance lamp was turned off and a further 128 signals subtracted in order to remove the residual flash tail and any other spurious fluorescences from the OH resonance fluorescence signal. This process was repeated at several atom concentrations for each temperature.

RESULTS

Measurements were made in the temperature-variable apparatus at 250 ± 5 , 300 ± 5 , 375 ± 5 , 445 ± 5 and 515 ± 5 K; those at 300 K have been combined with the previously published room-temperature results.¹² At each temperature the atom concentrations were varied from *ca*. 0.6×10^{13} to 5.0×10^{13} atom cm⁻³; upper limits for the initial OH concentrations range from 10^{11} to 3×10^{12} molecule cm⁻³ which is typically 1–5% and never more than 15% of the atom concentration.

The averaged resonant fluorescent signals were fitted to a single exponential by computer, using a regression analysis routine with baseline, pre-exponential factor and decay constant as variable parameters. The fit was normally started from ca. 0.5 ms after the flash to avoid contributions from improper subtraction of the flash tail; only fits with 99% confidence intervals better than 5% were accepted. The data are summarised in table 1.

Apart from reaction with the known atom concentrations, the removal of OH radicals was caused by diffusion to the walls and subsequent loss, convection due to the flow and reaction with any background concentrations of reactive species such as O atoms produced from an O₂ impurity passing through the discharge. The bimolecular recombination of OH⁴⁴ is negligible at the concentrations present in our experiment. These background removal processes are grouped together into a first-order rate constant k_b (see table 1). In the room-temperature reaction vessel k_b can be safely ignored;¹² however, in the narrower variable-temperature flow tube k_b is small but significant, indicating that the major contributions are the diffusive and convective processes. The value of k_b was determined at each temperature in the absence of added N₂ in the Ar flow but with the microwave cavity MC switched on. Consequently, the decay of OH is given by the equation:

$$-d[OH]/dt = k_{1st}$$
$$= k_b + k_1[N] \text{ or } k_2[O].$$

temp. /K	number of experiments	[N] or [O] $/10^{13}$ molecule cm ³	$k_{1\rm st}/{ m s}^{-1}$	$k_{\rm b}/{ m s}^{-1}$	$k_1 \text{ or } k_2$ /10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹
1) $N + OH$					
250 ± 5	18	0.93 - 3.80	570 - 2502	100	$5.56 \pm 0.34^{\circ}$
300 ± 5^{b}	20	1.03 - 5.14	518-3990	135	4.74 ± 0.44
375 ± 5	11	0.59 - 2.56	466 - 1427	161	4.97 ± 0.21
445 ± 5	15	1.19 - 4.21	694 - 2698	176	5.07 ± 0.44
515 ± 5	22	0.76 - 3.78	430-2284	179	4.25 ± 0.37
2) <i>O</i> + <i>OH</i>					
250 ± 5	20	0.92 - 4.52	421 - 2088	100	4.04 ± 0.18
300 ± 5^{b}	21	0.98 - 6.04	341 - 2165	135	3.53 ± 0.31
375 ± 5	17	0.55 - 3.56	310 - 1866	161	3.36 ± 0.24
445 ± 5	25	1.09 - 3.86	516-1633	176	3.10 ± 0.27
515 ± 5	56	0.69-4.34	366 - 1653	179	2.76 ± 0.14

TABLE 1.—SUMMARY OF EXPERIMENTAL RESULTS^a

^a Full experimental details are available from the authors. ^b Includes previously published room-temperature data;¹² k_b is less than 50 s⁻¹ and therefore neglected. ^c Errors in the second-order rate coefficients are 95% confidence intervals.

Values of k_1 and k_2 at each temperature, calculated from the means of $(k_{1st} - k_b)/[N]$ or [O], are presented in table 1; the errors are the 95% confidence intervals in the means. A further systematic error of ca. 5% due to the titration is possible.

Fig. 2 is a plot of log k against log T for both sets of data; the solid lines have been fitted by a weighted least-squares method which leads to the rate expressions:

$$k_1 = (2.21 \pm 0.18) \times 10^{-10} T^{-0.25 \pm 0.17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

 $k_2 = (6.65 \pm 0.23) \times 10^{-10} T^{-0.50 \pm 0.12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

where the quoted errors represent 95% confidence intervals within the range of temperature covered in the experiments.

DISCUSSION

There has only been one previous determination of k_1 , in a flow-tube experiment at 320 K.³² Active nitrogen was partially titrated with NO and the resulting concentrations of N and O atoms were deduced from the intensities of the N₂ and NO afterglows. Removal of both N and O was catalysed by addition of H₂, presumably *via* reactions (1) and (2) with OH formed in the reaction of O atoms with H₂. The relative rates at which the N and O atoms decayed indicated a value of $(k_1/k_2) =$ 1.40 ± 0.1 , in excellent agreement with our $(k_1/k_2) = 1.4 \pm 0.3$ at the same temperature.

Table 2 lists the available data on reaction (1), including our own. The first five values of k_2 were determined in indirect flow-tube experiments. The three highest results²⁷⁻²⁹ were obtained in essentially similar experiments in which reaction (5) was

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FIG. 2.—Plots of $\log_{10} k$ against $\log_{10} T$ for the reactions of OH radicals with N or O atoms; error bars are 95% confidence intervals, those at room temperature are omitted for clarity. (a) N+OH: \blacksquare , this work. (b) O+OH: \blacksquare , this work; \heartsuit , Lewis and Watson;¹¹ \square , Westenberg *et al.*;³⁰ (---) Cohen and Westberg's evaluation;⁴⁵ (---) "maximum free-energy" calculation.

used to generate an initial concentration of OH. The only significant subsequent reactions were assumed to be the bimolecular reaction

$$OH+OH \rightarrow H_2O+O$$
 (6)

heterogeneous removal of OH, and reaction (2). Therefore, a steady-state concentration of O atoms was reached, determined by (k_6/k_2) and the absoulute concentration of OH. By using high initial [OH] and long observation times, Clyne²⁷ was able to deduce k_2 from the steady-state O atom concentration alone, determining this from the intensity of the air afterglow. Kaufman²⁸ and Breen and Glass²⁹

temp./K	$/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	ref.
300	5.0 ± 1.7	Clyne, 1963. ²⁷
300	5.0 ± 1.7	Kaufman, 1964. ²⁸
300	4.3 ± 0.2	Breen and Glass, 1970. ²⁹
425	4.2 ± 0.3^{a}	Campbell and Handy, 1977. ³¹
228-340	3.3 ± 0.5^{b}	Westenberg et al., 1970. ³⁰
220-500	$3.4 \pm 0.3 - 2.8 \oplus 0.08$	Lewis and Watson, 1980. ¹¹
250-515	$4.0 \pm 0.2 - 2.8 \pm 0.1$	this work.

TABLE 2.—RATE COEFFICIENTS FOR THE REACTION $O + OH \rightarrow O_2 + H$

^a Relative to OH+CO, reaction (7), $k_7 = 1.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{.}^{44}$ ^b Interpreted by authors as temperature independent; see fig. 2 for actual data.

monitored [OH] as well, using ultraviolet absorption and e.p.r. spectrometry, respectively.

The rate of reaction (2) has also been measured relative to the rate of

$$OH+CO \rightarrow CO_2+H,$$
 (7)

by observing the decay of O atoms in a discharged $H_2 + CO + N_2$ mixture at 425 K.³¹ The ratio (k_2/k_7) was found to be 260 ± 20 , giving the tabulated value of k_2 if k_7 is 1.6×10^{-13} cm³ molecule⁻¹ s^{-1.44}

Two groups have studied the temperature dependence of k_2 ; their results, as well as our own, are shown in fig. 2. Westenberg *et al.*³⁰ observed the relative concentrations of O atoms in a gas containing O and H flowing through a homogeneous e.p.r. reactor, with and without NO₂ added. Combined with an absolute measurement of [OH], this yielded a value of k_2 that is independent of k_6 . Because of the limited temperature range and fairly wide error limits, Westenberg *et al.* concluded from their results that k_2 is temperature invariant between 228 and 340 K.

Finally, Lewis and Watson's recent direct experiments,¹¹ between 220 and 500 K, yield rate coefficients in good agreement with our own and a similar, small but significant, negative temperature dependence. In their experiments, flows of O and H atoms were mixed and then a much smaller flow of NO₂ was added to generate a small concentration of OH *via* reaction (5). Relative concentrations of OH were observed by resonance fluorescence. To ensure the rapid formation of OH at the NO₂ injector, and hence good time resolution, large excess concentrations of H atoms ($[H]_0 \approx 1.5 \times 10^{13} \text{ cm}^{-3}$; $[OH]_0 \approx 1.5 \times 10^{11} \text{ cm}^{-3}$; $[O]_0 \approx 1-7 \times 10^{12} \text{ cm}^{-3}$) were used. Under these conditions, significant concentrations of OH radicals were produced *via* the reactions:

$$H + O_2 + M \rightarrow HO_2 + M \tag{8}$$

and

$$H + HO_2 \rightarrow 2OH$$
 (9)

or

$$O + HO_2 \rightarrow OH + O_2. \tag{10}$$

Lewis and Watson's computer simulation of their system indicated that this caused their observed value of k_2 to be 6–10% lower than the "true" value, and an appropriate correction was made.

Measurements on reaction (2) and its reverse have been recently evaluated.^{44,45} The recommended⁴⁵ expression for k_2 , based on high-temperature determinations of k_{-2} and application of the principle of detailed balance, on model calculations, and on previous room-temperature determinations of k_2 agrees with our results quite well (see fig. 2).

Reactions (1) and (2) presumably proceed via a collision complex corresponding to a state (or states) of the triatomic radical which can form without the system having to surmount any barrier on the potential energy surface (or surfaces). $N({}^{4}S) + OH(X {}^{2}\Pi)$ adiabatically correlate with ${}^{3}A'$, ${}^{5}A'$, ${}^{3}A''$ and ${}^{5}A''$ terms of a collision complex with C_s symmetry, but only the ${}^{3}A''$ term correlates through to $NO(X {}^{2}\Pi) + H({}^{2}S)$ and electronically excited products are energetically inaccessible. Intuitively, one expects a collision complex closer to an HON configuration than the more familiar HNO radical. Indeed, *ab initio* calculations⁴⁶ on the lowest singlet and triplet states of HNO have shown that there is an appreciable barrier between the HNO and HON structures and that the ground state of the latter species is a triplet. There are, however, no available spectroscopic data on HON, so a calculation of the rate of reaction (1) via the methods proposed by Quack and Troe²⁵ has not been attempted. What one can do is to estimate rate coefficients for adiabatic reaction across the ³A" surface of HON by multiplying k_1 by the ratio of electronic partition functions: $f_{el,N}f_{el,OH}/f_{el,NOH(\bar{X}^3A'')}$. This procedure yields rate coefficients of 2.1× 10^{-10} and 1.9×10^{-10} cm³ molecule⁻¹ s⁻¹ at 250 and 500 K, respectively, corresponding to simple collision theory mean reaction cross-sections of 25 and 16 Å².

The adiabatic correlations of $OH(X^2\Pi) + O({}^{3}P)$ are with $3^{2}A'$, $3^{2}A''$, $3^{4}A'$ and $3^{4}A''$ terms of an HO₂ collision complex with C_{s} symmetry. Only one ${}^{2}A''$, $3^{4}A'$ and one ${}^{4}A''$ term correlate through to $O_{2}({}^{3}\Sigma_{g}^{-})$ and $H({}^{2}S)^{1}$ and electronically excited products are energetically inaccessible. No ${}^{4}A''$ state of HO₂ is known spectroscopically and the one correlating with both $OH({}^{2}\Pi) + O({}^{3}P)$ and $O_{2}({}^{3}\Sigma_{g}^{-}) + H({}^{2}S)$ is presumed to play no part in the reaction. The common ${}^{2}A''$ term is the electronic ground state of HO₂.⁴⁷ Combining orbital and spin symmetries, 48 both this term and the low-lying ${}^{2}A'$ excited state become ${}^{2}E_{1/2}$ and a non-crossing rule becomes probable although not rigorous. Calculating, as before, rate coefficients associated with adiabatic reaction across the lowest surface of the triatomic radical yields values varying from 3.8×10^{-10} cm³ molecule⁻¹ s⁻¹ at 250 K to 3.4×10^{-10} cm³ molecule⁻¹ s⁻¹ at 500 K, corresponding to simple collision theory mean reaction cross-sections decreasing from 47 to 30 Å.²

Since spectroscopic information on HO₂ is available, estimates of k_2 have been made using Quack and Troe's simplification²⁵ of their adiabatic channel model. This was designed for calculating the rates of unimolecular dissociation reactions, in the limit of high pressure. The rate of association reactions, under these conditions, corresponds to the rate of formation of the energised complex. This is also the case in reactions (1) and (2) as long as the complex breaks down to products much more rapidly than it dissociates to reagents.

In such calculations, the partition function for the system is expressed as a function of the reaction coordinate q, taken to be the O-O bond distance in reaction (1). This variation depends on an exponential interpolation formula, containing a single parameter γ , to connect the rovibrational partition function of the reactants, *i.e.* at $q = \infty$, to that of equilibrium HO₂, *i.e.* at $q = q_e$. The electronic potential is assumed to be a Morse function and the centrifugal contribution is represented by a simple two-body expression. The transition state is then located where the total partition function is a minimum corresponding to the position of maximum free energy.

Using the recommended²⁵ value of $\gamma = 0.75 \text{ Å}^{-1}$ and a Morse parameter $\beta = 2.5 \text{ Å}^{-1}$, estimated from the O—OH dissociation energy and the force constant for this bond in HO₂, one obtains $k_2 = 3.2 \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹ at 250 K and $3.3 \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹ at 500 K; this is shown on fig. 2. The magnitude of the calculated rates are in good agreement with experiment; however, the fit to the temperature dependence is poor and is not improved significantly by varying β and γ . Nevertheless, the general picture of the transition state becoming less extended at higher temperatures is probably correct.

In order to explain the negative temperature dependence of k_2 , Lewis and Watson¹¹ have proposed that reaction proceeds *via* a collision complex which can dissociate to products or redissociate to reagents:

$$O + OH \xleftarrow{k_t}{k_r} (HO_2)^{\dagger} \xrightarrow{k_p} H + O_2$$

so that $k_2 = k_f k_p / (k_r + k_p)$. As the temperature, and therefore the mean energy in $(HO_2)^{\dagger}$, is raised, k_r increases more rapidly than k_p so that $k_p / (k_r + k_p)$ falls.

However, for there to be a significant effect on the observed reaction rate, it is necessary that k_r and k_p are roughly equal within the temperature range of interest. Lewis and Watson examined their proposition on the basis of RRK (Rice-Ramsberger-Kassel) theory,¹ in which the specific rate constant, k(E), for unimolecular decomposition of an energised molecule with internal energy E is given by $A[(E - E_0)/E]^{s-1}$, where E_0 is the critical or threshold energy and s the number (or 'effective' number) of oscillators in the molecule. They argued that the large difference between $[(E - E_0)/E]^{s-1}$ for the two $(HO_2)^{+}$ dissociation channels might be compensated for by differences in the A factors.

Partly because of theoretical interest and partly because the rate of reaction between O and OH might depend on pressure if Lewis and Watson's hypothesis is correct, we have examined the proposed mechanism using the extensions of RRKM (Rice-Rambsberger-Kassel-Marcus) theory¹ due to Quack and Troe²⁵ and Troe⁴⁹. As already indicated, the model of Quack and Troe estimates a value of k_f in reasonable agreement with the observed value of k_2 . The ratio (k_f/k_r) describes the equilibrium between thermally equilibrated OH+O and the energised (HO₂)[†] complexes formed by association of these species; it can be estimated via a procedure developed by Troe⁴⁹ for calculating the rates of dissociation and association reactions in the limit of low pressure. Using the estimated value of k_f , this calculation yields k_r , which we find to be ca. 7×10^{10} s⁻¹ at 298 K.

The rate constant k_p for dissociation of $(HO_2)^{\dagger}$ to $H + O_2$, where the complex is formed in thermal collisions of O and OH, has been estimated using the expression:¹

$$k_{\rm p} = k(E) = N^*(E^\dagger) / h\rho(E)$$

where $N^*(E^{\dagger})$ is the number of "active" states in the transition state at energy E. In estimating $N^*(E^{\dagger})$ we have assumed that $E^{\dagger} = E + \Delta E_0 = 70.7$ kJ mol⁻¹. This means that the energies associated with the adiabatic degrees of freedom in the $(HO_2)^{\dagger}$ complex and in the transition state for its dissociation to $H + O_2$ are taken to be the same and equal to the thermal energy present in collisions between O and OH. Any errors introduced by these assumptions will be small since E^{\dagger} and E are both much greater than kT. Counting of states to yield $N^*(E^{\dagger})$ was carried out according to the simple harmonic approximation, which would cause us to underestimate $N^*(E^{\dagger})$ and hence k_p . Frequencies in the transition state were estimated via the interpolation formulae of Quack and Troe.²⁵ This calculation gives $k_p \approx 10^{12} \text{ s}^{-1}$, *i.e.* 15 times the value estimated for k_r .

The calculations outlined in the two previous paragraphs suggest that there is unlikely to be significant redissociation of collision complexes[‡] formed from OH and O. Two further arguments appear to support this conclusion. First, if $k_r \approx k_p$, then $k_f \approx 2k_2$. Because of the number of surfaces which correlate with OH(²II) and O(³P), formation of HO₂($\tilde{X}^2 A''$) would then have to occur with a collision cross-section of $ca. 100 \text{ Å}^2$ to be consistent with the observed k_2 . This is larger than could be explained even in the limit of a "loose" transition state determined only by the need to conserve angular momentum. Secondly, a growing number of radical-radical reactions are being shown to have rates which decrease significantly with temperature. The mechanism of competing dissociation channels cannot be responsible for this in association reactions, *e.g.* OH+NO₂(+M) \rightarrow HNO₃(+M),⁵⁰ and seems inherently improbable in more than a fraction of atom-transfer reactions.

 $[\]ddagger$ It is important to recognise that the calculations only treat the fate of genuine collision complexes. It may be that, as the temperature increases, collision complexes are formed in a smaller fraction of O + OH collisions as a result, for example, of the system passing through the transition state for formation of HO₂ twice before energy is randomised and a proper complex is formed [see also ref. (1), p. 37].

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Despite the absence of a satisfactory simple theoretical model, it appears that these observations reflect the decrease in rate constant associated with formation of a collision complex from two radicals as the temperature is raised. Unfortunately, there have been very few theoretical calculations of potential surfaces in the important regions where two radicals just start to interact appreciably.

SUMMARY

The experiments described in this paper demonstrate a new, versatile technique for measuring the rate coefficients of radical-radical reactions, which is perhaps less susceptible to systematic errors than methods based only on the flow tube. The results reported for the reactions of OH with N and O atoms are in satisfactory agreement with those of other workers and reduce the uncertainties in the rate coefficients; for k_2 , from factors of two⁴⁴ and three⁴⁵ quoted in recent evaluations to *ca.* 20%. The negative temperature dependence of k_2 found by Lewis and Watson is confirmed. However, our calculations indicate that there is unlikely to be significant redissociation to O + OH of the collision complex formed in this reaction, although it is not possible to match the observed temperature dependence by any other simple theoretical model.

We thank the S.R.C. and the Central Electricity Research Laboratories for a S.R.C./C.A.S.E. research studentship (M.J.H.) and for other financial support.

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