Ic[29,30] and several other radical–radical reactions (e.g., NO + $HO_2 \rightarrow NO_2$ + OH).[32]

There have been no previous studies of reaction VI (O + I_2) at 298 K to our knowledge. The nearly gas kinetic value of the room-temperature rate coefficient is consistent with the trend observed in the rate coefficients of the other oxygen atom plus diatomic halogen reactions:

$$k(O + F_2) < 3.3 \times 10^{-15}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{(ref 23 and 24)}$$

$$k(O + Cl_2) = 4.2 \times 10^{-14}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{(ref 17)}$$

$$k(O + Br_2) = 1.4 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{(ref 14)}$$

$$k(O + I_2) = 1.38 \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

In addition, the molecular beam study of Parrish and Herschbach[33] suggests a value of zero for the activation energy of reaction VI, which supports our result.

These results will have a minimal impact on the predictions of atmospheric photochemical model calculations as they have confirmed prior expectations. However, those studies that have assumed a value of $\sim 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for k_{Ia} and k_{Id} have now been provided with a less uncertain basis.

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Temperature Dependence of the Self-Reaction of CH_3O_2 Radicals

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The flash photolysis–ultraviolet absorption technique was used to measure the rate constants for the reaction $CH_3O_2 + CH_3O_2 \rightarrow$ products (1) over the temperature range 248–417 K and the pressure range 60–700 torr of N_2. Rate constants were measured by observing the second-order disappearance of CH_3O_2 radicals. The measured Arrhenius expression is $k_1 = (1.40 \pm 0.20) \times 10^{-13} \exp[(223 \pm 41)/T]$ cm^3 molecule^{-1} s^{-1}, where the rate constant is defined by the expression $-d[CH_3O_2]/dt = 2k_1[CH_3O_2]^2$.

Introduction

The self-reactions of peroxy radicals, besides being of potential importance in atmospheric and combustion chemistry, present a number of intriguing mechanistic problems. For example, the disproportionation of HO_2 radicals

$$HO_2 + HO_2 \rightarrow \text{products}$$

exhibits a marked pressure dependence[1,2] and a negative temperature dependence,[2,3] indicating that the reaction mechanism is apparently not a simple hydrogen abstraction and that multiple pathways may be involved. For the self-reaction of methylperoxy radicals, at least four reaction channels have been postulated:

$$CH_3O_2 + CH_3O_2 \rightarrow 2CH_3O + O_2 \quad \text{(1a)}$$

$$\rightarrow HCHO + CH_3OH + O_2 \quad \text{(1b)}$$

$$\rightarrow CH_3OOCH_3 + O_2 \quad \text{(1c)}$$

$$\rightarrow CH_3OOH + CH_2O_2 \quad \text{(1d)}$$

with heats of reaction of +3.5,[4] −77.4,[4] −42.8,[4] and −14[5] kcal mol^{-1} for reactions 1a–d, respectively. There have been several measurements of the overall rate constant.[6-11] The preferred value according to the most recent review is 4.0 $\times$ 10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K,[12] where the rate constant, k_1, is defined by the relation

$$-d[CH_3O_2]/dt = 2k_1[CH_3O_2]^2$$

The branching ratios of reaction 1 have been studied extensively by a number of methods, mostly indirect. These measurements have been summarized by Kan et al.,[13] who also carried out an FT-IR study of the reaction products. The results of their work are qualitatively consistent with other studies, namely, that $k_{1b}/k_{1a} \sim 1.2$ and that reaction 1c accounts for less than 10% of the

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observed CH_3O_2 decay. A similar FT-IR study has recently been carried out by Niki et al.,[14] who obtained $k_{1b}/k_{1a} \sim 1.9$. Reaction 1d, which was recently proposed by Nangia and Benson,[5] was also investigated by Kan et al.[13] and Niki et al.,[14] who concluded that this branch is of negligible importance.

In this work we report the first measurements of k_1 made over a wide temperature range (248–417 K). The results are discussed in terms of the mechanism of reaction 1.

Experimental Section

The study was carried out in a Pyrex flash photolysis system employing ultraviolet absorption detection. The apparatus has been described in detail previously.[11,15] CH_3O_2 radicals were monitored in their absorption continuum at 250.0 nm using path lengths of 357–689 cm. Averaging the absorption signals of multiple flashes resulted in a detection limit for CH_3O_2 of $\sim 5 \times 10^{11}$ molecules cm^{-3} ($\sim$0.1% absorption). The accumulated absorption signals recorded on a multichannel analyzer were processed and displayed by using a Tektronix 4052 graphics system. The temperature of the cell was controlled by flowing methanol (248–298 K) or ethylene glycol (298–417 K) from a thermostated circulator through the cell jacket.

CH_3O_2 radicals were produced by the photolysis of Cl_2–CH_4–O_2 mixtures by the following mechanism:

$$Cl_2 + h\nu\ (\lambda > 300\ \text{nm}) \rightarrow 2Cl \qquad (2)$$

$$Cl + CH_4 \rightarrow HCl + CH_3 \qquad (3)$$

$$k_3 = 1.04 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K} \qquad \text{(ref 4)}$$

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

$$k_{4,\infty} = 2.0 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \qquad \text{(ref 4)}$$

The ranges of reagent concentrations (in molecules cm^{-3}) were as follows: $[Cl_2]$, 6.7×10^{14}–4.46×10^{16}; $[CH_4]$, 0.90×10^{17}–9.40×10^{17}; $[O_2]$, 0.48×10^{17}–8.44×10^{17}. Conditions were adjusted so that the time required for the formation of CH_3O_2 (10–100 μs) was always much shorter than its decay (>25 ms). $[CH_3O_2]_0$ varied from 3.5×10^{12} to 2.0×10^{14} molecules cm^{-3}. Flash-lamp energy was varied between 518 and 850 J per flash. Most experiments were conducted at a total pressure of 250 torr by using N_2 as the diluent gas. A few runs were conducted at 75- and 600-torr total pressure.

The effective optical path lengths at 250.0 and 330.0 nm were determined by measuring the absorbance of gas mixtures of known composition and absorption cross section. At 330.0 nm, Cl_2 was used ($\sigma_{Cl_2} = 2.56 \times 10^{-19}$ cm^2 $molecule^{-1}$)[16] as the calibrating gas. At 250 nm, where the kinetic measurements were made, CH_3Br was used. The CH_3Br cross section was determined experimentally with a 10-cm absorption cell and a Cary 14 spectrophotometer. A value of $(1.03 \pm 0.03) \times 10^{-20}$ cm^2 $molecule^{-1}$ was obtained from the slope of a Beer's law plot. Using this cross section, we determined the path lengths to be 689 cm (eight passes) and 357 cm (four passes).

Diluent gases had the following stated purities: He, Linde UHP grade, 99.999%; N_2, Linde UHP grade, 99.999%; O_2, Linde UHP grade, 99.99%. Chlorine (Matheson research purity, 99.96%) and methane (Matheson purity, 99.99%) were used without further purification.

Results

The rate law for the second-order decay of CH_3O_2 radicals is

$$1/[CH_3O_2] - 1/[CH_3O_2]_0 = 2k_1t$$

or, in terms of the CH_3O_2 optical density, γ

$$1/\gamma - 1/\gamma_0 = 2k_1t/\sigma l$$

where σ is the CH_3O_2 absorption cross section and l is the path length. Plots of $1/\gamma$ vs. time were observed to be linear over at least three half-lives. The residual absorption at 250.0 nm was never larger than 0.1%, which is very close to the measurement noise level. The slope of the decay plots gives the quantity $2k_1/\sigma l$; therefore, determination of the rate constant requires that both σ and l be known.

The path length was measured as described previously. The cross section was measured by the following procedure. CH_3O_2 decay plots were back-extrapolated to the time of the flash to obtain the initial optical density, γ_0. Since $\gamma_0 = \sigma l[CH_3O_2]_0$, it can be shown that

$$\sigma = \gamma_0/(2lf[Cl_2]) \qquad (I)$$

where f is the fractional dissociation of Cl_2 per flash. The derivation of this equation assumes that each chlorine atom is rapidly converted to a CH_3O_2 radical with unit stoichiometry and that the initial chlorine atom concentration is strictly proportional to $[Cl_2]$. The parameter f was measured by flashing samples of chlorine in helium and observing the change in Cl_2 absorption at 330.0 nm on time scales short compared to the chlorine atom recombination time. It can be shown that f is given by

$$f = \ln\ (I''/I')/(\sigma_{Cl_2}l[Cl_2]) \qquad (II)$$

where I'' and I' are the transmitted light intensities before and after the flash, respectively. $[Cl_2]$ was measured by calculating its partial pressure from flow-rate measurements. From eq II, a plot of $\ln\ (I''/I')$ vs. $l[Cl_2]\sigma_{Cl_2}$ should give a straight line with zero intercept and slope f. As indicated in Figure 1, this equation is obeyed. The resulting value of f is $(2.28 \pm 0.21) \times 10^{-3}$ at a flash energy of 518 J.

Validation of the assumption of rapid and stoichiometric conversion of Cl to CH_3O_2 requires that the CH_3O_2 formation mechanism be examined in detail. The principal reactions are

$$Cl + CH_4 \rightarrow CH_3 + HCl \qquad (3)$$

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

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

Possible secondary reactions include

$$CH_3 + Cl_2 \rightarrow CH_3Cl + Cl \qquad (5)$$

$$CH_3 + Cl \xrightarrow{(M)} CH_3Cl \qquad (6)$$

$$CH_3 + CH_3 \xrightarrow{(M)} C_2H_6 \qquad (7)$$

$$CH_3 + CH_3O_2 \rightarrow \text{products} \qquad (8)$$

Of reactions 5–8, only the rate constant for reaction 7 has been directly measured; its value is 5.1×10^{-11} cm^3 $molecule^{-1}$ s^{-1}.[6] There are no direct measurements of k_5, but it is expected to be quite fast. An upper limit of 5×10^{-11} cm^3 $molecule^{-1}$ s^{-1} is assumed. Rate constants of 1×10^{-11} and 1×10^{-10} cm^3 $molecule^{-1}$ s^{-1} are estimated for k_6 and k_8, respectively. These are worst-case estimates, and the

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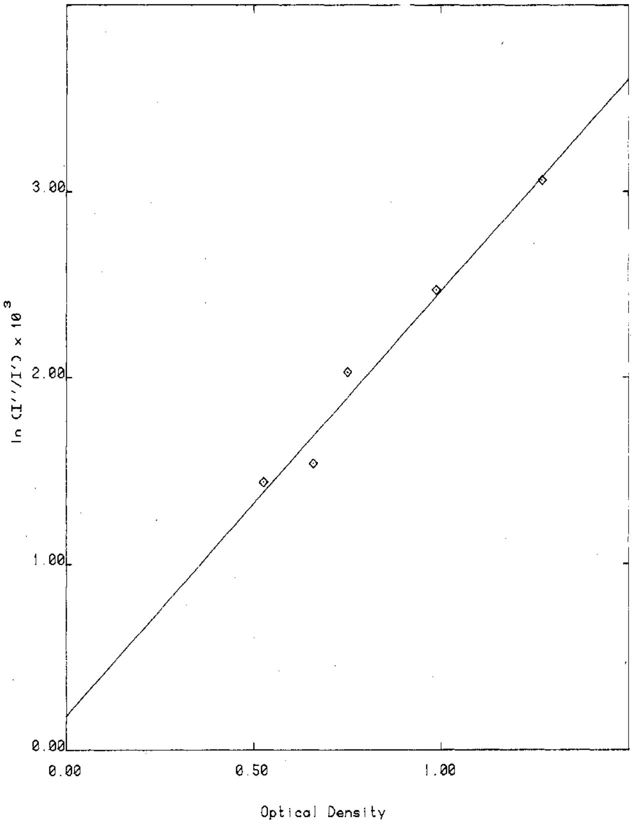

Figure 1. Plot of ln (I''/I') vs. the Cl_2 optical density at 330.0 nm at 298 K using a flash energy of 518 J. The resulting slope, (2.28 ± 0.21) × 10^{-3}, is the fractional dissociation of Cl_2.

actual rate constants are probably substantially smaller. For typical conditions employed in this study ($[CH_3O_2] < 1 \times 10^{14}$ molecules cm^{-3}), reactions 6–8 are unimportant. Reaction 5 is competitive with reaction 4 in removing methyl radicals when $[Cl_2]$ is 1×10^{16} molecules cm^3 or greater. However, because reaction 5 regenerates atomic chlorine, and thus CH_3, the net effect of the cycle consisting of reactions 3–5 is to delay the time of the CH_3O_2 formation peak. A computer simulation of the complete mechanism (reactions 2–8) was carried out to investigate the effect of reaction 5. Under worst-case conditions ($[Cl_2] = 1.0 \times 10^{16}$ molecules cm^{-3}, $[Cl]_0 = 1.0 \times 10^{14}$ molecules cm^{-3}), it was discovered that the time required to reach the CH_3O_2 peak was increased from 154 to 229 μs as k_5 was increased from 0.0 to 5×10^{-11} cm^3 $molecule^{-1}$ s^{-1}. The magnitude of the peak remained unchanged and was within 3% of the initial chlorine atom concentration. Because of the relatively long time scales for the CH_3O_2 decay by reaction 1 (initial $t_{1/2} > 12$ ms) and the much lower CH_3O_2 and Cl_2 concentrations typically used, it can therefore be concluded that the back-extrapolation procedure used to obtain γ_0 is valid.

The second assumption required in the derivation of eq I, that $[Cl]_0$ is proportional to $[Cl_2]$, is valid since Cl_2 is optically thin to the photolysis flash. From eq I, a plot of γ_0 vs. $2[Cl_2]$ should give a straight line with zero intercept and slope $f\sigma$. The data taken at 298 K and 518-J flash energy are plotted in Figure 2. γ_0 values were obtained by back-extrapolating the kinetic decay plots to zero time. The resulting line has a slope of (6.08 ± 0.17) × 10^{-21} cm^2 $molecule^{-1}$. Similar plots were also made for the data at other temperatures to investigate any possible dependence of f with temperature. The results are listed in Table I. There appears to be no significant variation of $f\sigma$ over the temperature range 270–417 K. The mean value of the slopes at all temperatures is (5.58 ± 0.72) × 10^{-21} cm^2 $molecule^{-1}$. Combining this result with the value of f gives a temperature-independent CH_3O_2 cross section of (2.45 ± 0.39) × 10^{-18} cm^2 $molecule^{-1}$ at 250.0 nm.

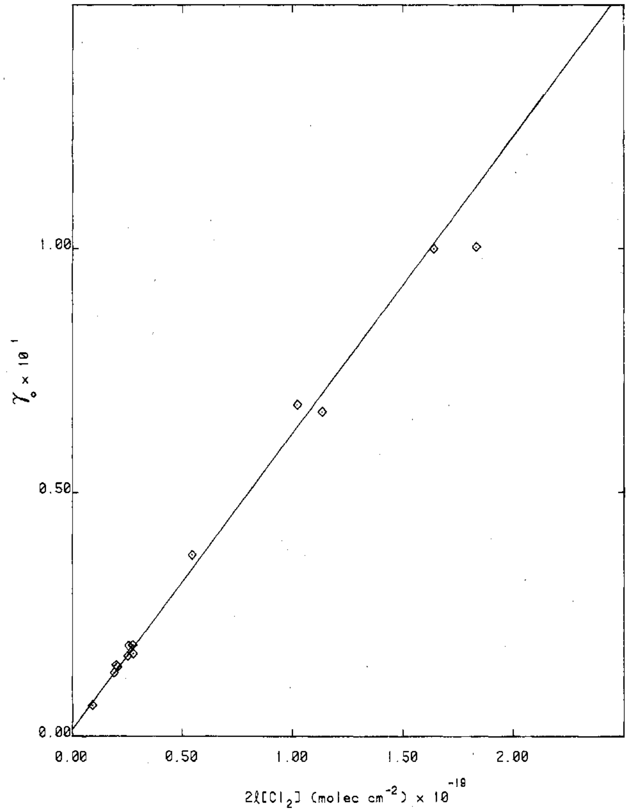

Figure 2. Plot of γ_0 at 250.0 nm vs. $2l[Cl_2]$ at 298 K using a flash energy of 518 J. The slope, (6.08 ± 0.17) × 10^{-21} cm^2 $molecule^{-1}$, is the product $f\sigma$.

TABLE I: Measured Values of $f\sigma$[a]

temp, K	no. of points	l, cm	$10^{21}f\sigma$, cm^2 $molecule^{-1}$
270	8	689	4.62 ± 0.27
298	13	689	6.08 ± 0.17
	6	357	5.41 ± 0.25
329	6	689	6.25 ± 0.14
373	10	689	6.26 ± 0.33
417	12	689	4.88 ± 0.12
		mean:	5.58 ± 0.72

[a] Analysis wavelength = 250.0 nm; flash energy = 518 J.

A total of 103 kinetic runs were performed over the temperature range 248–417 K. Total pressure was varied from 75 to 600 torr of N_2. Wide variations in the concentrations of all reagents were also made as indicated in the Experimental Section with no observable effects being noticed. The data analysis procedure was identical with that employed in our earlier room-temperature study[11] with the exception that, in this study, a pretriggering circuit from the MCA allowed the preflash and postflash analyzing light intensities to be checked for the presence of any possible residual absorbing species. Plots of 1/(CH_3O_2 optical density) vs. time were observed to be linear over a concentration change of a factor of 10–50; however, as observed before,[11] the slopes of the decay plots were extremely sensitive to the choice of I_0, the analyzing beam intensity at long reaction times. No residual absorbing species could be observed within the detection limit of ~0.1% absorption. Of the possible products (HCHO, CH_3OH, CH_3OOCH_3, and CH_3OOH), only methyl hydroperoxide ($\sigma = 5.8 \times 10^{-20}$ cm^2 $molecule^{-1}$ (ref 17)) would

TABLE II: Reaction Rate Data for $CH_3O_2 + CH_3O_2 \rightarrow$ Products (1)

temp, K	no. of runs	$10^{-5}(2k_1/\sigma)$,[a] cm s^{-1}	$10^{13}k_1$,[a,b] cm^3 $molecule^{-1}$ s^{-1}
248	9	2.62 ± 0.23	3.21 ± 0.58
270	13	2.79 ± 0.32	3.42 ± 0.67
298	50	2.43 ± 0.18	2.98 ± 0.52
329	8	2.36 ± 0.12	2.89 ± 0.48
373	11	2.04 ± 0.16	2.50 ± 0.44
417	12	1.90 ± 0.12	2.33 ± 0.40

[a] Quoted uncertainties are 1σ. [b] $\sigma = (2.45 \pm 0.39) \times 10^{-18}$ cm^2 $molecule^{-1}$ at 250.0 nm (this work).

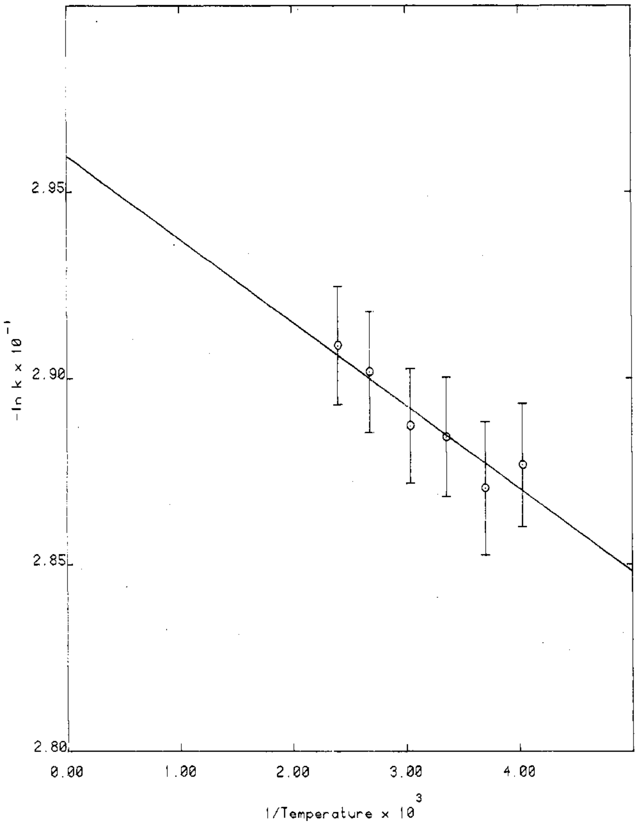

Figure 3. Arrhenius plot of the rate constant for reaction 1.

absorb strongly enough at 250.0 nm to be detected, and only if the quantum yield for the formation of this species was near unity.

Results of the kinetic runs at each temperature are summarized in Table II, and an Arrhenius plot of the data is shown in Figure 3. The data show a small negative activation energy with the best-fit Arrhenius expression being $k_1 = (1.40 \pm 0.20) \times 10^{-13} \exp[(223 \pm 41)/T]$ cm^3 $molecule^{-1}$ s^{-1}, where the rate constant is defined by the expression

$$-[CH_3O_2]/dt = 2k_1[CH_3O_2]^2$$

No significance is attached to the fact that the rate constant at 248 K is slightly lower than the value at 270 K. This is attributed to random scatter in the data.

As discussed by other workers,[9,11,18] secondary reactions involving CH_3O_2

$$CH_3O_2 + CH_3O \rightarrow \text{products} \qquad (9)$$

$$CH_3O + O_2 \rightarrow HO_2 + HCHO \qquad (10)$$

$$CH_3O_2 + HO_2 \rightarrow \text{products} \qquad (11)$$

may result in an enhancement in the apparent second-order rate constant. While k_9 and k_{11} are not known with certainty, reactions 9–11 will be rapid on the time scale of reaction 1. The true second-order rate constant will be given by

$$k_1 = k_1'/(1 + \alpha)$$

where α is the branching ratio for reaction 1a and k_1' is the measured second-order rate constant. Because of the large variation in the measured values of α, reliable corrections to k_1' cannot be made, and the values listed in Table II are derived from apparent decays without corrections being applied.

Discussion

The absorption spectrum of CH_3O_2 radicals in the 200–300-nm spectral region has been studied by several groups,[6,8,9,18,19] and both absolute and relative cross sections have been determined. In this study, an absolute σ value was derived only at 250 nm, which is near the CH_3O_2 absorption maximum. Previous measurements of σ at 250 nm are summarized in Table III. Although the technique used to measure the cross section is similar for most of these studies, relying on the measurement of azomethane loss or N_2 formation in $(CH_3)_2N_2$–O_2 photolyses, substantial discrepancies in the reported σ values exist. This study is the only one to use the Cl_2–CH_4–O_2 system to measure σ, although Sanhueza et al.[10] used this method to measure k_1/σ. The value determined here, $(2.5 \pm 0.4) \times 10^{-18}$ cm^2 $molecule^{-1}$, is in excellent agreement with the results of Hochanadel et al.[6] and Kan et al.[9], both of whom obtained 2.7×10^{-18} cm^2 $molecule^{-1}$. However, the results of Adachi et al.[18] and Parkes et al.[19] differ by almost a factor of 2 from our determination. The reason for this discrepancy is not known; however, support for the lower set of values comes from the earlier work of Sander and Watson[11] on the CH_3O_2 + NO reaction

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \qquad (12)$$

$$k_{12} = 7.4 \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1} \qquad \text{(ref 12)}$$

Under the conditions of this study, the only significant loss path for methoxy radicals is by reaction with NO

$$CH_3O + NO \xrightarrow{(M)} CH_3ONO \qquad (13a)$$

$$\rightarrow HCHO + HNO \qquad (13b)$$

$$k_{13a} + k_{13b} = 2.1 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1} \qquad \text{(ref 20)}$$

$$k_{13b}/k_{13a} < 0.05 \qquad \text{(ref 21)}$$

A residual absorption spectrum was observed which showed a wavelength dependence very similar to the well-characterized CH_3ONO spectrum. However, the magnitude of this absorption was consistent with the stoichiometric conversion of CH_3O_2 to CH_3ONO if the CH_3O_2 cross sections of Hochanadel et al.[6] were used. Although the rates and the products of CH_3O reactions are not completely understood, it is unlikely that this inter-

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TABLE III: Comparison of Previous Determinations of k_1 and σ at 250 nm Near Room Temperature

ref	$10^{18}\sigma$-(250 nm), cm^2 molecule^{-1}	$10^{-5}k_1/\sigma$, cm s^{-1}	$10^{13}k_1$, cm^3 molecule^{-1} s^{-1}	T, K	technique for σ measurement
6	2.7	1.4	3.8 ± 0.7	295	$(CH_3)_2N_2$ loss/flash photolysis
18	5.0	1.2	5.8 ± 0.5	298(?)	N_2 formation from $(CH_3)_2N_2$ flash photolysis
9	2.7	1.6	4.2 ± 0.5	296	N_2 formation from $(CH_3)_2N_2$ flash photolysis
8, 19[a]	4.8	0.96	4.6 ± 1.2	298	molecular modulation, $(CH_3)_2N_2$-O_2 mixtures
this work	2.5 ± 0.4	1.2	3.0 ± 0.5	298	Cl_2 loss in Cl_2-CH_4-O_2 system/flash photolysis

[a] Cross sections from Parkes et al.[19] were rescaled in accordance with the unpublished work of Kirsch and Parkes as quoted in ref 8.

pretation is subject to an error as large as a factor of 2, as would be required to account for the larger CH_3O_2 cross-section values obtained by Adachi et al. and Parkes et al.

Previous direct determinations of k_1 in which both the experimental parameters k_1/σ and σ were measured in the same study are listed in Table III. There are two other direct studies in which only k_1/σ was measured.[10,11] In both cases, the experimental CH_3O_2 spectrum of Hochanadel et al. was used to derive k_1. The results were $k_1 = (3.6 \pm 0.7) \times 10^{-13}$ (our earlier work, ref 11) and $(3.7 \pm 0.3) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (ref 10). Thus, the measured room-temperature rate constants range from $(3.0 \pm 0.5) \times 10^{-13}$ (this work) to $(5.8 \pm 0.5) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (ref 18). Examination of Table III indicates that there is no obvious connection between the relative magnitudes of k_1 and k_1/σ in any of the studies; e.g., the study with the highest measured value of σ does not have the highest measured value of k_1/σ, and conversely. The spread in σ is somewhat greater than the spread in k_1/σ; therefore, future studies should emphasize the CH_3O_2 absorption spectrum measurement rather than the decay rate.

This is the first study of reaction 1 over a wide range of temperature. Anastasi et al.[8] measured k_1/σ at 298 and 325 K and obtained values of $(8 \pm 1) \times 10^4$ and $(6 \pm 2) \times 10^4$ cm s^{-1}, respectively. This is perhaps suggestive of the negative temperature dependence observed here although the temperature range is too small to be significant. In contrast, measurements by Anastasi et al.[8] on the mutual reaction of *tert*-butylperoxy radicals indicate a factor of 4 increase in k/σ from 298 to 325 K.

The interpretation of the slightly negative (or approximately neutral) temperature dependence of k_1 has several elements. As mentioned above, if the reaction branch forming CH_3O contributes significantly to the overall reaction rate, as previous studies have suggested,[7,13,14] and k_{1a} is endothermic by 3.5 kcal mol^{-1}, then a significant positive activation energy might have been observed. However, when the uncertainty in the CH_3O_2 enthalpy of formation is factored in, (±2 kcal mol^{-1}), reaction 1a could be thermoneutral or even slightly exothermic. As a result, this temperature-dependence measurement cannot be used to verify the relative importance of this channel.

The experimental A factor for reaction 1 is considerably smaller than the value expected if the $CH_3O_2 + CH_3O_2$ reaction proceeded entirely through a hydrogen abstraction mechanism as proposed by Nangia and Benson[5]

$$CH_3O_2 + CH_3O_2 \rightarrow CH_3OOH + CH_2O_2 \qquad (1d)$$

These authors predict a lower limit for A_{1d} as being $\sim 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Additional experimental evidence contradicting this mechanism has been provided by Kan et al.,[13] who observe that the $[O_2]$ dependence of the CH_3OOH formation rate in the photolysis of $(CH_3)_2N_2$-O_2 mixtures cannot be explained by reaction 1d.

The absence of any observable dependence of the rate constant on total pressure between 75- and 600-torr total pressure may be contrasted with the behavior observed for the HO_2 radical disproportionation

$$HO_2 + HO_2 \rightarrow \text{products} \qquad (11)$$

k_{11} has been observed to be pressure dependent in at least two studies,[22,23] and recent results from this laboratory show a substantial pressure dependence in the 50–700-torr (N_2) pressure range. If reaction 1 forms a long-lived adduct, and therefore has a pressure-dependent channel, it is possible that the rate constant for this channel has reached its high-pressure limit at 75 torr of N_2, owing to the larger number of available vibrational modes than in the $HO_2 + HO_2$ case. Investigation of reaction 1 in flow systems at lower pressures would therefore be illuminating.

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