Flash Photolysis Study of the UV Spectrum and Kinetics of Reactions of the Acetonylperoxy Radical

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The flash-photolysis–UV-absorption method was used to study the UV spectrum and the kinetics of the $CH_3C(0)CH_2O_2$ radical formed in the presence of oxygen *via* the reaction between CI atoms and acetone. Results were analysed in the light of the results of the preceding article describing work using end-product analysis. The peroxy radical $CH_3C(0)CH_2O_2$ absorbs in the UV with two maxima at around 230 and 290 nm. This peroxy radical reacts according to: $2CH_3C(0)CH_2O_2 \rightarrow 2CH_3C(0)CH_2O + O_2$ (7a) and $\rightarrow CH_3C(0)CH_2OH + CH_3C(0)CHO + O_2$ (7b) with $k_7 = (8.0 \pm 2.0) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ and $k_{7e}/k_7 = (0.75 \pm 0.1)$. The kinetics of the reactions between $CH_3C(0)CH_2O_2$ and the $CH_3C(0)O_2$, CH_3O_2 and HO_2 radicals were determined by adding acetaldehyde, methane or methanol to the photolysis mixtures: $CH_3C(0)CH_2O_2 + CH_3C(0)CH_2O + CH_3 + CO_2$ (11a); $\rightarrow O_2 + CH_3C(0)OH + CH_3C(0)CHO$ (11b); $k_{11} = (5.0 \pm 2.0) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹; $CH_3C(0)CH_2O_2 + CH_3C(0)CH_2O + CH_3O$ (14a); $\rightarrow O_2 + CH_3C(0)CHO + CH_3O$ (14b); $\rightarrow O_2 + CH_3C(0)CH_2O + CH_3O$ (14c); $k_{14} = (3.8 \pm 0.4) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ and $k_{14e}/k_{14} = 0.3 \pm 0.1$ while k_{14b} and k_{14c} could not be distinguished; $CH_3C(0)CH_2O_2 + HO_2 \rightarrow CH_3C(0)CH_2O_2H + O_2$ (16), $k_{16} = (9.0 \pm 1.0) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. All experiments were performed at 298 K and 760 Torr.

In the atmosphere, acetone is present at a low concentration (around 0.5 ppbv) as a result of direct emission from various sources, and as a degradation product of some hydrocarbons $(\geq C_3)$.¹ Its oxidation is initiated either by photolysis or by reaction with OH radicals. The major photolysis pathway produces methyl and acetyl radicals² whose oxidation has been investigated thoroughly:^{3,4}

$$CH_3C(O)CH_3 + h\nu \rightarrow CH_3CO + CH_3$$
 (1)

 $CH_{3}CO + O_{2} + M \rightarrow CH_{3}C(O)O_{2} + M$ (2)

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \tag{3}$$

Acetone is thus a precursor for peroxyacetyl nitrate (PAN) formed in the reaction between the acetylperoxy radical and NO_2 .⁵

Under tropospheric conditions, the reaction with OH forming the acetonyl radical

$$OH + CH_3C(O)CH_3 \rightarrow H_2O + CH_3C(O)CH_2 \qquad (4)$$

occurs twice as quickly as photolysis, and leads to the production of acetonylperoxy radicals:

$$CH_3C(O)CH_2 + O_2 + M \rightarrow CH_3C(O)CH_2O_2 + M$$
 (5)

The UV spectrum and the kinetics of the acetonylperoxy radical have been investigated only once by $Cox \ et \ al.^6$ using the pulsed radiolysis of a mixture of SF₆, acetone and O₂ for the production of the radicals and UV absorption for their detection. In our work, the flash photolysis technique was used to produce the peroxy radicals, which were detected by UV absorption. The UV absorption spectrum of the peroxy radical was measured, and the kinetics of its self-reaction and of its reactions with the acetyl-, methyl- and hydroperoxy radicals were investigated. A complementary study of the same chemical system, using end-product analysis (FTIR and UV spectroscopy) is described in the preceding paper.⁷

Experimental

The experimental apparatus has been described in detail elsewhere.⁸ Briefly, it consists of a 70 cm long thermostatted Pyrex cell provided with a second, outer, evacuated jacket. The flash is generated by discharging two capacitors through external argon flash lamps. The analysis beam from a deuterium lamp passes twice through the cell and impinges onto a monochromator-photomultiplier unit. Individual experimental absorption curves are fed into a transient recorder and passed to a microcomputer for averaging and further data analysis. The gas mixtures are flowed through the cell and regulated by Tylan flow-controllers. All experiments were performed at atmospheric pressure and 298 K. The acetonylperoxy radicals were produced *via* the reaction of chlorine atoms with acetone:

$$Cl + CH_3C(O)CH_3 \rightarrow HCl + CH_3C(O)CH_2$$
 (6)

$$CH_3C(O)CH_2 + O_2 + M \rightarrow CH_3C(O)CH_2O_2 + M$$
 (5)

The gas mixture was renewed between flashes to ensure that no products were photolysed, yielding secondary radicals. Acetone (Prolabo, 99.8% or Aldrich 99.8%) was used without further purification. In the experiments, nitrogen was bubbled through acetone maintained at 298 K. The concentration of acetone in the photolysis cell: $(0.3-8.3) \times 10^{17}$ molecule cm⁻³, was measured by its absorption at 280 nm ($\sigma = 5.2 \times 10^{-20}$ cm² molecule⁻¹).⁹ Acetaldehyde (Prolabo, 99%, *ca*. 10¹⁷ molecule cm⁻³ in the cell) was added by bubbling nitrogen through it at 0 °C. Its concentration in the photolysis cell was measured by absorption at 290 nm ($\sigma = 4.75 \times 10^{-20}$ cm² molecule⁻¹).⁹ Between experiments, it was kept in the dark at 4 °C. The concentration of chlorine (L'Air Liquide, 5% in nitrogen) was maintained in the range (3-5) $\times 10^{16}$ molecule cm⁻³ and was measured by its absorption at 330 nm ($\sigma = 25.6 \times 10^{-20}$ cm² molecule⁻¹).¹⁰

Absorption profiles were analysed using non-linear leastsquare fitting that allowed simultaneous simulation of up to four traces recorded at various wavelengths.¹¹

Results and Discussion

Determination of the UV spectrum of CH₃C(O)CH₂O₂

Mixtures of chlorine (1.6 Torr[†]), acetone (5.8 Torr) and air at atmospheric pressure were photolysed using a constant flash energy. In a series of runs at different wavelengths in the UV, the time-profiles of the absorption were recorded and analysed. The concentration of chlorine atoms formed in the flash was ca. 5×10^{13} molecule cm⁻³. In a preliminary analysis, initial values of the absorbance, extrapolated to time zero assuming pseudo-second-order kinetics, were used to determine a raw spectrum which was calibrated at 240 nm, using the CH₃O₂ radical as a reference.¹¹ In order to obtain a more accurate spectrum, however, great care had to be taken to allow for absorption by radicals other than $CH_3C(O)CH_2O_2$, that are formed rapidly in the decay and which could distort the shape of the spectrum. For this purpose, a comprehensive reaction scheme similar to that presented in the preceding paper⁷ was used in the simulations, starting with:

$$2CH_{2}C(O)CH_{2}O_{2} \rightarrow 2CH_{2}C(O)CH_{2}O + O_{2}$$
(7a)

$$\rightarrow CH_3C(O)CH_2OH + CH_3C(O)CHO + O_2$$
(7b)

followed by the decomposition of the acetonoxy radical formed in reaction (7a)

$$CH_3C(O)CH_2O \rightarrow CH_3CO + HCHO$$
 (8)

forming the acetylperoxy radical in the presence of oxygen:

$$CH_3CO + O_2 + M \rightarrow CH_3C(O)O_2 + M$$
(9)

There also exists the possibility of the reaction with O_2 , occurring in competition with reaction (8):

$$CH_3C(O)CH_2O + O_2 \rightarrow HO_2 + CH_3C(O)CHO$$
 (10)

However, under our experimental conditions (298 K, 1 atm. \ddagger air), the rate of reaction (10) was found to be negligible compared with that of reaction (8). This was verified in a series of experiments in which the concentration of oxygen was varied from 10 to 700 Torr, with no resultant effect on the observed absorption-time profiles. A similar conclusion was reached in the collaborative work described in the preceding paper.⁷

An optimised absorption spectrum was obtained simultaneously with the kinetic parameters for reactions of $CH_3C(O)CH_2O_2$ as described below, using a detailed kinetic analysis of the whole system. In this way, decay traces could be extrapolated to time zero, whilst allowing for the distortion resulting from the absorption of strongly absorbing species such as $CH_3C(O)O_2$, which are formed rapidly in the system, as shown above. The final optimised spectrum of the $CH_3C(O)CH_2O_2$ radical is shown in Fig. 1, together with the absorption spectrum obtained by Cox *et al.*⁶ The error bars correspond to the standard deviation at wavelengths where more than four measurements were performed (210, 220, 230, 240, 250, 270 and 290 nm) and represent the upper and lower limits of acceptable fit to the initial optical densities at other wavelengths. Values of the cross-sections are given in Table 1.

Unlike those of alkylperoxy radicals, this spectrum has two absorption maxima. The first, at around 230 nm, is typical of a simple alkylperoxy radical, whereas the second at around 290 nm, can be attributed to the presence of the carbonyl group in the radical. The observation of two bands in the spectrum is in agreement with the only other determination.⁶ However, the cross-section at 290 nm determined in the

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Fig. 1 UV spectrum of the acetonylperoxy radical; (\diamondsuit) this work; ($\cdot \cdot \cdot$) spectrum of ref. 6

present study is 60% larger than that reported in ref. 6, in which no maximum was observed at 230 nm. These discrepancies may be explained by the lower sensitivity at short wavelength of the apparatus used in ref. 6, and the lack of a complete kinetic scheme for the simulations, which would allow the contribution to the total absorption made by acetylperoxy radicals to be taken into account.

Kinetics of the Reaction between CH₃C(O)CH₂O₂ Radicals

Absorption-time traces obtained at various wavelengths during the photolysis of chlorine, acetone and air mixtures were analysed to determine the kinetics of reaction (7). The initial concentration of the peroxy radical was (0.5-1.0) × 10¹⁴ molecule cm⁻³. A crude second-order analysis performed on a 330 nm data set, where the radical $CH_3C(O)CH_2O_2$ is the only species to absorb, gave $k_{7 obs} =$ 9.0×10^{-12} cm³ molecule⁻¹ s⁻¹. Further analysis was carried out with time profiles obtained at 230 and 260 nm where the absorption of other species, particularly that of the acetylperoxy radical, had to be taken into account. Fig. 2 shows experimental profiles and simulations done at these two wavelengths. The contribution of the two channels of reaction (7) could be evaluated since the radicals formed in reaction (7a) or subsequent reactions absorb, particularly the acetylperoxy radical which aborbs strongly at short wavelengths peaking at 207 nm, while the products formed in reaction (7b) do not. Table 2 gives the results of kinetic analyses performed at various wavelengths using the full kinetics scheme given in Table 3, which provided the following mean kinetic parameters: $k_7 = (8.0 \pm 2.0) \times 10^{-12} \text{ cm}^3$

 Table 1
 Experimental values of the cross-section of the acetonylperoxy radical

λ/nm	$\sigma \pm \text{SD}/10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$		
200	0.86 ± 0.68		
210	1.32 ± 0.58		
220	1.82 ± 0.26		
230	2.19 ± 0.22		
240	1.85 ± 0.35		
250	1.42 ± 0.25		
260	1.39 ± 0.39		
270	1.95 ± 0.14		
280	2.07 ± 0.11		
290	2.47 ± 0.31		
300	2.36 ± 0.11		
310	2.34 ± 0.11		
320	2.00 ± 0.20		
330	1.57 ± 0.22		
340	1.30 ± 0.20		

^{† 1} Torr = (101 325/760) Pa.

 $[\]ddagger 1 \text{ atm} = 101 325 \text{ Pa}.$



Fig. 2 Experimental and calculated kinetic profiles at A, 210 and B, 230 nm. Simulations were done using the full kinetic scheme described in the text and Table 3. (a) Acetonylperoxy; (b) acetylperoxy; (c) methylperoxy and (d) hydroperoxy radicals.

molecule⁻¹ s⁻¹; with $\alpha_7 = k_{7a}/k_7 = (0.75 \pm 0.1)$. This value of k_7 is not much below that determined by a pure secondorder analysis, but reactions between peroxy radicals, following reaction (7), affect the shape of the decays. The reactions between the CH₃C(O)CH₂O₂ radical and CH₃C(O)O₂, CH₃O₂ and HO₂ all play a role, as described in the preceding paper,⁷ which had to be taken into consideration. Thus,

Table 2 Determination of k_7 . Kinetic analysis of photolysis of acetone-chlorine air experiment

wavelength nm	k _{7a}	k _{7b}
200	6 ± 3	
210	6 ± 2	1.8 ± 1
220	6 ± 2	_
230	5 ± 2	2 ± 2
240	6 ± 2	2 ± 1
250	7 ± 2	2.7 ± 1
260	6 ± 2	1.7 ± 1

Error bars correspond to acceptable limits of the goodness of fit. Initial concentration of radical = 8.9×10^{13} molecule cm⁻³. All rate constants values in Table 3.

we performed kinetic determinations concerning these three reactions in separate experiments in which similar initial concentrations of $CH_3C(O)CH_2O_2$ and one of the other peroxy radicals were prepared, as described in the following sections. These results were incorporated into the full kinetic analysis, from which the values of k_7 and α_7 given above were obtained.

The only previous determination of k_7 by Cox et al.⁶ gave a preliminary upper-limit value of $(8.3 \pm 1.6) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ in apparent agreement with the one obtained here in a similar manner (9 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ in a second-order analysis at 330 nm). However, the former value was obtained using $\sigma(RO_2) = 1.48 \times 10^{-18}$ cm² molecule⁻¹ at 310 nm while our value is 2.3×10^{-18} cm² molecule⁻¹ at the same wavelength, indicating that the close agreement of the derived rate coefficients is fortuitous.

Kinetics of the Reaction between $CH_3C(O)CH_2O_2$ and $CH_3C(O)O_2$ Radicals

Kinetic analysis of absorption decays obtained in the photolysis of chlorine in the presence of acetone and oxygen

reaction		$k/10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
acetonylperoxy radical chemistry		
$2CH_3C(O)CH_2O_2$		
$\rightarrow 2CH_3C(O)CH_2O + O_2$	(7 <i>a</i>)	6.0
\rightarrow CH ₃ C(O)CH ₂ OH + CH ₃ C(O)CHO + O ₂	(7 <i>b</i>)	2.0
$CH_3C(O)CH_2O_2 + CH_3C(O)O_2$		
$\rightarrow O_2 + CH_3C(O)CH_2O + CH_3 + CO_2$	(11 <i>a</i>)	2.5
$\rightarrow O_2 + CH_3C(O)OH + CH_3C(O)CHO$	(11 <i>b</i>)	2.5
$CH_3C(O)CH_2O_2 + CH_3O_2$		
$\rightarrow O_2 + CH_3C(O)CH_2O + CH_3O$	(14 <i>a</i>)	1.2
$\rightarrow O_2 + CH_3C(O)CHO + CH_3OH$	(14 <i>b</i>)	2.6
$\rightarrow O_2 + CH_3C(O)CH_2OH + HCHO$	(14 <i>c</i>)	
$CH_3C(O)CH_2O_2 + HO_2$		
\rightarrow CH ₃ C(O)CH ₂ O ₂ H + O ₂	(16)	9.0
other chemistry ^a		
$CH_{2}C(O)CH_{2}O \rightarrow CH_{3}CO + HCHO$	(8)	rapid
$CH_3CO + O_3 \rightarrow CH_3C(O)O_3$	(9)	rapid
$CH_3 + O_2 \rightarrow CH_3O_2$	(12)	rapid
CH ₃ O + O, → HCHO + HO,	(15)	rapid
$2CH_3C(O)O_2 \rightarrow 2CH_3 + 2CO_2 + O_2$		16.0
$CH_3C(O)O_2 + CH_3O_2 \rightarrow CH_3 + CO_2 + CH_3O + O_2$		5.5
\rightarrow CH ₃ C(O)OH + HCHO + O ₂		5.5
$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OH + O_3$	(19 <i>a</i>)	4.5
$\rightarrow CH_3C(O)O_2H + O_2$	(19 <i>b</i>)	8.5
$2CH_3O_2 \rightarrow 2CH_3O + O_2$		0.1
\rightarrow CH ₃ OH + HCHO + O ₂		0.24
$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$		4.8
$2HO_2 \rightarrow H_2O_2 + O_2$		2.8

Table 3 Reactions used in the kinetic simulations. Rate constants at 298 K

^a Rapid reactions are assumed instantaneous on the experimental timescale. Rate coefficients for reactions are taken from the literature as indicated in the preceding paper.⁷

$$CH_{3}C(O)CH_{2}O_{2} + CH_{3}C(O)O_{2}$$

$$\rightarrow O_{2} + CH_{3}C(O)CH_{2}O + CH_{3} + CO_{2} \quad (11a)$$

$$\rightarrow O_2 + CH_3C(O)OH + CH_3C(O)CHO$$
 (11b)

This is followed by reactions producing methylperoxy radicals and regenerating acetylperoxy radicals:

$$CH_3C(O)CH_2O \rightarrow CH_3CO + HCHO$$
 (8)

$$CH_3CO + O_2 + M \rightarrow CH_3C(O)O_2 + M$$
(9)

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$$
(12)

Since both reactions (7) and (11) are fast, the kinetic measurement of k_{11} is difficult in this chemical system. In order to confirm the preliminary determination of k_{11} further experiments were performed with both acetone (22 Torr) and acetaldehyde (2 Torr) present, so that acetylperoxy radicals [$(4.0 \pm 0.2) \times 10^{13}$ molecule cm⁻³] were formed in comparable concentrations to acetonylperoxy radicals [$(3.0 \pm 0.2) \times 10^{13}$ molecule cm⁻³] via the following reactions:

$$Cl + CH_3CHO \rightarrow HCl + CH_3CO$$
 (13)

$$CH_{3}CO + O_{2} + M \rightarrow CH_{3}C(O)O_{2} + M \qquad (9)$$

Kinetic determinations were performed at 210, 220, 230 and 245 nm, but could not be carried out at 310 nm because of the strong absorption of acetone in the cell at this wavelength due to the high concentration used in this experiment in order that reactions (6) and (13) could be competitive. Determination of k_{11a} from this chemical system proved difficult, since acetylperoxy radicals consumed by reaction (11a) are rapidly regenerated by reaction (9), and the decay in absorption due to the loss of acetonylperoxy radicals is compensated for by production of CH_3O_2 in reaction (12). Consequently, only an upper limit for $k_{11b} \le 4 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ could be estimated for the molecular channel, from the time-resolved measurements alone. However, incorporation of the branching ratio $\alpha_{11} = k_{11a}/k_{11} = (0.5$ \pm 0.2), inferred from the product studies described in the preceding paper,⁷ into the present analysis, placed an extra constraint on the optimisation procedure, allowing the following value of k_{11} to be determined:

$$k_{11} = (5.0 \pm 2.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

This is the first direct kinetic determination of the rate constant for a reaction between different peroxy radicals that each contain a carbonyl group. The value of this rate coefficient, and those for the self-reactions of acetonylperoxy radicals (see above) and acetylperoxy radicals,^{3,4} are much larger than those for the self-reactions of small primary alkylperoxy radicals that do not contain a carbonyl group (*i.e.* $< 0.5 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ for self-reactions of methylperoxy or ethylperoxy radicals).^{3,4} However, the reaction between methylperoxy and acetylperoxy radicals occurs at a rate comparable to reaction (11).^{3,4}

Kinetics of the Reaction between $CH_3C(O)CH_2O_2$ and CH_3O_2 Radicals

In the initial chemical system based on the photolysis of chlorine in the presence of acetone, the reactions of methylperoxy radicals with acetonylperoxy radicals and acetylperoxy radicals were important since the rate of the self reaction of

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 CH_3O_2 is low (see Table 3). The cross-reaction of acetylperoxy and methylperoxy radicals has been studied previously.^{3,4} In order to obtain a rate coefficient for the cross-reaction of acetonylperoxy and methylperoxy radicals further experiments were performed with both acetone and methane present. The experiments were performed with [methane]/[acetone] = 40. Under these conditions, the initial concentrations of radicals are: $[CH_3O_2] = 5 \times 10^{13}$ and $[CH_3C(O)CH_2O_2] = 2.5 \times 10^{13}$ molecule cm⁻³.

The reaction between acetonylperoxy and methylperoxy radicals has one channel forming radicals and two channels producing molecules:

$$CH_{3}C(O)CH_{2}O_{2} + CH_{3}O_{2}$$

 $\rightarrow O_2 + CH_3C(O)CH_2O + CH_3O \qquad (14a)$

$$\rightarrow O_2 + CH_3C(O)CH_2OH + HCHO$$
 (14b)

 $\rightarrow O_2 + CH_3C(O)CHO + CH_3OH \qquad (14c)$

reaction (14a) is followed by reactions (8) and (9) forming $CH_3C(O)O_2$ radicals and by the reaction forming HO_2 :

$$CH_{3}O + O_{2} \rightarrow HCHO + HO_{2}$$
(15)

Kinetic analysis of time-profiles obtained at 230 and 260 nm gave: $k_{14a} = (1.2 \pm 0.4) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹; $k_{14b} + k_{14c} = (2.6 \pm 0.4) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹; which corresponds to a branching ratio $\alpha_{14} = k_{14a}/k_{14} = (0.3 \pm 0.1)$ for the radical channel. Because of the very small absorption cross-sections of the molecular products of reactions (14b) and (14c), it was not possible to determine the branching ratios for these two channels from the present kinetics experiments. However, the end-product analysis presented in the preceding paper allowed estimates of these parameters, $k_{14b}/k_{14} = (0.2 \pm 0.1)$ and $k_{14c}/k_{14} = (0.5 \pm 0.1)$.

Kinetics of the Reaction between $CH_3C(O)CH_2O_2$ and HO_2 Radicals

The reaction between acetonylperoxy and hydroperoxy radicals is a termination reaction which is likely to yield a hydroperoxide:

$$CH_{3}C(O)CH_{2}O_{2} + HO_{2} \rightarrow CH_{3}C(O)CH_{2}O_{2}H + O_{2} \quad (16)$$

Since this was a minor reaction in the preliminary photolysis of chlorine-acetone mixtures, no value of k_{16} could be obtained from the kinetic analysis. Thus, further experiments were performed with methanol also present in the photolysis mixture, allowing the formation of HO₂ radicals via the sequence of reactions:

$$CH_3OH + Cl \rightarrow CH_2OH + HCl$$
 (17)

$$CH_2OH + O_2 \rightarrow HCHO + HO_2$$
(18)

With a concentration ratio [acetone]/[methanol] = 24, the two radicals were formed in equal amounts. Kinetic analysis of time-profiles obtained at 210 and 230 nm gave the following value of the rate constant for reaction (16): $k_{16} = (9.0 \pm 1.0) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. In this kinetic determination, the accuracy was better than for the other reactions because of the large rate constant and the distinct absorptions of the two radicals.

In constrast with the situation for the reaction between acetylperoxy and hydroperoxy radicals:¹²

$$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OH + O_3$$
 (19a)

$$\rightarrow$$
 CH₃C(O)O₂H + O₂ (19b)

which forms ozone with a branching ratio of ca. 0.3, or between the propionylperoxy and hydroperoxy radicals:¹³

$$CH_3CH_2C(O)_2 + HO_2 \rightarrow CH_3CH_2C(O)OH + O_3$$
 (20a)

$$\rightarrow CH_3CH_2C(O)O_2H + O \qquad (20b)$$

which has a branching ratio of 0.23, there was no measurable residual absorption that could have been attributed to ozone formed in reaction (16).

The formation of ozone from the reactions of the acylperoxy radicals with HO_2 has been attributed to the possibility of the formation of a seven membered ring containing the sequence OHO (*i.e.* involving the carbonyl group) facilitating the simultaneous elimination of the carboxylic acid product by a concerted mechanism:

$$RC(O)O_2 + HO_2 \rightarrow RC(O)OOOOH \rightarrow RC(O)OH + O_3$$

In the case of the acetonylperoxy radical, however, the carbonyl group is not adjacent to the peroxy radical centre, and cannot participate in an analogous mechanism. Thus, the organic product of reaction (16) is believed to be a hydroperoxide species analogous to those formed from the reactions of CH_3O_2 and $C_2H_5O_2$ with HO_2 .^{3,4}

Conclusion

The results of these experiments have shown that it was only possible to determine an accurate spectrum for the acetonylperoxy radical, by taking into account the complexity of the reaction scheme initiated by the self-reaction of acetonylperoxy radicals. A full confirmation and determination of the rate constant for reactions between the acetonylperoxy radical and the other radicals involved in the reaction system was carried out by preparing mixtures such that two peroxy radicals were formed rapidly from the initial photolysis, so that their mutual reaction was preponderant. A comprehensive analysis was made possible by the complementary nature of kinetic determinations described in this paper and the end-product analysis described in the preceding one.³ This analysis shows that the rate constants measured in the present study for reactions of acetonylperoxy radicals with itself and other organic peroxy radicals are significantly higher than those reported for simple alkylperoxy radicals such as CH₃O₂ and C₂H₅O₂. This confirms recent observa2997

tions that any substituent on the above radicals tends to increase the rate constant dramatically.^{3,4} Further work is necessary, however, before definite structure-reactivity rules can be drawn.

The situation is clearer, however, for reactions of peroxy radicals with HO_2 , which have a strong atmospheric relevance. The rate constant increases by a factor of 2–3 compared with the rate constant of the CH_3O_2 reaction,^{3,4} when the peroxy radical becomes bigger and more complex. The present result confirms this rule for the acetonylperoxy radical.

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