# The CH<sub>3</sub>C(O)O<sub>2</sub> Radical. Its UV Spectrum, Self-Reaction Kinetics, and Reaction with CH<sub>3</sub>O<sub>2</sub>

## M. Matti Maricq\* and Joseph J. Szente

Research Laboratory, Ford Motor Company, P.O. Box 2053, Drop 3083, Dearborn, Michigan 48121 Received: November 10, 1995; In Final Form: December 12, 1995<sup>®</sup>

The reactions of CH<sub>3</sub>C(O)O<sub>2</sub> with itself and with CH<sub>3</sub>O<sub>2</sub> are investigated using flash photolysis combined with time-resolved UV spectroscopy and transient infrared absorption. The UV spectrum of CH<sub>3</sub>C(O)O<sub>2</sub> exhibits two bands; the stronger short wavelength component has a maximum cross section of  $6.5 \times 10^{-18}$ cm<sup>2</sup> at 206 nm and the weaker one a cross section of  $2.9 \times 10^{-18}$  cm<sup>2</sup> at 250 nm. These bands are used to monitor the disappearance of CH<sub>3</sub>C(O)O<sub>2</sub> and the secondary formation of CH<sub>3</sub>O<sub>2</sub>, yielding a self-reaction rate constant of  $(3.0^{+1.7}_{-1.1}) \times 10^{-12} e^{(504\pm114)/T}$  cm<sup>3</sup> s<sup>-1</sup> and a cross reaction rate constant of  $(8.5^{+2.6}_{-2.0}) \times 10^{-13} e^{(726\pm75)/T}$  cm<sup>3</sup> s<sup>-1</sup>. Transient IR monitoring of the formation of CH<sub>2</sub>O reveals CH<sub>3</sub>C(O)O<sub>2</sub> + CH<sub>3</sub>O<sub>2</sub>  $\rightarrow$ CH<sub>2</sub>O + CH<sub>3</sub>COOH + O<sub>2</sub> to be the dominant channel for the cross reaction over the entire 209–358 K temperature range. This contrasts with previous studies that indicate a steep temperature dependence for the branching ratio, with a channel leading to CH<sub>3</sub>C(O)O + CH<sub>3</sub>O + O<sub>2</sub> dominant at high temperatures.

#### I. Introduction

Organic peroxy radicals represent an important class of intermediates formed in the course of the atmospheric oxidation of hydrocarbon compounds.<sup>1,2</sup> One of the more notable constituents of this class of radicals is the acetylperoxy radical. It is formed as a consequence of the photooxidation of a variety of carbonyl compounds, either from their direct emission into the atmosphere or from their appearance as secondary products of hydrocarbon oxidation. The acetylperoxy radical is a significant contributor to smog formation owing to the reaction that it undergoes with NO<sub>2</sub> to form peroxyacetylnitrate (PAN). Furthermore, this reaction is important to the understanding of the ozone photochemical steady state since, due to its relative chemical and thermal stability, the formation of PAN effectively sequesters NO<sub>2</sub>.

The self-reaction of acetylperoxy radicals, while of minor consequence in the atmosphere, is often an important consideration in laboratory studies. The reason is that, under the high radical concentrations typical of laboratory measurements, the self-reaction competes with the reaction under investigation, whether it be PAN formation or the removal of acetylperoxy radicals by reaction with NO, HO<sub>2</sub>, or other peroxy radicals. Clearly, a good understanding of the self-reaction kinetics is required to extract useful information about the reactions of acetylperoxy radicals with these important atmospheric trace species. Furthermore, owing to significant secondary chemistry, the investigation of the self-reaction also yields information about the atmospherically more relevant cross reaction between acetylperoxy and methylperoxy radicals.

There are relatively few previous studies of the acetylperoxy UV spectrum, of its self-reaction, or of its reaction with methylperoxy radicals. An examination of the literature reveals that the previously published values for these quantities exhibit sizable discrepancies. UV cross sections of the acetylperoxy radical by Addison et al.,<sup>3</sup> Basco and Parmar,<sup>4</sup> and Moortgat et al.<sup>5</sup> differ both in their wavelength dependence as well as in their absolute intensities. The self-reaction rate constant has been measured at ambient temperature by the first two groups

cross reaction with  $CH_3O_2$  has only been investigated by Moortgat et al.<sup>5</sup> The kinetic measurements reported in the present paper make use of time-resolved UV spectroscopy to disentangle the

and at three temperatures by Moortgat et al., with the values at 298 K disagreeing by up to a factor of 7. The kinetics of the

use of time-resolved UV spectroscopy to disentangle the secondary chemistry that complicates the study of the acetylperoxy radical self-reaction. The secondary complications arise because the  $CH_3C(O)O$  product of the self-reaction,

$$CH_3C(O)O_2 + CH_3C(O)O_2 \rightarrow 2CH_3C(O)O + O_2 \quad (1)$$

rapidly dissociates, leading in the presence of molecular oxygen to  $CH_3O_2$  formation:

$$CH_3C(O)O \rightarrow CH_3 + CO_2 \tag{2}$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$$
(3)

Because the UV spectrum of methylperoxy radical significantly overlaps that of acetylperoxy radical, a simple analysis of the change in the UV absorption of the reaction mixture with time fails to yield the desired rate constant.

A further difficulty arises from the possibility that two channels exist for the cross reaction between acetylperoxy and methylperoxy radicals:

$$CH_3C(O)O_2 + CH_3O_2 \rightarrow CH_3C(O)O + CH_3O + O_2$$
(4a)

$$CH_3C(O)O_2 + CH_3O_2 \rightarrow CH_3COOH + CH_2O + O_2$$
 (4b)

In fitting their UV absorption vs time profiles, Moortgat et al.<sup>5</sup> found it necessary to postulate that reaction 4b dominates at low temperatures (<295 K) but that, due to a steep temperature dependence of the branching ratio, reaction 4a becomes the more important one at high temperatures (368 K). In a subsequent product study, Horie and Moortgat<sup>6</sup> refined the branching ratio but still found it to be steeply temperature dependent. The present study provides acetylperoxy UV cross sections and rate constants for reactions 1 and 4 in good agreement with Moortgat et al.<sup>5</sup>, but the fits of the kinetic data do not reproduce the steep temperature variation in the branching ratio of reactions 4a and

<sup>\*</sup> Author for correspondence.

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4b. Instead, transient infrared absorption experiments reveal that  $CH_2O$  is formed immediately and suggest that channel 4b dominates over the entire 232–348 K temperature range. A more complete discussion of this result, as well as of the self-reaction kinetics, is provided following a description of the experimental techniques and the presentation of the results.

#### **II. Experimental Section**

Acetylperoxy radicals, at concentrations of  $5 \times 10^{14}$  to  $1.4 \times 10^{15}$  cm<sup>-3</sup>, are generated by 351-nm excimer laser photolysis of Cl<sub>2</sub> in the presence of acetaldehyde and oxygen via the reactions

$$Cl + CH_3CHO \rightarrow CH_3CO + HCl$$
 (5)

$$CH_3CO + O_2 + M \rightarrow CH_3C(O)O_2 + M$$
 (6)

The radicals are produced in an approximately cylindrical volume 51 cm long and roughly 1.5 cm in diameter (based on the excimer laser beam shape), the central 0.8 cm of which is sampled by the probe beam. For the acetylperoxy UV absorption cross-section measurements, the acetaldehyde concentration was varied from 0.5 to 1.7 Torr and the oxygen concentration between 4 and 47 Torr in order to ascertain conditions under which the photolyzed chlorine atoms are stoichiometrically converted to CH<sub>3</sub>C(O)O<sub>2</sub>. The kinetics experiments were carried out with acetyladehyde concentrations of 0.5-1.6 Torr and an oxygen partial pressure of ~22 Torr, values that ensure that reactions 5 and 6 reach completion before the radical-radical reactions can proceed to any significant extent.

The reaction is followed by monitoring the absorbance due to  $CH_3C(O)O_2$  and  $CH_3O_2$  using time-resolved UV spectroscopy, a detailed description of which is provided in refs 7 and 8. Spectra are recorded at various delay times following the photolysis pulse using probe light from a cw deuterium lamp and a gated diode array spectrometer. They are deconvoluted by comparison against reference spectra of  $CH_3C(O)O_2$  and  $CH_3O_2$  along with the residual absorbance found after the reactions initiated by photolysis have gone to completion; thus,

$$Abs(\lambda, t) = l(\sigma_{CH_3C(O)O_2}(\lambda)[CH_3C(O)O_2]_t + \sigma_{CH_3O_2}(\lambda)[CH_3O_2]_t + c(t)Abs(\lambda, \infty))$$
(7)

where *l* represents the path length,  $\sigma_i(\lambda)$  is the cross section of component i, and  $[i]_t$  denotes the time-dependent concentration of component i. The last term accounts for the accumulation of UV-absorbing reaction products. Abs $(\lambda,\infty)$  represents the absorbance of these products, and c(t) is proportional to their concentration.

Initial radical concentrations are found by substituting ethane for acetaldehyde and measuring, via the method just described, the formation of  $C_2H_5O_2$  radicals. This is a convenient and accurate method for determining the yield of Cl atoms from photolysis since the UV cross section of  $C_2H_5O_2$  has been well established,<sup>8–10</sup> the reactions forming ethylperoxy radicals are rapid, and the removal of the radicals via self-reaction is very slow.<sup>1,2</sup> This procedure is used both to assign absolute cross sections to the acetylperoxy UV spectrum and to provide initial radical concentrations for fitting model predictions to the kinetic data.

Additional experiments were carried out to measure, via a previously described transient IR absorption method,<sup>11</sup> the rate and extent of formaldehyde production from the Cl-initiated oxidation of acetaldehyde. IR light from a Pb-salt diode laser is directed through the reaction mixture and detected by a

CH<sub>3</sub>COO<sub>2</sub> self reaction



**Figure 1.** Time-resolved UV spectra following the photolysis of  $Cl_2$  in the presence of CH<sub>3</sub>CHO and O<sub>2</sub>. The change in the shape of the UV spectrum with time indicates the formation of a secondary UV absorbing species, namely CH<sub>3</sub>O<sub>2</sub>.

HgCdTe detector having a time response of 0.3  $\mu$ s. CH<sub>2</sub>O is monitored via vibration—rotation lines of the  $\nu_2$  carbonyl stretch mode at 1729 cm<sup>-1</sup> ( $\sigma_{IR} = 3.6 \times 10^{-18}$  cm<sup>2</sup> at 30 Torr and 345 K) and 1766 cm<sup>-1</sup> ( $\sigma_{IR} = 2.7 \times 10^{-18}$  cm<sup>2</sup> at 110 Torr and 345 K). Acetaldehyde also absorbs at these frequencies ( $\sigma_{IR} \approx 5 \times 10^{-19}$  cm<sup>2</sup>); however, at the 30–110-Torr total pressure of these experiments, the individual rotational transitions are not resolved; rather, the spectrum is nearly continuous over regions of the width of the formaldehyde lines. Therefore, a comparison of transient absorptions on vs off the CH<sub>2</sub>O resonances enables the contributions from formaldehyde vs acetaldehyde to be distinguished.

Acetaldehyde was obtained from Aldrich (99%) or Fisher (99.5%) and freeze-pump-thawed prior to use. Nitrogen (99.999%) and oxygen (ultrazero grade) were obtained from Michigan Airgas. Chlorine was obtained from Matheson as a 9.7% mixture in helium. Gas flows are controlled by Tylan flow controllers, except for chlorine which is set by a needle valve. Partial pressures are determined by timing the pressure rise into a fixed volume. Temperature control is achieved using a Neslab ULT-80dd recirculating chiller. The gases are precooled/preheated prior to entering the reaction vessel.

## **III. Results**

A. UV Spectrum. Figure 1 illustrates the variation in the UV spectrum of a CH<sub>3</sub>CHO/Cl<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> gas mixture with the delay time after chlorine photolysis. The spectrum at 10  $\mu$ s reveals two broad and apparently unstructured absorption features centered at approximately 210 and 250 nm. As time progresses, the short-wavelength band decreases rapidly in intensity, whereas the long-wavelength band initially remains at nearly constant intensity and only later decreases in amplitude. Clearly the spectra do not arise from absorption by a single compound. Instead, the temporal behavior of the spectra can be explained by reactions 1-4. The early spectrum is almost entirely due to absorption by CH<sub>3</sub>C(O)O<sub>2</sub>. Each molecule lost by self-reaction is replaced, essentially instantaneously, by CH<sub>3</sub>O<sub>2</sub> owing to the rapid dissociation of CH<sub>3</sub>C(O)O and the facile addition of  $O_2$  to the  $CH_3$  fragment. Methylperoxy radicals absorb in the UV in a single, broad, Gaussian-shaped band centered at 238 nm. The lack of a CH<sub>3</sub>O<sub>2</sub> feature at 210 nm explains why the absorbance in this spectral region decreases rapidly whereas the absorbance at 250 nm does not.

Because of the fast decay of  $CH_3C(O)O_2$  and the interference from the  $CH_3O_2$  that is produced, care must be taken in measuring the acetylperoxy spectrum and assigning to it absolute

TABLE 1: CH<sub>3</sub>C(O)O<sub>2</sub> Self-Reaction Mechanism

	reaction <sup>a</sup>	rate constant		
1.	$CH_3C(O)O_2 + CH_3C(O)O_2 \rightarrow 2CH_3C(O)O + O_2$	$k = 3.0 \times 10^{-12} \mathrm{e}^{504/T} \mathrm{cm}^3 \mathrm{s}^{-1} \mathrm{b}$		
2.	$CH_3C(O)O \rightarrow CH_3 + CO_2$	$k \ge 1 \times 10^6  \mathrm{s}^{-1}$		
3.	$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$	$k = 4.5 \times 10^{-31} (T/300)^{-3} \text{ cm}^6 \text{ s}^{-1.15}$		
4a.	$CH_3C(O)O_2 + CH_3O_2 \rightarrow CH_3C(O)O + CH_3O + O_2$	$k = 0 \text{ cm}^3 \text{ s}^{-1 b}$		
4b.	$CH_3C(O)O_2 + CH_3O_2 \rightarrow CH_3COOH + CH_2O + O_2$	$k = 8.5 \times 10^{-13} \mathrm{e}^{726/T} \mathrm{cm}^3 \mathrm{s}^{-1} \mathrm{b}$		
9a.	$CH_3O_2 + CH_3O_2 \rightarrow 2CH_3O + O_2$	$k = (1 - b) \times 9.1 \times 10^{-14} e^{416/T} \text{ cm}^3 \text{ s}^{-1} ^{1.2}$		
9b.	$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + CH_2O + O_2$	$k = b \times 9.1 \times 10^{-14} e^{416/T} \text{ cm}^3 \text{ s}^{-1} {}^{1,2}$		
		$b = (1 + 25e^{-1165/T})^{-1}$		
10.	$CH_3O_2 + CH_3O \rightarrow products$	$k = 1.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$		
11.	$CH_3O + CH_3O \rightarrow products$	$k = 3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$		
12.	$CH_3O + O_2 \rightarrow CH_2O + HO_2$	$k = 3.9 \times 10^{-14} \mathrm{e}^{-900/T} \mathrm{cm}^3 \mathrm{s}^{-1} \mathrm{i}^2$		

<sup>a</sup> Reaction numbers correspond to those used in the text. <sup>b</sup> Measured in the present study.

absorption cross sections. The measurements presented here were accomplished in two stages: (1) ascertaining conditions under which the chlorine atoms formed by photolysis are quantitatively converted to acetylperoxy radicals and (2) correcting the raw spectrum for the short time delay (5  $\mu$ s) between photolysis and spectral measurement.

CH<sub>3</sub>C(O)O<sub>2</sub> is formed via reactions 5 and 6, i.e., attack of acetaldehyde by chlorine atoms followed by oxygen addition to the acyl radical. The first step can be made rapid by the addition of a sufficient quantity of CH<sub>3</sub>CHO ( $k_5 = 7.6 \times 10^{-11}$ cm<sup>3</sup> s<sup>-1</sup> at 295 K implies a lifetime of 0.4  $\mu$ s at 1 Torr).<sup>12</sup> Too much will enhance the chain reaction propagated by the reaction between CH<sub>3</sub>CO and Cl<sub>2</sub>; however, this fortunately has little effect on the quantity of  $CH_3C(O)O_2$  produced. Similarly, the oxygen concentration can be increased to enhance the rate of the O<sub>2</sub> addition reaction ( $k_6 = 5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  at 295 K implies a lifetime of 0.6 µs at 10 Torr).<sup>12</sup> If the [O<sub>2</sub>]/[CH<sub>3</sub>-CHO] ratio is too high, however, peroxy radicals are formed before all of the chlorine atoms have been consumed. As a consequence, the very rapid reaction typically found between peroxy radicals and chlorine atoms<sup>13</sup> can significantly reduce the conversion of Cl to  $CH_3C(O)O_2$ . The quantities of both acetaldehyde and oxygen were varied in order to locate a plateau region over which the  $CH_3C(O)O_2$  yield shows little dependence on changes in their concentrations. This region occurs for [CH<sub>3</sub>-CHO] >  $\sim 0.5$  Torr and  $[O_2]$  >  $\sim 10$  Torr.

Spectra recorded with the above conditions undergo a variation in time such as depicted in Figure 1. The raw spectrum, measured at 5  $\mu$ s, is corrected to zero time by the following procedure. Using the presently measured values of  $k_1$  and  $k_4$ , predictions from the reaction model of Table 1 indicate that, for an initial CH<sub>3</sub>C(O)O<sub>2</sub> concentration of  $10^{15}$  cm<sup>-3</sup>, 14% of the molecules are converted to CH<sub>3</sub>O<sub>2</sub> in the intervening 5  $\mu$ s. The contribution from the methylperoxy radicals is subtracted using the known wavelength-dependent cross sections of this species,<sup>8</sup> and the remainder is increased by 14% to compensate for the loss of CH<sub>3</sub>C(O)O<sub>2</sub>. The resulting acetylperoxy spectrum is shown by the solid line in Figure 2 and compared to previously measured spectra.

The broad featureless spectra of peroxy radicals are often well fit by a Gaussian shape of the  $form^{14}$ 

$$\sigma(\lambda) = \sigma_m \exp(-\alpha [\ln(\lambda_m/\lambda)]^2)$$
(8)

Assuming that the CH<sub>3</sub>C(O)O<sub>2</sub> spectrum consists of two such bands, a good fit of the spectrum, as illustrated by the dashed line in Figure 2, is obtained with the parameters  $\sigma_{1m} = 6.5 \times 10^{-18}$  cm<sup>2</sup>,  $\lambda_{1m} = 206$  nm,  $\alpha_1 = 119$  and  $\sigma_{2m} = 2.9 \times 10^{-18}$  cm<sup>2</sup>,  $\lambda_{2m} = 250$  nm,  $\alpha_2 = 81$ . The parameterization according to eq 8 affords a compact representation of the UV cross sections of CH<sub>3</sub>C(O)O<sub>2</sub>.





**Figure 2.** UV absorption spectrum of  $CH_3C(O)O_2$ . The spectrum measured in the present work is given by the solid line. The dashed line represents a fit of the spectrum to two Gaussian-shaped absorption bands (see text). The symbols represents results from previous studies.

**B.** CH<sub>3</sub>C(O)O<sub>2</sub> Reaction Kinetics. Time-dependent concentrations of CH<sub>3</sub>C(O)O<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub> are calculated from time-resolved spectra, such as those shown in Figure 1, by fitting them to a superposition of the UV cross sections of the peroxy radicals plus a fraction of the residual absorbance recorded at 20 ms, as per eq 7. The residual absorbance accounts for stable species, such as CH<sub>2</sub>O and CH<sub>3</sub>COOH, that are generated from the photooxidation of acetaldehyde and absorb weakly in the UV. An example of the resulting concentration vs time profiles is provided by Figure 3. These are then fit to the reaction model of Table 1 in order to extract values for the unknown rate constants  $k_1$  and  $k_4$ .

The principal reactions required to explain the concentration dependences depicted in Figure 3 are reactions 1 and 4. The self-reaction of CH<sub>3</sub>C(O)O<sub>2</sub> determines the initial decay rate of this species. On the time scale of the radical-radical reactions, the dissociation of the CH<sub>3</sub>C(O)O formed by reaction 1 and the subsequent addition of O<sub>2</sub> to the methyl radical fragment occur very rapidly. Thus, under our experimental conditions, each CH<sub>3</sub>C(O)O<sub>2</sub> lost by self-reaction appears to be instantly replaced by a CH<sub>3</sub>O<sub>2</sub> radical, as is evident in Figure 3 from the fact that the initial rate of CH<sub>3</sub>O<sub>2</sub> rise matches the rate of CH<sub>3</sub>C(O)O<sub>2</sub> decay.

The observation that the methylperoxy level does not rise to the initial acetylperoxy concentration indicates that it is lost by subsequent reactions. The self-reaction of  $CH_3O_2$  alone is too slow to account for this, and it does not explain the non-secondorder decay of  $CH_3C(O)O_2$ . Instead, one postulates the existence of a cross reaction between the two peroxy radicals. According to the previous work of Moortgat et al.<sup>5</sup> and Horie and Moortgat<sup>6</sup> two channels are possible: reactions 4a and 4b. The principal difference between the two, for the purpose of



**Figure 3.** Time dependence of the CH<sub>3</sub>C(O)O<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub> concentrations obtained by deconvoluting time-resolved UV spectra. Error bars represent  $2\sigma$  of the fitting error. Both sets of concentrations are fit simultaneously for the two unknowns  $k_1$  and  $k_4$ . Solid lines illustrate best fits of the reaction model to the data using a branching fraction of b = 1. Dashed lines show the best fits for the value of b = 0.06 obtained from Horie and Moortgat,<sup>6</sup> for which  $k_1 = 1.3 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> and  $k_4 = 2.2 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>.

fitting the RO<sub>2</sub> concentration vs time profiles, is that channel 4b causes a net loss of  $CH_3O_2$ , whereas channel 4a does not; the methylperoxy lost on the left-hand side of (4a) is replaced, after reactions 2 and 3, by the  $CH_3C(O)O$  produced on the right side. As demonstrated below, the branching ratio has a minor influence on the value of  $k_1$  but a major effect on  $k_4$ .

Whereas channel 4b yields stable products, channel 4a and channel 9a of the methylperoxy self-reaction,

$$CH_3O_2 + CH_3O_2 \rightarrow 2CH_3O + O_2$$
 (9a)

$$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + CH_2O + O_2 \qquad (9b)$$

produce methoxy radicals. These are formed too late to have anything but a negligible effect on the acetylperoxy concentration; however, they participate in secondary reactions via

 $CH_3O_2 + CH_3O \rightarrow products$  (10)

$$CH_3O + CH_3O \rightarrow products$$
 (11)

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \tag{12}$$

Very little is known about reaction 10; a channel leading to CH<sub>2</sub>O and CH<sub>3</sub>OOH may constitute about 20% of the total products.<sup>12</sup> Somewhat more information is available for the methoxy self-reaction.<sup>12</sup> At ambient temperatures and above, the predominant products may be CH<sub>2</sub>O and CH<sub>3</sub>OH; however, the recombination reaction could become important at low temperature and high pressure. Fortunately, reactions 10 and 11 have only a minor influence on the determinations of  $k_1$  and  $k_4$ . The reaction of CH<sub>3</sub>O with O<sub>2</sub> is well-known but is included here only for completeness, since at the O<sub>2</sub> concentrations of the present study this reaction proceeds too slowly to affect the kinetics measurements.

Fits of the reaction model to the time-dependent RO<sub>2</sub> concentrations involves three unknowns:  $k_1$ ,  $k_4$ , and b, the branching fraction of reactions 4a and 4b. b = 0 implies that



**Figure 4.** Variation of CH<sub>3</sub>C(O)O<sub>2</sub> self-reaction rate constant with temperature. Error bars represent deviations of  $2\sigma$ . Filled circles show the present measurements assuming b = 1. Crosses indicate the rate constants determined with *b* derived from the branching ratio of Horie and Moortgat,<sup>6</sup> eq 13. Open triangles indicate the values obtained by Moortgat et al.<sup>5</sup> The solid line gives the best fit of the present data to the Arrhenius expression.



**Figure 5.** Variation of the CH<sub>3</sub>C(O)O<sub>2</sub> + CH<sub>3</sub>O<sub>2</sub> reaction rate constant with temperature. Error bars represent deviations of  $2\sigma$ . Filled circles show the present measurements assuming b = 1. Crosses indicate the rate constants determined with *b* derived from the branching ratio of Horie and Moortgat.<sup>6</sup> Open triangles indicate the values obtained by Moortgat et al.<sup>5</sup> The solid line gives the best fit of the present data to the Arrhenius expression. Dashed line gives best fit of data (×'s) to a sum of two Arrhenius expressions related by  $\beta$  from eq 13 assuming that the branching ratio for reaction 4 is temperature dependent.

100% of the reaction proceeds via channel 4a; b = 1 implies that it goes entirely by (4b). Allowing all three parameters to vary always gives a best fit with b = 1 over the entire temperature range of the study, 209–358 K. Unfortunately, a drawback of the three-parameter fit is that it leads to large error bars for both b and the cross reaction rate constant. An alternative procedure is, therefore, adopted. Two parameter fits are performed by setting b = 1 and, for comparison, setting bto the value obtained from Horie and Moortat.<sup>6</sup> Section IIIC presents evidence supporting the b = 1 value favored by the three-parameter fits of the RO<sub>2</sub> concentration vs time data.

The temperature-dependent rate constants derived by the above fitting procedure are illustrated in Figures 4 and 5. The preferred results, with b = 1, are also given in Table 2 along

TA	BL	Е	2:	Measu	red	Rate	Constant
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			results				
temp, K	CH <sub>3</sub> CHO, Torr	Cl <sub>2</sub> , Torr	O <sub>2</sub> , Torr	$P_{\rm tot}$ , Torr	$[Cl]_{o}$ , $10^{14} \text{ cm}^{-3}$	$k_1$ , $10^{-11}$ cm <sup>3</sup> s <sup>-1</sup>	$k_4$ , $10^{-11}$ cm <sup>3</sup> s <sup>-1</sup>
209	1.2	0.26	22	106	7.3	$3.2 \pm 0.5$	$3.0 \pm 0.8$
216	1.2	0.53	23	110	13.6	$2.7 \pm 0.4$	$2.3 \pm 0.4$
224	1.3	0.21	23	108	5.2	$3.5 \pm 0.4$	$2.0 \pm 0.4$
226	1.2	0.28	22	105	7.7	$2.8 \pm 0.5$	$2.0 \pm 0.4$
233	1.5	0.51	23	112	13.5	$2.2 \pm 0.3$	$1.8 \pm 0.3$
253	0.76	0.47	23	110	6.2	$2.6 \pm 0.5$	$1.6 \pm 0.5$
273	1.5	0.43	22	109	10.5	$2.0 \pm 0.3$	$1.3 \pm 0.2$
295	1.5	0.56	22	112	12.4	$1.6 \pm 0.4$	$1.0 \pm 0.2$
295	0.52	0.59	13	112	7.2	$1.5 \pm 0.2$	$1.1 \pm 0.15$
327	1.5	0.35	23	112	7.3	$1.4 \pm 0.3$	$0.76 \pm 0.25$
358	1.6	0.38	24	120	6.4	$1.2 \pm 0.2$	$0.58 \pm 0.15$

with the experimental conditions. The CH<sub>3</sub>C(O)O<sub>2</sub> self-reaction (Figure 4) has a negative temperature dependence and is little affected by the choice of branching fraction. The largest effect, at 358 K, is an increase of 26% upon changing *b* from 0 to 1. The cross reaction (Figure 5) also exhibits a negative temperature dependence for b = 1; however, when *b* is set to the previously reported temperature-dependent values,  $k_4$  increases with increasing temperature between about 260 and 295 K before returning to the negative temperature dependence.

Errors in the rate constants (aside from the effect of b) derive primarily from two sources: noise and uncertainty in the peroxy radical UV cross sections. A comparatively negligible contribution arises from uncertainties in the secondary chemistry, reactions 9-12. The noise in the concentration vs time data introduces on average a 15% fitting error for  $k_1$  and a 20% error for  $k_4$ . The methylperoxy and ethylperoxy UV spectra have been well studied, and their intensities are known to within about 5%. The uncertainty in the acetylperoxy UV cross sections is somewhat higher, about 10%, owing to the corrections necessitated by its rapid self-reaction. However, the fact that both the  $CH_3C(O)O_2$  and  $CH_3O_2$  data can be fit simultaneously suggests that these cross sections are internally consistent. Adding statistically a roughly 10% contribution from uncertainties in the reference UV spectra to the noise error yields the overall errors of 12–22% for  $k_1$  and 14–33% for  $k_4$  listed in Table 2.

**C.**  $CH_3C(O)O_2 + CH_3O_2$  **Product Channel.** It is apparent that an accurate determination of the acetylperoxy plus methylperoxy reaction rate constant requires information about the branching of this reaction. The product study of Horie and Moortgat<sup>6</sup> and the kinetic measurements of Moortgat et al.<sup>5</sup> indicate the branching ratio to have a steep temperature dependence, with

$$\beta = k_{4a}/k_{4b} = 2.2 \times 10^6 \mathrm{e}^{-3870/T} \tag{13}$$

In contrast, the present time-resolved peroxy radical measurements are best fit with  $b = (1 + \beta)^{-1} = 1$ . Although the fits with b = 1 are superior to those based on eq 13, this is not sufficient to rule out the possibility that setting b = 1compensates for some other shortcoming of the reaction model or for a systematic error in the experimental measurements. As an independent means to investigate the branching ratio, timedependent measurements of CH<sub>2</sub>O formation were undertaken, since formaldehyde is produced by channel 4b but not channel 4a. This procedure is not as ideal as might be hoped because reactions 9b and 10–12 also form CH<sub>2</sub>O. To make matters worse, the increase in  $k_4$ , found upon setting b to the value of Horie and Moortgat,<sup>6</sup> increases the CH<sub>2</sub>O contribution from the latter reactions, making it more difficult to distinguish between reactions 4a and 4b.



**Figure 6.** Time dependence of CH<sub>2</sub>O formation upon photolysis of a CH<sub>3</sub>CHO/Cl<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> gas mixture at 345 K. The solid line illustrates the predictions of the reaction model using b = 1; the dashed line shows CH<sub>2</sub>O formation for b = 0.03, assuming that the reactions of CH<sub>3</sub>O with itself and with CH<sub>3</sub>O<sub>2</sub> produce CH<sub>2</sub>O at 100% yield. The dotted line assumes no CH<sub>2</sub>O is produced by reaction 10; the dot-dash line assumes no CH<sub>2</sub>O from either reaction 10 or 11. The inset compares the transient IR absorption with the diode laser locked to a CH<sub>2</sub>O absorption line vs an off-resonant transient absorption (see text).

CH<sub>2</sub>O was probed by vibration-rotation lines of the carbonyl stretch mode. These lines are overlapped by the corresponding band of the acetaldehyde precursor. However, at the 30-110 Torr total pressures of these experiments, the latter absorption features are considerably broader than the CH<sub>2</sub>O lines. The inset to Figure 6 illustrates the raw changes in IR absorption following Cl<sub>2</sub> photolysis. Off the CH<sub>2</sub>O resonance there is an abrupt increase in the transmitted light intensity which occurs because acetaldehyde is removed by reaction with chlorine atoms. With the IR probe beam tuned to the CH<sub>2</sub>O resonance, there is a nearly identical abrupt increase in transmitted light; however, this is followed by an increase in absorption with a half-life of approximately 200  $\mu$ s. The abrupt increase in light intensity is, again, due to loss of acetaldehyde, whereas the subsequent loss of transmitted light arises from the formation of formaldehyde. In order to ensure that the absorption is indeed due to CH<sub>2</sub>O and not because of an accidental spectral coincidence with another molecule, the measurements were repeated at two well-separated frequencies, 1729 and 1766 cm<sup>-1</sup>, with consistent results.

Using measured IR line strengths, CH<sub>2</sub>O absorbance traces are converted to concentration vs time profiles, such as the one illustrated in the main portion of Figure 6. The key point to notice is that, after photolysis, CH<sub>2</sub>O formation commences with almost no delay; the small delay that can be observed occurs because of interference from the excimer laser pulse. This sharp rise was noted uniformly from 232 K, at which temperature our UV experiments and Horie and Moortgat's<sup>6</sup> results agree that channel 4b predominates to 345 K, where there is disagreement. At the high temperature, the [CH<sub>2</sub>O] time dependence can be compared to differing model predictions based on (i) b = 1 and  $k_1$  and  $k_4$  taken from Table 2 vs (ii) bfrom ref 6 and the alternative rate constants exhibited by x's in Figures 4 and 5. These are illustrated, respectively, by the solid and dashed curves in Figure 6. In agreement with the data, the solid line exhibits only a very small delay in rising after the photolysis pulse. In contrast, the prediction based on a temperature-dependent branching ratio, with b = 0.03 at 345 K, indicates a noticeable delay in CH<sub>2</sub>O production, that, in spite of interference from the excimer laser, is not observed in the data. The discrepancy between the data and predictions based on b = 0.03 increases if it is assumed (as is likely) that reaction 10 produces no CH<sub>2</sub>O (dotted line) or if neither reaction 10 nor 11 produces CH<sub>2</sub>O (dot-dash line). Although not conclusive because CH<sub>2</sub>O is formed by reactions other than (4b), the CH<sub>2</sub>O formation measurements agree with the UV data that channel 4b represents the principal  $CH_3C(O)O_2 + CH_3O_2$ reaction pathway over the 210-350 K temperature range.

## **IV.** Discussion

Figure 2 compares the UV spectrum of CH<sub>3</sub>C(O)O<sub>2</sub> presented in this work to previous measurements. All the spectra reveal two bands: an intense one at about 207 nm and a somewhat weaker one at 240 nm. The intensities and exact positions of the peaks, however, vary considerably, except that the spectrum of Moortgat et al.<sup>5</sup> agrees well with the present work. The spectrum of Addison et al.<sup>3</sup> was recorded in the presence of NO<sub>2</sub> and, therefore, required subtraction of the UV absorption contributed by PAN. Since PAN absorbs more strongly over the short-wavelength portion of the  $CH_3C(O)O_2$  spectrum than the long-wavelength portion, this may explain why the spectrum of Addison et al.3 agrees relatively well with ours above 225 nm but much more poorly below 225 nm. The spectrum of Basco and Parmar<sup>4</sup> differs from ours in both overall intensity and in the relative intensity of the 207- and 240-nm peaks. The discrepancy in overall intensity may result from their use of Cl<sub>2</sub> loss as a means of determining radical production, a method inherently less sensitive than the present one based on  $C_2H_5O_2$ production. Although Basco and Parmar<sup>4</sup> claim to measure their spectrum "immediately" after photolysis, as shown by the present work, even a small delay causes a substantial change in the shape of the spectrum because of the rapid conversion of acetylperoxy radicals to methylperoxy radicals. It is likely that this is responsible for the enhanced absorption recorded by Basco and Parmar<sup>4</sup> in the 230–260-nm region relative to the 207-nm peak.

The spectrum of Moortgat et al.<sup>5</sup> was measured relative to the absorption of HO<sub>2</sub> at 210 nm and has, therefore, been rescaled to account for the change in the accepted HO<sub>2</sub> cross section at this wavelength since their work.<sup>1</sup> This rescaling gives very good overall agreement with the present spectrum. Close comparison reveals small discrepancies; at 207 nm, the present spectrum is less intense by about 10%, whereas it is more intense above 250 nm. The discrepancy at 207 nm is well within the error bars of the respective intensity measurements. However, calibration differences alone cannot account for the fact that the spectral shapes are different; i.e., the relative intensities at 207 nm vs 260 nm are different. The latter occurrence likely arises from uncertainites in correcting the acetylperoxy spectrum for the conversion of  $CH_3C(O)O_2$  to  $CH_3O_2$ , a procedure required by both studies.

The acetylperoxy self-reaction rate constant has been measured previously at room temperature by Addison et al.<sup>3</sup> ( $k_1 =$  $2.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ ) using molecular modulation and by Basco and Parmar<sup>4</sup> ( $k_1 = 8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ ) using flash photolysis. More recently, Moortgat et al.<sup>5</sup> reported rate constants at 253, 298, and 368 K. The earlier rate constants are substantially smaller than both the present value and that of Moortgat et al.<sup>5</sup> at 295 K. The rate constant of Addison et al.<sup>3</sup> is based on measurements at 210 and 240 nm; however, the CH<sub>3</sub>C(O)O<sub>2</sub> UV cross sections they employed are  $\sim$ 50% smaller than the present ones, and they do not account for residual absorption by stable reaction products. Although they attempt to correct for methylperoxy formation, these authors use a rate constant  $k_4$  that is about 6 times smaller than the value reported herein. While these factors might explain an underestimate of  $k_1$ , that the rate constant is over 5 times smaller than the present value is difficult to rationalize. Basco and Parmar<sup>4</sup> base their rate constant on the time dependence of the absorbance in the 198-208-nm region assuming no contribution from methylperoxy radicals, whereas, in fact, it contributes roughly 25%. This and the lack of accounting for the cross reaction between CH<sub>3</sub>C(O)O<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub> are likely reasons for the low value of  $k_1$  reported by Basco and Parmar.<sup>4</sup>

As is apparent from Figure 4, the self-reaction rate constants measured by Moortgat et al.<sup>5</sup> agree extremely well with the present results based on the preferred branching fraction for reaction 4b of b = 1. Even if we set b to the temperaturedependent values from Horie and Moortgat,<sup>6</sup> the agreement for  $k_1$  remains very good. Of course, this is somewhat fortuitous; Moortgat et al.<sup>5</sup> derived rate constants based on their original "unscaled" CH<sub>3</sub>C(O)O<sub>2</sub> UV cross sections, and they did not account for the residual absorbance due to stable products in their kinetic simulations. Still, these shortcomings should not influence the rate constant determinations by more than about 20%, implying that the agreement would remain very good.

The principal issue concerning the cross reaction of  $CH_3C(O)O_2$  with  $CH_3O_2$  is the branching between the radical channel yielding  $CH_3C(O)O$  and  $CH_3O$  vs the molecular channel that produces formaldehyde and acetic acid. From flash photolysis/UV absorption data, Moortgat et al.<sup>5</sup> determined self-reaction and cross reaction rate constants by fitting model simulations to absorbance vs times traces at a few fixed wavelengths in the 200–260-nm range. Fits of their traces gave a branching ratio of

$$\beta = 4.4 \times 10^5 e^{-3900/T}$$

Unfortunately, this determination must be viewed with some skepticism because, as Figure 3 shows, the peroxy radical concentration vs time data cannot with accuracy provide unique values for  $\beta$  and  $k_4$ . On the basis of a product study of biacetyl photolysis, Horie and Moortgat<sup>6</sup> later revised this to the expression given by eq 13. The major effect of the revision is to decrease the temperature at which channels 4a and 4b contribute equally from 300 to 265 K.

The results of the present study indicate that channel 4b is the major channel over the entire 209–358 K temperature range. We base this on two types of experimental measurements and on two observations. First, consider the experiments. The fits of the UV data for  $[CH_3C(O)O_2]_t$  and  $[CH_3O_2]_t$  invariably

Next, consider two observations concerning the issue of branching ratio. First, experiments have been conducted to measure the self-reaction rate constant of the CF<sub>3</sub>C(O)O<sub>2</sub> radical using the same time-resolved UV spectroscopy technique as described here.<sup>16</sup> Fits of the data in that case revealed a  $CF_3C(O)O_2 + CF_3O_2$  rate constant of  $< 2 \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup>. Presumably, the reason for the small rate constant is that, as with acetylperoxy, the radical channel is slow and that, due to fluorine substitution, the molecular channel becomes unaccessible. Second, we can examine the consequence of the branching ratio given by eq 13 and the values of  $k_4$  determined under this assumption (marked by x's in Figure 5). A best fit of these rate constants to a sum of two Arrhenius expressions yields  $k_{4a} = 6.8 \times 10^{-9} e^{-1870/T} cm^3 s^{-1}$  and  $k_{4b} = 3.1 \times 10^{-9} e^{-1870/T} cm^3 s^{-1}$  $10^{-15}e^{2000/T}$  cm<sup>3</sup> s<sup>-1</sup> and the dashed curve in Figure 5. As is apparent, the curve gives a poor fit to the data, suggesting that the branching ratio is not consistent with the measured overall rate constants and the assumption of Arrhenius behavior for each channel. Moreover, the preexponential factors are unphysical for both channels. In contrast, fixing b = 1 over the temperature range of the present experiments leads to a consistent interpretation of both the UV and IR data.

A comparison between the  $CH_3C(O)O_2 + CH_3O_2$  rate constants measured in the present work and those determined by Moortgat et al.<sup>5</sup> is presented in Figure 5. Except at 368 K, the agreement is extremely good when the branching fraction for channel 4b is set to b = 1. Again, this is in part fortuitous since Moortgat et al.<sup>5</sup> employed a temperature-dependent branching ratio in their fits. For comparison, poor agreement is obtained above 270 K when we force the temperature dependence of Horie and Moortgat<sup>6</sup> on the fits of our UV data.

The question remains as to the origin of the discrepancy in the branching ratio of reactions 4a and 4b. The present work has shown that, even if time-resolved UV spectra are recorded, fits of the data to  $k_1$ ,  $k_4$ , and b produce rather large error bars for the branching ratio. Moortgat et al.<sup>5</sup> found that, in order to fit their UV absorbance vs time traces, they needed to introduce into their model a third adjustable parameter, a temperaturedependent branching ratio for reactions 4a and 4b. Because their data were recorded at just a few fixed wavelengths, it is likely that another effect, such as residual absorption by stable products or a systematic discrepancy in the UV cross sections employed in their model, could have been introduced instead with equal success. The reason for the discrepancy with the product study of Horie and Moortgat<sup>6</sup> is less clear. They base their results on measurements of the temperature dependence of a variety of products from the photooxidation of biacetyl; however, the mechanism is rather complex. For the analogous reaction between CH<sub>3</sub>C(O)O<sub>2</sub> and HO<sub>2</sub>, they are able, rather directly, to base the branching ratio on the ratio of certain products. That procedure does not work for reactions 4a and 4b. Instead, they had to employ an indirect means to determine the branching ratio. Interestingly enough, they find a much smaller temperature dependence for the reaction of  $CH_3C(O)O_2$  with  $HO_2$  as opposed to  $CH_3O_2$ . It appears at this

point that more work is needed to fully understand the reaction between acetylperoxy and methylperoxy radicals.

### V. Conclusion

The techniques of time-resolved UV spectroscopy and transient infrared absorption have been used to investigate the  $CH_3C(O)O_2$  self-reaction and its reaction with  $CH_3O_2$ . The UV spectrum of  $CH_3C(O)O_2$  has been corrected for secondary production of methylperoxy radicals, unlike some earlier measurements.<sup>3,4</sup> After recalibrating the previous spectrum of Moortgat et al.,<sup>5</sup> it is found to be in good agreement with the present work. Similarly, very good agreement is found for both the absolute magnitudes and the temperature dependence of the  $CH_3C(O)O_2$  self-reaction rate constants between the present results and the work of Moortgat et al.<sup>5</sup> In contrast, two earlier studies that lacked as careful an analysis of the secondary chemistry reported much smaller rate constants.<sup>3,4</sup>

The magnitudes and temperature dependence of the cross reaction between  $CH_3C(O)O_2$  and  $CH_3O_2$  found in the present work also agree well with those of Moortgat et al.<sup>5</sup> However, the present results are based on channel 4b being the dominant pathway over the entire 209–358 K temperature range, whereas the latter results have channel 4a dominant above 300 K. The present paper concludes that reaction 4 proceeds nearly exclusively via channel 4b and supports this by IR measurements of  $CH_2O$  production and the fact that the values of  $k_4$  measured in the present work are inconsistent with two product channels both exhibiting Arrhenius temperature dependences, but related by the branching ratio of Horie and Moortgat.<sup>6</sup>

**Note Added in Proof.** After submission of this paper we became aware of the measurements of  $CH_3C(O)O_2$  kinetics by Roehl, Bauer, and Moortgat [*J. Phys. Chem.*, in press]. Their UV cross sections are virtually identical to the measurements presented here. Their values of  $k_1$  and  $k_4$ , at 295 K, are in very good agreement with the ones in this work.

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