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Fourier-transform Infrared Product Study of the Reaction of $CH_3O_2 + HO_2$ over the Pressure Range 15–700 Torr at 295 K

Timothy J. Wallington
Research Staff SRL E-3083, Ford Motor Company, P.O. Box 2053, Dearborn, MI 48121, USA

Fourier-transform infrared spectroscopy was used to establish methyl hydroperoxide as the dominant product of the gas-phase reaction of methylperoxy radicals with hydroperoxy radicals. Over the pressure range 15–700 Torr† of either air or oxygen, 92 ± 5% of the reaction of CH_3O_2 with HO_2 proceeds *via* channel (1*a*)

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \qquad (1a)$$

Quoted errors represent 2σ. This result is discussed with respect to previous kinetic and mechanistic studies of peroxy radicals and computer models of atmospheric chemistry.

The reaction of methylperoxy radicals, CH_3O_2, with hydroperoxy radicals, HO_2, plays a key role in the oxidation of methane in the earth's atmosphere and is an important reaction occurring in many laboratory chemical systems designed to study peroxy radical chemistry.

$$CH_3O_2 + HO_2 \rightarrow \text{products} \qquad (1)$$

It was thought that reaction (1) proceeded through one channel, *via* a hydrogen-abstraction mechanism, leading to CH_3OOH and O_2 as products. However, this has been challenged recently by Jenkin *et al.*[1] with the detection of HDO as a product of the reaction of $CD_3O_2 + HO_2$ which suggests that reaction of CD_3O_2 with HO_2 proceeds *via* two channels:

$$CD_3O_2 + HO_2 \rightarrow CD_3OOH + O_2 \qquad (1a)$$

$$CD_3O_2 + HO_2 \rightarrow DCDO + HDO + O_2 \qquad (1b)$$

From the observed rate of HDO formation at 11 Torr total pressure, Jenkin *et al.*[1] tentatively proposed a branching ratio of $k_b/(k_a + k_b) = 0.4$ for the reaction of CD_3O_2, and by analogy CH_3O_2, radicals with HO_2. This result is supported by the measurements of Moortgat *et al.*[2] of the rate of CH_3OOH production during photolysis of acetaldehyde in 700 Torr of air. In their study they found the rate of CH_3OOH production to be *ca.* 30% less than the rate of loss of CH_3O_2 and HO_2 radicals, implying the existence of a reaction channel other than (1*a*).

In contrast to the results of Jenkin *et al.*[1] and Moortgat *et al.*[2] Wallington and Japar[3] recently reported results from a study of the products of reaction (1) at 700 Torr which showed that CH_3OOH was the dominant product, with a yield of 92 ± 8%. It is difficult to reconcile this result with the observations of Moortgat *et al.*[2] which were made under essentially identical conditions. However, the results of Wallington and Japar may be consistent with those of Jenkin *et al.* if total pressure affects the branching ratio, with k_{1a}/k_1 decreasing at lower pressures.

To model accurately hydrocarbon oxidation in the atmosphere, and in laboratory systems designed to simulate atmospheric chemistry, it is important to establish the effect, if any, of pressure on the branching ratio of reaction (1). To provide such information the FTIR spectroscopic technique has been used to study the products of reaction (1) over the pressure range 15-700 Torr at 295 ± 2 K.

Experimental

The apparatus and experimental techniques used have been described in detail previously[3,4] and are discussed only briefly here. Methylperoxy and hydroperoxy radicals were generated by the photolysis of molecular fluorine in the presence of methane and hydrogen in either ultra-pure synthetic air (at 700 Torr) or oxygen (at 15, 25 and 50 Torr);

$$F_2 + h\nu \rightarrow 2F \qquad (2)$$

$$F + CH_4 \rightarrow CH_3 + HF \qquad (3)$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \qquad (4)$$

$$F + H_2 \rightarrow H + HF \qquad (5)$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad (6)$$

The loss of methane and the formation of products were monitored using FTIR spectroscopy. The pathlength for the analysing IR beam was 26.6 m. The spectrometer was operated at a resolution of 0.25 cm^{-1}. IR spectra were derived from 32 co-added interferograms. Reference spectra were obtained by expanding known volumes of the reference material into the long-pathlength cell. Methane had a stated purity of >99.996% and was used as received. Methyl hydroperoxide, CH_3OOH, was synthesized by alkylation of hydrogen peroxide (30%) in basic solution using dimethylsulphate as described by Vaghjiani and Ravishankara.[5] Uncertainties associated with quantitative analyses using these reference spectra are estimated to be <5% for methane and *ca.* 5% for CH_3OOH.

Products were quantified by fitting reference spectra of the pure compounds obtained at appropriate total pressures to the observed product spectra using integrated absorption features. The procedure was as follows: the CH_4 reactant was first quantified and subtracted from the product spectra using characteristic absorption features over the wavelength regions 1320–1370 and 2800–3000 cm^{-1}. Methylhydroperoxide, formic acid, formaldehyde, methyl fluoride, CO and CO_2 were then identified and quantified using features over the following wavelength ranges 800–900 and 2800–3000; 1700–1900; 1500–1700; 1000–1100; 2000–2200; and 2250–2350 cm^{-1} respectively.

Initial concentrations of the gas mixtures used were 0.10–0.16 Torr of methane (>99.996% purity), 0.5–1.1 Torr of hydrogen (>99.9% purity) and 0.1–0.4 Torr of fluorine (>97% purity, supplied as a 5% mixture in He). Ultra-pure synthetic air was used as diluent for experiments at 700 Torr

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† 1 Torr = 101 325/760 Pa.

Table 1 Reaction mechanism

reaction	rate constant /cm^3 molecule^{-1} s^{-1}
$F_2 + h\nu \rightarrow F + F$	
$F + CH_4 \rightarrow CH_3 + HF$	8.0×10^{-11}
$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$	2.3×10^{-13} [a]
$F + H_2 \rightarrow H + HF$	2.7×10^{-11}
$H + O_2 + M \rightarrow HO_2 + M$	9.1×10^{-14} [a]
$CH_3O_2 + CH_3O_2 \rightarrow 2CH_3O + O_2$	1.3×10^{-13}
$CH_3O_2 + CH_3O_2 \rightarrow HCHO + CH_3OH$	2.1×10^{-13}
$CH_3O + O_2 \rightarrow HCHO + HO_2$	1.9×10^{-15}
$CH_3O_2 + HO_2 \rightarrow$ products	4.5×10^{-12}
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	1.7×10^{-12} [a]

[a] Value appropriate for 50 Torr total pressure.

and oxygen was used at lower total pressures. Experiments were performed at 295 ± 2 K.

Results

As described previously,[3] the formation of CH_3O_2 radicals in the reaction chamber is followed by a competition between reactions (1) and (4) for the available radicals:

$$CH_3O_2 + HO_2 \rightarrow \text{products} \quad (1)$$

$$CH_3O_2 + CH_3O_2 \rightarrow \text{products} \quad (7)$$

By suitable choice of initial conditions, reaction (1) can be made the major loss process for the methylperoxy radicals. To select the initial conditions, the chemistry within the chamber was simulated using the Acuchem kinetic modelling program[6] and the chemical mechanism given in Table 1. The kinetic data used in this mechanism were taken from the latest NASA[7] and IUPAC[8] recommendations. The value of k_1 is the subject of debate in the literature with reported values in the range $2.9\text{–}6.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[9] In the present work, $k_1 = 4.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} was used. To select the optimal initial $[H_2]/[CH_4]$ concentration ratio one must compromise the desire to work under conditions where the largest fraction of CH_3O_2 radicals react with HO_2 with the need to measure appreciable carbon containing products for a given F atom flux. In the present series of experiments, concentration ratios of $[H_2]/[CH_4]$ of 4.8–8.7 were used. Under these conditions 89–95% of the loss of CH_3O_2 will be *via* reaction (1).

In all experiments, the dominant product observed was methyl hydroperoxide. Minor carbon containing products identified were; CO, HCHO, HCOOH, CH_3F and CO_2. Carbon containing product yields measured at 15, 25 and 50 Torr total pressure in the present work are given in Table 2. Yields of CO_2 were in all cases small (<2% of methane loss) and are not listed. Yields given in Table 2 are the experimentally observed concentrations in the chamber immediately following irradiation and have not been subject to any corrections. As a check of the experimental reproducibility, two experiments were conducted at 700 Torr total pressure to compare with data previously reported at this pressure. In the 700 Torr experiments the initial CH_4 and H_2 concentrations were 160 and 1400 mTorr, respectively. Irradiation of the mix for 1.5 and 3 min led to the loss of 3.09 and 7.70 mTorr of CH_4 and the formation of 3.12 and 7.70 mTorr of CH_3OOH. These results are consistent with those reported earlier from this laboratory.[3] The observed product yields at 700 Torr in the present experiments are not listed in Table 2, they are, however, given in Fig. 1.

At all total pressures a small amount of H_2O product was observed by virtue of its IR features over the range 1500–1700 cm^{-1}. This H_2O product was present at yields of 10–20%. When reaction mixtures were left to stand in the dark the H_2O product was observed to increase and H_2O_2, a product of the self-reaction of HO_2 radicals in the chamber, slowly decreased (H_2O_2 lifetime *ca.* 1 h). The loss of H_2O_2 accounts for the majority of the H_2O product observed, additional sources for the observed H_2O features include, changes in the efficiency of the purging of optical elements external to the chamber, or possibly channel (1*b*). In view of the ubiquitous nature of H_2O and the observed dark source of this species in the chamber no mechanistic inference concerning reaction (1) is drawn from the formation of H_2O.

To calculate the methyl hydroperoxide product yield in reaction (1) allowance must be made for, (i) loss of methyl radicals *via* reaction with molecular fluorine, (ii) the fact that not all of the CH_3O_2 radicals react with HO_2 and (iii) potential losses of hydroperoxide in the chamber.

Regarding the first point, reaction of CH_3 radicals with fluorine is a complication caused by the competition of reac-

Table 2 Product yields[a] following the irradiation of CH_4–H_2–F_2 mixtures

irradiation time[b]/min	$[CH_4]_0$	$[H_2]_0$	$\Delta[CH_4]$	$\Delta[CH_3OOH]$	$\Delta[CO]$	$\Delta[HCHO]$	$\Delta[HCOOH]$	$\frac{\Delta[CH_3OOH]}{\Delta[CH_3F]}$	$\frac{\Delta[CH_3OOH]}{\Delta[CH_4]}$	carbon balance (%)
0	131	1140	(50 Torr total pressure)							
5			5.25	4.22	0.18	0.30	0.22	trace[c]	0.80	94
10			7.22	5.37	0.58	0.61	0.37	0.11	0.74	97
15			10.5	9.20	0.77	0.76	0.65	0.11	0.88	109
20			12.5	10.9	1.55	0.91	0.90	0.21	0.87	116
25			13.1	11.5	1.92	0.61	1.31	0.21	0.88	119
0	105	502	(25 Torr total pressure)							
25			7.37	5.75	0.69	0.91	0.75	0.21	0.78	113
0	137	804	(15 Torr total pressure)							
5			6.88	3.83	0.23	1.52	0.19	2.78	0.56	124
10			13.75	7.29	0.58	1.83	0.56	3.61	0.53	101
15			17.9	9.59	0.58	1.83	0.94	4.71	0.53	99
20			20.6	11.1	0.81	1.67	1.32	4.98	0.54	96
0	158	870	(15 Torr total pressure)							
10			7.90	5.75	0.50	1.21	0.37	1.33	0.73	116

[a] All concentrations are in units of mTorr. [b] These times are not absolute; the fluorescent lamps employed in this work were not equipped with pre-ignition coils, thus there was a small variable time delay between switching the lamps on and the lamps igniting. [c] Trace amount detected, *i.e.* $[CH_3F] < 0.06$ mTorr.

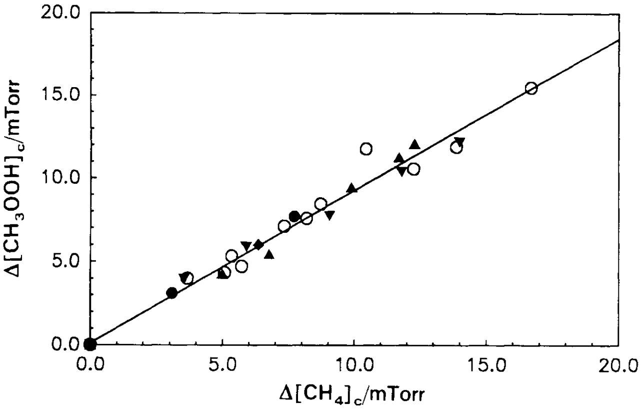

Fig. 1 Observed increase in CH_3OOH concentration, corrected for loss *via* reaction with F atoms, as a function of the methane loss, corrected for CH_3F formation and CH_3O_2 self-reaction. Data acquired at different pressures; ●, 700 Torr; ▲, 50 Torr; ◆, 25 Torr; and ▼, 15 Torr. Open symbols represent previous data[3] acquired at 700 Torr for comparison. The solid line is a linear least-squares fit to all the data

tions (4) and (8) for available methyl radicals:

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \quad (4)$$

$$CH_3 + F_2 \rightarrow CH_3F + F \quad (8)$$

The rate of reaction (4) decreases with decreasing pressure whereas reaction (8) is independent of pressure; hence formation of CH_3F is favoured at lower pressures. To reduce the formation of CH_3F at low pressures, pure O_2 was used as the diluent at 50, 25 and 15 Torr total pressure. Nevertheless, as seen from Table 2, CH_3F was a significant product at the lowest pressures. Indeed, it was the increasing importance of CH_3F formation through reaction (8) which placed a limit on the lowest pressures at which experiments could be performed without unduly large corrections being required.

With regard to the second point, the experimental conditions were chosen so that 89–95% of the methylperoxy radicals reacted with HO_2 radicals. Thus, the amount of methylperoxy radicals reacting with HO_2 was 5–11% less than the amount of methylperoxy radicals produced.

Finally, possible loss mechanisms for the hydroperoxide in the reaction chamber include photolysis, heterogeneous loss, and reaction with F atoms. It has been demonstrated recently that within the reaction chamber there is no observable photolysis or heterogeneous loss of CH_3OOH at 700 Torr total pressure.[10] In the present work, CH_3OOH was admitted into the chamber in oxygen diluent at 15 Torr total pressure, left in the dark for 10 min, then irradiated with the output of all UV lamps for 30 min. No loss (<4%) of CH_3OOH was observed, indicating that both photolysis and heterogeneous reactions are unimportant. To assess the loss of CH_3OOH through reaction with F atoms requires knowledge of the rate constant for this reaction. This rate constant has not yet been determined. Based upon the available kinetic data base for the reactions of F and Cl atoms with alkanes and oxygenated organics[7,11] it seems reasonable to ascribe a rate constant of $k_9 = (1.0 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

$$F + CH_3OOH \rightarrow \text{products} \quad (9)$$

To assess the potential impact of this reaction on the measured CH_3OOH yields it was added to the chemical mechanism given in Table 1 and simulations of each of the experiments were performed. Under the experimental conditions, assuming a value of $k_9 = 1.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, reaction with F atoms leads to a small (2–10%) loss of the hydroperoxide.

Fig. 1 shows a plot of the observed CH_3OOH product yield, corrected for loss due to reaction with F atoms, as a function of the observed loss of methane, corrected for the formation of CH_3F and that fraction of CH_3O_2 radicals that is lost *via* self-reaction. As seen from Fig. 1 there is no observable effect of pressure on the yield of methyl hydroperoxide from reaction (1). Linear least-squares analysis of all the data given in Fig. 1 yields a value of 92 ± 5% for the hydroperoxide yield from reaction (1), independent of pressure over the range 15–700 Torr (quoted errors represent 2σ).

All errors thus far represent random errors. At this point potential systematic errors will be considered. Sources of potential systematic error in the determination of the product yield of reaction (1) are: errors in measurement of $\Delta[CH_4]$ and $\Delta[CH_3OOH]$ and errors in the corrections applied to these quantities. With regard to the measurement of $\Delta[CH_4]$ and $\Delta[CH_3OOH]$ it is estimated that systematic errors in these values could, when combined, add an additional 10% uncertainty. The estimation of potential systematic errors in the correction factors applied to the data is more difficult. The largest single correction applied was to account for CH_3F formation at 15 Torr total pressure. Based upon the calibration of the infrared features of CH_3F over the range 1000–1100 cm^{-1} it is estimated that systematic errors in this correction add <5% additional uncertainty. Potentially the most significant source of systematic error lies in the values of k_1 and k_7 that are used to calculate the fraction of CH_3O_2 radicals which are lost *via* reaction (11). The value of k_7 used in this work was taken from the latest IUPAC recommendation. Uncertainties in k_7 are small as the recommendation is based upon nine previous determinations; in contrast k_1 is less well defined with reported values of k_1 spanning the range $(2.9\text{–}6.8) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[9] To assess the sensitivity of the results to the value of k_1, the data were analysed with k_1 varied over the range $3\text{–}7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Using a value of $k_1 = 3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} increases the CH_3OOH yield to 99% and using a value of $k_1 = 7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} decreases the yield to 87%.

Discussion

Results from the present study are consistent with the reaction of $CH_3O_2 + HO_2$ proceeding through a single channel, yielding CH_3OOH as the sole carbon-containing product, over the pressure range 15–700 Torr at 295 K. Although small amounts of CH_3F, HCHO, HCOOH and CO were detected, these were minor products whose formation can be explained by secondary chemistry. While the present results do not preclude the existence of a small, *ca.* 10%, contribution from reaction channel(s) leading to products other than CH_3OOH, they are inconsistent with the 40% contribution of channel (1*b*) proposed previously.[1]

This discrepancy implies the presence of systematic errors in one or both studies. As noted above, systematic errors in the present work may add an additional *ca.* 10% uncertainty in the determination of k_{1a}/k_1. However, such errors, if present in this work, cannot explain the difference between the two studies.

Systematic errors in the work of Jenkin *et al.*[1] could arise as a result of either the overestimation of the HDO product from channel (1*b*) or an underestimation of the amount of CD_3O_2 consumed. The former possibility has been discussed previously[3] and is not dealt with here. The latter possibility has been addressed recently by Jenkin *et al.*[12] In the derivation of $k_{1b}/k_1 = 0.4$, Jenkin *et al.*[1] calculated the CD_3O_2 production rate by assuming that the rate of reaction of CD_3 radicals with O_2 was equal to that of CH_3 radicals with O_2.

$$CD_3 + O_2 + M \rightarrow CD_3O_2 + M \qquad (10)$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \qquad (4)$$

Knowledge of the reaction rate was important in the system, since the reaction of CD_3 with O_2 was occurring in competition with the reaction of CD_3 with Cl_2. However, because of the greater density of vibrational states in CD_3O_2 compared with CH_3O_2, and the correspondingly larger low-pressure limiting rate constant, reaction (10) is probably significantly faster than reaction (4). In a recent reappraisal of the system, Jenkin *et al.*[12] used literature data for the vibrational frequencies in CD_3O_2 and CH_3O_2 [13] and estimated that $k_{10}/k_4 \approx 4$ at the low-pressure limit. Thus, the production rate of CD_3O_2 was probably significantly underestimated in the original calculations of Jenkin *et al.*[1]

A further way in which the rate of formation of CD_3O_2 radicals could be underestimated is if the rate of reaction of Cl with CH_3OH employed was overestimated. In the experimental system employed by Jenkin *et al.*,[1] CD_4 and CH_3OH compete for the available Cl atoms. Use of a lower value for k_{11} will lead to an increase in the calculated CD_3O_2 flux.

$$Cl + CH_3OH \rightarrow \text{products} \qquad (11)$$

The sole available literature value of $k_{11} = 6.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} was used by Jenkin *et al.*[1] in the simulation of their data. Recently three further determinations of k_{11} have been published using both absolute[11] and relative rate techniques[14,15] which report values of $k_{11} = (5.0 \pm 1.0) \times 10^{-11}$, $(4.6 \pm 0.4) \times 10^{-11}$ and $(5.3 \pm 1.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively. All these values are lower than that used by Jenkin *et al.*[1]

In their recent reappraisal of the system, Jenkin *et al.*[12] used an average of the recent values of k_{11} (5×10^{-11} cm^3 molecule^{-1} s^{-1}) together with an updated value of k_{10} to reanalyse their original data[1] and derived a revised value of $k_{1b}/k_1 = 0.25$. This reanalysis reduces, but does not eliminate, the discrepancy between the two studies.

The chemical system used in the present work is more direct than that employed by Jenkin *et al.*[1] Hence results from the present work are less likely to be subject to significant systematic errors. Although the results from Jenkin *et al.*[1,12] claim to provide evidence for the presence of channel (1*b*) the present experiments indicate that this channel makes a minor, or zero, contribution to reaction (1) over the pressure range 15–700 Torr at 295 K.

Conclusion

Results from the present work show that methyl hydroperoxide is the sole product, within experimental error, of the reaction of CH_3O_2 radicals with HO_2 over the pressure range 15–700 Torr. This conclusion is consistent with the previous determination that ethyl hydroperoxide is the sole product following the reaction of $C_2H_5O_2$ radicals with HO_2.[16] In the absence of experimental evidence to the contrary, it is recommended that reactions of the general type $RO_2 + HO_2$, where R is an unsubstituted alkyl group (CH_3, C_2H_5, C_3H_7 *etc.*), should have the following single channel in models of atmospheric chemistry:

$$RO_2 + HO_2 \rightarrow ROOH + O_2$$

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