DIRECT RATE MEASUREMENTS ON THE REACTIONS N + OH → NO + H AND O + OH → O_2 + H

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Rate constants for the radical–radical reactions N + OH → NO + H (1), and O + OH → O_2 + H (2) have been measured for the first time by a direct method. In each experiment, a known concentration of N or O atoms is established in a discharge-flow system. OH radicals are then created by flash photolysis of H_2O present in the flowing gas, and the disappearance of OH is monitored by time-resolved observations of its resonance fluorescence. The experiments yield $k_1 = (5.0 \pm 1.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $k_2 = (3.8 \pm 0.9) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, for the rate constants of these reactions at 298 ± 5 K.

1. Introduction

The deployment of techniques which can monitor extremely small concentrations of atomic and small molecular free radicals has dramatically improved the quality of the kinetic data which are available for many elementary reactions. Detection by resonance fluorescence has been employed widely, both in steady-state flow experiments and in time-resolved measurements following the creation of radicals by pulsed photolysis. The chief advantage of high detection sensitivity is that side and secondary reactions can be safely ignored [1]. Consequently, the concentration of the radical decays exponentially, and the second-order rate constant for the primary reaction is found by observing how the first-order decay constant varies with the concentration of the second reagent. In the case of a reaction between a radical and a "stable" molecule, the concentration of the molecule can usually be determined without difficulty, and the measurement of rate constants for such reactions, at least for some radicals such as OH [2], has become almost routine. However, the same measurement for reactions between two different radicals presents a more formidable challenge, since the first-order disappearance of one radical must be observed in the presence of an excess of the second radical, whose concentration must be known *absolutely*.

The experiments which are described in this paper combine discharge-flow and flash photolysis techniques. The discharge creates a relatively large steady-state concentration of one free radical, whilst photolysis produces a much smaller concentration of a second radical, whose rate of removal is then observed. This general method has been employed previously by Wolfrum and co-workers [3,4] to study the reaction between O atoms and CN. They used kinetic absorption spectroscopy to follow the disappearance of CN [3], or cw laser absorption or gain to observe the formation of CO [4]. In the present experiments, time-resolved resonance fluorescence is used to monitor the removal of OH radicals. As well as being very sensitive, this technique can be applied to a rather large number of radical–radical reactions. Here, we report rate constants for the reactions

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

and

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

Previously, it has only been possible to infer the rates of these reactions from indirect measurements [5–9], most of which yielded ratios of rate constants: for example, k_2/k_3 [6,7], where k_3 is the rate constant for

$$OH + OH \rightarrow H_2O + O, \qquad (3)$$

or k_1/k_2 [9].

2. Experimental

A full-length paper will report measurements of k_1 and k_2 at temperatures other than room temperature and it will also describe the experimental method and procedures in detail. Here, we give a short account of the main features of our experiments.

A schematic diagram of the central part of the apparatus is shown in fig 1. The Pyrex reaction vessel forms part of a flow system through which gases can be pumped at ≈4 ℓ s^{-1} The total pressure can be measured at point P and was 3.75 Torr in all the experiments described in this paper. The measurements were performed at room temperature, 298 ± 5 K.

The main stream of gas, consisting of a dilute mixture of N_2 (1.2–0.05%) in Ar, passed through a microwave discharge cavity (MC), operated at 50–70 W. The N_2 was partially dissociated (2–8%) and the flow-rate of N atoms, and hence their steady-state concentration, was determined by titration with NO [10], using the photomultiplier tube PM2 (EMI, 9781B) and a suitable filter, to observe the N_2, the NO, or the NO_2 afterglow emission. As indicated in fig. 1, the NO could be added at either of two points so that the extent to which N atoms were removed by recombination on the uncoated Pyrex wall of the main reaction vessel could be determined. This loss was certainly <3% and was therefore ignored.

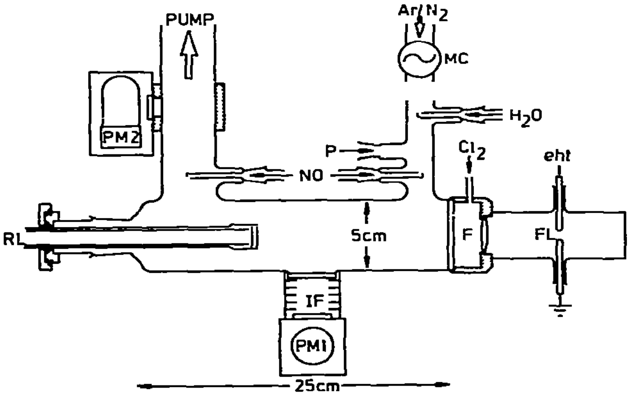

Fig 1 Schematic diagram of the apparatus. Symbols are identified in the text.

For experiments on reaction (2), O atoms were generated in a known steady-state concentration by adding NO to just beyond the end-point of the

$$N + NO \rightarrow N_2 + O \qquad (4)$$

titration reaction. To assess the loss of O atoms by surface-catalysed recombination, a slight excess of NO was added at the two titration points and the intensities of the NO_2 afterglows compared. These measurements indicated that 5% of the O atoms were lost between the first titration point and the centre of the reaction vessel and this loss was allowed for in calculating values of k_2.

Once the steady-state concentration of atoms for a particular experiment had been established, 40–90 mTorr of H_2O was added via an injector 20 cm downstream of the discharge. The H_2O was partially photolysed by radiation from a small flash lamp (FL) which was fired at 100–170 J once every 2 or 5 s. The light from this lamp was collimated with a CaF_2 lens, passed through a stainless-steel filter cell (F), and entered the reaction vessel through a CaF_2 window. N_2 was flowed through the flash lamp at atmospheric pressure. Despite this precaution, this part of the apparatus has to be dismantled fairly frequently so that the CaF_2 lens could be cleaned. The filter cell was filled with 400 Torr of Cl_2 to absorb light from the flash lamp at ≈308 nm [11], the wavelength of the OH resonance fluorescence.

The OH radicals produced in the H_2O photolysis were excited using a resonance lamp (RL) powered by a microwave discharge through He containing ≈1% H_2O [11]. This lamp was positioned at the other end of the reactor from the flash lamp. Radiation from it entered the reaction vessel along an aluminised tube terminating in a quartz window. The OH fluorescence was observed, through a quartz window and a narrow band interference filter (IF) with peak transmission at 308.3 nm and a bandwidth at half maximum of 3.2 nm, using the gated photomultiplier tube PM1 (RCA, 1P28).

Output from PM1 was passed, via a current-to-voltage converter, to a transient recorder (Data Laboratories, DL 905), and the digitised signals were accumulated in a signal averager (Data Laboratories, system DL 4000). We recorded the resonance fluorescence signals from 128 experiments and subtracted the same number of signals from PM1 with the resonance lamp switched off, but everything else the same. The results were then transferred to paper tape for subsequent computer analysis. Usually, measurements on reactions (1) and (2) were performed in pairs. First, an experiment was carried out on reaction (1), ample time having been allowed for the microwave discharge producing N atoms to stabilise. Next, the N atom flow-rate was determined by titration with NO Finally, an experiment was performed on reaction (2), the NO flow having been left on just beyond the titration end-point. The intensity of the N_2 afterglow at PM2 was observed at intervals throughout this procedure, to guard against changes in the efficiency of atom production in the discharge

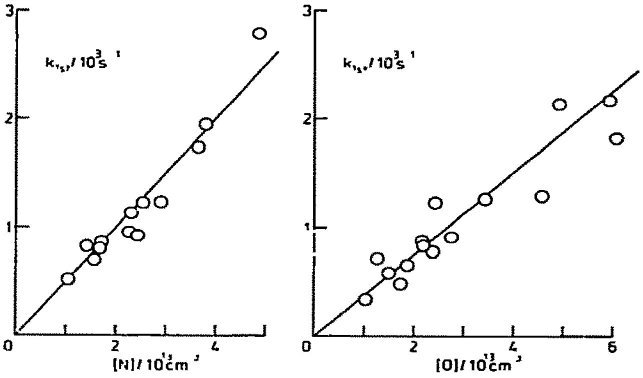

Fig 2 First-order rate constants for removal of OH in the presence of N or O atoms

3. Results

Before attempting kinetic measurements, two series of preliminary experiments were performed to determine the sensitivity of our system for detecting OH. In the first, the reaction vessel was converted into a conventional flow-tube, by replacing the flash lamp and filter cell with an assembly incorporating a movable injector This enabled us to observe the resonance fluorescence signals from known steady-state concentrations of OH, which were generated by titrating H atoms with NO_2 [10]. Allowance for removal of OH could be made by observing the intensity of resonance fluorescence as the injector was withdrawn different distances upstream of the observation zone.

The results from the flow-tube experiments were checked by observing the intensity of NO β band emission, following flash photolysis of H_2O in an excess of N atoms. Because reaction (1) was followed by reaction (4), OH radicals were converted quantitatively to O atoms. The reaction products were swept past PM2 and the integrated intensity of the NO afterglow provided a measure of the concentration of O atoms – and hence of OH radicals produced in the photolysis of H_2O.

Although the second method was less accurate than the first, it gave a similar value for the detection sensitivity Together, these experiments showed that the initial concentration of OH in our rate measurements on reactions (1) and (2) was approximately 10^{12} cm^{-3}, corresponding usually to <5% and never >8% of the concentration of N or O atoms. In the absence of radical atoms, the decay of the OH resonance fluorescence was very slow, and was probably determined simply by convective and diffusive removal of OH from the observation zone Consequently, in the presence of N or O atoms, the concentration of OH decayed according to the equations

$$-\mathrm{d}\ln[\mathrm{OH}]/\mathrm{d}t = k_{1st},$$

$$= k_1 [\mathrm{N}] \text{ or } k_2 [\mathrm{O}]$$

Fig. 2 shows plots of k_{1st} against [N] and against [O] Values of k_1 and k_2 were obtained by taking the mean values of (k_{1st}/[N]) and (k_{1st}/[O]), yielding

$$k_1 = (5\ 0 \pm 1\ 2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k_2 = (3\ 8 \pm 0.9) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

The errors quoted correspond to a single standard deviation plus a 5% allowance for possible systematic error in the titration.

4 Discussion

Reaction (1) has only been studied previously in a discharge-flow experiment [9]. By observing the relative intensities of the N_2 and NO emissions when H_2 was added to a flow of active nitrogen which had been partially titrated with NO, Campbell and Thrush deduced that $k_1/k_2 = 1.4 \pm 0.1$ at 320 K. This solitary experiment has been the basis of subsequent evaluations [12,13] The ratio of our directly determined values of k_1 and k_2 is in excellent agreement with Campbell and Thrush, confirming their analysis and decreasing the uncertainty in the absolute value of k_1.

There have been several previous determinations [5–8] of k_2, all of them in flow-tube experiments, none of them direct, but all yielding similar values of k_2. The most recent evaluations suggest. $k_2 = 4\,2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} [13] and $k_2 = 4.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} [14] Our work should improve the "reliability" or "uncertainty" in these evaluations, given as a factor of two [13] and a factor of four [14].

The rate constants which we find for reactions (1) and (2) correspond to reaction about once in every five gas kinetic collisions. Superficially, such large rate constants occasion no surprise, since a radical–radical reaction can usually proceed via a collision complex whose formation is not impeded by the existence of a barrier on the potential surface. Thus, reaction (2) can occur via the $\tilde{X}\,^2A''$ ground electronic state of the HO_2 radical. However, it should be remembered that the interaction of $O(^3P)$ with $OH(^2\Pi)$ gives rise to no fewer than six quartet and six doublet states Of these, only one $^2A''$ and one $^4A''$ also correlate with $H(^2S) + O_2(^3\Sigma_g^-)$ Reaction to give electronically excited O_2 is too endothermic to make any appreciable contribution to the overall reaction rate at room temperature.

The doublet electronic states of HO_2 have been the subject of several theoretical studies [15]. In simple terms, the lowest four of these states arise from different distributions of 7 electrons among the 4 orbitals which, in the linear conformation, are π and π^* orbitals on the O_2 moiety It appears that the lowest quartet state must lie considerably above the energy of separated $O(^3P) + OH(^2\Pi)$, so that reaction across this surface is very unlikely to be important. If this is so, the rate constant for adiabatic reaction across the HO_2 ($\tilde{X}\,^2A''$) ground-state surface can be estimated by multiplying k_2 by a ratio of electronic partition functions. $f_{\mathrm{el,OH}} f_{\mathrm{el,O}} / f_{\mathrm{el,HO_2}(\tilde{X})}$. This yields a value of 4.0×10^{-10} cm^3 molecule^{-1} s^{-1}, or, on a simple collision theory basis, a reaction cross section of about 45 Å^2, indicating the absence of any steric hindrance to reaction on this surface.

An alternative estimate of k_2 can be made using a method devised by Quack and Troe [16] for calculating the rate constants of radical–radical association reactions in the limit of high pressure. Their procedure requires that one finds the point along the reaction path at which the system acquires maximum free energy. The partition function of the reacting system and the potential is assumed to change continuously along the reaction coordinate and these changes are described in terms of a single, universal, length parameter. Assuming that reaction (2) proceeds only across the $\tilde{X}\,^2A''$ surface of HO_2, application of this method gives a value of $k_2 = 3.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K, with the two O atoms being separated by 3.8 Å in the transition state.

Reaction (1) is less amenable to the treatment just described. Again the adiabatic correlations should be considered. The reagents interact to give four surfaces, $^3A'$, $^3A''$, $^5A'$, $^5A''$; the products yields, $^1A'$, $^1A''$, $^3A'$, $^3A''$ The only spectroscopic information available for the HNO radical relates to the $\tilde{A}\,^1A''$–$\tilde{X}\,^1A'$ transition [17]. In any case, the important regions of the triplet potential surface (or surfaces) across which reaction (1) can occur are presumably those with the H atom close to O rather than to N. Ab initio calculations have been carried out on the lowest singlet and triplet states of NOH, as well as for HNO [18,19]. They indicate that for the NOH conformation the $^3A''$ state lies lower than the $^1A'$ state and that there is appreable binding energy relative to N + OH and H + NO. If one assumes that reaction (1) proceeds only across the $^3A''$ surface and allows for the electronic degeneracy of the reagents, one obtains a cross section of 23 Å^2 for reaction on this surface only.

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