A flash photolysis study of the $HO_2+HCHO \rightarrow H_2O_2+HCO$ reaction between 541 and 656 K

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The kinetics of the reaction $HO_2+HCHO \rightarrow H_2O_2+HCO$ have been studied between 541 and 656 K, using the flash photolysis/UV absorption technique. The results are in good agreement with the only existing, single-temperature literature measurement of Baldwin and co-workers. An unweighted, logarithmic Arrhenius fit to the present data and the literature measurement gives $k_1 = 3.5\times10^{-13}\exp(-38.4\ \mathrm{kJ\ mol^{-1}}/RT)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ over the temperature range 541–773 K.

1. Introduction

The hydroperoxy radical, HO_2, is ubiquitous in oxidation systems and a knowledge of its chemistry is central to our understanding of hydrocarbon combustion [1]. The abstraction reactions of hydroperoxy and other peroxy radicals are important elementary steps in combustion processes, producing hydroperoxide species which act as branching agents in autoignition processes [2]. Despite their admitted importance, these reactions are quite poorly understood. No direct studies of the abstraction reactions of HO_2 have been published and the available data are largely due to the work of a single group: over a number of years, Walker and co-workers have built up an extensive database on HO_2 abstraction reactions, using classical product analysis techniques in which small quantities of hydrocarbons are added to slowly reacting hydrogen–oxygen mixtures [3–7]. Until now, there has been no experimental confirmation of the HO_2 abstraction rate constants obtained using this technique.

In this article, we present data, derived from time-resolved flash photolysis experiments, on the rate constant for the abstraction reaction of hydroperoxy radicals with formaldehyde,

$$HO_2+HCHO \rightarrow H_2O_2+HCO \qquad (1)$$

between 541 and 656 K.

2. Experimental

The apparatus used in the present study has already been described in detail [8]. Briefly, hydroperoxy radicals were generated by flash photolysis of slowly flowing gas mixtures in a quartz cell located in an electrically heated oven. Typical residence times in the cell were of the order of 20 s. The radicals were monitored by time-resolved UV absorption at 210 nm, with a 2 nm bandpass. Transient optical density traces were collected on a digital storage oscilloscope and transferred to a microcomputer for averaging and data processing by numerical integration/non-linear least-squares analysis. All experiments were performed at a total pressure of 760 Torr.

Two methods of radical generation were employed. In the majority of experiments, broad band (200–360 nm) flash photolysis of formaldehyde was used. Owing to the low output of the flash lamp at wavelengths below 220 nm and the low absorption cross sections of formaldehyde in the same region [9], photolysis of formaldehyde certainly occurred

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almost exclusively in the 300 nm band, where two photolysis channels are possible [9]:

$$\mathrm{HCHO}+h\nu\rightarrow\mathrm{H}+\mathrm{HCO}\,, \qquad (\mathrm{P1})$$

$$\mathrm{HCHO}+h\nu\rightarrow\mathrm{H_2}+\mathrm{CO}\,. \qquad (\mathrm{P2})$$

The second of these channels gives molecular products which are inert for the purposes of the present experiment. The formyl radicals produced in channel (P1) react rapidly on the millisecond timescale of the present experiments to produce HO_2:

$$\mathrm{HCO}+\mathrm{O_2}\rightarrow\mathrm{HO_2}+\mathrm{CO}. \qquad (2)$$

Concentrations of molecular oxygen were sufficiently elevated that the unimolecular decomposition of HCO [10], its self-reaction [11] and reaction with H [12] were negligible compared to reaction (2) [13]. The hydrogen atoms produced in channel (P1) similarly reacted rapidly on the timescale of the present experiments, either with formaldehyde, giving formyl radicals [14]:

$$\mathrm{H}+\mathrm{HCHO}\rightarrow\mathrm{H_2}+\mathrm{HCO}\,, \qquad (3)$$

which were again quickly converted to HO_2 via reaction (2), or with molecular oxygen [15]:

$$\mathrm{H}+\mathrm{O_2}+\mathrm{M}\rightarrow\mathrm{HO_2}+\mathrm{M}\,, \qquad (4)$$

again producing HO_2.

For some experiments, hydroperoxy radicals were generated by the flash photolysis of molecular chlorine in the presence of formaldehyde:

$$\mathrm{Cl_2}+h\nu\rightarrow 2\mathrm{Cl}\,, \qquad (\mathrm{P3})$$

$$\mathrm{Cl}+\mathrm{HCHO}\rightarrow\mathrm{HCl}+\mathrm{HCO} \qquad (5)$$

(ref. [15]),

$$\mathrm{HCO}+\mathrm{O_2}\rightarrow\mathrm{HO_2}+\mathrm{CO}\,. \qquad (2)$$

For these latter experiments, a Pyrex filter was used for the flash lamp, restricting the photolysis radication to wavelengths above 280 nm. Under such conditions, the radical yield from the photolysis of molecular chlorine, at the concentrations employed in the present experiments, was around ten times greater than that from the photolysis of formaldehyde, owing to the much greater integrated absorption cross section of chlorine around 300 nm [15].

Following the production of the radicals, which was complete within 100 μs, time-resolved optical density profiles were recorded over up to 1 s. Under conditions where reaction (1) is unimportant, the only loss process for hydroperoxy radicals is their self-reaction:

$$\mathrm{HO_2}+\mathrm{HO_2}\rightarrow\mathrm{H_2O_2}+\mathrm{O_2}\,. \qquad (6)$$

Reaction (6) has been studied at temperatures up to 777 K in this laboratory [16]. In the present experiments, the removal of hydroperoxy radicals was monitored at 210 nm, using previously determined temperature-dependent absorption cross sections [17]. The hydrogen peroxide product of reaction (6) gives rise to a weak residual absorption at the monitoring wavelength, where $\sigma(\mathrm{H_2O_2})=35.7\times10^{-20}$ $\mathrm{cm^2\ molecule^{-1}}$, less than 10% of that of the hydroperoxy radical [15].

Under the present experimental conditions of relatively high $[\mathrm{O_2}]$, even when reaction (1) competes with reaction (6) for the removal of hydroperoxy radicals, the radical decay is unchanged as HO_2 is rapidly regenerated via reaction (2). The net effect of the occurrence of reaction (1) (and subsequently reaction (2)) is the conversion of formaldehyde to hydrogen peroxide:

$$\begin{array}{lll} \mathrm{HO_2}+\mathrm{HCHO} & \rightarrow\mathrm{H_2O_2}+\mathrm{HCO} & (1)\\ \mathrm{HCO}+\mathrm{O_2} & \rightarrow\mathrm{HO_2}+\mathrm{CO} & (2)\\ \hline \mathrm{HCHO}+\mathrm{O_2} & \rightarrow\mathrm{H_2O_2}+\mathrm{CO}. & \end{array}$$

As the absorption cross section of formaldehyde is very small compared to that of hydrogen peroxide at 210 nm [9], the above chain results in an increased residual absorption when reaction (1) is important. The basis of the present experiments was thus to monitor the HO_2 decay and to look for residual absorptions over and above that expected on the basis of reaction (6) alone.

Gaseous formaldehyde was generated by passing nitrogen over solid paraformaldehyde held at 388 K in a thermostatted heat bath. a triple U-bend trap at 198 K was used downstream of the formaldehyde generator to condense out water vapour and any formaldehyde polymers. All parts of the gas handling system in contact with gaseous formaldehyde were kept hot by means of heating tape. In this way, stable concentrations of formaldehyde of $\approx2\times10^{17}$ $\mathrm{molecule\ cm^{-3}}$ could be routinely achieved at one atmosphere total pressure, with total flows of 1000 sccm, of which 10% passed over the solid formaldehyde.

The concentration of formaldehyde was measured in situ, before and after each set of experiments using its UV absorption spectrum [18]. A digitized spectrum, kindly supplied by Dr. J.N. Crowley (MPI, Mainz) was used rather than published spectra as it could be easily convoluted with the present experimental resolution of 2 nm. The usual monitoring wavelength was 285.5 nm, corresponding to a peak in the highly structured formaldehyde spectrum, where $\sigma(\mathrm{HCHO})=4.6\times10^{-20}$ cm^2 molecule^{-1}. By using a rather low monitoring wavelength resolution and a peak of the formaldehyde spectrum, it was hoped that the effect of temperature on the formaldehyde cross sections was minimized (see below). A few confirmatory experiments were also performed using a monitoring wavelength of 304.4 nm, again corresponding to a peak in the formaldehyde spectrum and where $\sigma(\mathrm{HCHO})=7.0\times10^{-20}$ cm^2 molecule^{-1} [18].

Typical concentrations in experiments where the direct photolysis of formaldehyde was used to generate the radicals were (in molecule cm^{-3}) HCHO: $(0.5\text{–}1.6)\times10^{17}$; O_2: $(0.25\text{–}2.0)\times10^{18}$; N_2: balance to 760 Torr; initial radical concentration: $(1\text{–}3)\times10^{13}$. In experiments where the UV photolysis of molecular chlorine was used to generate the radicals, typical concentrations were (in molecule cm^{-3}) Cl_2: 3×10^{16}; HCHO: $(1\text{–}3)\times10^{17}$; O_2: $(0.25\text{–}2.0)\times10^{18}$; N_2: balance to 760 Torr; initial radical concentration: $(1.5\text{–}2.5)\times10^{14}$. Materials used in the present study were paraformaldehyde (Prolabo), O_2 (AGA Gaz Spéciaux), Cl_2 (5% in N_2, AGA Gaz Spéciaux) and N_2 (AGA Gaz Spéciaux).

3. Results and discussion

Below 541 K, the removal of hydroperoxy radicals could be well described by a second-order process and the experimental traces were fitted with two adjustable parameters: the initial radical concentration and k_6. The values of k_6 returned were in good agreement with those previously determined in this laboratory, using both the photolysis of $Cl_2/CH_3OH/O_2/N_2$ and O_2/CH_3OH mixtures for radical generation [16,19]. At 541 K and above, the residual absorption was significantly greater than that expected on the basis of reaction (6) alone, demonstrating the occurrence of the chain involving reactions (1) and (2). At 541 K and above, a three parameter fit was hence employed, with the initial radical concentration, k_6 and k_1 as variables. A typical decay trace and fit is shown in fig. 1 for a temperature of 656 K. Simulations showed that a pseudo first-order rate constant, $k_1[\mathrm{HCHO}]$, of approximately 20 s^{-1} was necessary for reaction (1) to be detectable in the present experiments. For example, for the experiment shown in fig. 1, $k_1[\mathrm{HCHO}]=28.6$ s^{-1} and the final yield of hydrogen peroxide is equal to $1.99[\mathrm{HO_2}]_{t=0}$, corresponding to 1.49 cycles of reactions (1) and (2) during the lifetime of the radicals. The experimental results are summarized in table 1 and the values of k_1 plotted in Arrhenius form in fig. 2.

Between 541 and 656 K, the optimized values of k_6 were in good agreement with those previously obtained [16,19]. At higher temperatures, however, the returned values of k_6 were no longer in accord with our previous work, increasing rapidly with temperature. In addition, at these elevated temperatures and for experiments where molecular chlorine was used to generate the radicals, there was evidence for the occurrence of chain decomposition of the reaction mixture over its residence time in the reactor: the formaldehyde concentration was not stable and the transmitted light intensity at 210 nm was very low, suggesting the production of significant quantities of hydrogen peroxide. In view of the possibility of thermal reactions, perhaps initiated on the walls of the reactor, we prefer not to include any results obtained at temperatures above 656 K. In order to check for potential problems with thermal decomposition at 656 K and below, the oxygen concentration was varied systematically over a factor of at least four at most temperatures. No systematic dependence of the results on oxygen concentration was observed. Similarly, no systematic dependence of the results on variation of the formaldehyde concentration within the limits given above, or on the wavelength employed to monitor the formaldehyde concentration was observed. It can be seen from table 1 that the results obtained with the two radical generation systems are in good agreement, despite very (an order of magnitude) different initial radical concentra-

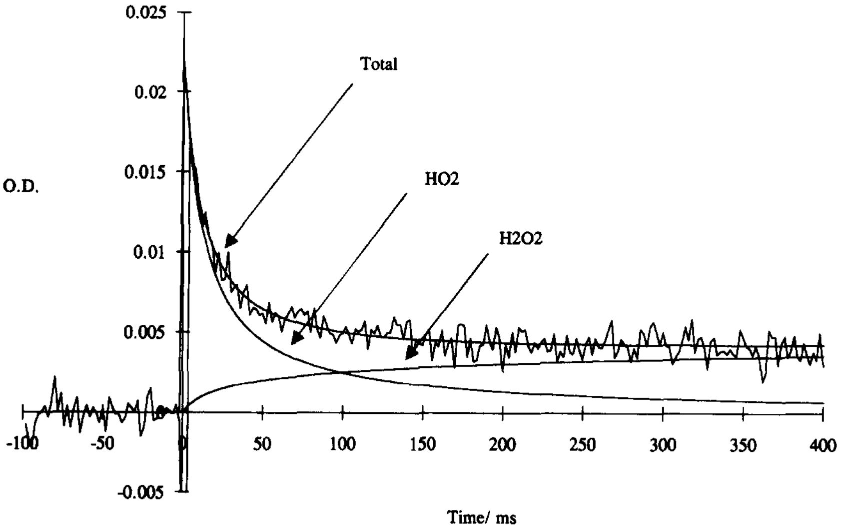

Fig. 1. Typical trace of optical density (natural logarithms) versus time, plus fit, 656 K. [HCHO] $= 1.38\times10^{17}$ molecule cm^{-3}; $O_2 = 1.86\times10^{18}$ molecule cm^{-3}; $[HO_2]_{t=0} = 3.98\times10^{13}$ molecule cm^{-3}; $k_1 = 2.07\times10^{-16}$ cm^3 molecule^{-1} s^{-1}; $k_2 = 1.01\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Table 1
Bimolecular rate constants

T (K)	Radical generation	$10^{-13}k_6$ [a]	Exp.	$10^{-16}k_1$ [a]	Exp.
418	Cl_2/HCHO	20.0±0.3	[2]		
470	Cl_2/HCHO	11.9±1.0	[4]		
516	HCHO	8.8±0.9	[2]		
516	Cl_2/HCHO	10.5	[1]		
525	Cl_2/HCHO	9.5±0.7	[6]		
541	HCHO	9.5±1.5	[7]	0.66±0.24	[7]
592	HCHO	6.1±1.2	[7]	1.56±0.65	[9]
592	Cl_2/HCHO	9.8±0.4	[5]	1.81±1.02	[5]
616	HCHO	9.2±1.9	[7]	1.7±1.09	[7]
621	Cl_2/HCHO	9.3±1.4	[5]	1.66±0.22	[3]
624	HCHO	9.2±1.6	[11]	2.07±1.14	[11]
656	HCHO	11.1±0.2	[9]	3.19±1.33	[9]
773				9.26±1.07 [b]	

[a] Units cm^3 molecule^{-1} s^{-1}; errors 1σ, including a Student's t.
[b] Value of Baldwin and Walker [3].

tions, lending further confidence to the experimental results.

As far as we are aware, the only existing experimental determination of k_1 is the single temperature measurement of Baldwin and Walker at 773 K [3]. In fact, the ratio $k_1/(k_6)^{1/2} = (9.4\pm1.0)\times10^{-10}$ cm$^{-3/2}$ molecule$^{-1/2}$ s$^{-1/2}$ was derived, rather than k_1 directly. Using $k_6/\sigma(HO_2, 210\text{ nm}) = (2.6\pm0.2)\times10^5$ cm s^{-1} at 775 K [16], and $\sigma(HO_2, 210\text{ nm}, 775\text{ K}) = 3.76\times10^{-18}$ cm^2 molecule^{-1} [17], we calculate $k_1 = (9.3\pm1.1)\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 773 K. As can be seen from fig. 2, this value is entirely consistent with the present experimental results. In view of this consistency and the limited temperature range of our experiments, both the present data and the data of Baldwin and Walker were

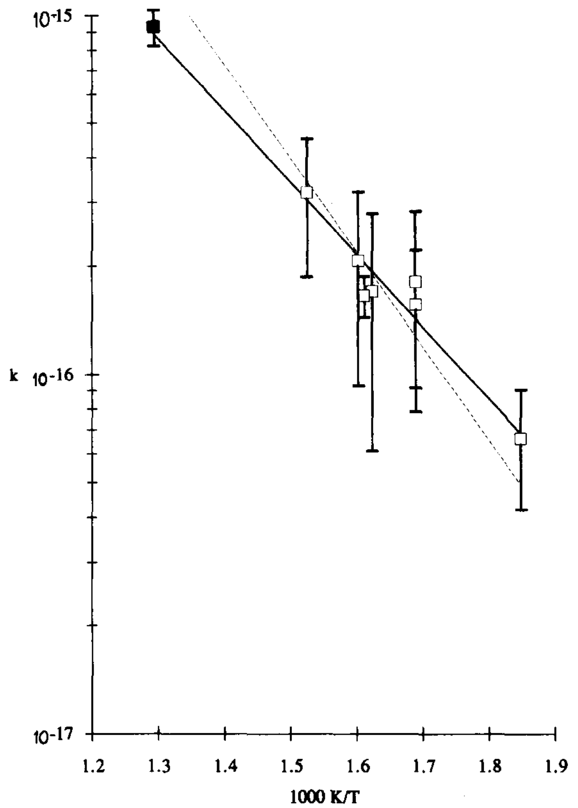

Fig. 2. Arrhenius plot for k_1 in units of cm^3 $molecule^{-1}$ s^{-1}. (□) This work; (■) ref. [3]. Error bars represent 1σ statistical uncertainties. The solid line represents a non-weighted fit to $k=A\exp(-E/RT)$; the dotted line represents a fit to $k=A\exp(-50\ \mathrm{kJ\ mol^{-1}}/RT)$. See text for discussion.

fitted to the Arrhenius expression. As it is difficult to estimate possible systematic errors in the present work and the work of Baldwin and Walker, an unweighted logarithmic fit was performed, giving

$$k_1=(3.5^{+2.7}_{-1.5})\times10^{-13}\exp[-(38.4\pm2.9)\ \mathrm{kJ\ mol^{-1}}/RT]\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ .$$

The low statistical uncertainties on the A factor and the activation energy arise from the low scatter of the data about the unweighted fit. In view of the experimental uncertainties on the present experimental determinations at each temperature, realistic uncertainties would be rather greater. Indeed, the A factor appears perhaps a little low for an abstraction reaction and the activation energy is significantly lower than the value of 50 kJ mol^{-1} estimated by Baldwin and Walker [3] on the basis of activation energies found for other HO_2+RH reactions and the corresponding C–H bond strengths. Fitting the present data and the data of Baldwin and Walker using $E_1=50$ kJ mol^{-1} gives $A=(3.3\pm0.3)\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. As can be seen from fig. 2, the fit to the experimental data, although not as good as the two-parameter fit, is not unreasonable; it is clear that a range of pairs of Arrhenius parameters could be accommodated by the present data over its limited temperature range. Furthermore, many hydrogen atom abstraction reactions are now believed to demonstrate non-Arrhenius behaviour – a $T^{2.5}$ term in the pre-exponential factor is not uncommon [20]. Such a strong pre-exponential term would result in an activation energy of 50 kJ mol^{-1} at around 1200 K for the present data. The above expression for k_1 is thus only valid over the range 500–800 K; extrapolation outside of this temperature range should be treated with caution.

Possible sources of systematic error in the present experiments lie in the temperature dependences of the absorption cross sections of hydrogen peroxide and formaldehyde – the measured values of k_1 are directly dependent on the absorption cross sections of these species. Nicovich and Wine studied the temperature dependence of the hydrogen peroxide spectrum over the range 285–381 K, with an aim to extrapolating the data down to lower temperatures [21]. Although a pronounced temperature dependence was observed at wavelengths above 250 nm, no systematic temperature dependence was found over the range 193–230 nm. Similarly, in shock tube experiments, Kijewski and Troe [22] observed no change in the spectrum over the range 190–230 nm from 650 to 1100 K. It seems thus justified to use the currently recommended room temperature cross section at 210 nm [15] for the present data analysis. The temperature dependence of the formaldehyde absorption cross sections is rather more difficult to estimate, owing to the absence of high temperature data and the highly structured nature of the spectrum. The concentration of formaldehyde was monitored at the resolution of 2 nm used for kinetic experiments, rather than at higher resolution, in order to reduce the effects of changes in rotational population on the absolute cross sections. We believe that it is unlikely that the cross sections used in the present experiments, and hence the rate constants derived, are erroneous by more than a factor of two and could easily be corrected if a high-temperature formaldehyde spectrum becomes available.

The values of k_1 obtained in this study, which represent the first determination of rate constants for a HO_2 abstraction reaction using a time-resolved technique, are in good agreement with the single-temperature measurement of Baldwin and Walker, obtained using an entirely different technique [3]. As such, the present results also provide indirect support for the values measured by the same group for the HO_2 abstraction reactions with methane [7], ethane [5], tetramethylbutane [4] and 2,3-dimethylbutane [6]. Although the results were obtained over a narrow temperature range, they cover a significant part of the range (500–1000 K) important for HO_2/H_2O_2 chemistry in combustion systems.

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