THE RATE CONSTANT FOR THE HO2+HO2 REACTION AT ELEVATED TEMPERATURES

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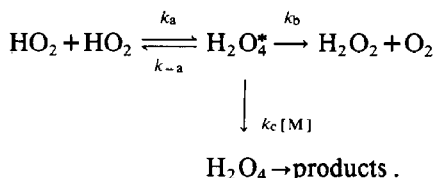*33405 Talence Cedex, France*

The HO2+HO2 reaction has been studied at atmospheric pressure between 298 and 777 K, using a new high-temperature flash photolysis/UV kinetic spectroscopy apparatus. An upward curvature of the Arrhenius plot is observed at temperatures above 600 K, supporting a recent suggestion that – in addition to the well-established low-temperature association complex mechanism – a direct abstraction reaction with a positive activation energy operates at combustion temperatures. Arrhenius parameters for this direct reaction are estimated.

1. Introduction

The hydroperoxy radial, HO2, is known to be an important intermediate in hydrocarbon combustion. The self-reaction

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (R1)$$
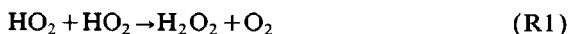
is particularly interesting, as it acts as a chain-termination step at low (< 800 K) temperatures, but as a chain-branching step at higher temperatures, owing to the thermal decomposition of the hydrogen peroxide product into two highly reactive hydroxy radicals [1]. The mechanism of reaction (R1) has aroused a great deal of experimental and theoretical interest. Sander and co-workers [2,3] have demonstrated that k_1 increases linearly with pressure, but displays a non-zero intercept at low pressures. In addition, both the zero pressure and third-order rate constants decrease with temperature. The reaction is thought to proceed via an association complex:

$$HO_2 + HO_2 \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} H_2O_4^* \overset{k_b}{\longrightarrow} H_2O_2 + O_2$$

$$\downarrow k_c[M]$$

$$H_2O_4 \rightarrow products .$$

Although reaction (R1) has been much studied

under conditions pertaining to atmospheric hydrocarbon oxidation [4–17], very little is known of its behaviour at combustion temperatures. Only the single temperature value of Troe [18] at 1100 K exists above 510 K, which is about a factor of five greater than the value obtained by extrapolation of the low-temperature data. In a recent paper, Walker et al. [19] suggested that an additional, direct bimolecular pathway becomes accessible at high temperatures:

$$HO_2 + HO_2 \overset{k_{1d}}{\longrightarrow} H_2O_2 + O_2 , \qquad (R1d)$$
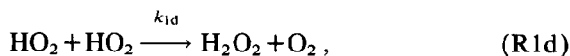
causing the overall rate constant to increase with temperature above 500 K, thereby reconciling the high-temperature point of Troe with the substantial body of data at lower temperatures.

In this paper we present new rate constant data for reaction (R1), at temperatures up to 777 K. These experiments form the first part of a series of direct studies of peroxy radical reactions at high temperatures.

2. Experimental

The apparatus used in the present study will be discussed in detail elsewhere [20]. Only the principal features will be described here. The cylindrical

reaction cell was made entirely of quartz, with a diameter of 4 cm and a central photolysis section of length 70 cm. The analysis beam was passed twice through the cell, giving an effective path length of 1.40 m. Photolysing radiation was provided by a single 80 cm quartz flash lamp, mounted parallel to the cell and capable of delivering 200 J in a 5 μs pulse. The flash lamp was operated with a Pyrex sleeve to cut out far-UV radiation. The cell was mounted in a cylindrical oven, capable of achieving temperatures of up to 1300 K. In practice, the operation of the flash lamp limited the experimental temperatures to 800 K and below, although it is hoped to extend the temperature range towards 900 K in the near future. The temperature, as measured by four thermocouples along the length of the photolysis volume, was stable to ±1%. The inside of the oven was lined with crinkled aluminium foil, to improve the homogeneity of the flash radiation.

Hydroperoxy radicals were monitored by time-resolved UV absorption spectroscopy at 200–227.5 nm (2.0 nm bandpass), following the flash lamp photolysis of suitable flowing gas mixtures at atmospheric pressure. Residence times were around 30 s, during which time the gas mixtures were typically photolysed once or twice. The much used $Cl_2/CH_3OH/air/h\nu$ system was employed to generate HO_2:

$$Cl_2 \xrightarrow{h\nu} 2\,Cl\,,$$

$$Cl + CH_3OH \rightarrow HCl + CH_2OH\,,$$

$$CH_2OH + O_2 \rightarrow H_2CO + HO_2\,.$$
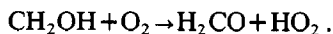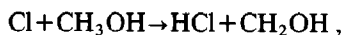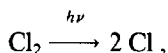
The majority of experiments were performed at 210 nm, which is close to the maximum of the HO_2 absorption.

Decay traces were signal averaged over typically 16 shots and analysed by non-linear least-squares analysis, which returned values of the initial concentration and k_1 ($-d[HO_2]/dt = 2k_1[HO_2]^2$) for each experiment. Absorption cross sections for H_2O_2 were taken from the NASA evaluation [21]. Reactant concentrations (in molecules cm^{-3}) and purities were: $[Cl_2]$ (l'Air Liquide, 5% in N_2) (2–6)×10^{16}; $[CH_3OH]$ (Merck, spectroscopic grade purity) (1–15)×10^{15}; synthetic air (l'Air Liquide, purity N_2: 99.95%, purity O_2: 99.5%) to 760 Torr.

3. Results

Experiments were performed between 298 and 777 K. Experiments at higher temperatures were hindered by the poor operation of the flash lamp and consequent low flash energies. In addition, a reduction in signal, which could not be wholly attributed to the reduction in flash energy, was observed above 800 K. The drop in signal was accompanied by a distortion of the kinetics away from true second order and a reduction in the steady-state light level at short (<210 nm) wavelengths. Under all other conditions, good second-order decay traces were obtained. At each temperature, k_1 was measured at atmospheric pressure. The concentrations of Cl_2 and CH_3OH, the flash energy and the time between flashes were routinely varied by factors of four. A typical decay trace and fit are shown in fig. 1.

A relative spectrum for HO_2 was obtained between 200 and 250 nm at each temperature. The shape of the spectrum was, within experimental error, independent of temperature between 200 and 227.5 nm. With increasing temperature, the value of σ at longer wavelengths increased somewhat in size relative to the maximum. Full details of these spectra will be discussed in a future publication [20]. The values of $\sigma(HO_2)$ were normalised to 3.0×10^{-18} cm^2 at 227.5 nm, in line with the NASA recommendation [21]. Only experiments performed at wavelengths between 200 and 227.5 nm, where the signal-to-noise ratio was much better than at longer wavelengths, were used in the calculation of k_1. The values of
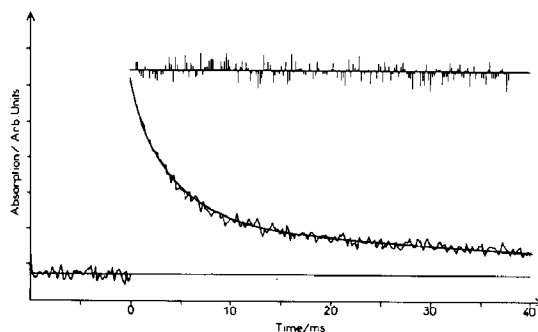

Fig. 1. HO_2 decay trace and fit to second-order kinetics with an absorbing product (H_2O_2). Residuals are expanded by a factor of two. Experimental conditions: 777 ± 5 K, 760 Torr air, 16 shots, $[Cl_2] = 3.5 \times 10^{16}$ molecules cm^{-3}, $[CH_3OH] = 2.0 \times 10^{15}$ molecules cm^{-3}, $[HO_2]_0 = 1.75 \times 10^{14}$ molecules cm^{-3}.

Table 1
Values of $\sigma(HO_2)$ obtained in the present study [a]

λ (nm)	$10^{18}\sigma(HO_2)$ (cm^2)
200	4.8 ± 0.4 [b]
210	4.4 ± 0.3
220	3.7 ± 0.4
227.5	3.0

[a] The relative values obtained in this work are normalised to the value of $(3.0\pm0.4)\times10^{-18}$ cm^2 obtained by Sander and co-workers at 227.5 nm and subsequently recommended by the NASA evaluation.

[b] Errors are 1σ.

$\sigma(HO_2)$ obtained at the appropriate experimental wavelengths and averated over all temperatures are given in table 1. No systematic dependence of k_1 on experimental conditions other than temperature was found. The values of k_1/σ obtained at 210 nm are given in table 2.

Experiments of this nature obviously yield k/σ, rather than k directly and any dependence of σ on temperature will be reflected in the experimental measurements. Kijewski and Troe [22] have performed calculations on the effect of temperature on $\sigma(HO_2)$, assuming a steeply repulsive upper state; the shape of the absorption spectrum was obtained from a reflection of the ground-state wavefunction in the excited-state wavefunction. At low temperatures, when only the ground vibrational level is populated, this procedure gives rise to an approximately Gaussian absorption profile. As the temperature increases and vibrational levels other than the ground state become populated, a gradual broadening of the spectrum and a consequent decrease in the absorption cross section in the centre of the band with increas-
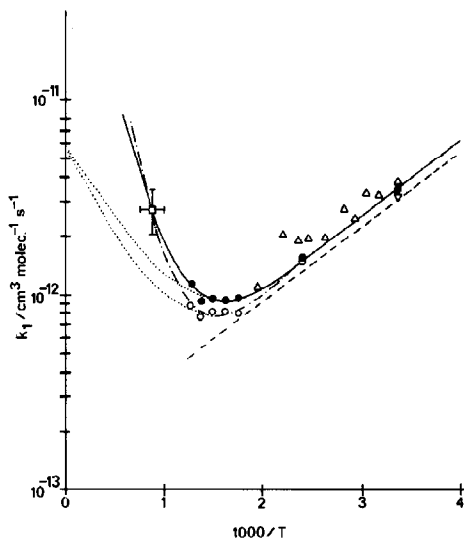
Table 2
Values of k_1/σ obtained in the present study

T (K)	$10^{-5} k/\sigma$ (s^{-1})	Number of experiments
298	7.6 ± 2.0 [a]	13
418	3.5 ± 1.1	6
577	2.2 ± 0.3	8
623	2.1 ± 0.5	4
677	2.2 ± 0.4	7
723	2.1 ± 0.4	5
777	2.6 ± 0.7	14

[a] Errors are 2σ and include a Student's t.

Fig. 2. Arrhenius plot of k_1. ($\triangle$)Patrick and Pilling [11]. (∇) Kurylo et al. [17]. (– – –) Exponential fit to the data of Kircher and Sander [3]. ($\square$) Troe [18]. ($\bullet$) Present data, uncorrected for the temperature dependence of $\sigma(HO_2)$. ($\bigcirc$) Present data, corrected for the temperature dependence of $\sigma(HO_2)$ according to the prescription of Kijewski and Troe [22]. (- - -) Fit of the sum of two exponentials to the present uncorrected data, plus that of Troe [18]. (–.–.–) The same fit, using our corrected data. (...) Fits to the corrected and uncorrected data, using $A_{1d}=5.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1}. See text for details.

ing temperature is predicted. Using their expression for $\sigma(\lambda, T)$, the absorption cross section at 210 nm can be represented by

$$\sigma(210\,\text{nm}, T)/\sigma(210\,\text{nm}, 300\,\text{K})$$

$$= 1.00-2.16\exp(-1801/T). \qquad (1)$$

A 21% decrease in the value of σ at 210 nm is thus estimated between 300 and 777 K. Our observations of a broadening of the spectrum at high temperatures is consistent with these calculations. The present data, with and without a correction for the estimated change in σ with temperature, are shown in fig. 2.

4. Discussion

At pressures above a few tens of Torr, a direct comparison of the results obtained in different laboratories is complicated by the dependence of the rate constant for the termolecular reaction on tempera-

ture, pressure and the nature of the bath gas. All studies at pressures above 20 Torr have used UV absorption spectroscopy to monitor the concentration of the hydroperoxy radical.

The most extensive data to date are those of Sander and co-workers [2,3], who studied k_1 over a wide range of temperature (230–417 K), pressure (100–700 Torr) and used both argon and nitrogen as bath gases. For nitrogen, a global expression for k_1 (in cm^3 molecule^{-1} s^{-1}) was obtained:

$$k_1 = 2.2 \times 10^{-13} \exp(620/T)$$
$$+ 1.9 \times 10^{-33} [M] \exp(980/T), \qquad (2)$$

which is virtually identical to the expression recently obtained by Veyret and Lesclaux [23], after minor differences in $\sigma(HO_2)$ are accounted for. In view of the good agreement between our own values and those predicted by Kircher and Sander (vide infra), we have used the above expression to correct values from other laboratories to 760 Torr. Kurylo et al. [17] have recently shown that the third-body collision efficiencies of nitrogen and oxygen are very similar in this system. A direct comparison between results obtained in nitrogen and those obtained in air should thus be valid. The correction procedure involved fitting eq. (2) to an Arrhenius form over the appropriate temperature range, at 760 Torr and at the pressure of the study to be corrected. Comparison of the two sets of Arrhenius parameters gave the appropriate correction over the required temperature range.

The results of previous studies of the dependence of k_1 on temperature at high pressure are summarised in table 3. Where minor corrections have been made to the published parameters, owing to differences in experimental pressures or in the values used for $\sigma(HO_2)$, these are indicated. For the purposes of comparison, eq. (2) was fitted to an exponential form between 250 and 500 K. The four sets of Arrhenius parameters produce rate constants which are in reasonable agreement over their quoted temperature ranges, although there is a good deal of scatter in the individual values of A_1 and E_1/R. The curve calculated from eq. (2) at 760 Torr is plotted in fig. 2, together with the present data, the data of Patrick and Pilling [11], the single point of Troe and the value derived for 298 K and 760 Torr of air from the recent work of Kurylo et al. [17]. At 298 K, all the data coincide within their quoted 1σ uncertainties. In general, the data of Patrick and Pilling lie around 25% above the values predicted by Kircher and Sander. Up to 577 K, our own values lie close to the values predicted using the data of Kircher and Sander (which stop at 420 K), but then cease to decrease and begin to increase with increasing temperature. At our highest temperature (777±8 K), our value of k_1 is approximately a factor of two greater than that predicted using the data of Kircher and Sander.

The high value of k_1 found at around 1100 K in the early study of Troe [18] formed the basis for the suggestion of Walker and co-workers [19] that a further reaction channel with a positive activation energy exists, and so must be considered in some detail.

Table 3
Previous determinations of the temperature dependence of k_1

Ref.	Technique [a]	Temperature range (K)	Pressure (Torr)	Bath gas	$10^{13}A_1$ (cm^3 molecule^{-1} s^{-1})	$-E_1/R$ (K)
[6] [b]	MMS/UV	273–339	760	O_2, N_2, SF_6	0.40±0.15 [f]	1245±92
[7] [c]	PR/UV	276–400	1200	H_2	1.37±0.19	981±45
[11] [d]	FP/UV	298–510	700	N_2	4.10±1.14	693±115
[2,3] [e]	FP/UV	230–420	100–700	N_2	1.56	885

[a] MMS/UV: molecular modulation spectroscopy; PR/UV: pulse radiolysis/UV absorption, FP/UV: flash photolysis/UV absorption.
[b] Used $\sigma(HO_2) = 3.5 \times 10^{-18}$ cm^2 at 220 nm. Corrected to 3.7×10^{-18} cm^2.
[c] Used $\sigma(HO_2) = 2.17 \times 10^{-18}$ cm^2 at 230 nm. Corrected to 2.5×10^{-18} cm^2. Corrected to 760 Torr, assuming similar third-body behaviour for H_2 and N_2.
[d] Corrected to 760 Torr.
[e] Arrhenius parameters are from a fit to the values predicted by eq. (1) from 250 to 500 K. See text.
[f] Errors 1σ.

Troe monitored the concentrations of both H_2O_2 and HO_2, following the shock heating of H_2O_2/Ar mixtures. A complex reaction scheme was used to model the system. The data between ≈ 980 and ≈ 1250 K could be fitted if values of k_1 between 1.7×10^{-12} and 3.3×10^{-12} cm^3 molecule^{-1} s^{-1} were used. At 1100 K a value of 3.5×10^{-18} cm^2 molecule^{-1} for $\sigma(HO_2)$ at 220 nm was obtained, very close to the value of 3.7×10^{-18} cm^2 molecule^{-1} used in the present study, although a factor of two was quoted as the error limits on σ. For the purposes of the present study, a value of $k_1(1100 \text{ K}) = (2.5 \pm 0.8) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} has been assumed.

Walker and co-workers [19] used an estimated value of 5.7×10^{-12} cm^3 molecule^{-1} s^{-1} for the A factor of the postulated direct reaction A_{1d}, and Troe's value for k_1 at 1100 K to estimate an activation energy, E_{1d}, of 6.7 kJ mol^{-1} for the direct reaction. These Arrhenius parameters were used to correct the low pressure values of Kircher and Sander: the negative activation energy was doubled in magnitude and the A factor was decreased by an order of magnitude. The resulting model predicts a minimum at around 400 K for the low-pressure rate constant and around 460 K for the effective rate constant at 700 Torr. It was suggested that the highest temperature point of Patrick and Pilling could be seriously in error, as it lay well below the suggested curve. Our own results are, however, in good agreement with their results at high temperature. The present results suggest a minimum in k_1 between 600 and 700 K, supporting the idea of a further reaction channel with a positive activation energy, although a much higher value of E_{1d} than that predicted by Walker and co-workers [19] is implied.

In an attempt to extract Arrhenius parameters for the direct reaction, our own data, with that of Troe, were fitted to the sum of two exponentials:

$$k_1 = A_1 \exp(-E_1/RT) + A_2 \exp(-E_2/RT) . \quad (3)$$

The best method of fitting involved the floating of three parameters, A_1, E_1 and A_2, and fixing E_2 to the value derived from eq. (2). This procedure prevented the slight discrepancies between our own data and those of Kircher and Sander from biasing the fit, yet made use of the extensive low-temperature literature and enabled E_{1d} to be determined with better precision. The results of the three-parameter fits were

not strongly dependent on the Troe measurement, owing to its poor precision and consequent small weighting in the weighted fit, although the estimated errors are improved by its inclusion. The best fit values of A_1, E_1 and A_2 are (using $E_2 = -7.36$ kJ mol^{-1}): $A_1 = (5.9 \pm 3.9) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, $E_1 = 31 \pm 5$ kJ mol^{-1} and $A_2 = (1.8 \pm 0.2) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} for the data uncorrected for the temperature dependence of σ and $A_1 = (2.1 \pm 1.6) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, $E_1 = 42 \pm 6$ kJ mol^{-1} and $A_2 = (1.8 \pm 0.1) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} for the corrected data. It is clear that A_1 is very poorly determined and, particularly for the corrected data, rather too high. If the more realistic estimate of Walker and co-workers [19] (5.7×10^{-12} cm^3 molecule^{-1} s^{-1}) is used, then the present data can be well reproduced with $E_2 = 16 \pm 3$ kJ mol^{-1} (uncorrected data) and $E_2 = 20 \pm 4$ kJ mol^{-1} (corrected data). Such a value for A_1 is, however, incompatible with the result of Troe [18]. The results of the various fitting procedures are shown in fig. 2. One important consequence of such a large activation energy is that the contribution of k_{1d} to k_1 in the experiments performed below 600 K will be negligible and results derived from them require no reinterpretation.

The existence (or non-existence) of an increase in the value of k_1 with temperature above 600 K is clearly of importance in the modelling of combustion systems. The question which must be posed is whether the present experiments demonstrate the existence of such an effect, or whether the increase seen here is either within experimental error, or due to some experimental artefact.

At the highest temperature at which k_1 is reported here (777 K), the value obtained is a factor of two greater than that predicted by eq. (2), well outside the 2σ confidence limits.

The practical upper temperature limit was fixed by the thermal reaction of the precursor mixture. At 777 K and below, all decay traces displayed good second-order behaviour. At 800 K, a slight, unidentified first-order component to the decay profiles was noticed, together with a slight reduction in signal. At 825 K, the distortion of the decay traces was marked and the signal level further reduced. The reduction in signal and change in kinetic behaviour is presumably a consequence of chain reactions of the $CH_3OH/$

O_2 system: 800 K is very close to the ignition temperature for dilute mixtures of methanol in an atmosphere of air [24]. A rapid thermal oxidation of the precursor under such conditions is not unexpected. It is well known that the rate of thermal oxidation of simple organic molecules increases very rapidly as the ignition temperature is approached. Conversely, at 777 K, more than 20 K below the temperature where minor problems associated with the thermal decomposition of the precursor were first noticed, such processes should be negligible on the timescale (≈ 20 s) of the present experiments.

The possibility of the reaction of HO_2 with precursor molecules or a steady-state radical concentration caused by the thermal reaction and the subsequent introduction of an additional first-order loss term into the HO_2 decay can be excluded. If a value of k_1 calculated from eq. (2) at 777 K is used, then the magnitude of the first-order loss term which is required to bring the HO_2 decay back to the correct timescale is more than enough to make the resulting decay trace obviously non-second-order. Indeed, particular care was taken at 777 K to ensure that the observed kinetics were truly second order and showed no systematic dependence on experimental variables such as the chlorine and methanol concentrations, the flash energy and the residence time of the gas mixture in the cell.

In addition, preliminary results in this laboratory using the far-UV photolysis of molecular oxygen in the presence of methanol as the source of hydroperoxy radicals [25] confirm that k_1 does not decrease between 575 and 675 K. It thus seems very likely that the observed upturn in k_1 with temperature is real.

5. Conclusions

The rate constant for the self-reaction of hydroperoxy radicals appears to increase with temperature above 700 K, in accordance with a recent suggestion by Walker and co-workers [19] that a direct abstraction mechanism with a positive activation energy may operate at high temperature. The observed increase does, however, need confirmation and further experiments are clearly required at temperatures beyond the range of the present apparatus, particularly if the Arrhenius parameters for the abstraction reaction are to be determined.

Experiments are in progress in this laboratory with the present experimental arrangement. It is hoped to extend the working temperature range of the apparatus towards 900 K in the near future and to verify the present findings with further chemical systems for generating HO_2. In addition, we hope to define the A factor for the abstraction better by the use of semi-empirical quantum methods. Experiments in the region 800 to 1200 K, using different techniques, are clearly needed.

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