# THE RATE OF REACTION BETWEEN HO<sub>2</sub> RADICALS AT LOW PRESSURES

B A. THRUSH and G.S. TYNDALL

University of Cambridge, Department of Physical Chemistry, Lensfield Road, Cambridge CB2 1EP, UK

Received 14 August 1982

The rate coefficient of the bimolecular disproportionation of HO<sub>2</sub> radicals has been measured at total pressures between 7 and 20 Torr using flash photolysis and tunable diode laser spectroscopy. The rate coefficient is found to be (1.6  $\pm$  0.1) × 10<sup>-12</sup> cm<sup>3</sup> s<sup>-1</sup> at 298 K and can be expressed as 2.4 × 10<sup>-13</sup> exp(560/T) cm<sup>3</sup> s<sup>-1</sup> between 298 and 358 K

#### 1. Introduction

The reaction between  $HO_2$  radicals is an important atmospheric sink for odd-hydrogen radicals:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$
. (1)

It is the dominant source in the stratosphere of  $H_2O_2$ , a species which has been sought unsuccessfully by infrared spectroscopy. Several groups have reported a pressure-dependent rate coefficient for reaction (1) but the exact form of this dependence, and the overall reaction mechanism, are not yet clear [1-3].

We have measured the rate coefficient of reaction (1) at room temperature over the pressure range 7-20 Torr [4], and found no dependence on total pressure in this range, although the rate coefficients are almost a factor of two lower than those measured at atmospheric pressure. This is in overall agreement with the results of Sander et al. [3] who found a pressure dependence for a number of carriers over the range 100-700 Torr, and extrapolated their data to an intercept of  $\approx 1.6 \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup> at zero pressure.

The observed rate coefficient therefore consists of two components -a pressure-independent bimolecular process, and a termolecular step dependent on the nature of the carrier gas

At atmospheric pressure, the overall reaction shows a negative temperature coefficient which is characteristic of most third-order combination processes. We have measured the temperature coefficient of reaction (1) at low pressures, where the bimolecular process is dominant, to determine whether this is a direct hydrogen abstraction reaction (which would be expected to have a small activation energy) or proceeds via an  $H_2O_4$  complex which would give a negative temperature coefficient. In these experiments, which were made at total pressures corresponding to those in the middle stratosphere, we have combined the techniques of flash photolysis and tunable diode laser spectroscopy.

# 2. Experimental and results

The apparatus and experimental technique have been described [4]. HO<sub>2</sub> was produced by the flash photolysis of  $Cl_2-CH_3OH-O_2$  mixtures and detected by using a diode laser to scan part of the  $v_3$  band at 1117.54 cm<sup>-1</sup> with Doppler-limited resolution. The reaction vessel, 50 cm long and 2.5 cm in diameter, could be heated to 100°C by electrical heating of the reflective housing. The only modification to the system is the use of a transient recorder to store the detector output digitally. This has led to an improved signal-to-noise ratio, which also allows the decay to be followed for longer times.

Previously we reported that the rate coefficient for reaction (1) is independent of pressure between 7 and 20 Torr at 298 K. Further measurements given in table 1 have confirmed thus lack of pressure dependence and yield a rate coefficient of  $k_1 = (1.6 \pm 0.1) \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup>, the uncertainty being one standard deviation of the experimental measurements.

Table 1

Тетр. (К)	Pressure (Torr)	10 <sup>-14</sup> [HO <sub>2</sub> ] <sub>0</sub> (molecules cm <sup>-3</sup> )	NO. OF determinations	10 <sup>12</sup> k <sub>1</sub> (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )
298	6 3	98	2	1.6
	9.3	10	6	17
	9.6	12	2	15
	10	8.41	2	16
	12	10.4	3	1 55
			mean	1.6 ± 0.1
323	6	9.4	3	1.2
	8 5	58	5	1 35
	13	11	2	12
			mean	1 28 ± 0.15
333	10.5	73	8	1 35 ± 0 2
359	115	83	3	12
	115	68	2	1.1
			mean	1 15 ± 0 2

Measurements of rate coefficient for  $HO_2 + HO_2$ 

The experiments at 50°C reported in table 1 gave  $k_1 = (1.28 \pm 0.15) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , also independent of pressure.

Finally, the reaction rate was measured between 25 and 85°C at 10 Torr total pressure. Although it was not possible to monitor the fractional dissociation of  $Cl_2$  at all temperatures, a relative sensitivity for HO<sub>2</sub> could be calculated at various temperatures from the known variation of the parameters controlling the line intensities. The calculated yields were within 10% of those based on the dissociation as measured at room temperature.

The value obtained at 85°C was  $(1.15 \pm 0.2)$ X  $10^{-12}$  cm<sup>3</sup> s<sup>-1</sup>. Taken together, these results correspond to a negative temperature dependence which can be represented by

$$k = 2.4 \times 10^{-13} \exp[(560 \pm 200)/T] \text{ cm}^3 \text{ s}^{-1}$$

#### 3. Discussion

Our measurements at 7–20 Torr total pressure, taken with the measurements of Sander et. al. [3], confirm that the rate coefficient of the bimolecular reaction between HO<sub>2</sub> radicals extrapolates to a limiting value of  $(1.6 \pm 0.2) \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup> at zero pressure and 298 K. This rate coefficient increases approximately linearly with total pressure and for  $M = N_2$  or SF<sub>6</sub>, it can be represented by

 $k_1 = (1.6 \times 10^{-12} + 6 \times 10^{-32} [M]) \text{ cm}^3 \text{ s}^{-1}$ at 298 K,

where [M] is in units of molecules cm<sup>-3</sup>. As Sander et al. [3] point out, the pressure-dependent term has a magnitude commonly found for three-body combination reactions. Such a process would normally be interpreted in terms of the formation and redissociation of an H<sub>2</sub>O<sub>4</sub><sup>\*</sup> species which can be collisionally stabilised. The products observed require that the stabilised H<sub>2</sub>O<sub>4</sub> decomposes rapidly, predominantly to H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub>.

The negative temperature coefficient which we find for the bimolecular process is also consistent with a reaction which proceeds via an  $H_2O_4$  complex, but involves direct decomposition to yield  $H_2O_2 + O_2$ . Thus both terms in  $k_1$  can be rationalised by a single reaction mechanism:

$$HO_{2} + HO_{2} \stackrel{\approx}{\to} H_{2}O_{4}^{*} \stackrel{\leftarrow}{\to} H_{2}O_{2} + O_{2}$$
  
$$\downarrow M$$
  
$$H_{2}O_{4} \rightarrow H_{2}O_{2} + O_{2} .$$

~

Neglecting any complications which might arise from the energy dependence of some of the rate process involved, a steady-state analysis yields

$$k_{1} = \frac{1}{[HO_{7}]^{2}} \frac{d[H_{2}O_{2}]}{dt} = \frac{k_{a}(k_{c} + k_{d}[M])}{k_{b} + k_{c} + k_{d}[M]}$$

which has the required form providing  $k_b \ge k_c$ . The assumption that stabilised  $H_2O_4$  decomposes predominantly into  $H_2O_2 + O_2$  and not  $HO_2 + HO_2$  is justifiable because the former is exothermic and the latter endothermic.

The negative temperature coefficients observed at atmospheric pressure are about twice the low-pressure value. exp[(1250 ± 100)/T] [1] and exp[(1050 ± 45)/T] [5]. This is clearly due to process (c) becoming more important relative to (d) as the temperature and the energy of H<sub>2</sub>O<sub>4</sub> are increased. If we assume that N<sub>2</sub> and SF<sub>6</sub> have a collisional efficiency of ≈0.5 for stabilisation, then  $k_d \approx 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup>, giving  $k_c \approx 3 \times 10^9$  s<sup>-1</sup> at ambient temperatures.

The rates of processes (a) and (b) are somewhat harder to estimate. Data on the limiting second-order rate coefficients for association of small molecules suggest a value of  $k_0 \approx 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> which with the values of  $k_c$  and  $k_d$  adopted here gives  $k_b \approx 1.5$  $\times 10^{10}$  s<sup>-1</sup>, satisfying the condition that  $k_{\rm b} \ge k_{\rm c}$ . However it is not immediately obvious why channel (b) should be favoured over the much more exothermic channel (c). If  $H_2O_4$  were a chemically bound species, e g. HO<sub>4</sub>H, it would have a singlet ground state, and a low transmission coefficient could be associated with intersystem crossing to triplet potential surfaces arising from the ground-state products  $H_2O_2 + O_2$ . This argument would not hold for our preferred mechanism in which H<sub>2</sub>O<sub>4</sub> is a hydrogenbonded HO2 dimer, either cyclic or open chain, where the triplet and singlet states would be very close in energy. Here the small value of  $k_c$  relative to  $k_{\rm b}$  can be attributed to the difficulty of coupling vibrational energy from the low-frequency modes associated with the O...H hydrogen bond to the highfrequency H-O stretching vibration which is essential for reaction (c) to occur.

The theoretical calculations of Ewing [6] and of Beswick and Jortner [7] on the closely related problem of vibrational predissociation in hydrogen-bonded dimers show this energy exchange to be a very inefficient process. However, experimental observations on vibrational spectra of these species can be interpreted in terms of rapid predissociation [7] and it is therefore unprofitable to estimate  $k_c$  for either a cyclic or an open-chain hydrogen-bonded HO<sub>2</sub> dimer.

In this connection, it should be noted that Lorenz and Zellner [8] and Margitan and Watson [9] have recently confirmed earlier suspicions that the rate coefficient of the hydrogen transfer reaction [10]

$$HO + HNO_3 = H_2O + NO_3$$
 (2)

increases with total pressure, almost doubling between zero pressure and one atmosphere at 298 K [8]. Reaction (2), like (1), also has a negative temperature coefficient and it is plausible that it also proceeds by a mechanism involving a hydrogen-bonded complex.

The acceleration by water vapour (and by ammonia) of the reaction between two HO<sub>2</sub> radical has been attributed to the formation of a strongly hydrogen-bonded H2O ... HO2 species which reacts more rapidly with HO<sub>2</sub>. This would be implausible if the HO<sub>2</sub> + HO<sub>2</sub> reaction were a simple atom-transfer process. However, the energised species formed by association between H<sub>2</sub>O... HO<sub>2</sub> would have a much longer lifetime for redissociation  $(1/k_b)$  than one formed from HO<sub>2</sub> + HO<sub>2</sub>. Thus the ratio  $k_a/k_b$  would be much greater for the hydrogen-bonded species. This is consistent with the observation by Sander et al. [3] that added water vapour appears to give similar proportionate accelerations in the bimolecular and termolecular terms in the  $HO_2 + HO_2$  reaction. In other words H<sub>2</sub>O is not simply acting as an efficient third body. This interpretation of the effect of water vapour favours an open-chain hydrogen-bonded structure for  $H_2O_4$  unless it is assumed that  $H_2O_4$ ... $HO_2$ and HO<sub>2</sub> combine to form a cyclic trimer.

The DO<sub>2</sub> + DO<sub>2</sub> reaction is 3.3 times slower at a number of total pressures than the HO<sub>2</sub> + HO<sub>2</sub> reaction [3]. This suggests that the isotope effect is primarily on the ratio  $k_a/k_b$  although it is not obvious why the ratio  $k_c$  to  $k_d$  [M] does not also exhibit an isotope effect.

Since the initial observation a few years ago of a pressure-dependent rate coefficient for the reaction

the needs of atmospheric modelling have greatly increased the measurement accuracy for many transfer reactions. The interpretation given here suggests that a number of hydrogen atom transfer reactions involvVolume 92, number 3

ing HO, HO<sub>2</sub> and other highly polar species could exhibit pressure-dependent rate coefficients over the range important to atmospheric chemistry.

### Acknowledgement

We thank the Natural Environment Research Council for financial support.

# References

 R A. Cox and J.P Burrows, J. Phys. Chem 83 (1979) 2560.

- [2] B.A. Thrush and J P T Wilkinson, Chem. Phys. Letters 66 (1979) 441
- [3] S P. Sander, M. Peterson, R T. Watson and R Patrick, J Phys Chem 86 (1982) 1236
- [4] B.A. Thrush and G S. Tyndall, J. Chem. Soc. Faraday II 78 (1982), to be published.
- [5] R.-R Lu, R.A. Gorse Jr., M.C. Sauer Jr and S. Gordon, J. Phys. Chem. 83 (1979) 1803.
- [6] G.E. Ewing, J. Chem Phys. 72 (1980) 2096
- [7] J.A. Beswick and J. Jortner, Advan. Chem. Phys. 47 (1981) 363
- [8] K Lorenz and R. Zellner, Inf. Photochem Conf Stanford (1982) abs. G-4.
- [9] J J. Margitan and R T. Watson, J. Phys. Chem to be published.
- [10] Chemical Kinetic and Photochemical Data for Use in Stratospheric Modelling, No. 4., J P.L. Pasadena (1981)