The Temperature Dependence of the Rate Coefficients for *β*-Hydroxyperoxy Radical Self Reactions

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ABSTRACT: A laser-flash photolysis/UV absorption technique has been used to study the temperature dependence (from $T = 300-470$ K) of the self-reaction kinetics of representative primary, secondary, and tertiary β-hydroxyperoxy radicals:

$$\begin{aligned}
2\,\mathrm{HOCH_2CH_2O_2} &\longrightarrow 2\,\mathrm{HOCH_2CH_2O} + \mathrm{O_2} && \text{(1a)}\\
&\longrightarrow \mathrm{HOCH_2CH_2OH} + \mathrm{HOCH_2CHO} + \mathrm{O_2} && \text{(1b)}\\
2\,\mathrm{HOCH(CH_3)CH(CH_3)O_2} &\longrightarrow 2\,\mathrm{HOCH(CH_3)CH(CH_3)O} + \mathrm{O_2} && \text{(2a)}\\
&\longrightarrow \mathrm{HOCH(CH_3)CH(CH_3)OH}\\
&\qquad + \mathrm{HOCH(CH_3)C(CH_3)O} + \mathrm{O_2} && \text{(2b)}\\
2\,\mathrm{HOC(CH_3)_2C(CH_3)_2O_2} &\longrightarrow 2\,\mathrm{HOC(CH_3)_2C(CH_3)_2O} + \mathrm{O_2} && \text{(3)}
\end{aligned}$$

The following Arrhenius expressions were derived for the rate coefficients of reactions (1)–(3) (in $\mathrm{cm^3 molecule^{-1} s^{-1}}$) and for the product branching ratios of reactions (1) and (2) as a function of temperature (all errors 1σ):

$$\begin{aligned}
k_1 &= (6.9_{+2.1}^{-1.5}) \times 10^{-14} \exp[(1040 \pm 100)/T]\\
\beta_1 &= (3100_{+3700}^{-1700}) \exp[(-2400 \pm 280)/T] \text{ (where } \beta_1 = k_{1a}/k_{1b})\\
k_2 &= (7.7_{+12.8}^{-4.8}) \times 10^{-15} \exp[(1330 \pm 350)/T]\\
\beta_2 &= (4.0_{+0.2}^{-0.1}) \times 10^{4} \exp[(-3600 \pm 100)/T]\\
k_3 &= (4.7_{+6.5}^{-2.7}) \times 10^{-13} \exp[(-1420 \pm 320)/T]
\end{aligned}$$

The calculated rate coefficients for reactions (1)–(3) at 298 K are therefore (in $10^{-13}\ \mathrm{cm^3 molecule^{-1} s^{-1}}$) 23 ± 2, 6.7 ± 1.3, and 0.040 ± 0.012, respectively, which compare well with the values measured elsewhere at this temperature using a similar technique. The product branching ratios and the Arrhenius parameters are compared with those for other substituted and unsubstituted peroxy radical self reactions. © 1997 John Wiley & Sons, Inc. Int J Chem Kinet **29:** 323–331, 1997.

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INTRODUCTION

The addition of the hydroxy radical to alkenes leads, under tropospheric conditions, to the formation of peroxy radicals with an OH group in the β position to the carbon possessing the peroxy functionality [1]. Kinetic studies of such reaction systems containing β-hydroxyperoxy radicals are thus important in understanding the atmospheric oxidation of alkenes, which are an important class of volatile organic compound (VOC). In the absence of NO_x, reactions of such radicals with HO_2, with themselves (self reactions), and with other peroxy radicals (cross reactions) may be in competition [2]. While the cross reactions of a peroxy radical with CH_3O_2 or $CH_3C(O)O_2$ are generally more important than its self reaction from an atmospheric point of view, investigations of self-reaction kinetics nevertheless remain essential in laboratory studies used to determine cross-reaction rate coefficients. Furthermore, the results are of use in improving the validity of tropospheric degradation models both for these simple alkenes and for more complex unsaturated VOCs, since such models rely on the extrapolation of structure-reactivity relationships based on the kinetics of various types of RO_2 radical [2–5].

Jenkin and Hayman recently reported [6] revised room temperature measurements of the UV absorption spectra of three simple primary, secondary, and tertiary β-hydroxyperoxy radicals and the following rate coefficients for their self reactions (1)–(3) at 298 K.

$$2\,HOCH_2CH_2O_2 \longrightarrow 2\,HOCH_2CH_2O + O_2 \qquad (1a)$$

$$\longrightarrow HOCH_2CH_2OH + HOCH_2CHO + O_2 \qquad (1b)$$

$$k_1 = 2.1 \times 10^{-12}\ \mathrm{cm^3 molecule^{-1} s^{-1}}$$

$$2\,HOCH(CH_3)CH(CH_3)O_2 \longrightarrow 2\,HOCH(CH_3)CH(CH_3)O + O_2 \qquad (2a)$$

$$\longrightarrow HOCH(CH_3)CH(CH_3)OH + HOCH(CH_3)C(CH_3)O + O_2 \qquad (2b)$$

$$k_2 = (4.2 - 8.4) \times 10^{-13}\ \mathrm{cm^3 molecule^{-1} s^{-1}}$$

$$2\,HOC(CH_3)_2C(CH_3)_2O_2 \longrightarrow 2\,HOC(CH_3)_2C(CH_3)_2O + O_2 \qquad (3)$$

$$k_3 = 5.7 \times 10^{-15}\ \mathrm{cm^3 molecule^{-1} s^{-1}}$$

For reaction (1), Jenkin and Hayman derived their rate coefficient using the only previous reported study of the branching ratio towards alkoxy radical formation for this β-hydroxyperoxy self reaction ($\alpha_1 = k_{1a}/k_1 = 0.5$ [7]). A study of reaction (1) has also been reported by Anastasi et al. [8], who found a value for k_1 of 7.7×10^{-12} cm^{3}molecule^{-1}s^{-1}, the difference between their value and the preferred value of Jenkin and Hayman having been previously explained [9]. For reaction (2), no branching ratio measurement had been carried out and this is reflected in the large uncertainty range for k_2 at room temperature (corresponding to the branching ratio extremes of 0 and 1 and hence a k_2 range given by $k_{obs}/(1 + \alpha_2)$ where k_{obs} is the measured global second-order rate coefficient for $HOCH_2CH_2O_2$ loss).

In this article we have used a laser-flash photolysis technique to extend measurements of the self-reaction rate coefficients to elevated temperatures, allowing the Arrhenius parameters for reactions (1)–(3) and also the branching ratios for reactions (1) and (2) to be derived where possible. Possible trends are highlighted for these parameters and comparisons are made with corresponding data available for the self reactions of other classes and sizes of peroxy radical.

EXPERIMENTAL

The laser-flash photolysis technique and radical-generation method used have both recently been described in detail [4,6,10]. In summary, hydroxy radicals are generated by the longitudinal laser-flash photolysis (at $\lambda = 248$ nm) of H_2O_2 flowing slowly through a heatable cell (70 cm long, 1.5 or 2.3 cm i.d.) at atmospheric pressure. This leads, in the presence of excess O_2 and the appropriate alkene, to the formation of the β-hydroxyperoxy radical of interest on a near instantaneous timescale compared to that for its subsequent decay, the decay being monitored by UV absorption spectrometry. For example, with ethylene:

$$H_2O_2 + h\nu \longrightarrow 2\,OH \qquad (4)$$

$$HO + CH_2{=}CH_2 + M \longrightarrow HOCH_2CH_2 + M \qquad (5)$$

$$k_5\,(298\ \mathrm{K}) = 9 \times 10^{-12}\ \mathrm{cm^3 molecule^{-1} s^{-1}}\ \text{in 1 atm of air [11]}$$

$$HOCH_2CH_2 + O_2 + M \longrightarrow HOCH_2CH_2O_2 + M \qquad (6)$$

$$k_6\,(298\ \mathrm{K}) = 3 \times 10^{-12}\ \mathrm{cm^3 molecule^{-1} s^{-1}}\ \text{in 1 atm of air [1]}$$

Similar reaction schemes with excess *trans*-2-

butene and 2,3-dimethyl-2-butene (tetramethylethylene, TME) lead to the stoichiometric conversion of OH into $HOCH(CH_3)CH(CH_3)O_2$ and $HOC(CH_3)_2C(CH_3)_2O_2$ radicals [1,6,11]. The purities of the gases and precursor alkenes used were as follows: N_2 (AGA Gaz Spéciaux, $>99.995\%$), O_2 (AGA, $>99.995\%$), C_2H_4 (AGA, 99%), C_4H_8 (Aldrich, $>99\%$), and C_6H_{12} (Aldrich, $>99\%$). The low vapor pressure of hydrogen peroxide required the passage of most of the nitrogen or synthetic air carrier gas through a bubbler containing a concentrated solution of H_2O_2 (85%, Air Liquide). Resulting gas-phase hydrogen peroxide concentrations were in the range $0.9–2.8 \times 10^{16}$ molecule cm^{-3}, as measured by absorption at 220 nm (where $\sigma (H_2O_2) = 2.6 \times 10^{-19}$ $cm^2molecule^{-1}$) and yielding initial OH concentrations of $2.5–8.5 \times 10^{13}$ molecule cm^{-3}. The determination of OH radical concentrations was through simulation of the initial HO_2 absorbance signal obtained in the absence of alkene (using the known HO_2 cross section at 220 nm). The OH radical was rapidly converted to HO_2 in the absence of alkene by the reaction:

$$HO + H_2O_2 \longrightarrow H_2O + HO_2 \qquad (7)$$

$$k_7\,(298\text{ K}) = 1.7 \times 10^{-12}\ cm^3molecule^{-1}s^{-1}\ [12]$$

Allowances were also made in the kinetic model for minor signal contributions from H_2O_2 photolysis and the reactions of HO_2 with OH and with itself.

Dichroic mirrors allowed only light in the wavelength range 235–265 nm to be reflected through the cell (including the photolyzing laser radiation at 248 nm) and hence restricted the transmitted analysis wavelengths provided by a deuterium lamp source to those regions where the peroxy radicals absorb on either side of this range. Radical decays were therefore generally monitored at 220 and 270 or 280 nm for a given set of experimental conditions, with the signal-to-noise ratio being improved by the averaging of several tens of such decays.

RESULTS AND DISCUSSION

Reaction Mechanism used for Kinetic Simulations

The following general mechanism was used in kinetic simulations and was valid for all three reaction systems (comprising reactions (1), (2), or (3) and their associated secondary chemistry, where R’, R” = H or CH_3):

$$2\ HOC(R')(R'')C(R')(R'')O_2 \longrightarrow 2\ HOC(R')(R'')C(R')(R'')O + O_2 \quad \alpha_{1-3} \times k_{1-3}\ \text{(see text)}$$

$$HOC(R')(R'')C(R')(R'')O + M \longrightarrow HOCR'R'' + R'C(O)R'' + M\ \text{(fast) [Ref. [1]]}$$

$$HOC(R')(R'') + O_2 \longrightarrow R'C(O)R'' + HO_2\ \text{(fast) [Ref. [1]]}$$

$$HOC(R')(R'')C(R')(R'')O_2 + HO_2 \longrightarrow HOC(R')(R'')C(R')(R'')OOH + O_2\ \ k_8\ \text{(see text)}$$

$$HO_2 + HO_2 \longrightarrow H_2O_2\ \ k_9\ \text{[Ref. [12]]}$$

The molecular channel of the generalized self-reaction is not included because the products of this channel neither absorb significantly nor react with any other absorbing species during the subsequent secondary chemistry and thus are not required in the mechanism used to analyze decay curves. The kinetic model does however still contain a term for the total loss of peroxy radicals by both channels. None of the carbonyl compounds resulting from either alkoxy radical decomposition or subsequent reaction of the hydroxyalkyl radical produced with O_2 are likely to contribute significantly to the total absorbance at the UV analysis wavelengths of interest. Hence, only HO_2, H_2O_2, and the corresponding alkyl hydroperoxide (taken equivalent to CH_3OOH) had to be taken into account as products in the kinetic simulations at 220 nm (with inclusion of their known absorption cross sections [12]).

Kinetics and Branching Ratio of Reaction 1

Kinetic decays corresponding to the self reaction of the $HOCH_2CH_2O_2$ radical and associated secondary chemistry were recorded at analysis wavelengths of 220, 270, and 280 nm. Figure 1 shows typical decay traces obtained at $T = (400 \pm 2)$ K. Extrapolation to $t = 0$ for decays recorded over shorter timescales both in the presence and absence of ethylene allowed the absorption cross section of the radical of interest to be measured relative to that known for HO_2 at a given wavelength, as described by Jenkin and Hayman [6]. Use of the same $HOCH_2CH_2O_2$ cross sections determined by Jenkin and Hayman indicated the correct starting point for the simulation if the previously estimated initial concentration of HO_2 was used, confirming their cross sections at these wavelengths [6] and allowing accurate initial radical concentrations to be employed in the kinetic simulations.

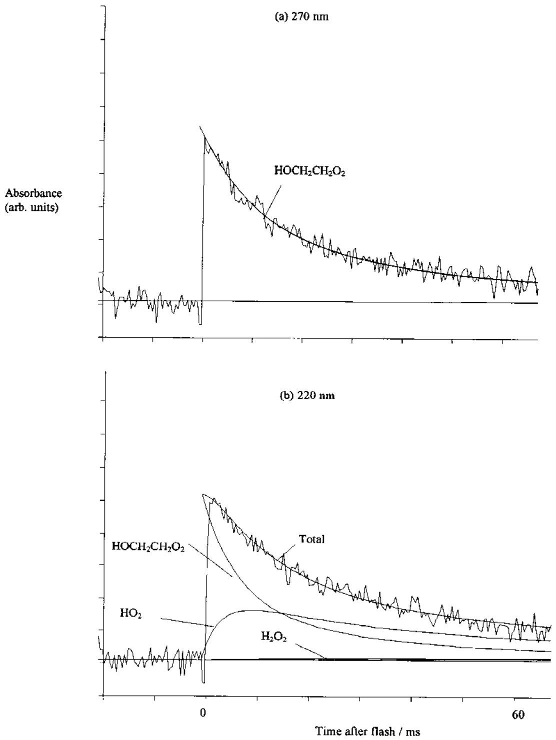

Figure 1 Typical decay traces obtained over 60 ms reaction time for the $HOCH_2CH_2O_2$ self reaction at $T = 400$ K and analysis wavelengths of (a) 270 nm and (b) 220 nm. The simulated lines used to extract k_1 and α_1 show the contributions of various absorbing species to the total absorbance profile, the best-fit simulations for both traces being obtained iteratively using $[HOCH_2CH_2O_2]_0 = 2.5 \times 10^{13}$ molecule cm^{-3} and the optimized parameters $\alpha_1 = 0.90 \pm 0.06$, $k_1 = (9.6 \pm 0.5) \times 10^{-13}$ cm^{3}molecule^{-1}s^{-1}. The errors quoted for the optimized parameters result from the nonlinear least-squares fitting procedure.

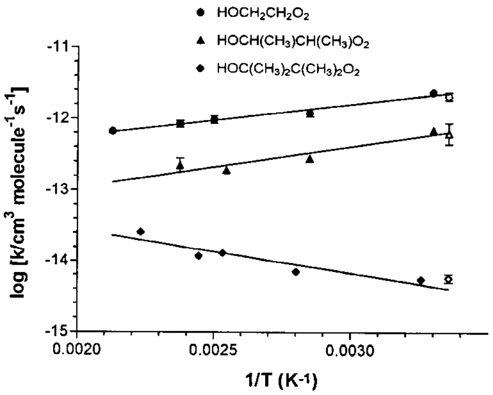

Figure 2 Arrhenius plots for the self reactions of the β-hydroxyperoxy radicals: (●)–$HOCH_2CH_2O_2$; (△)–$HOCH(CH_3)CH(CH_3)O_2$; and (◆)–$HOC(CH_3)_2C(CH_3)_2O_2$. Filled symbols, this work; open symbols, room temperature data of Jenkin and Hayman [6] for comparison.

In particular, the different contributions of HO_2 (formed from the alkoxy-radical-forming channel 1a) to the total absorption at 220 nm and 270/280 nm allowed the value of the branching ratio α_1 to be estimated, as described previously using an iterative procedure performed for a pair of decays recorded under identical experimental conditions but at different analysis wavelengths [10]. At elevated temperatures, the rate coefficient for the secondary reaction with HO_2 (k_8) was estimated by calculating the pre-exponential factor A using the literature value at room temperature (1.5×10^{-11} cm^{3}molecule^{-1}s^{-1} [16]) and a temperature dependence similar to that recently measured for $HOC(CH_3)_2CH_2O_2 + HO_2$ (E/R = −1650 K) [13], and then extrapolating to the temperature of interest. The derived values of k_1 and α_1 at each of the temperatures studied are given in Table I. The Arrhenius plot for k_1 is shown in Figure 2 along with the room temperature value of Jenkin and Hayman for comparison [6], while Figure 3 includes the temperature dependence of α_1 in the form $\beta_1 = \alpha_1/(\alpha_1 - 1)$ vs. $1/T$ for $T = 303$–470 K. The best fits shown correspond to the linear regressions (errors 1σ):

$$k_1 = (6.9_{+2.1}^{-1.5}) \times 10^{-14} \exp[(1040 \pm 100)/T] \ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

$$\beta_1 = (3100_{+3700}^{-1700}) \exp[(-2400 \pm 280)/T]$$

Table I Rate Coefficients and Branching Ratios Derived for the $HOCH_2CH_2O_2$ Radical Self Reaction (1) as a Function of Temperature

T/K	$k_1{}^{a}/10^{-12}$cm^{3}molecule^{-1}s^{-1}	No. of Meas.	$\alpha_1{}^{b}$
303	2.35 ± 0.21	5	0.55 ± 0.04
352	1.20 ± 0.12	5	0.73 ± 0.08
400	0.98 ± 0.12	3	0.90 ± 0.06
422	0.84 ± 0.14	2	0.91 ± 0.08
470	0.66 ± 0.03	3	≈ 1

[a] Errors 1σ for number of measurements indicated.

[b] Errors based on best fit to two pairs of decays recorded at 220 and 270 (or 280) nm.

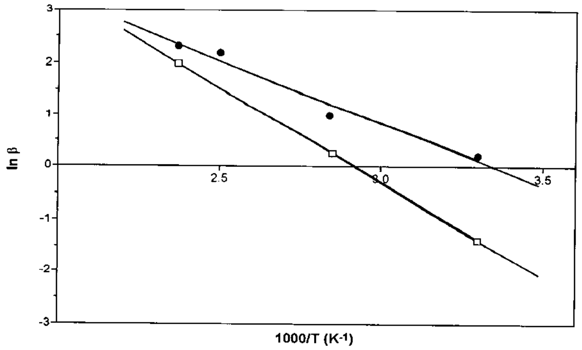

Figure 3 Plots of ln β vs. $1/T$ for the $HOCH_2CH_2O_2$ (●) and $HOCH(CH_3)CH(CH_3)O_2$ (□) self reactions ($\beta = \alpha/(1 - \alpha)$, $\alpha_1 = k_{1a}/k_1$ and $\alpha_2 = k_{2a}/k_2$).

Kinetics and Branching Ratio of Reaction 2

As with reaction 1, absorption cross sections of the $HOCH(CH_3)CH(CH_3)O_2$ radical from the previously measured spectrum of Jenkin and Hayman [6] were used to estimate the initial concentration at the wavelengths of interest. Such concentrations again agreed with the initial concentration of HO_2 radicals measured in the absence of *trans*-2-butene (allowing for an error of around 5% in extrapolating the signals to $t = 0$), confirming their absorption cross sections. A typical decay recorded at 270 nm is shown in Figure 4. At room temperature, very little deviation from second order behavior was detected at 220 nm, with α_2 requiring a value of ≤ 0.3 in the model to reproduce well the shape of the experimental decays recorded at this wavelength. In contrast, at higher temperatures, a good fit to decays at both 220 and 270 nm could only be obtained for iterated values of k_2 and a significantly greater branching ratio for the reaction channel towards alkoxy radical products (using the common chemical mechanism shown above, the known room temperature value for k_8 of 1.5×10^{-11} $cm^3molecule^{-1}s^{-1}$, and an assumed temperature dependence for reaction (8) of −1300 K, i.e., similar to that measured for other secondary peroxy radical reactions with HO_2 [12]). This room temperature branching ratio could also be estimated to lie in the range 0.1–0.3 by using the k_2 values measured here at 351 and 421 K and an assumed temperature dependence of 1750 K (the average of the E/R values measured for two other secondary peroxy radicals [14]). The results are summarized in Table II, with Figure 2 showing the Arrhenius plot for reaction (2) for $T = 303–421$ K (with the value of Jenkin and Hayman measured at 298 K for comparison), and corresponding to:

$$k_2 = (7.7_{+12.8}^{-4.8}) \times 10^{-15} \exp[(1330 \pm 350)/T] \quad cm^3molecule^{-1}s^{-1}$$

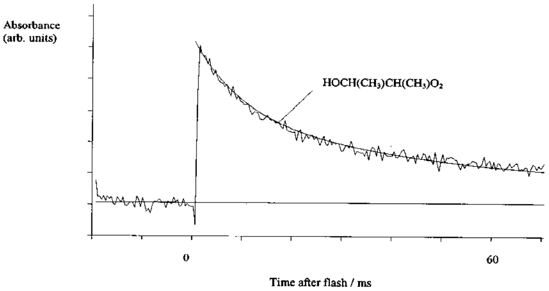

Figure 4 Typical decay trace obtained for the $HOCH(CH_3)CH(CH_3)O_2$ self reaction at $T = 392$ K and 270 nm. The best-fit simulation shown was obtained using $[HOC(CH_3)C(CH_3)O_2]_0 = 6.9 \times 10^{13}$ molecule cm^{-3}, α_2 estimated at 0.8 (see text), and with the optimized parameter $k_2 = (1.97 \pm 0.02) \times 10^{-13}$ $cm^3molecule^{-1}s^{-1}$.

Although α_2 was only accurately derived at two temperatures, fixing α_2 a reasonable room temperature value of 0.2 allowed an approximate representation of β_2 as a function of temperature to be derived (Fig. 3):

$$\beta_2 = (4.0_{+0.2}^{-0.1}) \times 10^4 \exp[-(3600 \pm 100)/T] \quad \text{(errors } 1\sigma\text{, precision only)}$$

Furthermore, this expression could be used to estimate α_2 at 393 K and thus to derive k_2 at this temperature where, for technical reasons, no direct branching ratio measurement had been performed (see Table II).

Kinetics of Reaction 3

A typical decay recorded at 270 nm for self reaction (3) is shown in Figure 5. Again, measured initial radical concentrations and those estimated using the spectrum of Jenkin and Hayman [6] for this radical were in good agreement. The tetramethylethylene precursor absorbed a large fraction of the incident light intensity of the deuterium lamp at 220 nm and hence no decays with a reasonable signal-to-noise ratio could be recorded at this wavelength. The lack of an abstractable hydrogen atom on the peroxy carbon in the radical concerned means that the branching ratio, by definition, is unity and the reaction proceeds completely via *t*-alkoxy radical formation, followed by its rapid decomposition and the subsequent secondary chemistry included in the general mechanism given above (with k_8 taken as 1.5×10^{-11} $cm^3molecule^{-1}s^{-1}$ at room temperature [6]). At higher tem-

Table II Rate Coefficients and Branching Ratios Derived for the $HOCH(CH_3)CH(CH_3)O_2$ Radical Self Reaction (2) as a Function of Temperature

T/K	$k_2{}^{a}/10^{-13}$cm^{3}molecule^{-1}s^{-1}	No. of Meas.	α_2
303	6.79 ± 0.41	5	0.2[b]
351	2.81 ± 0.24	5	0.56 ± 0.05[c]
392	1.88 ± 0.09	4	0.8[d]
421	0.84 ± 0.14	4	0.88 ± 0.10[c]

[a] Errors 1σ.

[b] Fixed at this value in simulations used to derive k_2 at 303 K (see text).

[c] Errors based on best fit to two pairs of decays recorded at 220 and 270 (or 280) nm.

[d] Estimated using the expression derived for β_2 as a function of temperature and then fixed at this value in simulations used to derive k_2 at 393 K (see text).

peratures, the rate coefficient for the secondary reaction (8) was again estimated using a similar temperature dependence to that for the reaction $HOC(CH_3)_2CH_2O_2 + HO_2$ [13]. Figure 2 shows the Arrhenius plot for reaction (3) using the results from Table III for $T = 307-448$ K and again with the room temperature measurement of Jenkin and Hayman for comparison. The best-fit linear regression corresponds to:

$$k_3 = (4.7_{+6.5}^{-2.7}) \times 10^{-13} \exp[(-1420 \pm 320)/T] \ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

with the errors again representing 1σ.

Some rate coefficient measurements were also attempted at more elevated temperatures (up to 540 K) but did not fit well to the above Arrhenius relationship, the deviation suggesting a change in the mechanism used in the simulations. The discrepancy may be at least in part explained by increasing competition between H-atom abstraction by OH and its addition to the double bond, combined perhaps with the onset of a different alkoxy radical decomposition mechanism at such elevated temperatures [11].

Structure-Reactivity Trends

It is of interest to compare the kinetic and product yield data of the peroxy radical self reactions studied here with those of other related substituted and unsubstituted peroxy radicals of various sizes. Table IV shows these collected data, grouping peroxy radicals as primary, secondary, and tertiary according to their previously recognized general reactivities ($k_{prim} > k_s > k_{tert}$) [15], but with the recently recommended parameters of Lesclaux [16].

Product Branching Ratios. From Table IV, the striking feature of the room temperature product branching ratios (α_{298}) for the self reactions of the eight primary peroxy radicals of size $\geq C_2$, is that, whether unsubstituted or β-substituted, all such reactions have a value for this parameter in the range 0.4–0.65, irrespective of the size of the radical or the nature of the β substituent. Thus, it would appear that a reasonable recommended mean value for this class of peroxy radical self reaction would be $\alpha = 0.55 \pm 0.10$ at 298 K. For secondary radical self reactions, the branching ratio is generally slightly lower than for

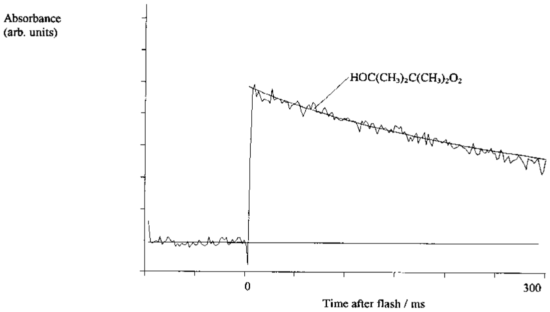

Figure 5 Typical decay trace obtained for $HOC(CH_3)_2C(CH_3)_2O_2$ self reaction at $T = 409$ K and 270 nm. The best-fit simulation shown over 250 ms was obtained using $[HOC(CH_3)C(CH_3)O_2]_0 = 4.8 \times 10^{13}$ molecule cm^{-3} and with the optimized parameter $k_3 = (1.13 \pm 0.02) \times 10^{-14}$ cm^{3}molecule^{-1}s^{-1}.

Table III Rate Coefficients Derived for the $HOC(CH_3)_2C(CH_3)_2O_2$ Radical Self Reaction (3) as a Function of Temperature

T/K	$k_3{}^{a,b}/10^{-14}$cm^{3}molecule^{-1}s^{-1}	No. of Meas.
307	0.55 ± 0.08	2
357	0.66 ± 0.15	3
395	1.30 ± 0.12	3
409	1.19 ± 0.16	3
448	2.58 ± 0.20	5

[a] $\alpha_3 = 1$.

[b] Errors 1σ.

Table IV Arrhenius Parameters for the Self Reactions of β-Hydroxyperoxy Radicals and some Related Alkylperoxy Self Reactions

Radical	k(298 K)[a]	A[a]	E/R[b]	α_{298}	Ref.
primary					
$HOCH_2CH_2O_2$	2.3×10^{-12}	6.9×10^{-14}	−1040	0.50[c]	This work
	2.1×10^{-12}			0.50	[6,7]
	7.7×10^{-12}				[8]
$BrCH_2CH_2O_2$	5.6×10^{-12}	5.4×10^{-14}	−1390	0.57	[17,18]
$ClCH_2CH_2O_2$	3.3×10^{-12}	1.1×10^{-13}	−1020	0.69	[16]
$HOC(CH_3)_2CH_2O_2$	4.6×10^{-12}	1.4×10^{-14}	−1740	0.60	[12]
$C_6H_5CH_2O_2$	7.7×10^{-12}	2.7×10^{-14}	−1680	0.40	[19]
$CH_2{=}CHCH_2O_2$	6.8×10^{-13}	5.4×10^{-14}	−760	0.61	[5,10]
neo-$C_5H_{11}O_2$	1.2×10^{-12}	1.7×10^{-15}	−1961	0.41	[16]
$C_2H_5O_2$	6.8×10^{-14}	6.8×10^{-14}	0	0.63	[16]
secondary					
$HOCH(CH_3)CH(CH_3)O_2$	6.7×10^{-13}	7.7×10^{-15}	−1330	≈0.2[c]	This work
	7×10^{-13}				[6][d]
$BrCH(CH_3)CH(CH_3)O_2$	6.8×10^{-13}	1.3×10^{-14}	−1185	≈0.5[c]	[17,18]
i-$C_3H_7O_2$	1.1×10^{-15}	1.7×10^{-12}	2188	0.56	[12]
c-$C_5H_9O_2$	4.5×10^{-14}	2.9×10^{-13}	555	–	[14]
c-$C_6H_{11}O_2$	4.2×10^{-14}	7.7×10^{-14}	184	0.30	[14]
tertiary					
$HOC(CH_3)_2C(CH_3)_2O_2$	4.0×10^{-15}	4.7×10^{-13}	1420	1.00[e]	This work
	5.7×10^{-15}				[6]
$BrC(CH_3)_2C(CH_3)_2O_2$	2.5×10^{-14}	–	–	1.00[e]	[17]
t-$C_4H_9O_2$	3.0×10^{-17}	4.0×10^{-11}	4200	1.00[e]	[15]

[a] Units $cm^3 molecule^{-1} s^{-1}$, calculated using the Arrhenius parameters shown.

[b] Units, *K*.

[c] Calculated using the appropriate expression for β as a function of temperature.

[d] Calculated using the k_{obs} value of Jenkin and Hayman and $\alpha = 0.2$ as estimated here ($k_{obs} = k_2(1 + \alpha_2)$).

[e] By definition for a tertiary peroxy radical self reaction assuming no adduct formation under these conditions.

primary radicals, an effect which might be related to the fact that the C—H bond dissociation energy is lower in the case of the secondary radical, thus favoring the internal H-atom transfer in the intermediate RO_4R complex which leads molecular products (channel b). The variations of β_1 and β_2 with temperature are the first to be investigated for β-substituted peroxy radicals and show positive 'activation energies' which are larger than those reported for other peroxy radical self reactions [15]. However, a limited database and large total uncertainty in these expressions (particularly in the measured preexponential factors), preclude the drawing of more detailed conclusions between the temperature dependence of β and the structure of the peroxy radical.

Arrhenius Parameters. Some general comments can be made concerning apparent trends in the Arrhenius parameters measured for the self reactions of substituted primary, secondary, and tertiary peroxy radicals (see Table IV).

For primary radical reactions, the three C_2 radicals which have been studied possessing a β-substituent ($HOCH_2CH_2O_2$, $BrCH_2CH_2O_2$, $ClCH_2CH_2O_2$) have all, within a factor of two, the same preexponential factors ($A = (0.5-1) \times 10^{-13}$ $cm^3 molecule^{-1} s^{-1}$) and similar, fairly large, 'negative' activation energies ($E/R = -(1000-1400)$ K). The ethylperoxy self reaction also has a preexponential factor in this range but shows practically no variation with temperature so that the difference in activation energy alone appears to explain why the rate coefficient at room temperature is some 30–50 times smaller for $C_2H_5O_2$ than for the substituted radicals.

A similar enhancement of the self-reaction rate constant has also been observed for several types of α-substituted peroxy radicals [13], suggesting that this large substituent effect is independent of whether the substituent is in the α or β position. It would be worthwhile assessing up to which distance this substituent effect is significant. In particular, any effect induced by the presence of a δ-OH group could be important for peroxy radicals formed from the 1,5 isomerization of alkoxy radicals formed during the oxidation of $\geq C_5$ alkanes and during the OH-initiated oxidation of dienes such as isoprene [1,6]. Unfortunately, to date, there is no known method for the clean generation of δ-hydroxyperoxy radicals under conditions which would allow us to study their self-reaction kinetics. Upon passing to larger primary peroxy radicals, the rate constant enhancement induced by the presence of the hydroxyl group seems lower than for C_1 or C_2 radicals. For example, the room temperature rate constant is only four times larger for the self reaction of $(CH_3)_2C(OH)CH_2O_2$ than for $(CH_3)_3CCH_2O_2$. It must be pointed out, however, that the rate constant for the neopentylperoxy radical self reaction is already significantly enhanced compared to that for $C_2H_5O_2$ (Table IV), probably as a result of the larger number of carbon atoms, as suggested recently [16]. It should be noted that this enhancement in reactivity for such large radicals is accompanied by a significantly larger negative temperature dependence ($ER = -(1700-2000)$ K).

It would also appear that the enhancement of reactivity for self reactions appears to be independent of whether the peroxy radical substituent is an electron-withdrawing group (such as a halogen atom) or an electron-donating group (such as CH_3O). All such substituents result in similar enhancements of the rate constant [15]. In contrast, the double bond in the allylperoxy radical has only a minor effect when compared with the *n*-propylperoxy radical, whereas the aromatic group in benzylperoxy induces a large enhancement, mainly resulting from a large increase in the negative temperature dependence [12]. Unfortunately, there is no current way of rationalizing these observations in terms of potential energy barriers on the reaction coordinate or of transition-state structures since no determinations of the molecular properties of such complex systems have as yet been reported.

As far as secondary radicals are concerned, the striking feature is the inversion of the temperature dependence resulting from β-substitution involving OH or Br [17] compared to unsubstituted secondary alkyl or cycloalkylperoxy radicals (Table IV). This difference is principally responsible for an enhancement of the room temperature rate constant by up to two orders of magnitude where β substitution is present. However, values remain a factor of 3 to 10 smaller than the rate constants for substituted primary radicals, a difference which would appear to be essentially determined by a smaller preexponential factor for substituted secondary radical reactions. Thus, as previously pointed out [6], a higher reactivity is observed for β-substituted primary radicals than for secondary radicals, but the difference is much smaller than that between unsubstituted primary and secondary alkylperoxy radicals (Table IV).

In the case of tertiary peroxy radicals, the activation energy is positive for the OH-substituted peroxy radical, but much smaller than for the *tert*-butylperoxy radical self reaction, resulting in a two orders of magnitude increase of the room temperature rate constant upon substitution. However, general trends cannot be given for this type of reaction as this is only the second reported measurement of the temperature dependence of a tertiary peroxy radical self reaction. The predicted positive temperature dependence was impossible to confirm for the β-brominated tertiary radical owing to mechanistic complications at higher temperatures [17]. Nevertheless, at room temperature, the rate constant enhancement is even larger than for the OH-substituted radical (see Table IV).

CONCLUSIONS AND RECOMMENDATIONS

Lesclaux has recently summarized the available data on peroxy radical self reactions, making some tentative recommendations concerning individual rate parameters and structure-reactivity trends [16]. Our values presented therein for the Arrhenius parameters of reactions (1)–(3) differ slightly from those presented herein since we have decided here not to include the room temperature data of Jenkin and Hayman [6], which were taken into account in our original Arrhenius plots [20].

The data presented in this article on the branching ratios and Arrhenius parameters of primary β-hydroxyperoxy radicals have been used in part to form the rate coefficient recommendations of Lesclaux [16] and may even allow some predictions for primary and secondary peroxy radicals to be made with slightly more confidence. We now suggest that for all primary peroxy radical self reactions for radicals of size $\geq C_2$, the branching ratio towards alkoxy radical formation, α, at room temperature can be taken as 0.55 ± 0.10. Also, for β-substituted primary radicals of size $\geq C_2$ (where the substituent is OH, a halogen atom, or an aryl group) we recommend that the self reaction rate constant at room temperature be taken as $(5 \pm 2) \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$ with $A = (6 \pm 4) \times 10^{-14}$ $cm^3 molecule^{-1} s^{-1}$ and $E_a/R = -(1400 \pm 300)$ K (averages for the five such peroxy radicals studied to date).

There remains, as of yet, very limited temperature dependent kinetic data available for tertiary peroxy radicals and no trends in reactivity with radical size or type can be suggested with any confidence. However, for β-substituted secondary radicals, a large and negative temperature dependence similar in magnitude to that for the primary analogues may be applicable in all cases but needs to be confirmed, as does the apparent inverse variation of both A-factor and activation energy with carbon number for unsubstituted secondary radicals (see Table IV). Measurements of the Arrhenius parameters for the linear secondary radicals $n\text{-}C_{12}H_{25}O_2$ and $n\text{-}C_5H_{11}O_2$ are planned with this confirmation in mind.

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