

RATE COEFFICIENT FOR THE REACTION OF CH_3O WITH CH_3CHO AT 25 °C

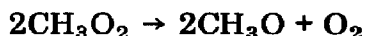
NELSON KELLY and JULIAN HEICKLEN

Department of Chemistry and Center for Air Environment Studies, The Pennsylvania State University, University Park, Pa. 16802 (U.S.A.)

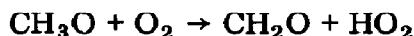
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Summary.

The rate coefficient ratio for the reaction of methoxy radicals with acetaldehyde and oxygen at 25 °C was determined by photolyzing azomethane in the presence of acetaldehyde and oxygen. The quantum yields for two of the products of the oxidation of the acetyl radicals, peracetic acid and CO_2 , were obtained. The methoxy radicals are generated from the methylperoxy radicals initially produced:



The methoxy radical is then scavenged by either acetaldehyde or O_2 :

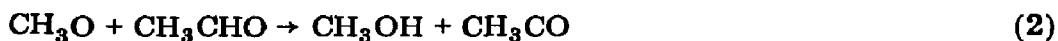


An analysis of the CO_2 quantum yield $\Phi\{\text{CO}_2\}$ in terms of a mechanism proposed earlier allows us to estimate $k_2/k_3 = 14$ with about a 20% uncertainty. This, together with a recent determination of $k_3 = 3.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 298 K, gives $k_2 = 5.0 \pm 1.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

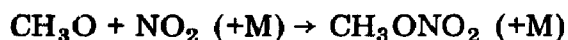
Introduction

Recently four papers have appeared from our laboratory concerned with the oxidation chemistry of methyl (CH_3), acetyl (CH_3CO) and formyl (HCO) radicals [1 - 3], and the photo-oxidation of acetaldehyde [4] at room temperature and 3130 Å. These investigations were part of a program to assess the role of aldehydes in photochemical smog. Acetaldehyde and aldehydes in general are important reactants in photochemical smog in two different ways. First, they may absorb solar radiation and the excited states formed can directly produce reactive free radicals [4, 5]. Secondly, acetaldehyde undergoes abstraction reactions by other free radicals to form acetyl radicals which eventually lead to peroxyacetyl nitrate (PAN) formation in polluted urban atmospheres [5, 6].

One pertinent rate coefficient ratio which is needed to analyze the free radical chemistry of the acetaldehyde system is k_2/k_3 for the reactions



The reaction numbers used are those used in the previous study of this system [2]. The rate of reaction (2) between the methoxyl radical and the acetaldehyde has never been measured to our knowledge. The difficulty in detecting CH_3O directly makes the use of indirect techniques of estimating rate coefficients for its reactions prevalent. Barker *et al.* [7] recently made CH_3O radicals by the decomposition of dimethyl peroxide and measured the rate of reaction (3) over a range of temperatures relative to the reaction



At 298 K their Arrhenius expression gives $k_3 = 3.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.

The previous work in our laboratory on the oxidation of acetyl radicals used a mass spectrometer to measure peracetic acid and a thermistor gas chromatograph to measure CO_2 as products. That work also measured methanol and dimethyl peroxide as products, and a relatively complete mechanism was deduced and rate coefficient ratios were obtained based on this mechanism [2]. However, from the data obtained by Weaver *et al.* [2] in their study of the oxidation of acetyl radicals, k_2/k_3 could only be estimated to lie between 10 and 20. The average value of 15 was adopted to rationalize the results of the study on the photo-oxidation of acetaldehyde at 3130 Å [4]. In the current study a long path infrared technique (LPIR) was used and this allowed us to go to much higher ratios of $[\text{O}_2]$ to $[\text{CH}_3\text{CHO}]$. Thus we can extend the mechanism of Weaver *et al.* [2] and obtain the important rate coefficient ratio k_2/k_3 .

Experimental

The azomethane used in this study was prepared by the procedure of Renaud and Leitch [8]. It was purified by trap-to-trap distillation from -86°C (isopropanol slush) to -130°C (n-pentane slush). The acetaldehyde was obtained from Fischer Scientific and was also purified by distillation from -86°C to -130°C . Gas chromatographic analyses of both of these compounds using a Chromosorb 103 column and flame ionization detection showed no impurities. The O_2 and N_2 were obtained from Phillip Wolf & Sons and were not less than 99.5% pure. Each was passed through a glass wool trap cooled in liquid nitrogen before use.

Authentic samples of peracetic acid and CO_2 were used for infrared calibrations. The peracetic acid was 40% pure and was obtained from FMC Corp., Buffalo, N.Y. The major impurity was acetic acid and this was corrected for by calibrating with pure acetic acid. The CO_2 was Matheson bone dry grade, and both this and the peracetic acid were degassed at -196°C and used without purification.

Irradiations were carried out in a three-mirror (White cell) multiple reflection long path infrared cell, made by Wilks Scientific, and mounted on a Beckman Model 10 infrared spectrometer. A diagram of this system is published elsewhere [9]. The vessel was Teflon coated and had a volume of about 10 l. The infrared windows were made of NaCl. For this study the path length was adjusted to 40 m.

The cell was evacuated to pressures less than 0.1 m Torr on a conventional grease free, mercury free high vacuum line using stopcocks with Viton O-rings and a three stage silicon oil diffusion pump. Pressure measurements were made on either a silicon oil manometer or a 0 - 800 Wallace & Tiernan pressure gauge. The gases were expanded into the cell from known volumes and N₂ was added before photolysis to bring the total pressure in the cell to 1 atm.

Irradiations were carried out through a small quartz side window in the cell. A Hanovia 140 W medium pressure mercury lamp was focused using a quartz lens and passed through a Corning 0 - 53 filter onto a gold plated mirror inside the cell. This mirror reflected the incident beam onto the same mirrors that multipass the infrared beam. However, the UV beam only made four passes. With this set-up and azomethane as the light absorber, the primary photolytic wavelength is 3660 Å.

Actinometry was done by photolyzing azomethane in 1 atm of helium diluent without adding acetaldehyde and O₂. The quantum yield of nitrogen under these conditions is known to be 1.0 [10]. An aliquot of the mixture was taken at various intervals and was injected into a gas chromatograph using a 13X molecular sieve column and an ice cooled thermistor detector. In order to obtain sufficient nitrogen for analysis, photolysis had to be performed over a period of 10 - 20 h.

Results

The photolysis of azomethane at 3660 Å in the presence of acetaldehyde and oxygen was studied at 25 °C. The pressure of azomethane was varied from 0.54 to 2.0 Torr, while the pressure of acetaldehyde ranged from 0.22 to 1.5 Torr and that of oxygen ranged from 0.16 to 120 Torr. The observed products under our conditions are peracetic acid and CO₂. The growth of peracetic acid with time was monitored by measuring its absorbance at 1230 cm⁻¹ and that of CO₂ was monitored at 2300 cm⁻¹. The other products of the reaction, methanol and dimethylperoxide, could not be observed by us because of interferences by the infrared peaks of the reactants azomethane and acetaldehyde.

The absorbances of both CO₂ and peracetic acid were converted to concentrations using extinction coefficients obtained from Beer's law plots on authentic samples of these products. For both peracetic acid and CO₂ the plots of concentration *versus* time were initially linear showing that these are initial photochemical products of the reaction. After prolonged exposure the

CO₂ is produced at an increasing rate and the peracetic acid at a decreasing rate. Presumably secondary reactions are occurring that destroy the peracetic acid, possibly to produce CO₂. Peracetic acid is known to decompose in the dark to acetic acid [4]. Under our conditions this decomposition is very slow, possibly because of the Teflon walls of our reactor. We checked that the dark decomposition of peracetic acid does not produce CO₂. Using the initial linear portion of the curves of concentration *versus* time we obtain the rate of production of products, and dividing this by the rate of light absorption I_a (obtained in separate actinometer experiments) gives the quantum yield of products.

Table 1 lists the initial concentrations of reactants, the quantum yields of products and the other fundamental variables of the system, $[O_2]/[CH_3CHO]$ and $[CH_3CHO]/I_a^{1/2}$. It should be noted that the measurements of products were made at sufficiently short times that the initial concentrations of reactants prevail.

The quantum yields $\Phi\{CO_2\}$ of CO₂ and $\Phi\{CH_3CO_3H\}$ of peracetic acid are listed in Table 1 as functions of decreasing $[O_2]/[CH_3CHO]$. It can be seen that $\Phi\{CO_2\}$ increases monotonically as $[O_2]/[CH_3CHO]$ decreases independent of $[CH_3CHO]/I_a^{1/2}$. $\Phi\{CH_3CO_3H\}$ also increases with decreasing $[O_2]/[CH_3CHO]$. However, $\Phi\{CH_3CO_3H\}$ is also strongly dependent on $[CH_3CHO]/I_a^{1/2}$ and increases as this variable is increased. The absolute quantum yields for CO₂ and peracetic acid obtained by us are slightly lower (approximately 20%) than those of Weaver *et al.* [2], where the two studies overlap, but this is well within our experimental error. It must be remembered that our peracetic acid quantum yields are based on the assumption that the peracetic acid used for calibrations was 40% pure. If this were untrue our quantum yields would have to be adjusted by a constant factor. Since this assumption gives reasonable agreement with the values for $\Phi\{CH_3CO_3H\}$ of Weaver *et al.* [2], it seems to be valid.

Discussion

The previous work in our laboratory on the oxidation of acetyl radicals [2] suggest the following mechanism:

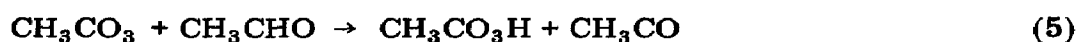
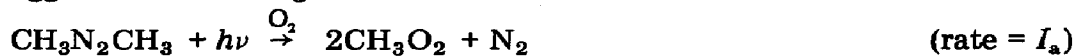
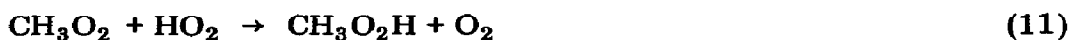
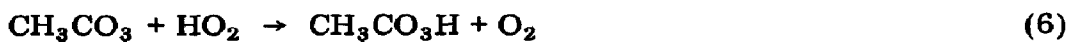


TABLE 1

Product quantum yields in the photolysis of $\text{CH}_3\text{N}_2\text{CH}_3$ in the presence of CH_3CHO and O_2

	$[\text{O}_2]/[\text{CH}_3\text{CHO}]$	$10^{-3}[\text{CH}_3\text{CHO}]/I_a^{1/2}$ (Torr s) ^{1/2}	$[\text{CH}_3\text{CHO}]$ (Torr)	$[\text{O}_2]$ (Torr)	$[\text{CH}_3\text{N}_2\text{CH}_3]$ (Torr)	$\Phi\{\text{CO}_2\}$	$\Phi\{\text{CH}_3\text{CO}_3\text{H}\}$
142		1.52	0.706	100	0.593	0.119	0.224
112		0.262	0.224	25.0	2.03	0.163	0.0883
100		1.37	0.703	70.9	0.718	0.123	0.431
86		1.63	1.39	120	2.02	0.238	0.575
74		2.73	1.42	105	0.747	0.303	0.654
61		1.37	0.690	41.9	0.703	0.258	0.577
47		2.82	1.45	68	0.731	0.309	0.957
44		2.85	1.47	65	0.731	0.452	0.900
44		0.445	0.228	9.94	0.725	0.340	0.227
39		1.76	1.35	53	1.62	0.489	0.939
24.3		0.269	0.221	5.38	1.86	0.653	0.336
19.8		1.46	0.680	13.5	0.601	0.985	1.47
18.1		0.454	0.226	4.09	0.684	0.754	0.467
10.6		1.67	0.778	8.24	0.599	1.26	1.85
2.82		1.88	1.34	3.78	1.40	1.91	3.81
2.07		0.453	0.217	0.450	0.637	3.13	0.985
0.93		1.26	0.605	0.565	0.631	3.50	3.00
0.17		1.96	0.955	0.164	0.655	3.30	4.23



In the study of Weaver *et al.* [2] the quantum yields for the products methanol, dimethylperoxide and peracetic acid were obtained. The fundamental parameter of the system was found to be $[\text{CH}_3\text{CHO}]/I_a^{1/2}$. The dependence of product yields on this parameter comes from the competition in reactions (5) and (7) between radical-molecule and radical-radical reactions. The quantum yields of CO_2 , methanol and peracetic acid were also observed to decrease at $[\text{CH}_3\text{CHO}]/[\text{O}_2]$ ratios less than 0.5. This effect is presumably due to the competition in steps (2) and (3) for CH_3O . Weaver *et al.* [2] were able to estimate a value for k_2/k_3 as discussed previously, but the majority of their experiments were done with $[\text{CH}_3\text{CHO}]/[\text{O}_2] > 0.5$. Under these conditions reactions (3), (6) and (9) - (12) are negligible.

At high $[\text{O}_2]/[\text{CH}_3\text{CHO}]$ reactions (3), (6), (11) and (12) are no longer negligible (but (9) and (10) are) and the complete reaction scheme (minus reactions (9) and (10)) is analyzed as follows. Under steady state conditions the rate of production of carbon-containing radicals is equal to the rate of removal. Thus

$$2I_a = R_{1b} + 2R_{1c} + \alpha R_3 \quad (I)$$

where $1 \leq \alpha \leq 2$ and R_{1b} is the rate of reaction (1b). At high $[\text{O}_2]/[\text{CH}_3\text{CHO}]$, reactions (2) and (6) are diminished and reactions (3) and (12) are enhanced so that $\alpha \rightarrow 1$. At low $[\text{O}_2]/[\text{CH}_3\text{CHO}]$ the reverse is true and $\alpha \rightarrow 2$.

Applying the steady state assumption to CH_3O gives

$$R_8 + 2R_{1a} = R_2 + R_3 \quad (II)$$

Thus

$$[\text{CH}_3\text{O}] = \frac{R_8 + 2\gamma I_a}{k_2[\text{CH}_3\text{CHO}] + k_3(1 + \alpha\gamma)[\text{O}_2]} \quad (III)$$

where $\gamma \equiv k_{1a}/(k_{1b} + k_{1c}) = 0.75$ [2].

If we note that only reactions that remove CH_3CO_3 radicals produce $\text{CH}_3\text{CO}_3\text{H}$ and CO_2 and that under steady state conditions the rate of removal of CH_3CO_3 equals the rate of production of CH_3CO_3 in reaction (4), then

$$R_2 + R_5 = R_4 = R\{\text{CH}_3\text{CO}_3\text{H}\} + R\{\text{CO}_2\} \quad (IV)$$

Since $R_5 + R_6 = R\{\text{CH}_3\text{CO}_3\text{H}\}$, then

$$R_6 + R\{\text{CO}_2\} = R_2 = k_2[\text{CH}_3\text{O}][\text{CH}_3\text{CHO}] \quad (\text{V})$$

Substituting for $[\text{CH}_3\text{O}]$, taking the reciprocal and multiplying by I_a to convert rates to quantum yields gives

$$(\Phi_6 + \Phi\{\text{CO}_2\})^{-1} = \frac{1}{\Phi_8 + 2\gamma} \left\{ 1 + \frac{k_3(1 + \alpha\gamma)[\text{O}_2]}{k_2[\text{CH}_3\text{CHO}]} \right\} \quad (\text{VI})$$

where Φ_6 and Φ_8 represent the quantum yields of reactions (6) and (8), respectively. At low $[\text{O}_2]/[\text{CH}_3\text{CHO}]$, $\Phi_6 \approx 0$ and $\alpha \approx 2$. Thus eqn. (VI) can be simplified to

$$\Phi\{\text{CO}_2\}^{-1} \approx \frac{1}{\Phi_8^0 + 2\gamma} \left\{ 1 + \frac{k_3(1 + 2\gamma)[\text{O}_2]}{k_2[\text{CH}_3\text{CHO}]} \right\} \quad (\text{VII})$$

where Φ_8^0 is the value of Φ_8 as $[\text{O}_2]/[\text{CH}_3\text{CHO}] \rightarrow 0$.

A plot of $\Phi\{\text{CO}_2\}^{-1}$ versus $[\text{O}_2]/[\text{CH}_3\text{CHO}]$ should approximate a straight line and should allow us to evaluate k_3/k_2 . Such a plot is shown in Fig. 1. The intercept is 0.30 and, since $\gamma = 0.75$, Φ_8^0 is therefore approximately 1.7. As $[\text{O}_2]/[\text{CH}_3\text{CHO}]$ increases, $\alpha \rightarrow 1$, Φ_6 will increase and Φ_8 will decrease since more and more of the CH_3CO_3 radicals will react with HO_2 .

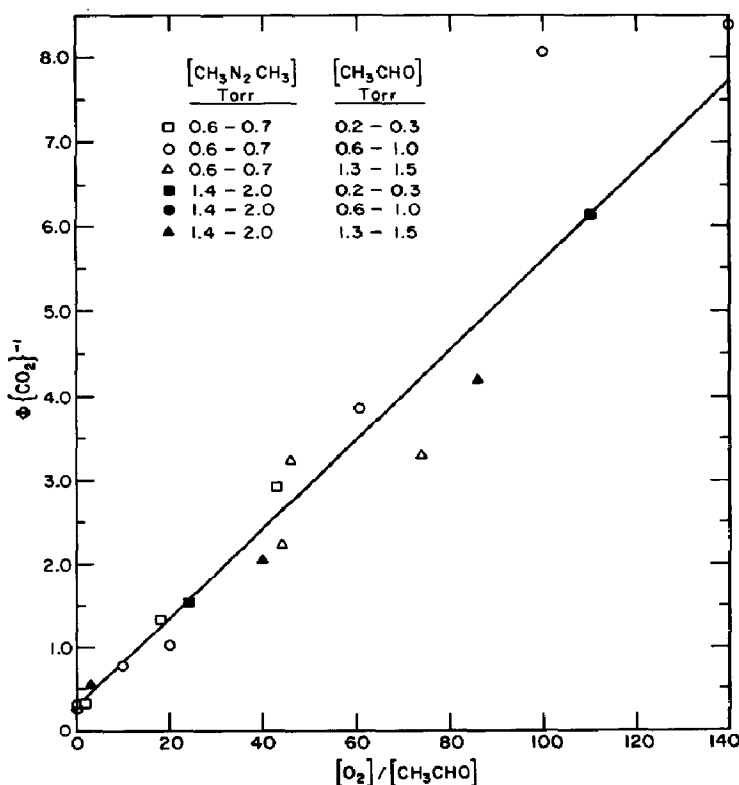


Fig. 1. Plot of reciprocal CO_2 quantum yield vs. $[\text{O}_2]/[\text{CH}_3\text{CHO}]$.

These three effects tend to cancel each other and the plot remains linear over the whole range of $[O_2]/[CH_3CHO]$ that we studied. The ratio of the slope, which is 0.053, to the intercept, which is 0.30, is equal to $(1 + \alpha\gamma)k_3/k_2$. With $\alpha = 2$ and $\gamma = 0.75$ [2], we obtain $k_2/k_3 = 14$ with about a 20% uncertainty. This is in good agreement with the estimate of 10 - 20 for this rate coefficient ratio by Weaver *et al.* based on their more limited data. Since Barker *et al.* [8] recently determined k_3 to be $3.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at room temperature, we may estimate k_2 to be $5.0 \pm 1.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at 298 K.

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