

UV ABSORPTION SPECTRA OF HO₂ AND CH₃O₂ RADICALS AND THE KINETICS OF THEIR MUTUAL REACTIONS AT 298 K

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Received 6 August 1986; in final form 18 October 1986

We report results of a flash photolysis study of the UV, spectra of HO₂ and CH₃O₂ radicals, obtained by using a calibration technique based on the reaction Cl + NO → NOCl. We also report preliminary results from our study of the kinetics of the reaction CH₃O₂ + HO₂ → products at room temperature and near atmospheric pressure. Our results are consistent with the only previous direct determination of the rate constant of the second reaction: $k_1 = (6.4 \pm 1.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. From the same study we derive rate constants for the self-reaction of HO₂ and CH₃O₂ radicals, which agree with recommended values.

1. Introduction

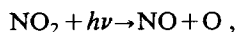
Under atmospheric conditions peroxy radical reactions are of great importance. A major factor influencing the rate of production of ozone in the troposphere is the competition between HO₂ and NO for methyl peroxy radicals in the following reactions:



removing HO₂, against



followed by



producing ozone.

In contrast to the extensive data base available concerning the self-reactions of peroxy radicals little is known about the cross-reaction (1).

To date there has been only one direct study reported on this reaction. The work of Cox and Tyndall [1], at atmospheric pressure, led to a value of $(6.0 \pm 0.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the rate constant (k_1) at room temperature. Experiments at 274 and 338 K gave a negative temperature dependence analogous to that for the HO₂ + HO₂ reaction, but no work was done to see if this similarity extended

to pressure and water vapour effects.

Recent work by Moortgat et al. [2] on the photo-oxidation of acetaldehyde has provided two preliminary values for the rate constant. By following the radical decays using UV absorption techniques they obtained $k_1 = 4.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The yield of methyl hydroperoxide in the reaction



provided the value $k_{1a} = 3.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Kan et al. [3] obtained a value of $k_{1a} = 1.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ from their FTIR product analysis of CH₃OOH yield in the self-reaction of methyl peroxy radicals.

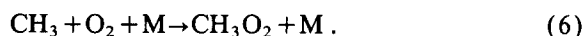
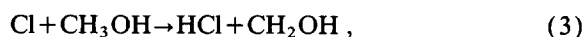
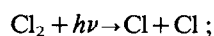
In view of the uncertainty of the value of the rate constant, and the important role of this reaction in determining tropospheric ozone levels, we have examined the kinetics of the cross-reaction at room temperature using flash photolysis kinetic spectroscopy, with UV absorption techniques to monitor the radical concentrations.

2. Experimental

All the experiments were carried out using our flash photolysis UV absorption apparatus. This apparatus will be described in full detail in a later publication. Briefly, it consists of a thermostatted pyrex reaction

cell with quartz windows to transmit the analysing light. The flash is generated by discharging two capacitors through two external argon flash lamps. The analysing beam, from a deuterium lamp, passes through the cell and impinges onto a monochromator-photomultiplier unit. The signal passes to a transient recorder and microcomputer for averaging and analysis.

The radicals were generated by the following reaction sequences:



For the determination of the spectra, these sources were used independently, but during the kinetic studies of the cross-reaction the radicals were produced by flashing $\text{Cl}_2/\text{CH}_4/\text{O}_2/\text{CH}_3\text{OH}/\text{N}_2$ mixtures. The gas mixtures flowed through the cell in all experiments.

Methanol (Merck, spectroscopic grade purity > 99.7%) was purified by several "freeze-pump-thaw" cycles before use. Oxygen, and nitrogen (l'Air Liquide, category "C", purity > 99.5% and 99.995% respectively), methane (l'Air Liquide, category "S", purity > 99.5%) and Cl_2 (l'Aire Liquide, 2% in N_2) were all used without further purification.

The amount of Cl produced during the flash was determined by a calibration technique involving NOCl. Samples of NOCl were prepared by mixing 100 Torr of chlorine with 250 Torr of NO in a well illuminated bulb for several days. It was degassed several times at -80°C , and used immediately.

3. Results

3.1. Spectra of HO_2 and CH_3O_2 radicals

A prerequisite for measurement of the kinetics of reaction (1) using UV spectroscopy is an accurate

Table 1

Previous determination of σ for CH_3O_2 at 250 nm (σ in $10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$, k/σ in 10^5 cm s^{-1})

| Ref. | σ (250 nm) | k/σ_{250} | Technique ^{a)} | |
|-----------|----------------------|------------------|--|-----|
| [1] | 3.9 | 1.33 | $\text{Cl}_2/\text{CH}_4/\text{O}_2$ | MMS |
| [5] | 2.5 | 1.2 | $\text{Cl}_2/\text{CH}_4/\text{O}_2$ | FP |
| [6] | 5.0 | 1.2 | $(\text{CH}_3)_2\text{N}_2/\text{O}_2$ | FP |
| [9] | 2.7 | 1.4 | $(\text{CH}_3)_2\text{N}_2/\text{O}_2$ | FP |
| [10] | 2.7 | 1.6 | $(\text{CH}_3)_2\text{N}_2/\text{O}_2$ | FP |
| [11] | 4.8 | 0.96 | $(\text{CH}_3)_2\text{N}_2/\text{O}_2$ | MMS |
| [12] | 4.0 ^{b)} | — | $(\text{CH}_3)_2\text{N}_2/\text{O}_2$ | LP |
| [2,14] | 3.8 | 1.18 | $\text{CH}_3\text{CHO}/\text{O}_2$ | MMS |
| this work | 4.4 | 1.34 | $\text{Cl}_2/\text{CH}_4/\text{O}_2$ | FP |

^{a)} LP: laser photolysis; FP: flash photolysis; MMS: molecular modulation spectroscopy.

^{b)} $\sigma = 3.7$ at 254 nm.

knowledge of the absorption cross section of the radicals at the appropriate monitoring wavelength. Although there is reasonable agreement between the various determinations of the HO_2 spectrum [4], the situation with CH_3O_2 is less satisfactory. For example, the values obtained for the cross section of CH_3O_2 at 250 nm range from 2.5×10^{-18} to $5.0 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ (table 1).

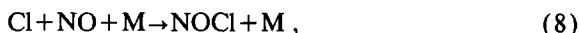
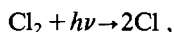
First we measured the absorption cross section of CH_3O_2 at 240 nm relative to the absorption cross section of HO_2 at 210 nm, which is fairly well established. This was achieved by using the same chlorine concentration and flash energy in each experiment, to produce the same initial peroxy radical concentration, and taking the ratio of the initial optical densities at the two wavelengths. The σ ratio obtained gave a value for the absorption cross section of CH_3O_2 at 240 nm of $4.4 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ using the value for HO_2 recommended in the NASA compilation [4].

Absolute cross sections were obtained by measuring the number of chlorine atoms produced from molecular chlorine during the flash. To do this, Cl was scavenged by NO to produce NOCl, which was monitored by its intense, well-characterised UV band at 218 nm ($\sigma = 10.7 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$, measured in this study under the same experimental conditions, in excellent agreement with the recent value obtained by Tyndall et al. [13]). Photolysis of $\text{Cl}_2/\text{NO}/\text{N}_2$ mixtures leads to the following reaction sequence

Table 2

Experimental values for the UV absorption cross sections of CH_3O_2 and HO_2 (in $10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$)

| Wavelength (nm) | σ^{HO_2} | $\sigma^{\text{CH}_3\text{O}_2}$ |
|-----------------|------------------------|----------------------------------|
| 200 | 5.25 | 1.65 |
| 205 | 5.44 | 1.91 |
| 210 | 5.37 | 2.31 |
| 215 | — | 3.18 |
| 220 | 4.37 | 3.78 |
| 225 | — | 4.15 |
| 230 | 2.86 | 4.92 |
| 240 | 1.77 | 4.86 |
| 250 | 0.85 | 4.41 |
| 255 | — | 4.12 |
| 260 | 0.35 | 3.68 |
| 265 | — | 3.12 |
| 270 | — | 2.60 |
| 272.5 | — | 2.35 |



By using a total pressure of 400 Torr, 15 Torr of NO and with $[\text{Cl}] = 6 \times 10^{13} \text{ molecules cm}^{-3}$, we ensured that reaction (8) dominated over (7) and (9) under our experimental conditions; thus all Cl atoms ultimately form NOCl. The observed yield of NOCl can be used to give the fractional dissociation of chlorine during the flash, which can then be used to give a direct measurement of the initial peroxy radical concentration in each experiment. A short back-extrapolation of the absorption, to zero time, allowed evaluation of the absolute σ for the peroxy radicals. The results are shown in table 2 and the spectra in fig. 1.

3.2. Kinetic studies of the self- and cross-reactions of CH_3O_2 and HO_2 radicals

On the basis of current knowledge [4] of the rates of reactions (1) and

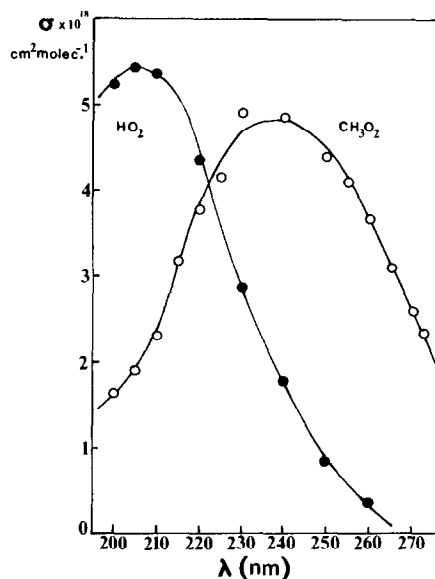
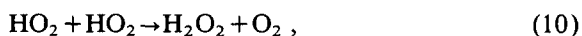


Fig. 1. UV absorption spectra of CH_3O_2 and HO_2 radicals. The spectra were determined five times, with each point shown the average of at least two measurements.



it was expected that the reaction between CH_3O_2 and HO_2 would occur in competition with the self-reactions (10) and (11) under our experimental conditions.

No simple algebraic expression is available to relate the decay rate of the radicals to the rate constant, k_1 , and consequently it was necessary to analyse the experimental curves using computer simulations. Predicted curves were compared directly to the experimental data stored on a floppy disc. The accuracy of this method was assessed from preliminary studies carried out on the self-reaction of each peroxy radical.

3.2.1. $\text{HO}_2 + \text{HO}_2$

The rate constant for this reaction and its pressure dependence is well documented [4]. By flashing flowing mixtures of $\text{Cl}_2/\text{CH}_3\text{OH}/\text{O}_2$ (with N_2 as diluent gas) over the pressure range 400–600 Torr, we observed the characteristic pressure dependence reported by other workers, and a value of $k = 2.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 400 Torr total pressure was measured.

The k/σ_{210} value agrees with the NASA recommended value [4] to within 12%.

3.2.2. $\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2$

Our value for this rate constant from simulations of the results obtained by flashing $\text{Cl}_2/\text{O}_2/\text{CH}_4$ mixtures gives $(5.9 \pm 1.0) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of pressure over the range 120–400 Torr. Although this value is 70% higher than the recommended value [4], the discrepancy arises from the different values for the absorption cross sections used here and in the compilation. Our value of $k/\sigma_{250} = 1.34 \times 10^5 \text{ cm s}^{-1}$ is in good agreement with previous values (see table 1).

3.2.3. $\text{CH}_3\text{O}_2 + \text{HO}_2$

Fig. 1 shows that at each wavelength there is some contribution to the optical density from both radicals. To obtain the individual radical concentrations, it was necessary to carry out two experiments, under identical conditions, at different wavelengths. The initial radical concentrations were thus obtainable by solving two simultaneous equations of the form

$$(\text{OD})_0 = (\sigma^{\text{HO}_2}[\text{HO}_2]_0 + \sigma^{\text{CH}_3\text{O}_2}[\text{CH}_3\text{O}_2]_0)/l$$

(l is the optical path length).

The two wavelengths were chosen to be 210 and 240 nm, as these values were close to the maxima of the HO_2 and CH_3O_2 spectra, thus ensuring strong absorptions, and hence low noise levels.

Experiments were carried out at pressures from 400 to 600 Torr and at 298 K, with total radical concentrations of the order of 6×10^{13} to $15 \times 10^{13} \text{ molecules cm}^{-3}$. A total of nine sets of experiments were performed, varying the initial $[\text{CH}_3\text{O}_2]/[\text{HO}_2]$ ratio by a factor 10. The values of the rate constant obtained from these experiments which gave the best fit, as judged visually, are presented in table 3. An example of an experimental decay curve is shown in fig. 2, together with the corresponding simulation curves with the value of k_1 set at 20% above and below its mean value. The shape of the simulation curve was found to be most sensitive to changes in the rate constant over the first 4 ms of the reaction. Hence these conditions were used in all of the experiments. The mean value from our results is

$$k = (6.4 \pm 1.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Table 3

Values of k_1 determined under different experimental conditions

| Total pressure (Torr) | $\frac{[\text{CH}_3\text{O}_2]_0}{[\text{HO}_2]_0}$ | $k_{210}^{\text{a)}}$ | $k_{240}^{\text{a)}}$ | Av. ^{a)} |
|-----------------------|---|-----------------------|-----------------------|-------------------|
| 386 | 0.58 | 6.5 | 6.5 | 6.5 |
| 417 | 0.63 | 7.5 | 6.8 | 7.3 |
| 417 | 2.2 | 7.0 | 6.5 | 6.8 |
| 417 | 0.39 | 6.3 | 5.7 | 6.0 |
| 481 | 0.9 | 5.7 | 5.5 | 5.6 |
| 580 | 1.21 | 6.7 | 6.5 | 6.6 |
| 581 | 0.67 | 6.2 | 6.0 | 6.1 |
| 581 | 0.23 | 6.0 | 6.2 | 6.1 |
| 582 | 1.64 | 6.5 | 6.5 | 6.5 |

average: 6.4

^{a)} k_{210} and k_{240} are obtained from the decays recorded at 210 and 240 nm respectively. Rate constants in $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The error limits given are ± 2 standard deviations.

This value for the rate constant was essentially independent of pressure over the range studied, but below 400 Torr it decreased with pressure. This aspect of the reaction will be considered in a later publication.

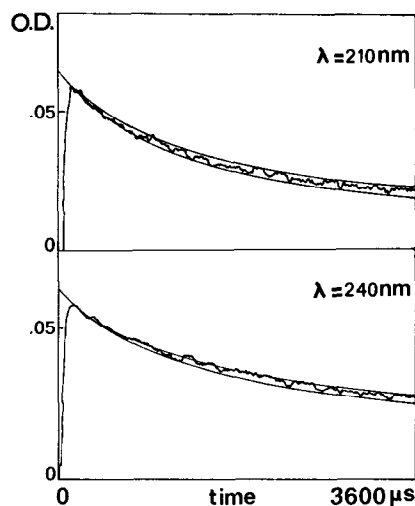


Fig. 2. Example of experimental and computer simulation curves. The curves shown are for values of $k_1 \pm 20\%$ of the average value of $6.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The experimental conditions were $[\text{CH}_3\text{O}_2]_0 = 7.1 \times 10^{13} \text{ molecules cm}^{-3}$, $[\text{HO}_2]_0 = 5.3 \times 10^{13} \text{ molecules cm}^{-3}$, and a total pressure of 581 Torr.

4. Discussion

4.1. Spectra of HO_2 and CH_3O_2 radicals

The shapes of the spectra obtained for both HO_2 and CH_3O_2 are in good agreement with those obtained previously. Our value for the absolute σ of HO_2 is in very good agreement with the value of Sander et al. [7] for σ at 227.5 nm ($3.0 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$) which was used as a basis for the NASA recommended values in the 250–200 nm region [4].

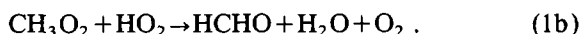
The cross sections observed in the present work are near the higher end of the range of the previously reported values for the CH_3O_2 spectrum. Due to the calibration of the Cl atom production, and our use of a relative technique, it is difficult to see how our CH_3O_2 spectrum may be too high, as any loss of Cl atoms through processes not producing CH_3O_2 would lead to lower values of σ .

4.2. Kinetic results

Our value for the rate constant, at atmospheric pressure, of $(6.4 \pm 1.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is in very good agreement with the value of $(6.0 \pm 0.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained by Cox and Tyndall [1].

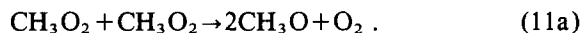
The value of $k_1 = 4.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained by Moortgat et al. [2] was based on a value for $\sigma_{\text{CH}_3\text{O}_2}$ ($3.8 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 250 nm), some 15% lower than the value obtained in this study. Reinterpretation of their results using our σ value would yield a rate constant close to the value of Cox and Tyndall [1] and ourselves.

The other two determinations, from analysis of the CH_3OOH product yields, $3.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ by Moortgat et al. [2], and $1.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ by Kan et al. [3] appear therefore to disagree with the direct determinations. The discrepancy between the values obtained from observation of the radical decays, and observation of product yields, could be an indication of the existence of alternative product pathways for this reaction, such as the exothermic route

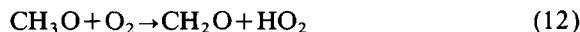


Alternatively, the calibrations on which the yields of CH_3OOH were based could be in error.

Possible complications to the chemistry may arise from the CH_3O radicals formed in one of the product channels of the self-reaction of CH_3O_2 radicals



Of the reactions available to CH_3O radicals the large excess of O_2 over two radical species (10^5 greater) will ensure that the reaction



will dominate and any CH_3O radicals formed will be rapidly converted to HO_2 ($\approx 20 \mu\text{s}$ time scale), causing an increase in $[\text{HO}_2]$ and therefore an increase in the rate of decay of CH_3O_2 radicals through reaction (1). This could lead to an overestimation of the rate constant of reaction (1). These reactions were included in the simulation program, and we found that under our experimental conditions omission of the methoxy radical chemistry had a negligible effect on the value of the rate constant.

Cox and Tyndall [1] observed the formation of a strongly absorbing product during their experiments, which they identified as methyl hydroperoxide. The spectrum of this compound has been measured [8] and is similar to that of H_2O_2 . The absorption of these species is unimportant at 240 nm, but needs to be considered at 210 nm, and was included in the simulations.

We are currently investigating the effects of pressure, temperature and water vapour on this reaction and will report our results shortly.

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