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FTIR Product Study of the Reactions $CH_3O_2 + CH_3O_2$ and $CH_3O_2 + O_3$

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The products of the self-reaction of methylperoxy radicals have been determined at 296 K in a 140-L chamber using continuous ultraviolet photolysis with FTIR detection. The branching fraction for the reaction channel giving methoxy radicals is found to be (41 ± 4)%, in good agreement with two earlier studies but somewhat higher than the most recent investigations. No evidence was found for the production of CH_3OOCH_3 (yield $<6\%$). The addition of ozone led to changes in the rates of formation of the major products, which could largely be explained by chemistry of the OH radical. However, some evidence was found for a slow reaction of CH_3O_2 with O_3 occurring with a rate coefficient of 1×10^{-17} cm^3 molecule^{-1} s^{-1}, with an uncertainty of a factor of 2. As part of the present work a relative rate technique was used to measure $k(Cl + CH_3N_2CH_3) = (4.8 \pm 0.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 296 K. The decay of peroxy radical concentrations in the nighttime clean troposphere is interpreted in terms of the product branching ratios and the rate coefficient for the reaction of $CH_3O_2 + O_3$.

Introduction

Organic peroxy radicals, RO_2 (where R is an alkyl or acyl group), are involved in the production of ozone in the troposphere through their interaction with active nitrogen species.[1−3]

$$RO_2 + NO \rightarrow RO + NO_2 \qquad (1)$$

$$RO + O_2 \rightarrow R'CHO + HO_2 \qquad (2)$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (3)$$

$$NO_2 + h\nu \rightarrow NO + O \qquad (4)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (5)$$

The sum of the peroxy radical concentrations present in the atmosphere ($RO_2 + HO_2$) has been measured under a variety of conditions using the chemical amplifier technique.[4−9] Models indicate that the sum of the concentrations of organic peroxy radicals is normally equal to, or slightly less than, the concentration of HO_2 radicals during daylight.[3,5]

Under conditions of low NO_x, such as the marine or free troposphere, the reaction of HO_2 radicals with O_3 can become a major loss of O_3.[3]

$$HO_2 + O_3 \rightarrow OH + 2O_2 \qquad (6)$$

Thus, depending on the NO_x level, peroxy radicals can be a source or sink for O_3. For clean background conditions with low hydrocarbon loading, methylperoxy radicals are expected to constitute almost 100% of the organic peroxy radicals.

At nighttime in the remote troposphere, peroxy radicals are removed slowly, and the balance changes from HO_2 being the major radical to CH_3O_2.[1,7,9] Under these circumstances the predominant loss process for RO_2 is the molecular channel of the peroxy radical self-reaction 7b or the reaction with HO_2.

$$CH_3O_2 + CH_3O_2 \rightarrow CH_3O + CH_3O + O_2 \qquad (7a)$$

$$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + HCHO + O_2 \qquad (7b)$$

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \qquad (8)$$

The self-reaction of CH_3O_2 radicals (reaction 7) has been the subject of many studies.[10−22] Current recommendations for the rate coefficient k_7 are based on studies that used time-resolved UV absorption spectroscopy coupled with either flash photolysis[10−13] or modulated photolysis.[14−16] The product branching ratio has been determined using continuous photolysis (with product measurements using mass spectrometry,[18] FTIR,[19,20] or gas chromatography[17,22]), flash photolysis with UV detection,[13] or a slow flow photolysis technique with matrix isolation/FTIR detection.[21] Studies of CH_3O_2 kinetics generally require a knowledge of the product branching ratios for reaction 7, since the methoxy radicals from reaction 7a lead to the formation of HO_2 radicals, which then contribute to the CH_3O_2 loss via reaction 8.[13−16]

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \qquad (9)$$

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \qquad (8)$$

While a branching fraction k_{7a}/k_7 of 35−45% was found in earlier studies,[17−20] more recent studies have suggested that the radical channel may be less than 30%.[13,21,22]

The reaction of CH_3O_2 with ozone has only been studied once before, by Simonaitis and Heicklen,[23] and the products were

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assumed to be analogous to those in reaction 6.

$$CH_3O_2 + O_3 \rightarrow CH_3O + 2O_2 \tag{10}$$

In that study, ozone photolysis was used as the source of free radicals. Ozone was the only chemical species measured, and the results were analyzed in terms of the quantum yield for ozone loss in a steady-state treatment.

We report here a study of the self-reaction of CH_3O_2 radicals using FTIR product analysis and examine the effect on product yields caused by the addition of O_3. Both the photolysis of $Cl_2-CH_4-O_2$ and that of azomethane$-O_2$ mixtures were used as sources of CH_3O_2. Some discrepancies between previous studies using the different sources are examined. The use of azomethane photolysis allows CH_3O_2 radicals to be produced independently of ozone photolysis, and a full product analysis constrains the number of unknowns in the system. The results obtained are used to interpret some recent atmospheric measurements of peroxy radicals.

Experimental Section

The experimental system has been described in detail elsewhere.[24] Experiments were carried out at 296 K in a large Pyrex chamber surrounded by 22 black lamps. Methyl radicals, produced by the photolysis of azomethane (AZM) or by the photolysis of Cl_2 in the presence of methane, were converted to methylperoxy by the presence of a large excess of oxygen:

$$CH_3N_2CH_3 + h\nu \rightarrow CH_3 + CH_3 + N_2 \tag{11}$$

$$Cl_2 + h\nu \rightarrow Cl + Cl \tag{12}$$

$$Cl + CH_4 \rightarrow HCl + CH_3 \tag{13}$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \tag{14}$$

The azomethane photolysis lasted up to 30 min, while the Cl_2-CH_4 mixtures required only 2-min photolysis. Reactants and products were monitored by FTIR spectroscopy at a resolution of 0.25 cm^{-1}. The oxygen partial pressure was varied between 8 and 700 Torr, with the total pressure made up to 700 Torr with N_2 where necessary. The initial pressures used in the experiments were azomethane, 22.5 or 255 mTorr; CH_4, 25−39 Torr; Cl_2, 93 mTorr; O_3, 35−51 mTorr. Ozone was produced by the action of a corona discharge on a slow flow of O_2, and the mixture was flowed directly into the photolysis chamber. The O_3 concentration in the cell was quantified using a calibrated reference spectrum taken from the library at Ford Motor Company (over the frequency range 975−1075 cm^{-1}, the integrated absorption cross section is 1.49×10^{-17} cm molecule^{-1}). Azomethane was synthesized in near-quantitative yields using the oxidation of 1,2-dimethylhydrazine with mercuric oxide.[25] When not in use, it was stored in liquid nitrogen. The infrared spectrum showed no signs of impurity based on comparison with the literature spectrum of Niki et al.[26] Formaldehyde was prepared by heating a sample of paraformaldehyde under vacuum. The formaldehyde cross sections were verified by producing HCHO in situ from the photolysis of $CH_3OH-Cl_2-O_2$ mixtures and by monitoring the loss of methanol and the production of HCHO.

$$Cl + CH_3OH \rightarrow HCl + CH_2OH \tag{15}$$

$$CH_2OH + O_2 \rightarrow HCHO + HO_2 \tag{16}$$

From the formation rate of HCHO in the photolysis of $Cl_2-CH_3OH-O_2$ mixtures, the Cl_2 photolysis rate was determined to be $(1.2 \pm 0.2) \times 10^{-3}$ s^{-1}.

To assess the reactivity of azomethane, and the potential for its loss by reaction with OH, the rate coefficients for the reaction of chlorine atoms with azomethane were measured relative to those of C_2H_6 and C_2H_4, both in the presence and in the absence of O_2. Pressures of reactants used in the relative rate experiments were AZM 50−71 mTorr, C_2H_4 6.4 mTorr, C_2H_6 15.2 or 28.2 mTorr, and Cl_2 310−490 mTorr, and the typical UV irradiation periods were 2−10 s.

Results

Relative Rate Study of the Reaction of Cl Atoms with $CH_3N_2CH_3$. The rate coefficient for the reaction of Cl atoms with azomethane was measured using the relative rate technique. Two experiments were performed using each of the reference gases ethane and ethene.

$$Cl + CH_3N_2CH_3 \rightarrow \text{products} \tag{17}$$

$$Cl + C_2H_6 \rightarrow HCl + C_2H_5 \tag{18}$$

$$Cl + C_2H_4 + M \rightarrow C_2H_4Cl + M \tag{19}$$

The slopes of plots of ln[AZM] versus ln[REF] gave values for the rate coefficient ratios of 0.84 ± 0.04 relative to ethane (in N_2 or air) and 0.52 ± 0.04 relative to ethene (in air). When combined with the literature values for k_{18}[27] and k_{19},[28] identical values of $k_{17} = (4.8 \pm 0.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 296 K are obtained. This result is similar in magnitude to $k_{18} = 5.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1},[27] indicating that the reactivity of the $-CH_3$ groups in azomethane and ethane with respect to Cl atom attack is comparable.

Methylperoxy Self-Reaction. Experiments were performed using the photolysis of $AZM-O_2$ or $Cl_2-CH_4-O_2$ mixtures to determine the product yield from the methylperoxy self-reaction. The major products observed were HCHO, CH_3OH and CH_3OOH with minor amounts of CO and HCOOH.

$$CH_3O_2 + CH_3O_2 \rightarrow CH_3O + CH_3O + O_2 \tag{7a}$$

$$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + HCHO + O_2 \tag{7b}$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \tag{9}$$

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \tag{8}$$

Wallington and co-workers[29−31] have shown that CH_3OOH is the major, if not sole (>92%), product of reaction 8. The CO and HCOOH are formed from secondary chemistry involving reactions of Cl atoms and HO_2 with HCHO.[32,33]

The most reliable experiments were those using the Cl_2-CH_4-air system, because the short photolysis times minimized secondary loss of HCHO and CH_3OOH. Since Cl atoms are much more reactive toward the reaction products (HCHO, CH_3OH, and CH_3OOH) than toward CH_4, high concentrations and low conversions of CH_4 must be used, and the depletion of CH_4 cannot be measured directly. However, the high methane concentrations did not interfere with the spectral analysis. The results of a typical experiment are shown in Figure 1. Four different experiments were carried out, using a range of oxygen pressures. The results of these experiments are shown in Table 1 and Figure 2. The ratios HCHO:CH_3OH and CH_3OOH:CH_3-

TABLE 1: Product Yields Obtained Using Cl_2-CH_4 Photolysis

$[Cl_2]_0$, mTorr	$[CH_4]_0$, Torr	$[O_2]_0$, Torr	time, s	HCHO, mTorr	CH_3OH, mTorr	CH_3OOH, mTorr	CO, mTorr	HCHO/ CH_3OH	CH_3OOH/ CH_3OH
93	25.3	700	60	5.0	2.0	2.6	0.7	2.50	1.30
93	29.6	140	120	11.4	4.1	7.6	3.0	2.56	1.46
93	26.4	140	60	5.0	2.0	2.8	0.7	2.50	1.40
93	38.8	10.3	60	5.2	2.2	2.4	0.6	2.36	1.10

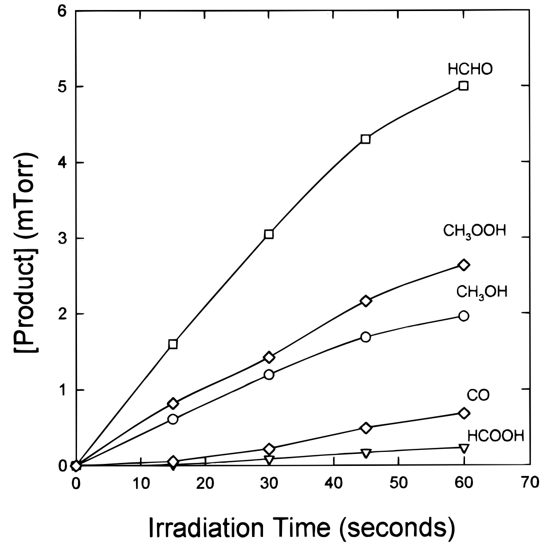

Figure 1. Time dependence of the products obtained in the photolysis of 93 mTorr of Cl_2 and 26.4 Torr of CH_4 in air at 296 K. The lines are for guidance only.

OH are 2.44 ± 0.10 and 1.3 ± 0.2, respectively (uncertainties are 2 standard deviations throughout the paper). As noted by Niki and co-workers,[20] each of these ratios gives an independent measure of the ratio k_{7a}/k_{7b}, provided that HO_2 radicals react exclusively with CH_3O_2 to give CH_3OOH and that the products are not lost to secondary reactions.

$$\frac{[HCHO]}{[CH_3OH]} = \frac{2k_{7a} + k_{7b}}{k_{7b}}$$

$$\frac{[CH_3OOH]}{[CH_3OH]} = \frac{2k_{7a}}{k_{7b}}$$

These measured HCHO:CH_3OH and CH_3OOH:CH_3OH ratios give consistent values of $k_{7a}/k_{7b} = 0.71 \pm 0.05$ and 0.65 ± 0.1. The mean of these values leads to a branching fraction $k_{7a}/k_7 = 0.41 \pm 0.03$. It should be noted that some secondary attack of Cl atoms on the reaction products is unavoidable even with the short reaction times used, as evidenced by the yield of CO (roughly 15% of the HCHO). Computer simulations[34] of the experiments with a chemical mechanism that accounts for secondary reaction of Cl atoms with all the products suggest that the observed HCHO and CH_3OOH yields are best reproduced with $k_{7a}/k_{7b} = 0.65 \pm 0.07$ or $k_{7a}/k_7 = 0.39 \pm 0.05$. The reaction of Cl atoms with CH_3O_2 does not play a part due to the low concentration of chlorine atoms. The experiment using 10 Torr of O_2 had a slightly lower yield of CH_3OOH, suggesting that not all the CH_3O radicals were being converted to HO_2. A rapid reaction of HO_2 with CH_3O could account for this change, but the effect was not large enough to allow a reliable correction to be made.

Experiments were also performed using the photolysis of azomethane. In the azomethane experiments both CH_3OH and CH_3OOH grew linearly with photolysis time, while formaldehyde concentrations appeared to roll off slightly at longer times; this was due partly to saturation of the absorption at higher HCHO but also to increased HCOOH formation. Control experiments were performed in which HCHO was subjected to photolysis under the same conditions as the azomethane; the measured photolysis rate was 5×10^{-5} s^{-1}. The photolysis rate of CH_3OOH has been measured to be less than 2×10^{-5} s^{-1} in this chamber.[30] Thus, the photolysis of HCHO and CH_3OOH is not expected to influence the product yields appreciably. Product yields were measured relative to loss of azomethane using partial pressures of O_2 in the range 8−700 Torr. The azomethane photolysis rate, determined from the slope of plots of ln[AZM] against time, was found to be $(1.8 \pm 0.1) \times 10^{-4}$ s^{-1}. This value was required for computer simulations of the $CH_3O_2 + O_3$ reaction.

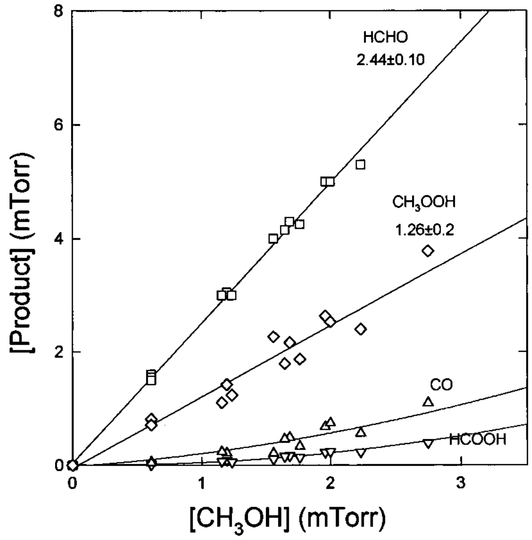

Figure 2. Product yields relative to that of CH_3OH from the combined Cl_2-CH_4 experiments. The HCHO and CH_3OOH yields have been fitted using linear least-squares regressions; the CO and HCOOH have been fitted using second-order polynomials to show the nonlinear growth.

Results from the azomethane experiments are presented in Table 2. For the experiments using low azomethane (shown in Figure 3), the average ratio HCHO:CH_3OH was 2.55 ± 0.10, while the ratio CH_3OOH:CH_3OH was 0.92 ± 0.1. The first ratio leads to $k_{7a}/k_{7b} = 0.78 \pm 0.09$, while the second gives $k_{7a}/k_{7b} = 0.46 \pm 0.05$. Thus, the experiments using azomethane do not appear to give reliable information on the branching fractions for reaction 7. At the lowest O_2 partial pressure used (8 Torr), there was again some indication that the CH_3OOH yield was reduced, possibly indicating a slow reaction between CH_3O radicals and azomethane.

In the experiment using high azomethane, the HCHO yields curved at longer times, as described above. The HCHO yield at shorter times (<25 mTorr total product yield) was 2.60 ± 0.15 times the CH_3OH yield, while the CH_3OOH yield was 1.01 ± 0.15 that of the methanol. These yields are indistinguishable from those at low azomethane, and the HCHO:CH_3OH ratios are also in good agreement with those using the Cl_2-CH_4 source. However, the methylhydroperoxide yields are distinctly

TABLE 2: Product Yields Obtained Using Azomethane Photolysis

[AZM]$_0$, mTorr	[O$_3$]$_0$, mTorr	[O$_2$]$_0$, Torr	time, min	HCHO, mTorr	CH$_3$OH, mTorr	CH$_3$OOH, mTorr	CO,[a] mTorr	HCHO/ CH$_3$OH	CH$_3$OOH/ CH$_3$OH
255	0	140	20	40.8	21.5	18.5	1.6	2.60[b]	1.01
22.5	0	700	30	7.5	2.9	2.6	0.4	2.61	0.92
22.6	0	140	30	7.1	2.8	2.45	0.4	2.61	0.91
22.6	0	8.4	30	6.9	2.8	2.3	0.3	2.57	0.79
255	35	140	20	42.8	22.3	15.9	3.5	2.9[b,c]	0.88
22.5	51	140	30	7.5	2.7	2.1	1.9	3.64[c]	0.77

[a] CO yield is nonlinear with time; value given corresponds to end of run. [b] HCHO yield given is for less than 15 mTorr conversion. [c] HCHO yield is time-dependent when O$_3$ is present; see text and Figure 4.

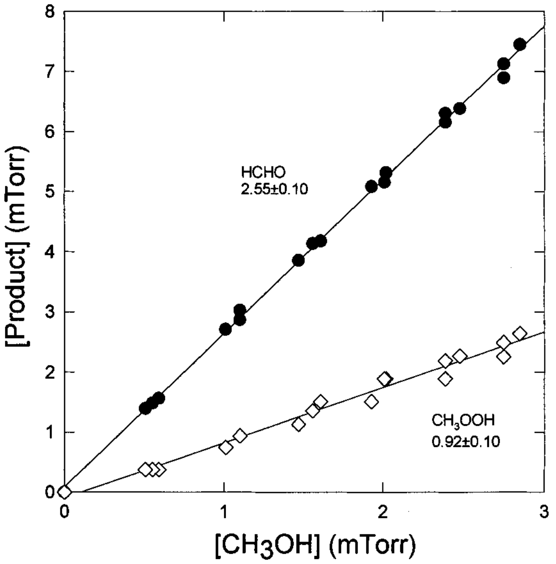

Figure 3. Yields of HCHO and CH$_3$OOH relative to that of CH$_3$OH for experiments using azomethane photolysis with partial O$_2$ pressures of 8−700 Torr.

lower than those found using the methane system. Both Niki et al.[20] and Kan et al.[19] used azomethane photolysis and found low yields of CH$_3$OOH relative to formaldehyde. Niki et al.[20] suggested that loss of CH$_3$OOH may be partly responsible for this discrepancy; however, the loss of CH$_3$OOH is known to be small in our chamber. Furthermore, the product yields after 6-min photolysis in the high-azomethane experiment are identical with those measured after 30 min using low azomethane, so significant loss of CH$_3$OOH cannot be occurring. The discrepancy can be resolved by lowering the rate coefficient for HO$_2$ + CH$_3$O$_2$, so that more HO$_2$ radicals are lost by self-reaction,[19] but, as described later, current measurements of the rate coefficient and product yield for reaction 8 do not support this explanation. An alternative explanation for the low yield of CH$_3$OOH is that an additional loss of HO$_2$ exists in the system. The appropriate loss rate required is about 1.5 s^{-1} in the low-azomethane experiments and 3.5 s^{-1} when the azomethane concentration was 10 times higher. The implications of this loss are explored in the discussion section.

One long-standing question about CH$_3$O$_2$ chemistry is whether CH$_3$OOCH$_3$ is produced in reaction 7.

$$CH_3O_2 + CH_3O_2 \rightarrow CH_3OOCH_3 + O_2 \qquad (7c)$$

Both Kan et al.[19] and Niki et al.[20] noted the presence of unidentified IR features after subtracting the absorptions due to known products. We also found weak, unidentified absorptions in the 1000−1050 cm^{-1} region, strongly overlapped by CH$_3$OH and CH$_3$OOH. The features may be due to CH$_3$OOCH$_3$, and an upper limit of 6% for the yield of this product can be estimated. The absorption spectrum did not correspond to that of HOCH$_2$OOH, an intermediate formed in the HO$_2$-initiated oxidation of HCHO,[33] and which may have been formed in this system. It is also worth noting that the shape of the residual absorption found here was not the same as that shown in the paper of Kan et al.,[19] suggesting that neither absorption is due to a primary product of reaction 7. The residual spectrum shown by Kan et al. actually resembles that of O$_3$ in the presence of another weak absorber to lower wavenumber. In view of these uncertainties, and the absence of any compelling evidence for peroxide formation in the self-reaction of other peroxy radicals,[35,36] we recommend that this channel be set to zero in future evaluations of the CH$_3$O$_2$ self-reaction.

Reaction between CH$_3$O$_2$ and O$_3$. Ozone was added to the azomethane photolysis system to investigate the potential reaction of CH$_3$O$_2$ with O$_3$.

$$CH_3O_2 + O_3 \rightarrow CH_3O + 2O_2 \qquad (10)$$

The Cl$_2$−CH$_4$ system was not used since the rapid reaction of Cl with O$_3$ leads to ClO radicals, which can react with CH$_3$O$_2$ to produce HCHO.[37] Control experiments were performed in which O$_3$ was photolyzed in the presence of 700 Torr of air. Under such conditions any O(^{1}D) atoms formed are quenched immediately to O(^{3}P) and reform O$_3$, so these experiments simply reflect the wall loss of O$_3$ in the experimental chamber. These experiments led to an apparent pseudo-first-order loss rate for O$_3$ of 2 × 10^{-5} s^{-1} either with the photolysis lights activated or in the dark. When ozone and azomethane were photolyzed together, the first-order ozone loss rate increased to about 6 × 10^{-5} s^{-1} with low azomethane, and 1.6 × 10^{-4} s^{-1} for high azomethane. Some increase is to be expected since HO$_2$ radicals produced following the self-reaction of CH$_3$O$_2$ react with ozone via reaction 6.

$$HO_2 + O_3 \rightarrow OH + 2O_2 \qquad (6)$$

The OH radicals produced in reaction 6 will also affect the observed product distribution. From a knowledge of the azomethane photolysis rate and the rate coefficient of the methylperoxy radical self-reaction, the CH$_3$O$_2$ concentration was estimated as 5 × 10^{11} and 1.3 × 10^{12} molecules cm^{-3} in the two experiments. If the entire observed ozone loss rate were due to CH$_3$O$_2$ + O$_3$, the apparent rate coefficient for reaction 10 would need to be ~1 × 10^{-16} cm^3 molecule^{-1} s^{-1}. However, it is expected that ozone would be subject to wall loss, as described above, and also to loss by reaction with HO$_2$. A better estimate for k_{10} can thus obtained by computer simulation of both the ozone loss rate and the observed distribution of carbon-containing products.

For the experiment with low azomethane, an increase (15−20%) in the first-order loss rate of azomethane was observed in the presence of O$_3$, along with a corresponding increase in the combined yield of reaction products. It was also observed that the HCHO:CH_3OH ratio was initially somewhat higher than in the absence of O_3 but decreased with time (initial ratio 3.7, decreasing to 2.8). The main loss of OH in the system is via reaction with HCHO, and an increase in the CO yield was indeed observed when O_3 was present, as shown in Table 2. There appears, then, to be an additional mechanism for the conversion of AZM to HCHO in these experiments, and the most likely candidate is a reaction between OH and azomethane. Unfortunately, there are no available kinetic data for this reaction. As discussed above, Cl atoms react with azomethane and ethane at comparable rates, and it seems reasonable to assume that the same will be true for OH radicals. On the basis of the reaction of OH with C_2H_6,[38,39] we estimate that reaction of OH with azomethane will occur with a rate coefficient between 1×10^{-13} and 1×10^{-12} cm^3 molecule^{-1} s^{-1}. The reactions expected to occur are

$$OH + CH_3N_2CH_3 \rightarrow H_2O + CH_3N_2CH_2 \qquad (20)$$

$$CH_3N_2CH_2 + O_2 + M \rightarrow CH_3N_2CH_2O_2 + M \qquad (21)$$

$$CH_3N_2CH_2O_2 + RO_2 \rightarrow CH_3N_2CH_2O + RO + O_2 \qquad (22)$$

$$CH_3N_2CH_2O + M \rightarrow CH_3 + N_2 + HCHO + M \qquad (23)$$

$$CH_3N_2CH_2O_2 + HO_2 \rightarrow CH_3N_2CH_2OOH + O_2 \qquad (24)$$

where RO_2 represents either $CH_3N_2CH_2O_2$ or CH_3O_2. It can readily be seen that this reaction sequence increases the yield of HCHO relative to that of CH_3OH.

The yields of HCHO, CH_3OH, and CH_3OOH were simulated using the Acuchem chemical kinetics modeling program,[34] with the additional HO_2 loss rate set equal to that required to explain the CH_3OOH yield in the absence of O_3 (1.5 or 3.5 s^{-1}), and a rate coefficient for OH with azomethane of $(2-20) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Rate coefficients for reactions 22 and 24 were estimated from analogous reactions involving primary RO_2 radicals.[35,36] The inclusion of reaction 20 with a rate coefficient of 1×10^{-12} cm^3 molecule^{-1} s^{-1} led to an increase in the combined product yield consistent with observations and also reproduced the CO:HCHO ratio well. The modeled ozone loss rate was then indistinguishable from that found in the experiments. If an additional loss of HO_2 was not included, the ozone loss rate was somewhat faster than that observed. With $k_{20} = 1.0 \times 10^{-12}$ and the HO_2 loss constrained as described above, simulations were made with $k_{10} = 0$, 1, and 3×10^{-17} cm^3 molecule^{-1} s^{-1}. Use of $k_{10} = 1 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} matched the measured HCHO:CH_3OH ratio very well and did not lead to an excessive loss of ozone, while a value of 3×10^{-17} cm^3 molecule^{-1} s^{-1} led to an ozone decay that was clearly too fast. Figure 4 shows the ratio HCHO:CH_3OH as a function of reaction time for the experiments and the simulations. The observations suggest that a slow reaction between methylperoxy radicals and ozone is occurring, with a rate coefficient of 1×10^{-17} cm^3 molecule^{-1} s^{-1}. The product yields in the experiments using high AZM were less sensitive to the rate coefficients k_{10} and k_{20}, since the OH reacts predominantly with AZM, so that the ratio HCHO/CH_3OH is closer to that in the absence of azomethane and does not vary with time. However, the ozone loss rate and CO/HCHO ratios were again best fit by a rate coefficient of 1×10^{-17} cm^3 molecule^{-1} s^{-1}. In light of the uncertainties associated with the chemistry of OH and the peroxy radicals derived from azomethane we estimate that k_{10} lies within the range $(0.5-2.0) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}.

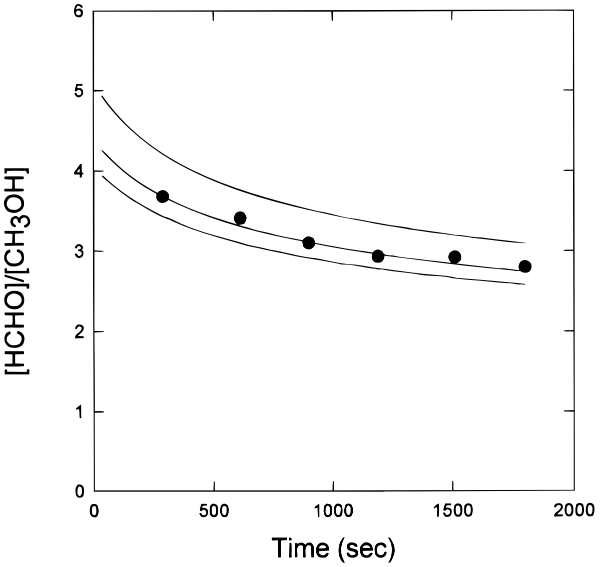

Figure 4. Plot of the ratio [HCHO]/[CH_3OH] as a function of time for the experiment using 22.5 mTorr of azomethane and 51 mTorr of ozone in air. The lines are computer-simulated values of the ratio using (in ascending order) $k_{10} = 0$, 1, and 3×10^{-17} cm^3 molecule^{-1} s^{-1}.

Discussion

The experiments carried out in the absence of O_3 give a measurement of the branching fraction k_{7a}/k_7 in excellent agreement with those of Kan et al.[19] and Niki et al.[20] Both of those studies used FTIR analysis in large environmental chambers. Whereas the two different methyl radical sources used here gave identical ratios for HCHO:CH_3OH, the yield of CH_3OOH was lower with azomethane photolysis than when the photolysis of Cl_2-CH_4 was used. This difference was also found by Niki and co-workers,[20] while the CH_3OOH yields of Kan et al.[19] (who only used azomethane) were low relative to the HCHO and CH_3OH yields. Kan et al. interpreted their results in terms of a low rate coefficient for the reaction $CH_3O_2 + HO_2$; however, more recent direct measurements[35,36,38,39] of k_8 have confirmed the original measurement of k_8 made by Cox and Tyndall,[15] which was disputed by Kan et al. on the basis of their product yields.[19] Jenkin et al.[14] and Moortgat et al.[40] suggested that the reaction between CH_3O_2 and HO_2 can proceed by two pathways—one to give $CH_3OOH + O_2$ and the other to give $HCHO + H_2O + O_2$—but that hypothesis is not consistent with the measurements of Wallington and co-workers.[29−31] Instead, we suggest that a small, unidentified loss of HO_2 can account for the observations in experiments using azomethane photolysis. It should further be pointed out that the CH_3OOH infrared absorption is overlapped by those of CH_3OH and azomethane, so some systematic underestimation of the yield is plausible. Finally, the yield of HCHO relative to CH_3OH is marginally higher in the azomethane experiments compared to the CH_4 experiments. It is conceivable that a conversion of CH_3OOH to HCHO is occurring, but its rate would have to be substantially larger than known losses of CH_3OOH in the system (photolysis, wall loss). It is likely that the methyl hydroperoxide absorption cross section used by Moortgat et al.[40] was too large, leading to a lower yield of CH_3OOH and hence the lower rate coefficient for reaction 8.

The uncertainties of the present measurements are estimated to be ±5% for the ratio HCHO/CH_3OH and ±10% for the CH_3-

TABLE 3: Measurements of $CH_3O_2 + CH_3O_2$ Branching Fractions near Room Temperature

investigator	substrate/ technique	reported[a] k_{7a}/k_7	reported[a] k_{7b}/k_7	reported[a] k_{7c}/k_7	normalized k_{7a}/k_7	normalized k_{7b}/k_7
Parkes[17]	AZM/GC	0.33	0.67	n.d.	0.33	0.67
Weaver et al.[18]	AZM/MS	0.43	0.50	0.07[b]	0.46	0.54
Kan et al.[19]	AZM/FTIR	0.40	0.53	<0.07	0.43	0.57
Niki et al.[20]	AZM/FTIR	0.35	0.57	<0.08	0.38	0.62
Niki et al.[20]	CH_4/FTIR	0.32	0.60	<0.08	0.35	0.65
Horie et al.[21]	CH_4/MI	0.30	0.70	n.d.	0.30	0.70
Anastasi et al.[22]	AZM/GC	0.17	0.77	0.08	0.18	0.82
this work	AZM/FTIR	0.45	0.55	n.d.	0.45	0.55
this work	CH_4/FTIR	0.39	0.61	n.d.	0.39[c]	0.61[c]

[a] Reported yields are those given by the investigator, i.e., including the possibility of CH_3OOCH_3 formation. Normalized yields assume only channels 7a and 7b. [b] Also found a 14–22% yield of CD_3OOCD_3 from CD_3 radicals. [c] These experiments deemed more reliable; corrected for secondary removal (see text).

OOH. The absorption cross sections of CH_3OH and HCHO used in the present work were shown to be consistent, by using the oxidation of CH_3OH as a source of HCHO. Niki et al.[20] found that the calibrations of CH_3OH and HCHO reference spectra were dependent on the relative amounts of O_2 and N_2 present in the bath gas. This may be an artifact of the higher resolution used by those authors. The use of pure O_2 or pure N_2 bath gas had no discernible effect (<2%) on the calibrations in the present experiments. As described earlier, the branching fraction k_{7a}/k_7 may be slightly overestimated in the Cl_2-CH_4 experiments due to the reaction of Cl atoms with the products. The reason for the low CH_3OOH yields in the azomethane experiments remains unknown, although they can be represented by a small loss of HO_2.

Measurements of the branching fractions for the reaction $CH_3O_2 + CH_3O_2$ at room temperature are summarized in Table 3. Values of k_{7a}/k_7 range between 0.18[22] and 0.46.[18] Note that in the table of branching ratios given by Lightfoot et al.,[13] a 30% branch for the reaction of $CH_3O_2 + HO_2$ to give HCHO was used to reinterpret the studies of Niki et al.[20] and Kan et al.,[19] and those numbers are consequently incorrect. The branching ratio reported by Anastasi et al.[22] has, to our knowledge, never been published in a peer-reviewed journal and is clearly much lower than the other values, so it is not discussed further here. The average room-temperature value from the other studies is 0.37 ± 0.05, and the current meaurements are in the middle of the observed range.

The most recent study of the branching ratio was made by Horie et al.[21] utilizing a slowly flowing photolysis system with matrix isolation collection of reaction products followed by FTIR analysis. The branching fraction k_{7a}/k_7 was 0.30 ± 0.02 near room temperature. Horie at al. were unable to detect CH_3OOH, and it is possible that the absorption features of CH_3OH and CH_3OOH near 1033 cm^{-1} overlap in the matrix phase. This would account for the nondetection of CH_3OOH and would also change the apparent value of the ratio HCHO:CH_3OH from that found in gas-phase experiments, where unequivocal detection of CH_3OH and CH_3OOH is possible. We measured the integrated band intensity for CH_3OOH to be about a factor of 4 less than that for CH_3OH, so considerable interference is possible. The value recommended by Horie et al., and adopted by the most recent evaluations,[38,39] is strongly weighted by their own measurements and also those of Anastasi et al.[22] We feel that the chamber/FTIR studies (Kan et al.,[19] Niki et al.,[20] and this work) are much less susceptible to sampling and calibration errors and should be more reliable, and we recommend that $k_{7a}/k_7 = 0.40 \pm 0.05$ and $k_{7b}/k_7 = 0.60 \pm 0.05$.

The experiments described here do not provide any direct evidence for CH_3OOCH_3 formation. The only study in which CH_3OOCH_3 was identified was that of Weaver et al.,[18] who reported a yield of 7%. The same group oxidized CD_3 radicals and found a CD_3OOCD_3 yield of 14–18%.[18,41] Most other studies have found less than 6% CH_3OOCH_3. Allowing for a 6% channel, the branching fractions for the methylperoxy self-reaction become $k_{7a}/k_7 = 0.38$, $k_{7b}/k_7 = 0.56$, and $k_{7c}/k_7 = 0.06$. However, we recommend for reasons given earlier that channel 7c be ignored and that the branching fractions for reactions 7a and 7b are 0.40 and 0.60.

The occurrence of the nonterminating radical channel 7a has an effect on measurements of the rate coefficient for reaction 7. The apparent rate coefficient measured in time-resolved experiments includes a contribution from the $CH_3O_2-HO_2$ reaction.[35,36,38,39] High concentrations of CH_3O_2 radicals are employed in laboratory kinetics studies, and in such an environment each HO_2 radical that is formed in reaction 9 rapidly removes an additional CH_3O_2 radical. Hence the measured rate constant k_{7obs} is related to k_7 by the expression $k_{7obs} = k_7(1 + k_{7a}/k_7)$. The NASA kinetics data evaluation panel[39] apparently recommend the use of the observed rate coefficient $k_{7obs} = 4.8 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} for use in atmospheric models. Using the value of $k_{7a}/k_7 = 0.40$ recommended here, the value for k_7 should be corrected to 3.5×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, as in most other evaluations.[35,36,38] The effects of this change are discussed in the next section. The recommended branching ratios lead to specific rate coefficients for reactions 7a and 7b of 1.4×10^{-13} and 2.1×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, respectively.

The only previous measurement of k_{10} is that of Simonaitis and Heicklen,[23] who photolyzed O_3 with 253.7-nm radiation in the presence of CH_4. From measurements of the rate of loss of O_3, they obtained an upper limit $k_{10} \leq 2.4 \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}. The present study has the advantage that a much more complete product study was carried out and that the methylperoxy radical concentration could be controlled independently of the ozone concentration. We cannot completely rule out the occurrence of reaction 10 but suggest that a slow reaction, with a rate coefficient of 1×10^{-17} cm^3 $molecule^{-1}$ s^{-1} (± a factor of 2), is occurring. DeMore[42] has also noted that reaction 10 is probably very slow near 200 K from measurements of the rate of decay of O_3 in the photolysis of $Cl_2-CH_4-O_3$ mixtures.

The reaction of HO_2 with O_3, reaction 6, is approximately 200 times faster than the value for the reaction of CH_3O_2 with O_3 measured here. Sinha et al.[43] and Nelson and Zahniser[44] have performed isotopic substitution experiments to show that the reaction of HO_2 with O_3 proceeds predominantly by H-atom transfer. Clearly, this mechanism is not favored for the methylperoxy radical. The results of the isotopic substitution experiments allowed for a small channel (about 5–10%) to occur via O-atom transfer. The upper limit measured here for the reaction of CH_3O_2 with O_3 is still a factor of 10 lower than that and suggests that O-atom transfer may actually be close to zero in the HO_2 reaction also.

Atmospheric Implications. Monks et al.[7] have reported measurements using the chemical amplifier technique of the total peroxy radical concentration ($CH_3O_2 + HO_2$) in the marine boundary layer of the Southern Ocean in Tasmania. Over the Southern Ocean the levels of NO_x are very low[45,46] (<3pptv), and the nighttime concentrations of CH_3O_2 and HO_2 radicals are controlled by their self-reactions, cross reaction, and reaction with ozone. Monks et al. deduced that CH_3O_2 was the dominant peroxy radical during the night with $[CH_3O_2]/[HO_2] > 60$. The nighttime overall peroxy radical decay could be described using a simple model with two reactions: second-order loss of CH_3O_2 via self-reaction using the rate coefficient given in the 1994 NASA compilation and a small first-order loss of 3.3×10^{-6} s^{-1}. Attributing the first-order loss solely to reaction with O_3 (present at 16 ppb) gives an upper limit of $k_{10} < 8 \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1}. As described in the previous section, the rate coefficient in the 1994 NASA compilation is an overestimate of the "true" bimolecular rate constant, k_7, since it has not been corrected for secondary loss of CH_3O_2 via reaction with HO_2 radicals.

In the atmosphere, the concentration of CH_3O_2 radicals is low and the fate of the HO_2 depends critically on the ratio O_3:CH_3O_2, which governs whether HO_2 leads to regeneration of CH_3O_2 (via reactions 6 and 25) or to radical loss by reaction 8.

$$CH_3O_2 + CH_3O_2 \rightarrow CH_3O + CH_3O + O_2 \qquad (7a)$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \qquad (9)$$

$$HO_2 + O_3 \rightarrow OH + 2O_2 \qquad (6)$$

$$OH + CH_4 \rightarrow H_2O + CH_3 \qquad (25)$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \qquad (14)$$

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \qquad (8)$$

$$OH + CO\ (+ O_2) \rightarrow HO_2 + CO_2 \qquad (26)$$

When O_3 is high, reaction 7a does not lead to a net loss of radicals; however, if the ozone mixing ratio is relatively low, reaction 7a leads to the loss of two radicals. Thus there is no a priori reason to expect the apparent rate coefficient for RO_2 loss in the atmosphere to be $k_{7a} + k_{7b}$. To a good approximation, the apparent second-order rate coefficient for loss of RO_2 (the sum of CH_3O_2 and HO_2) should be equal to $k_{7b} + k_8([HO_2]/[CH_3O_2])$. A reaction between CH_3O_2 and O_3 would also convert CH_3O_2 to HO_2 and would tend to increase the loss rate of RO_2 if the HO_2 reacts with CH_3O_2 and not with O_3. Thus, even though HO_2 is the minor radical at night, its rapid reaction with CH_3O_2 can impact the loss of both species (and their sum, which is measured by the chemical amplifier). During daytime hours, higher levels of NO are present and higher HO_2:CH_3O_2 ratios occur, so reaction 7 is not as important.

A box model[34] was used to simulate the effects of HO_2 cycling and reaction 10 on nighttime radical concentrations. The conditions were chosen to be similar to those encountered during the measurements of Monks et al.:[7] RO_2 2 ppt, O_3 16 ppb, and zero NO. The decay of the total RO_2 concentration was simulated with k_{10} equal to the extremes of the reported values, zero and 3×10^{-17} cm^3 $molecule^{-1}$ s^{-1}. In the first case, the apparent rate coefficient for RO_2 loss (3.2×10^{-13} cm^3 $molecule^{-1}$ s^{-1}) is given by the empirical relationship $k_{atm} = 0.8k_{7a} + k_{7b}$; i.e., most of the HO_2 radicals react with O_3 and simply recycle RO_2. The inclusion of reaction 10 with a rate coefficient of 3×10^{-17} cm^3 $molecule^{-1}$ s^{-1} leads to an increase of approximately 20% in the apparent rate coefficient for loss of RO_2. The increase expressed as a pseudo-first-order loss for RO_2 is 3×10^{-6} s^{-1}, which is very close to the "residual loss" of RO_2 radicals discussed by Monks et al. However, the actual first-order rate coefficient for CH_3O_2 reacting with O_3 is 1.2×10^{-5} s^{-1}, due to the recycling of HO_2 radicals. Thus, the effects of reactions 7, 8, and 10 cannot simply be separated, in contrast to the conclusions of Monks et al. The analysis employed by Monks et al. is thus too simplistic, and their upper limit for k_{10} should not be considered reliable.

For the nighttime conditions reported by Monks et al. of $[CH_3O_2] = 1$ ppt and $[O_3] = 16$ ppb with $k_7 = 3.5 \times 10^{-13}$ and $k_{10} = 1.0 \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}, the instantaneous pseudo-first-order loss rate of CH_3O_2 radicals via reaction with O_3 is approximately 20% of that of the CH_3O_2 self-reaction. Hence, the reaction of CH_3O_2 radicals with O_3 may play a minor role in the nighttime decay of CH_3O_2 radicals in very clean air. Under continental conditions such as those studied by Cantrell et al. in the southeast United States,[4] the influence of terrestrial nighttime NO sources is probably important and it is unlikely that reaction 10 is of any significance.

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