KINETICS OF THE REACTION OF HO_2 WITH $CH_3C(O)O_2$ IN THE TEMPERATURE RANGE 253–368 K

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The kinetics of the reaction between the HO₂ and CH₃C(O)O₂ radicals has been studied in the gas phase at atmospheric pressure between 253 and 368 K. Flash photolysis was used to produce the radicals which were detected by their absorption in the UV. The two reactive channels for this reaction are CH₃C(O)O₂+HO₂ \rightarrow CH₃C(O)OOH+O₂(1a) and \rightarrow CH₃C(O)OH+O₃(1b). The overall rate constant measurement gave a value of $k_1 = (4.3 \pm 1.2) \times 10^{-13} \exp[(1040 \pm 100)/T]$ cm³ molecule⁻¹ s⁻¹; the branching ratio $k_{1b}/(k_{1a}+k_{1b})$ was found to be independent of temperature and equal to 0.33 ± 0.07.

1. Introduction

Accurate kinetic data concerning the reactions of different peroxy radicals, such as HO₂, CH₃O₂ and CH₃C(O)O₂ are needed in order to understand the complex role of these species as important intermediates during the oxidation of organic compounds in combustion systems and in the atmosphere. Mutual and cross reactions between these radicals are important terminating steps in the oxidation chain of hydrocarbons and their role is particularly crucial in clean atmospheres where the NO_x concentrations are low [1].

Recent studies of the kinetics of the mutual reactions of HO₂, CH₃O₂ and CH₃C(O)O₂ radicals have been performed in this laboratory [2–5] as well as the kinetics of the reactions of CH₃O₂ radicals with HO₂ and CH₃C(O)O₂ [2,4,5]. In this paper, we report the results of a kinetic study of the reaction of HO₂ with CH₃C(O)O₂ radicals: the reaction rate coefficient and the product channels for this reaction were studied in the temperature range 258–368 K:

 $HO_2 + CH_3C(O)O_2 \rightarrow CH_3C(O)OOH + O_2$, (1a)

$$\rightarrow$$
CH₃C(O)OH+O₃. (1b)

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No kinetic data are available on this reaction, but the product distribution was determined recently in an FTIR study by Niki et al. [6], who estimated 75% and 25% for the yields of reactions (1a) and (1b), respectively.

In this work, flash photolysis kinetic spectroscopy was used with radical concentrations monitored by absorption in the UV.

2. Experimental

All experiments were carried out using the flash photolysis apparatus described in detail elsewhere [4]. Briefly, it consists of a 70 cm long thermostatted Pyrex cell provided with a second outer evacuated jacket. The flash is generated by discharching 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 were fed into a transient recorder and passed into a microcomputer for averaging and further data analysis.

 HO_2 and $CH_3C(O)O_2$ radicals were produced by the flash photolysis of $Cl_2/CH_3CHO/CH_3OH/O_2/N_2$ mixtures according to the reaction sequence

$$Cl_2 + h\nu \rightarrow 2Cl$$
, (2)

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$$Cl+CH_3CHO \rightarrow CH_3CO+HCl$$
, (3)

$$Cl + CH_3OH \rightarrow CH_2OH + HCl$$
, (4)

$$CH_3CO + O_2 \rightarrow CH_3C(O)O_2, \qquad (5)$$

$$CH_2OH + O_2 \rightarrow CH_2O + HO_2.$$
 (6)

The gas mixtures were flowed through the cell and regulated by Tylan flow controllers. Air was used as the carrier gas and the total pressure was kept constant in all experiments at between 600 and 650 Torr. The temperature of the cell was regulated with a thermostat using ethanol or water as cooling or heating fluids.

The total peroxy radical concentration was measured relative to the absorption cross section of HO₂ at 210 nm, which is fairly well established [3,4]. This was achieved by using the same chlorine concentration and flash energy in each experiment to produce the same initial peroxy radical concentration. The exact concentration of $CH_3C(O)O_2$ radicals was measured at wavelengths near 270 nm, using the recently measured absorption cross sections [5] listed in table 1. At 270 nm, the absorption of HO₂ is negligible in the present experiments. Knowing the total

Table 1

Cross-sections used in the kinetic simulations (10^{18} \mbox{cm}^2 molecule $^{-1}$)

Wavelength (nm)	HO ₂ ^{a)}	$CH_3C(O)O_2^{(a)}$	O3 ^b
195	5.00	5.00	0.39
200	5.20	8.20	0.32
205	5.35	9.30	0.36
207	5.33	9.50	0.42
210	5.30	9.00	0.57
215	4.95	7.15	1.02
220	4.35	5.70	1.78
225	3.55	4.15	2.94
230	2.90	3.40	4.48
235	2.30	3.50	6.32
240	1.80	3.65	8.31
245	1.25	3.70	9.93
250	0.90	3.35	11.2
255	0.55	2.95	11.6
260	0.30	2.50	10.8
265	0.20	2.15	9.66
270	0.10	1.70	7.98
275	-	1.40	5.91
280	-	1.10	4.00

^{a)} Ref. [5]. ^{b)} Ref. [8].

initial radical concentration from the HO₂ calibration run, the exact HO₂ radical concentration could be calculated after subtraction of the known $CH_3C(O)O_2$ concentration and the result was verified in simultaneous simulations with time profiles recorded at various wavelengths.

Typical total initial radical concentrations of 1×10^{14} molecules cm⁻³ were used and the initial ratio $[HO_2]_0/[CH_3C(O)O_2]_0$ could be controlled by variation of the CH₃OH and CH₃CHO concentrations respectively. The typical radical concentration ratio was varied between 0.8 and 1.2.

Acetaldehyde (Fluka, 99.7%) and methanol (Merck, Spectroscopic Grade purity 99.7%) were purified by several freeze-pump-thaw cycles before use. Oxygen, and nitrogen (l'Air Liquide purity 99.5% and 99.995%, respectively), synthetic air (same purities) and Cl₂ (l'Air liquide 2% in N₂) were all used without further purification. The Cl₂ concentration was measured between experiments by optical absorption at 330 nm, using $\sigma(Cl_2) = 2.56 \times 10^{-19}$ cm² molecule⁻¹ [7].

The composite transient absorption curves were measured in the wavelength range between 207 and 270 nm. Decay traces were analysed via non-linear least-squares (NL-LS), using numerical integration of the system of differential equations [4]. Because of the problem of overlapping spectra of the peroxy radicals, a programme was used which enables several decay traces, collected at different wavelengths but under identical physicsal conditions (e.g. temperature, pressure), to be simultaneously analysed.

3. Results

The kinetics of reaction (1) was studied near the maximum of the acetylperoxy radical at 210 nm. However, experimental results indicated that at wavelength longer than 225 nm, there is an additional long-lived product detected by its increased absorption at longer reaction times in agreement with Niki's results [6]. This species was identified as ozone, after incorporating the O₃ absorption cross sections from the recent measurements by Molina and Molina [8] in the simulations. The behaviour of the optical density time profiles was simulated at various wavelengths between 210 and 270 nm by optimising the overall reaction rate constant k_1 and the branching ratio for O_3 formation. One set of experiments at various wavelengths was performed at each of the three temperatures.

Reactions (2) to (6) were assumed instantaneous on the time scale of the radical decay. The NL-LS computer simulation programme contained reactions (1) and those reactions involving HO₂, CH_3O_2 and $CH_3C(O)O_2$ radicals, the rate constants of which were measured in earlier studies [2–5]:

$$2CH_3C(O)O_2 \rightarrow 2CH_3C(O)O + O_2$$
, (7)

 $k_7 = 2.8 \times 10^{-12} \exp[(530 \pm 100)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [5],$

$$CH_{3}C(O)O \rightarrow CH_{3} + CO_{2}, \qquad (8)$$

$$CH_3 + O_2 \rightarrow CH_3O_2, \qquad (9)$$

$$2CH_3O_2 \rightarrow HCHO + CH_3OH + O_2, \qquad (10a)$$

$$\rightarrow 2CH_3O + O_2, \qquad (10b)$$

 $k_{10} = (1.3 \pm 0.15) \times 10^{-13} \exp[(365 \pm 40)/T]$ cm³ molecule⁻¹ s⁻¹ [4],

 $CH_3C(O)O_2 + CH_3O_2$

$$\rightarrow CH_3C(O)O + CH_3O + O_2, \qquad (11a)$$

$$\rightarrow CH_3C(O)OH + HCHO + O_2, \qquad (11b)$$

$$k_{11} = (1.4 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ [5]},$$

 $CH_3O + O_2 \rightarrow HCHO + HO_2 , \qquad (12)$

 $CH_3O_2 + HO_2 \rightarrow products$, (13)

 $k_{13} = 4.4 \times 10^{-13} \exp(780/T)$ cm³ molecule⁻¹ s⁻¹ [4].

At 298 K, the overall absorbance decay was simulated at 210 nm. The best fit was obtained for $k_1 = k_{1a} + k_{1b} = (1.3 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ as shown in fig. 1a, middle trace. The upper and lower traces represent the limits 1.0×10^{-11} and 1.6×10^{-11} cm³ molecule⁻¹ s⁻¹.

At this wavelength the O₃ absorption is weak and it was verified that the other reaction products, i.e. CH₃OOH, CH₃C(O)OH and CH₃C(O)OOH have no significant contribution to the optical density. Experiments were thus performed at 210 and 245 nm on a 40 ms time base and simulations included all products except for CH₃C(O)OOH for which the



Fig. 1. Kinetic simulations of experiments done at 298 K. (a) 210 nm, with $k_1 = (1.3 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ (middle trace). The upper and lower traces represent the limit 1.0×10^{-11} and 1.6×10^{-11} cm³ molecule⁻¹ s⁻¹. (b) 260 nm, effect of the inclusion of O₃ formation with a branching ratio of 0.30 (middle trace), with the limits 0.35 (upper), 0.25 (lower) and 0.0 (bottom).

cross-section is not known. It was clear in the simulations that O_3 was the major contributor to the total absorption at both wavelengths and that the kinetics were not affected by absorption by the two organic acids.

As can be seen in fig. 1b, simulations of the experiments at 265 nm show the effect of inclusion of O_3 production in the system, where the fractional contribution was 0.30 (middle trace), with limits 0.35 (upper) and 0.25 (lower). The isolated lower curve represents a simulation where the O_3 contribution was set to zero. The value of the branching ratio was obtained from a NL-LS treatment at 210, 245 and 265 nm.

At 258 K, the overall reaction rate constant k_1 is much faster than that 298 K. The best fit was obtained for $k_1 = (2.7 \pm 0.5) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. The fractional O₃ contribution was 0.36 ± 0.05 , as deduced from the simultaneous simulations done at 245 and 260 nm. Finally at 368 K, the overall reaction rate constant was obtained from simulations done at 207 nm. The best fit was obtained for $k_1 = (7.45 \pm 3.0) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. The O₃ contribution was investigated at 245 and 265 nm, and an O₃ fraction of 0.39 ± 0.05 was obtained.

The temperature dependence of the rate constant for the overall reaction between HO_2 and $CH_3C(O)O_2$ radicals is displayed in fig. 2 and can be expressed in Arrhenius form as

$$k_1 = (4.3 \pm 1.2) \times 10^{-13} \exp[(1040 \pm 100)/T]$$

cm³ molecule⁻¹ s⁻¹.

The branching ratio defined as $k_{1b}/(k_{1a}+k_{1b})$ is 0.33 ± 0.07 independent of temperature between 253 and 368 K within experimental uncertainty (fig. 3).



Fig. 2. Temperature dependence of k_1 . Error bars indicate the acceptable range of variation of k_1 values in the kinetic simulations.



Fig. 3. Temperature dependence of the branching ratio $k_{1b}/(k_{1a}+k_{1b})$. Error bars correspond to the range of variation of the branching ratio values in the kinetic simulations.

4. Discussion

This study constitutes the first measurement of the rate constant of the reaction between HO_2 and $CH_3C(O)O_2$ radicals. Two product channels have been distinguished on the basis of O_3 formation:

$$HO_2 + CH_3C(O)O_2 \rightarrow CH_3C(O)O_2H + O_2$$
, (1a)

$$\rightarrow$$
CH₃C(O)OH+O₃. (1b)

The products $CH_3C(O)OH$ and $CH_3C(O)O_2H$ had been observed in the Cl-initiated oxidation of HCHO-CH₃CHO mixtures by Niki et al. [6] who estimated the relative contributions of reactions (1a) and (1b) to be 75% and 25%, respectively, in fairly good agreement with our results, within experimental uncertainties.

These two channels can be explained by the formation of a common adduct intermediate, which may decompose in two ways:

CH₃C(O)O₂ + HO₂
O
$$\rightarrow$$
H₃-C-C-O-O-O-O-H (RO₄H)

followed by either

$$\begin{array}{c} O \\ \parallel \\ RO_4H \rightarrow O_2 + H_3 - C - C - O - O - H \end{array}$$

which is the expected pattern for $RO_2 + HO_2$ reactions, or



This second pathway is made possible in this case by the presence of the carbonyl group which allows the formation of the C=O-H-O linkage. Such an intermediate is not possible for the analogous reaction between HO_2 and CH_3O_2 radicals which therefore does not produce ozone. In that case, a cyclic structure involving a C-H bond, as shown below, can explain the formation of formaldehyde and water which were recently observed [9]:

The particular mechanism involved in the formation of O_3 in reaction (1) is not typical of reactions between peroxy radicals ($RO_2 + HO_2$) and indeed, in no other case to date, has ozone been found as a product, but it should be looked for in the products of the reaction between HO_2 and other acylperoxy radicals.

The rate constant for reaction (1) can be compared with that for similar $RO_2 + HO_2$ reactions:

$$HO_2 + CH_3O_2 \rightarrow products$$
, (13)

 $k_{13} = 3.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, E/R = 780 \text{ K}$ [4],

$$HO_2 + HOCH_2O_2 \rightarrow products$$
, (14)

 $k_{14} = 8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, E/R = 2170 \text{ K}$ [10].

The enthalpies are similar for the three reactions $(\approx -43 \text{ kcal/mol})$ and the rate constants have similar values at 298 K with strong negative temperature dependences.

5. Conclusion

The kinetics of the reaction of HO_2 radicals with $CH_3C(O)O_2$ radicals has been determined with computer-aided simulation of experimental absorption traces generated in the flash photolysis of $Cl_2/$

CH₃CHO/CH₃OH/O₂ mixtures. The results are based on the knowledge of exact absorption cross sections of the peroxy radicals produced in the chemical system. The results show that ozone organic acids are produced. Consequently, this reaction might be a possible source of CH₃C(O)OH and CH₃C(O)O₂H in remote regions of the troposphere where the NO_x concentration is lower than 10 ppt, and where reactions between peroxy radicals predominate [1]. It can reasonably be anticipated that all reactions of acylperoxy radicals with HO₂ are also sources of organic acid and ozone and this should be confirmed experimentally.

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