THE TEMPERATURE DEPENDENCE OF THE HO₂ + HO₂ REACTION

Roger PATRICKth and Michael J. Pilling Physical Chemistry Laboratory, Oxford OXI 3QZ, UK

Received 21 June 1982, in final form 12 July 1982

The temperature dependence of the rate constant for the reaction $HO_2 + HO_2 \rightarrow H_2O_2 + O_2(2k_1)$ has been determined using flash photolysis techniques, over the temperature range 298-510K, in a nitrogen diluent at a total pressure of 700 Torr. The overall second order state constant is given by $k_1 = (4.14 \pm 1.15) \times 10^{-13} \exp[(630 \pm 115)/T] \text{ cm}^3$ molecule⁻¹ s⁻¹ where the quoted errors refer to one standard deviation. This result is compared with previous findings and the negative activation energy is shown to be consistent with the observation that the rate constant is pressure dependent at 700 Torr

1. Introduction

The importance of the hydroperoxy radical, HO_2 , in combustion and in atmospheric chemistry is widely recognized. Its low reactivity with many non-radical species lends particular importance to the disproportionation reaction

$$2\mathrm{HO}_2 \xrightarrow{2k_1} \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2, \qquad (1)$$

and this has been the subject of numerous studies [1-9]. In addition many other rate constants have been determined relative to k_1 , especially at higher temperatures $\{10,11\}$.

A recent paper by Sander et al. [12] reported a room-temperature study of the pressure dependence of k_1 in a variety of diluent gases at pressures between 100 and 700 Torr. The results show that the rate constant is linearly dependent on pressure whilst extrapolation to zero pressure indicates a pressure independent contribution, $k_{1,0}$, to the total rate constant of (1.6 \pm 0.2) \times 10⁻¹² cm³ molecule⁻¹ s⁻¹.

The work presented in this paper is intended to complement that of Sander et al. [12] by studying the temperature dependence of the overall rate constant at a fixed total pressure of nitrogen diluent gas.

2. Experimental

The apparatus is described in more detail elsewhere [13]. Conventional flash photolysis techniques using Xe/O₂ flashlamps which delivered a flash energy of 200 J per pulse were used to generate HO₂ from an anhydrous mixture of CH₃OH, Cl₂ and O₂. The following sequence has been shown [12] to operate in such a chemical system.

$$\operatorname{Cl}_2 \xrightarrow{h\nu} 2\operatorname{Cl}_2$$
 (2)

$$Cl + CH_3OH \rightarrow CH_2OH + HCl,$$
 (3)

$$CH_2OH + O_2 \rightarrow HO_2 + CH_2O. \tag{4}$$

The relevant rate constants, k_3 and k_4 , are 6 33 × 10⁻¹ cm³ molecule⁻¹ s⁻¹ and 2 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ respectively [14,15]

Typical pressures of the reagents were $CH_3OH \approx Cl_2 \approx 1.5$ Torr and $O_2 \approx 5$ Torr. The total pressure was maintained at 700 ± 10 Torr with an excess of N₂ diluent. The reaction mixture flowed through a pyrex cell, with spectrosil end-windows, whose overall length was 17.3 cm. The cell was enclosed in an electrically heated aluminum housing and its temperature was determined, after equilibration, to 0.5 K with a Hg/glass thermometer

 HO_2 was detected by its ultraviolet absorption at 227.5 nm where its cross section (base e) has been de-

^a Address for all correspondence. Department of Chemical Kinetics, SRI International, Menlo Park, California 94025, USA.

termined to be $(3 0 \pm 0.4) \times 10^{-18}$ cm² molecule⁻¹ [12]. Absorption profiles were recorded as a function of time over a range of temperatures from 298 to 513 K Initial absorbances varied from 4.0×10^{-3} to 1.2 $\times 10^{-2}$ corresponding to initial HO₂ concentrations of 7.6 $\times 10^{13}$ to 2.3 $\times 10^{14}$ molecule cm⁻³. In order to achieve an acceptable signal-to-noise ratio, signal averaging of up to 256 shots was used. The data were digitized (Datalab DL920) and averaged (Datalab DL4000) before analysis by an on-line microcomputer (Research Machines 380Z) and storage on floppy disk.

3. Results

 H_2O_2 produced in reaction (1) has a significant absorption cross section at 227.5 nm ($\sigma = 2.14 \times 10^{-19}$ cm² molecule⁻¹) [16] and so the experimentally observed absorption profile consists of the sum of contributions from both HO₂ and H₂O₂ Assuming second-order kinetics it can be shown that the time dependence of the total absorption is given exactly by [13]

$$\Delta I(t)/I_0 = 1 - \{\exp[(B - C)/(ABt + 1) + C]\}^{-1}, \quad (5)$$

where I_0 is the incident light intensity, $\Delta I(t)$ is the change in transmitted intensity at time $t, A = 2k_1 \sigma l, \sigma$ is the absorption cross section of HO₂, *I* is the path length, *B* is the initial absorbance at t = 0 and *C* is the final absorbance at $t = \infty$ Since the reaction is second order in HO₂, it was not practicable to obtain *C* experimentally as this would have required following the absorption to very long times Instead *C* was equated to 0.0353*B* on the basis of the known extinction coeffi-

Table 1 Experimental values of k_1

<i>T</i> (K)	10 ¹² k ₁ (cm ³ molecule ⁻¹ s ⁻¹)		
298	3.66 ± 0 46		
317	3.18 ± 0 23		
330	3.28 ± 0 20		
345	2.40 ± 0.06		
358	2.72 ± 0 21		
380	1.90 ± 0.18		
407	1.91 ± 0.06		
425	1 84 ± 0 43		
455	203 ± 015		
510	1.08 ± 0.16		



Fig. 1. Temperature dependence of k_1 . ---- data of Cox and Burrows [7], - - data of Lifet at [6]

cients for HO₂ and H₂O₂ and the known stoichiometry of the reaction [12,16]. The data were then fitted to eq. (5) using non-linear regression [13,17], with A and B as adjustable parameters.

The results of this analysis are given in table 1, and plotted in Arrhenius form in fig. 1. Each rate determination represents an average of 6–10 experiments and the quoted errors are one standard deviation. The room temperature value is in reasonable agreement with the value of $(2.97 \pm 0.45) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ obtained by Sander et al in 700 Torr N₂. The rate constant decreases with temperature and a weighted least-squares analysis of the Arrhenius plot gives

$$k_1 = (4.14 \pm 1.15) \times 10^{-13}$$

 $X \exp[(630 \pm 115)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

corresponding to an activation energy of $-5\ 24\pm 0.96$ kJ mol⁻¹. Expressing the rate constant in the form $k_1 = AT^{-n}$ gives $n = 1.9 \pm 0.1$.

4. Discussion

The temperature dependence of reaction (1) has been reported in two previous studies Cox and Burrows [7] generated HO₂ using the modulated photolysis of mixtures of H₂/O₂/Cl₂, in a variety of diluents, at a pressure of 760 Torr. They expressed k_1 as Volume 91, number 5

 $k_1 = (3.8 \pm 1.4) \times 10^{-14}$

 $X \exp[(1250 \pm 200)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$

Lu et al. [6] used pulse radiolysis of H_2/O_2 mixtures at a total pressure of 2 atm and found

 $k_1 = (1.14 \pm 0.16) \times 10^{-13}$

 $\times \exp[(1057 \pm 45)/T]$ cm³ molecule⁻¹ s⁻¹.

The best straight line fits to the data of Cox and Burrows and Lii et al. are included in fig. 1. The broad agreement between the three sets of data is important, particularly because of the difficulty of generating HO_2 directly and the need to use quite complex chemical systems.

The pressure dependence of the reaction has been cited as evidence for an associative mechanism proceeding via H_2O_4 [6-8,12]. Most of the necessary molecular parameters for a linear H_2O_4 species have been determined by Giguere and co-workers [18-20] and the HO_2-O_2H bond dissociation enthalpy has been estimated by Nangia and Benson [21], (see table 2). Thus it is possible to use unimolecular rate theory to calculate the rate constant, k_d , for dissociation of H_2O_4 and hence, via the equilibrium constant, to obtain the association rate constant, k_a , for the reaction

$$2\mathrm{HO}_2 \frac{k_{\mathrm{a}}}{k_{\mathrm{d}}} \mathrm{H}_2 \mathrm{O}_4. \tag{6}$$

Troe [24,25] has recently developed approximate formulae which may be readily used to calculate k_{2} in the limiting third-order region. Using the data in table 2 and assuming a strong collision model gives $k_{a,0} = 2.6 \times 10^{-33} \text{ cm}^6$ molecule⁻² s⁻¹, which is significantly smaller than the experimental value of 5.4×10^{-32} cm^6 molecule⁻² s⁻¹ found by Sander et al. [12] for a N2 diluent Adopting a more realistic weak collision model would reduce the calculated value of $k_{a,0}$ still further. The approximations made in the Troe model are unlikely to introduce an error of this magnitude. At a given concentration of the third body [M], $k_{a,0}$ [M] represents a maximum value for the secondorder rate constant, since k_a falls below this asymptotic limit as the pressure increases. Thus, given that an associative mechanism operates, it is clear that the H_2O_4 molecule must have a larger density of states or be more strongly bound than the species described by

Table 2					
Molecular	parameters	for	H ₂ O ₄	and	HO

Vibrational frequencies						
	ω (cm ⁻¹)	Туре	Ref			
H ₂ O ₄						
$\nu_{\rm I}$	3417	O-H stretch sym	[22			
12	2869	O-H bend sym	(22			
V3	855	O-O stretch sym	20			
ν_4	764	O-O stretch med	[20]			
ν_5	450	OOO bend sym	20			
ν ₆	-	free rotor	•			
ν	-	free rotor				
ν_8	1408	O-H stretch asym	[22]			
<i>v</i> 9	1435	O-II bend asym	[22]			
v_{10}	823	O-O stretch asym	[20]			
<i>v</i> 11	430	000 bend asym	[20]			
21 ⁴	-	free rotor				
HO ₂						
νı	3410	O-H stretch	[3]			
ν <u>2</u>	1390	bend	131			
μ3	1095	O-O stretch	[3]			
Moments	s of inertia ,	/ (amu/Ų) [3,23]				
H ₂ O ₄		HO ₂				
16 57		0 82				
113 24		14 97				
114 47		15 84				

HO2-O2H Bond dissociation energy (kJ mol-1)[21]

 $\Delta H_{298}^0 = 37.7 \qquad \Delta H_0^0 = 33.4$

Giguere et al. [18-20] and by Nangia and Benson [21]

If ΔH_0^0 , the dissociation energy at 0 K, is increased so as to match the calculated and experimental thirdorder rate constants, then a value of 73.0 kJ mol⁻¹ is required This assumes a weak collision model with a deactivation efficiency β_c of 0.35

The validity of the assumption of third order kinetic at 700 Torr pressure for an associative mechanism can be assessed using Luther and Troe's [25] approximate method, based on reduced Kassel integrals, for estimating the fall-off behavior of such reactions. If the highpressure rate constant is taken as 1.4×10^{-11} cm³ molecule⁻¹ s⁻¹, by analogy with the recombination of the isoelectronic ethyl radical [26], and the broadening parameter is taken as 0.6, then the predicted half pressure for HO₂ recombination is \approx 33 atm. Thus thirdorder kinetics for HO₂ recombination would be expected even at pressures greatly in excess of 1 atm

The strong negative temperature dependence of k_1 was discussed by Li et al [6] in terms of a competition between the back dissociation of a thermalized H2O4 species and its decomposition to H2O2 and O2. However it can be shown that the temperature dependence is easily accommodated within a pressure dependent association reaction. Following Tree [24], and assuming weak collisions, the model predicts an exponent n, for $k_{a,0}$ (= AT^{-n}), of 4 7. Comparison of this value with the experimental one of 1.9 ± 0.1 , which includes the temperature dependence of the pressure independent component, is not straightforward Experiments on the pressure dependence at elevated temperatures are needed before a quantitative treatment can be given, but it is clear that a strong negative temperature dependence of the type found experimentally can be adequately accounted for by the simple association mechanism.

Finally it is of interest to consider the nature of the pressure independent component of k_1 observed by Sander et al. [12]. Troe [2] measured k_1 over the temperature range 950-1450 K and obtained a value in the range $(17-33) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which is significantly greater than the value of 7.0 X 10-13 cm3 molecule-1 s-1 obtained at 1200 K by extrapolation of the present experimental results. One possible interpretation is that a direct abstraction mechanism, with a positive temperature dependence, sets in at higher temperatures. This mechanism may also account for the pressure independent component, $k_{1,0}$, but, if so, it must show a complex temperature dependence since the total experimental rate constant at 500 K is less than the value of $k_{1,0}$ at room temperature

A further possible mechanism for the pressure independent reaction can be invoked by considering the energetics of the overall reaction. Incorporating Howard's [27] value for $\Delta H_f(HO_2)$ and Nangia and Benson's estimated HO_2-O_2H bond dissociation enthalpy, gives the following enthalpies of reaction.

$$2HO_2 \rightarrow H_2O_4$$
, $\Delta H_{298}^0 = -37.7 \text{ mJ mol}^{-1}$;

 $H_2O_4 \rightarrow H_2O_2 + O_2(^3\Sigma), \Delta H_{298}^0 = -119.3 \text{ kJ mol}^{-1},$ $H_2O_4 \rightarrow H_2O_2 + O_2(^1\Delta), \Delta H_{298}^0 = -25.0 \text{ kJ mol}^{-1}.$ $O_2({}^{1}\Delta)$ is an energetically possible product although this route from H_2O_4 becomes increasingly endothermic if it is necessary to assume a larger dissociation enthalpy for $HO_2 - O_2H$. Thus two reaction channels, proceeding via H_2O_4 , may operate, although on surfaces of different multiplicity. Both would be expected to be pressure dependent, although these dependences may not be the same. A more detailed experimental study of the overall rate constant at pressures significantly lower than those examined by Sander et al. [12] is needed and it is relevant to note that Thrush and Wilkinson [5], working at pressures of 2-4 Torr

He, found no indication of a zero pressure intercept. A major problem for the associative mechanism is presented by the $DO_2 + DO_2$ reaction however. Analysis of the data of Sander et al. [12] leads to an apparent third-order rate constant of 1.9×10^{-32} cm⁶ molecule⁻² s⁻¹ for this reaction in a N₂ diluent; a factor of 2 8 times slower than the protonated case. It is interesting to note that a simple Troe calculation would suggest that the third-order rate constant should be faster by a factor of ≈ 2 on substituting deuterium, largely as a result of the increased density of states in D₂O₄ at the dissociation threshold.

More detailed calculations are in progress in an attempt to interpret this behavior [28].

Acknowledgement

The authors would like to thank Drs R.T. Watson and S.P. Sander for their collaboration in this work and Drs D.M. Golden and J.R. Barker for helpful discussions Financial support from S.E.R.C. and the Dixie Educational Foundation is gratefully acknowledged.

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