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THE RATE OF REACTION OF HO_2 RADICALS WITH HO AND WITH NO

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The rate coefficients for the reactions $HO_2 + NO = HO + NO_2$ (1) and $HO_2 + HO = H_2O + O_2$ (2) have been remeasured by laser magnetic resonance using an improved experimental arrangement. Values of $k_1 = (6.9 \pm 0.6) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $k_2 = (5.8 \pm 0.9) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (one standard deviation) were obtained at 298 K.

1. Introduction

The free radicals HO_2 and HO play a central role in the chemistry of the stratosphere, but reactions of the former have proved difficult to study in the gas phase. Laser magnetic resonance (LMR) spectroscopy has provided the most unequivocal method of following the concentration of HO_2 radicals in the gas phase, and was soon used to show that the reaction

$$HO_2 + NO = HO + NO_2 \qquad (1)$$

is much more rapid than indicated by previous studies [1,2]. Subsequent determinations of k_1 by a variety of techniques all gave values close to 8×10^{-12} cm^3 molecule^{-1} s^{-1} at 290–300 K [3–5]. Unfortunately no such agreement exists for the important atmospheric reaction

$$HO_2 + HO = H_2O + O_2\,, \qquad (2)$$

where published values of k_2 range from 2×10^{-10} cm^3 molecule^{-1} s^{-1} [6] to an upper limit of 3×10^{-11} cm^3 molecule^{-1} s^{-1} [7]. Although the high values of k_2 were in general obtained at higher total pressures than were the lower values, there is no reason to believe that this is associated with a pressure-dependent rate coefficient, as has been established for the related but considerably slower reaction [8]

$$HO_2 + HO_2 = H_2O_2 + O_2\,. \qquad (3)$$

We have therefore remeasured k_2 taking particular care to eliminate potential sources of error associated with our previous studies. We have also remeasured k_1 since its well-established value provides a good check of our experimental technique.

The methods used depend on establishing a steady state between the reactions (1) or (2) and the reaction

$$HO + H_2O_2 = HO_2 + H_2O\,, \qquad (4)$$

for which the accepted value has recently been revised upwards to 1.6×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K since our previous work [9,10]. The steady-state expressions for the two systems are respectively

$$[HO_2]/[HO] = k_4[H_2O_2]/k_1[NO]$$

and

$$[HO_2] = k_4[H_2O_2]/k_2\,.$$

The absolute sensitivity of the apparatus for free radicals is determined using the rapid stoichiometric reaction

$$H + NO_2 = HO + NO\,, \qquad (5)$$

the measured values of k_1 and k_2 therefore depend on the relative sensitivity of the spectrometer for HO and HO_2. Because it is not possible to have windows near the sampling zone where the laser tube intersects the flow tube, unequal diffusion of free radicals into the laser tube can cause the measured sensitivity ratio to differ from that calculated from the line strength factors and the dipole moments of the two species. For the geometry of the present system it has proved more

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satisfactory to control this by surface coatings which minimise the difference between the surface losses (and hence the spacial distribution of the two species) than by the use of large counter-flows of inert gas to limit diffusion into the laser tube.

2. Experimental

The laser magnetic resonance spectrometer which uses the 118.6 μm line of the water vapour discharge laser to detect both HO and HO_2 was similar to that described previously [2]. An Infrared Laboratories germanium bolometer at 1.5 K was invariably used as a detector.

All experiments were conducted in a 25 mm internal diameter flow tube containing a double concentric sliding injector constructed so that the flows and addition points for two reagents could be adjusted independently. This part of the apparatus was coated either with Dupont Teflon Enamel or with halocarbon wax [9]. The walls of the laser tube between the end mirror and the Brewster angle window were coated with boric acid as described by Howard and Evenson [11]. Great care was taken to ensure that the flow system was evacuated at all times. Exposure of the coated surfaces to the atmosphere resulted in activation of the walls which then required long periods of conditioning before reproducible results could again be obtained

Total pressures were measured with an MKS Baratron type 222 gauge. The main carrier flow was controlled by an ASM flow controller. Needle valves and calibrated capillary flowmeters were used for all other flows.

3. Results

To study reaction (2), hydrogen atoms ($\approx 10^{13}$ cm^{-3}) in an argon carrier, from a microwave discharge, at a total pressure of 2 Torr were pumped down the flow tube at 8 m s^{-1}. Hydrogen peroxide ($\approx 10^{14}$ cm^{-3}) in an argon carrier was added through the outer concentric injector. Nitrogen dioxide was then added through the inner injector a few centimetres upstream of the observation region; this stoichiometrically converted any remaining atomic hydrogen to hydroxyl radicals, which then established a steady state for HO_2 between reactions (2) and (4). Variation of the reaction time showed that this steady state was maintained over periods greater than 10 ms.

The number of HO radicals generated in the H + NO_2 reaction was used to calibrate the sensitivity of the spectrometer for each data point. The relative sensitivities of the spectrometer for HO and HO_2, using the same Zeeman components as before [8] was determined by converting known amounts of HO_2 to HO by addition of NO in reaction (2) which stoichiometrically converts HO_2 to HO. This gave a sensitivity ratio of 120 ± 4 (one standard deviation) for 10 sets of measurements taken over the duration of the experiments.

Taking $k_3 = 1.6 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K [9,10] the present measurements yield $k_2 = (5.8 \pm 0.9) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K (one standard deviation of seven measurements).

In the study of the HO_2 + NO reaction HO_2 radicals were generated in two ways. In one, ≈2% hydrogen peroxide in an argon carrier at 2 Torr total pressure was passed through a Tesla discharge before entering the flow tube. In the other, fluorine atoms were generated by a microwave discharge through a 2% mixture of carbon tetrafluoride in an argon carrier, again at 2 Torr total pressure. Hydrogen peroxide ($\approx 10^{14}$ cm^{-3}) in an argon carrier was added to this through the outer concentric injector. In both cases nitric oxide ($\approx 10^{13}$ cm^{-3}) was added through the inner injector some 5 mm from the observation region. Calibration was carried out as for reaction (2), and yielded the mean value of $k_1 = (6.9 \pm 0.6) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K (one standard deviation of five sets of measurements), this agrees well with Howard's value of $(8.0 \pm 1.0) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} [1] using different methods of determining k_1 from LMR measurements. Values close to 8.0×10^{-12} cm^3 $molecule^{-1}$ s^{-1} have also been obtained in discharge-flow systems using resonance fluorescence to detect the HO radicals formed in reaction (1) [3–5]. We therefore conclude that there are no serious errors in our present method for determining reaction rates of HO_2 by LMR, a view supported by modelling calculations on the reaction rates and transport in the system [12].

Our new measurement of k_2 agrees well with our previous value of $(5.1 \pm 1.7) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. It strengthens our view that the disagreement between other low-pressure measurements in discharge-flow systems [7,13] which give $k_2 = 3 \times 10^{-11}$ cm^3

molecule^{-1} s^{-1} and those obtained at higher pressures which give $k_2 = (10–20) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at room temperature [6,14,15] do not arise from a pressure dependence of k_2. The rate coefficient of the corresponding disproportionation reaction of two HO_2 radicals is dependent on pressure over this range [8, 16,17] and this behaviour can be rationalised in terms of the formation of a cyclic dimeric H_2O_4 species bound by two strong hydrogen bonds. Such a complex might also be formed between HO_2 and HO, but containing one less atom it would have a shorter lifetime than the H_2O_4 complex, which is of the order of 10^{-8} s. The contribution to reaction (2) of a pathway via an H_2O_3 intermediate should therefore be slower than the $HO_2 + HO_2$ reaction. Because the measured rate of reaction (2) is two orders of magnitude faster than that of reaction (3) there is no good reason to regard reaction (2) as other than a normal rapid hydrogen abstraction reaction with negligible dependence on pressure under the conditions which obtain in the Earth's atmosphere. Its rate coefficient would therefore be expected to have only a small temperature dependence (between $T^{1/2}$ and $T^{-1/2}$ to judge from related reactions).

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