THE OXIDATION OF ACETYL RADICALS*

JAMES WEAVER, JAMES MEAGHER, ROBERT SHORTRIDGE** and
JULIAN HEICKLEN

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

Summary

The oxidation of acetyl radicals at 25 °C was studied by photolyzing azomethane in the presence of acetaldehyde and oxygen. The quantum yields of methanol, carbon dioxide, dimethylperoxide and peracetic acid were obtained for the four isotopic combinations of $CH_3N_2CH_3$ or $CD_3N_2CD_3$ with CH_3CHO or CD_3CDO.

The initially formed methylperoxy radicals are self-annihilated by the reactions:

$$2CH_3O_2 \rightarrow 2CH_3O + O_2 \tag{1a}$$
$$\rightarrow CH_3OH + CH_2O + O_2 \tag{1b}$$
$$\rightarrow CH_3O_2CH_3 + O_2 \tag{1c}$$

The results from this study indicate that k_{1a}/k_1, k_{1b}/k_1, and k_{1c}/k_1 = 0.43, 0.50 and 0.07, respectively, for CH_3O_2 and 0.45, 0.41 and 0.14, respectively, for CD_3O_2. The methoxy radical is scavenged by either acetaldehyde or O_2:

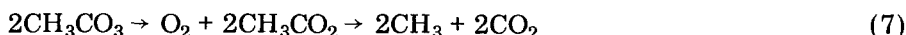$$CH_3O + CH_3CHO \rightarrow CH_3OH + CH_3CO \tag{2}$$
$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \tag{3}$$

Under most of our conditions, $[CH_3CHO]/[O_2] > 0.5$ and reaction (3) is negligible. At lower values of the ratio, reaction (3) plays some role and $k_2/k_3 \sim 10 - 20$.

The acetyl radical oxidizes entirely by addition:

$$CH_3CO + O_2 \rightarrow CH_3CO_3 \tag{4a}$$

since CO is not a product, and all the CO_2 is shown to come from the reactions:

$$2CH_3CO_3 \rightarrow O_2 + 2CH_3CO_2 \rightarrow 2CH_3 + 2CO_2 \tag{7}$$
$$CH_3CO_3 + CH_3O_2 \rightarrow CH_3O + O_2 + CH_3CO_2 \rightarrow CH_3 + CO_2 \tag{8}$$

with $k_8/(k_1k_7)^{1/2} = 2.8 \pm 0.4$ regardless of whether the radicals are protonated or deuterated.

Peracetic acid is produced from the abstraction reaction:

$$CH_3CO_3 + CH_3CHO \rightarrow CH_3CO_3H + CH_3CO \tag{5}$$

with $k_5/k_7^{1/2} = 6.0 \times 10^{-3}$ (Torr-s)$^{-1/2}$ for the protonated system and 1.29×10^{-3} (Torr-s)$^{-1/2}$ for the deuterated system.

Introduction

The oxidation of acetyl radicals is an important process both in photo-chemical smog [1] and in the slow combustion of hydrocarbons and their cool flames [2]. In most of the previous studies of acetyl radical oxidation, acetaldehyde has been photolyzed in the presence of oxygen. The first room temperature study of the photo-oxidation of acetaldehyde in both the vapor and liquid phases as well as in solution was made by Bowen and Tietz [3]. They found the major products of the reaction to be peroxides formed in a long chain. Carruthers and Norrish [4] also photo-oxidized both formal-dehyde and acetaldehyde and, except for the chain length, their results for acetaldehyde were consistent with those of Bowen and Tietz. In 1941, work by Mignolet [5] further substantiated the results of these studies. McDowell and coworkers [6 - 8] in 1958 confirmed the presence of peracetic acid as a product in the photo-oxidation of acetaldehyde and also proposed diacetyl-peroxide, $CH_3C(O)-O-O-(O)CCH_3$, which was found in small amounts [8], as the product of the chain terminating step. However, in a study by Calvert and Hanst [9] of acetaldehyde photo-oxidation at lower pressures ($\sim$ 42 Torr of CH_3CHO) no diacetylperoxide was obtained, although peracetic acid was again confirmed as a product. In 1964, Johnston and Heicklen [10] studied acetaldehyde photo-oxidation at even lower pressures ($[CH_3CHO]$ = 0.14 - 18 Torr, $[O_2]$ = 1.0 - 9.2 Torr) using mass spectral techniques. As principal products they reported CH_3OH and presumably CO and CO_2. Other products were H_2O, CH_2O, $HCOOH$, CH_3OOH, CH_3COOH, CH_3OOCH_3, and probably CH_3CO_3H. They also looked for, but could not find, diacetylperoxide as a product. However, they were unable to deduce a mechanism from their product analysis.

The photo-oxidation of acetaldehyde is complicated by the possible existence of long-lived excited states and by the number of different primary photolytic processes. In order to avoid these complications, this work was undertaken to study acetyl radical oxidation by photolyzing azomethane in the presence of acetaldehyde and oxygen. Azomethane, acetaldehyde and oxygen mixtures have previously been photolyzed by Subbaratnam and Calvert [11] in their work on the photo-oxidation of azomethane, but at very low $[CH_3CHO]/[O_2]$ ratios (6×10^{-4} to 2×10^{-3}). Under these conditions, the major observed products (methanol and methylhydroperoxide) were the same as those in the photo-oxidation of azomethane. In our work reported here, the $[CH_3CHO]/[O_2]$ ratio is much higher (0.1 - 12), and thus the products of the acetyl radical oxidation become important.

Experimental

The experimental apparatus and procedure are similar to those reported elsewhere [12, 13]. Reaction mixtures were photolyzed with 3655 Å radiation in a 500 cm^3 Kimax cell using a Hanovia medium pressure Hg lamp fitted with a Corning 0-52 filter. The reaction gases were excited continuously through a detachable pinhole into a differentially pumped intermediate chamber maintained at a pressure $\leqslant 1$ Torr. These gases could then pass through a second leak which was permanently mounted on the mass filter of an Extranuclear quadrupole mass spectrometer type II. The pressure in the spectrometer was $\sim 3 \times 10^{-6}$ Torr for all experiments. Total gas pressure in the reaction cell was ~ 100 Torr.

After the irradiation was completed, carbon dioxide and carbon monoxide were analyzed on a Gow-Mac gas chromatograph employing a thermistor detector at 0 °C. The CO_2 was separated from other reaction components on a 11 ft. $\times \frac{1}{4}$ in. o.d. copper column packed with Porapak QS and operated at room temperature with a helium carrier gas flow rate of 45.5 cm^3/min. The CO was separated from reaction components on an 8 ft. $\times \frac{1}{4}$ in. o.d. copper column packed with 13X molecular sieves and operated at room temperature with a helium carrier gas flow rate of 50 cm^3/min. Both CO_2 and CO calibrations were performed using standard samples.

Infra-red analyses were performed using a Beckman IR-10 infra-red spectrophotometer. Several experiments were performed in a 200 cm^3 Pyrex "T" cell with sodium chloride windows which permitted continuous infra-red analysis during photolysis. The top of the "T", which was in the sample beam of the spectrometer, was 12 cm long.

The non-deuterated azomethane was prepared by the procedure of Renaud and Leitch [14]. It was purified by trap-to-trap distillation from -90 °C to -130 °C. The non-deuterated acetaldehyde and acetic acid were obtained from Fisher Scientific Company. The acetaldehyde was purified by distillation from -79 °C to -130 °C. The azomethane-d_6 and acetaldehyde-d_4 (99% minimum isotopic purity) were obtained from Merck, Sharpe and Dohme of Canada Ltd. Mass spectral analysis confirmed that the isotopic purity was at least 95%. The azomethane-d_6 and acetaldehyde-d_4 were purified in the same manner as their non-deuterated counterparts. Gas chromatographic analysis showed $< 0.1\%$ of any chemical impurity in either the purified acetaldehyde or azomethane. The O_2, N_2 and CO_2 were Matheson extra dry, prepurified, and bone dry grades respectively. Before use, the azomethane and acetaldehyde were degassed at -130 °C and -196 °C respectively.

The values for the mass spectral sensitivity relative to the m/e 64 parent peak of azomethane-d_6 for the $CD_3O_2CD_3$ and $CD_3OD(H)$ products were the same as those obtained in previous work [12]. Although the parent m/e peak for the peracetic and peracetic-d_4 acids could not be detected in the mass spectrometer, their presence was confirmed by infra-red analysis of reaction mixtures, and their production could be followed with the mass
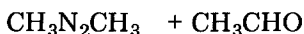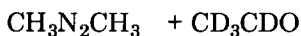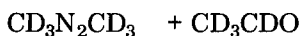
spectrometer by monitoring the m/e 60 and (63 + 64) peaks respectively. Mass spectral sensitivities for these per-acids were determined in an indirect manner by infra-red analysis of reaction mixtures after photolysis. The per-acetic acid produced in the reaction was collected at $-$ 83 °C and allowed to convert to acetic acid [15] in an infra-red gas cell.

Acetic acid calibrations were performed using standard samples with consideration given to the dimer—monomer equilibrium (K_p = 0.557 Torr at 25 °C) [16]. Thus, by measuring the acetic acid it was possible to deduce the amount of peracetic acid produced in the reaction and the mass spectral sensitivity of the peracetic acid. The sensitivity of the CD_3CO_3D lacked experimental precision but was found to agree with that for its non-deuterated counterpart to within 30%. Thus, the experimental sensitivity of 0.48 determined for the CH_3CO_3H was also used for the CD_3CO_3D (*i.e.* 0.48 Torr of $CH_3N_2CH_3$ gives the same mass spectral peak at m/e 58 as 1.0 Torr CH_3CO_3H at m/e 60).

In order to generate quantum yields the m/e peak height ratios corresponding to methanol, peracetic acid and dimethylperoxide-d_6 were plotted *versus* time. The slopes of these plots yielded the rates of production of these products, when corrected for the relative sensitivity calibration factors and multiplied by the pressure of azomethane. CO_2 production rates were obtained by measuring the amount of CO_2 in the reaction cell after photolysis by gas chromatography and dividing by the photolysis time. These product rates were converted to quantum yields by dividing by the N_2 production rate in separate actinometer experiments in the absence of O_2 and acetaldehyde, but at the same azomethane pressure.

Results

The photolysis of azomethane at 3655 Å in the presence of acetaldehyde and oxygen was studied at 25 °C. The pressure of azomethane was varied between 2 and 28 Torr while the pressures of acetaldehyde and oxygen each ranged between 8 and 100 Torr. The following isotopic combinations of reactants were examined:

$$CD_3N_2CD_3 \quad + CD_3CDO$$
$$CH_3N_2CH_3 \quad + CD_3CDO$$
$$CD_3N_2CD_3 \quad + CH_3CHO$$
$$CH_3N_2CH_3 \quad + CH_3CHO$$

In these systems the observed products were methanol, CO_2, peracetic acid and dimethylperoxide. Absolute quantum yields for these products for each of the above isotopic combinations are given in Tables 1 to 4 respectively. Since CD_3OD and CD_3CO_3D easily exchange D for H on the walls of the reaction vessel, the sum of the quantum yields for the OH and OD compounds are given. Values are not reported for the light methanol because of the interference of the large mass spectral parent peak of O_2. Likewise except

TABLE 1

Product quantum yields in the photolysis of $CD_3N_2CD_3$ in the presence of CD_3CDO and O_2 at 25 °C

$\dfrac{[CD_3CDO]}{I_a^{1/2}}$ (Torr·s)$^{1/2}$	$\dfrac{[CD_3CDO]}{[O_2]}$	$[CD_3CDO]$ (Torr)	$[O_2]$ (Torr)	$[CD_3N_2CD_3]$ (Torr)	$I_a \times 10^4$ (Torr/s)	$\Phi\{CD_3OD(H)\}$	$\Phi\{CO_2\}$	$\Phi\{CD_3O_2CD_3\}$
[CD$_3$CDO] study								
259	0.125	3.39	27.1	8.1	1.72	2.29	2.57	0.28
639	0.308	8.38	27.2	8.1	1.72	3.90	4.23	0.45
879	0.416	11.52	27.7	8.1	1.72	3.72	4.42	0.32
1609	0.793	21.1	26.6	8.1	1.72	4.92	5.76	—
2272	2.49	27.4	11.0	8.1	1.46	4.76	—	0.23
2845	1.39	37.3	26.9	8.1	1.72	5.23	7.09	0.47
3860	1.88	50.6	26.9	8.1	1.72	5.41	5.89	0.39
5156	2.19	67.6	31.1	8.1	1.72	4.71	5.50	0.33
8444	4.07	111	27.3	8.1	1.72	4.75	6.26	0.25
[O$_2$] study								
1716	2.25	22.5	10.0	8.1	1.72	5.02	5.39	0.39
1709	0.42	22.4	53.6	8.1	1.72	4.00	4.32	0.44
1716	0.21	22.5	108.5	8.1	1.72	2.86	4.02	0.23
Intensity study								
5152	2.37	24.6	10.4	1.19	0.228	5.92	7.00	0.44
3540	2.45	24.5	10.0	2.26	0.479	5.49	5.92	0.37
1863	2.29	23.3	10.2	8.15	1.57	5.88	6.77	0.37
1905	2.56	24.8	9.7	8.20	1.70	5.22	6.70	0.33
1296	2.59	25.4	9.8	20.0	3.84	5.63	6.33	0.32
958	2.61	24.8	9.5	31.7	6.71	4.63	4.86	0.27

TABLE 2

Product quantum yields in the photolysis of $CH_3N_2CH_3$ in the presence of CD_3CDO and O_2 at 25 °C

$\dfrac{[CD_3CDO]}{I_a^{1/2}}$ (Torr-s)$^{1/2}$	$\dfrac{[CD_3CDO]}{[O_2]}$	$[CD_3CDO]$ (Torr)	$[O_2]$ (Torr)	$[CH_3N_2CH_3]$ (Torr)	$I_a \times 10^4$ (Torr/s)	$\Phi\{CD_3OD(H)\}$	$\Phi\{CO_2\}$	$\Phi\{CD_3CO_3D(H)\}$
[CD₃CDO] study								
647	0.97	7.8	8.0	8.1	1.46	2.19	3.75	1.07
829	1.11	10.0	9.0	8.1	1.46	2.38	4.04	1.00
1250	1.89	15.1	8.0	8.1	1.46	3.21	5.08	1.57
2262	2.48	27.3	11.0	8.1	1.46	2.77	—	2.39
2164	3.24	26.1	8.1	8.1	1.46	3.50	5.52	2.13
2262	2.48	27.3	11.0	8.3	1.46	3.06	—	2.28
4115	6.16	49.6	8.1	8.1	1.46	3.87	6.16	3.18
7042	10.55	85.0	8.1	8.1	1.46	3.64	6.46	3.70
8230	12.55	99.2	7.9	8.1	1.46	3.40	5.84	4.44
[O₂] study								
831	1.12	10.0	9.0	8.1	1.46	2.38	4.04	0.99
837	1.08	10.1	9.4	8.1	1.46	2.04	3.78	0.89
829	0.33	10.0	30.2	8.1	1.46	1.29	2.42	0.68
837	0.17	10.1	61.2	8.1	1.46	0.89	1.34	0.81
837	0.12	10.1	88.0	8.2	1.46	—	0.80	—
837	0.10	10.1	97.0	8.1	1.46	0.45	0.74	0.38
Intensity study								
3876	2.43	24.8	10.2	2.29	0.41	2.87	4.55	3.39
1901	2.42	24.5	10.1	10.0	1.80	3.10	4.58	1.88
1399	2.51	24.8	9.9	20.1	3.60	3.36	4.38	1.43
1095	2.45	24.7	10.1	28.3	5.07	3.52	3.98	1.39

TABLE 3

Product quantum yields in the photolysis of $CD_3N_2CD_3$ in the presence of CH_3CHO and O_2 at 25 °C

$\dfrac{[CH_3CHO]}{I_a^{1/2}}$ $(Torr \cdot s)^{1/2}$	$\dfrac{[CH_3CHO]}{[O_2]}$	$[CH_3CHO]$ (Torr)	$[O_2]$ (Torr)	$[CD_3N_2CD_3]$ (Torr)	$I_a \times 10^4$ (Torr/s)	$\Phi\{CD_3OD(H)\}$	$\Phi\{CO_2\}$	$\Phi\{CH_3CO_3H\}$
[CH₃CHO] study								
613	0.93	7.7	8.3	8.1	1.57	1.28	4.63	3.44
1185	1.88	15.0	8.0	8.1	1.60	1.16	4.84	6.70
2075	3.52	26.0	7.4	8.1	1.57	1.31	5.62	9.83
3929	5.93	49.7	8.4	8.1	1.60	1.28	5.11	23.86
6734	10.4	85.3	8.2	8.1	1.60	1.27	6.38	39.40
7770	12.6	97.2	7.7	8.0	1.57	1.70	—	43.58
[O₂] study								
790	1.14	10.0	8.8	8.2	1.60	1.14	4.35	4.00
806	0.33	10.2	30.7	8.1	1.60	0.93	3.65	3.68
806	0.18	10.2	56.0	8.1	1.60	0.95	3.12	3.36
790	0.12	10.0	82.2	8.1	1.60	0.85	2.29	2.42
790	0.10	10.0	100.0	8.2	1.60	0.96	2.24	1.41
Intensity study								
3690	2.49	24.9	10.0	2.30	0.455	1.30	4.99	19.31
1754	2.58	24.8	9.6	10.15	2.01	1.25	4.75	10.35
1244	2.58	24.8	9.6	20.05	3.97	1.30	4.54	8.05
1053	2.38	24.8	10.4	28.0	5.54	1.29	4.06	7.39

TABLE 4

Product quantum yields in the photolysis of $CH_3N_2CH_3$ in the presence of CH_3CHO and O_2 at 25 °C

$\dfrac{[CH_3CHO]}{I_a^{1/2}}$ (Torr·s)$^{1/2}$	$\dfrac{[CH_3CHO]}{[O_2]}$	$[CH_3CHO]$ (Torr)	$[O_2]$ (Torr)	$[CH_3N_2CH_3]$ (Torr)	$I_a \times 10^4$ (Torr/s)	$\Phi\{CO_2\}$	$\Phi\{CH_3CO_3H\}$
1234	1.64	14.9	9.1	8.1	1.46	4.07	4.96
2169	3.19	26.2	8.2	8.1	1.46	4.30	8.82
2262	2.51	27.3	10.9	8.1	1.46	—	10.25
2262	2.58	27.3	10.6	8.1	1.46	—	10.92
4246	5.90	51.3	8.7	8.1	1.46	4.60	21.74
7576	11.35	91.4	8.1	8.1	1.46	4.55	38.12

for the $CD_3N_2CD_3$–CD_3CDO system, reliable values for the dimethylperoxide quantum yields could not be obtained because of the interference of product cracking peaks. In the $CD_3N_2CD_3$–CD_3CDO system, $\Phi\{CD_3CO_3D\}$ is not reported because of the interference from the mass spectral parent peak of $CD_3N_2CD_3$.

The quantum yields for methanol, dimethylperoxide and peracetic acid were obtained mass spectrometrically while those for CO_2 were obtained by gas chromatography. The presence of methanol and peracetic acid as primary products of the reaction was verified by infra-red analysis. Although acetic acid is also a product of the reaction, an *in situ* photolysis experiment employing continuous infra-red analysis confirmed that all the acetic acid came from the decomposition of the peracetic acid. Neither CO nor methylhydroperoxide was observed as a product of the reaction. Thus, these compounds must have quantum yields < 0.01 in this system. We looked for, but found no evidence for either diacetylperoxide or methyl acetylperoxide.

In regard to the peracetic acid–acetic acid products, the mass spectrum shows no parent peaks for peracetic acid. The only identifying mass spectral peak for these products is at the parent mass for acetic acid, and this peak grows without an induction period during the irradiation. Since the i.r. analysis, as well as almost all the earlier studies, show that peracetic acid, and not acetic acid, is the initial product, either the mass spectrum for peracetic acid is unusual and misleading or the peracetic acid is converted to acetic acid during the sampling procedure in the mass spectral analysis. Thus the acetic acid reported by Johnston and Heicklen [10], who used a similar mass spectral analytical technique, is really peracetic acid.
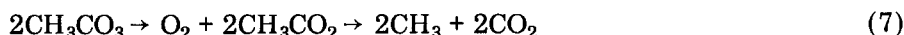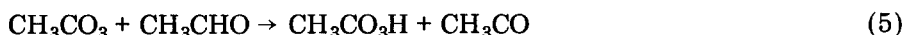
The fundamental parameter of the system is $[CH_3CHO]/I_a^{1/2}$ and it was varied by a factor of 32.6. To do this $[CH_3CHO]$ was varied by a factor of 32.7 and I_a by a factor of 29.4. The quantum yield for peracetic acid was found to increase as this factor was raised while the quantum yields for CO_2, methanol and dimethylperoxide were fairly constant. At the same $[CH_3CHO]/I_a^{1/2}$ value, the quantum yield for $CD_3CO_3D(H)$ was found to be a factor of ~ 4.6 lower than that for CH_3CO_3H. No similar isotope effect was observed for any of the other products.

The quantum yields for CO_2, methanol, and peracetic acid were also observed to decrease at [acetaldehyde]/$[O_2]$ ratios less than 0.5. However, $\Phi\{CD_3O_2CD_3\}$ was fairly constant for all values of this ratio, even though this ratio was varied by a factor of 21.

Discussion

On the basis of these results, the following mechanism for the photolysis of azomethane in the presence of acetaldehyde and oxygen at 25 °C is proposed:
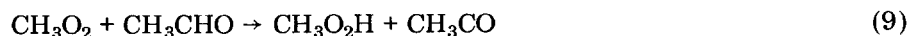
$$CH_3N_2CH_3 + h\nu \xrightarrow{\;O_2\;} 2CH_3O_2 + N_2 \qquad \text{Rate} = I_a$$

$$2CH_3O_2 \rightarrow 2CH_3O + O_2 \tag{1a}$$

$$\rightarrow CH_3OH + CH_2O + O_2 \tag{1b}$$

$$\rightarrow CH_3O_2CH_3 + O_2 \tag{1c}$$

$$CH_3O + CH_3CHO \rightarrow CH_3OH + CH_3CO \tag{2}$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \tag{3}$$

$$CH_3CO + O_2 \rightarrow CH_3CO_3 \tag{4a}$$

$$\rightarrow CH_3O + CO_2 \tag{4b}$$

$$CH_3CO_3 + CH_3CHO \rightarrow CH_3CO_3H + CH_3CO \tag{5}$$

$$CH_3CO_3 + HO_2 \rightarrow CH_3CO_3H + O_2 \tag{6}$$

$$2CH_3CO_3 \rightarrow O_2 + 2CH_3CO_2 \rightarrow 2CH_3 + 2CO_2 \tag{7}$$

$$CH_3CO_3 + CH_3O_2 \rightarrow CH_3O + O_2 + CH_3CO_2 \rightarrow CH_3 + CO_2 \tag{8}$$
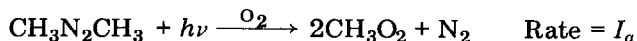
Reaction (1a), (1b), and (1c) are included on the basis of earlier work on the photo-oxidation of azomethane [12]. Since no acetic acid is produced, except from the decomposition of peracetic acid, the CH_3CO_2 radicals expected in reactions (7) and (8) must decompose prior to abstracting a H atom from acetaldehyde. Thus, either no CH_3CO_2 radicals are produced at all in the system, or if they are, they exist only as intermediates in reactions (7) and (8) decomposing to give CO_2 and CH_3 radicals. The CH_3CO_2 radical is thermodynamically unstable and decomposes exothermically to CH_3 and CO_2. ($\Delta H_{decomp} = -17$ kcal/mol) [17, 18]. Also Szwarc and Herk [19] consider that the decarbonylation of the acetate radical requires an activation energy of only 1 - 2 kcal/mol. In addition, they report [20, 21] that in both the gas and liquid phases, the reaction observed in the diacetyl-peroxide system is due to methyl radicals rather than to CH_3CO_2 radicals. Thus, it would seem that CH_3CO_2 radicals are kinetically unstable even at room temperature and in our system would immediately decompose to CO_2 and CH_3.

Since no CO was observed in any of the experiments, the reaction

$$CH_3CO + O_2 \rightarrow CH_3O_2 + CO \tag{4c}$$

must only occur to a negligible extent. The absence of methylhydroperoxide as a product suggests that the reactions

$$CH_3O_2 + CH_3CHO \rightarrow CH_3O_2H + CH_3CO \tag{9}$$

$$CH_3O_2 + CH_3O \rightarrow CH_3O_2H + CH_2O \tag{10}$$

$$CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2 \tag{11}$$

are not important in the acetyl radical oxidation system for values of the $[CH_3CHO]/[O_2]$ ratio greater than $\sim 10^{-1}$. Apparently reaction (9) is just too slow to be of consequence at our acetaldehyde pressures and absorbed intensities. Reactions (10) and (11), which are known to proceed rapidly [12], are suppressed because CH_3O is scavenged by acetaldehyde and HO_2

production is unimportant. Peroxide production *via* alternate paths to reactions (7) and (8) have also been omitted, since the corresponding peroxides were not found as products.

In order to account for the reduction in methanol, CO_2 and peracetic acid quantum yields at values of $[CH_3CHO]/[O_2] < 0.5$, reactions (3) and (6) have been included in the mechanism. However, since no methylhydroperoxide was found and the other product quantum yields are fairly constant for values of this ratio greater than 0.5, where most of our studies were done, these two reactions will not be considered further. With the elimination of reaction (6) from the mechanism, reactions (1b) and (1c) become the only termination reactions.

An analysis of reactions (1) - (8) (with reactions (3) and (6) eliminated) leads to the following steady-state concentration expressions for the radicals in the system:

$$[CH_3O_2] = \left(\frac{I_a}{k_{1b} + k_{1c}} \right)^{1/2} \tag{I}$$

$$[CH_3CO] = \frac{k_2[CH_3O][CH_3CHO] + k_5[CH_3CO_3][CH_3CHO]}{k_4[O_2]} \tag{II}$$

$$[CH_3CO_3] = \left[\frac{k_{1a}}{k_7} \left(\frac{I_a}{k_{1b} + k_{1c}} \right) \right]^{1/2} \tag{III}$$

$$[CH_3O] = \left\{ (2k_{1a}[CH_3O_2]^2 + k_8[CH_3CO_3][CH_3O_2] + \frac{k_{4b}}{k_4} k_5[CH_3CO_3][CH_3CHO] \right\} \Big/ \frac{k_2 k_{4a}}{k_4} [CH_3CHO] \tag{IV}$$

The quantum yields for the observed products of the reaction then become:

$$\Phi\{CH_3O_2CH_3\} = \frac{k_{1c}}{k_{1b} + k_{1c}} \tag{V}$$

$$\Phi\{CH_3OH\} = \frac{k_4 k_8}{k_{4a}(k_{1b} + k_{1c})} \left(\frac{k_{1a}}{k_7} \right)^{1/2} +$$
$$\left(k_{1b} + \frac{2k_4 k_{1a}}{k_{4a}} \right) \left(\frac{1}{k_{1b} + k_{1c}} \right) +$$
$$\frac{k_{4b} k_5}{k_{4a}} \frac{[CH_3CHO]}{I_a^{1/2}} \left(\frac{k_{1a}}{k_7(k_{1b} + k_{1c})} \right)^{1/2} \tag{VI}$$

$$\Phi\{CO_2\} = \frac{k_4}{k_{4a}} \left(\frac{2k_{1a} + k_8(k_{1a}/k_7)^{1/2}}{k_{1b} + k_{1c}} \right) +$$
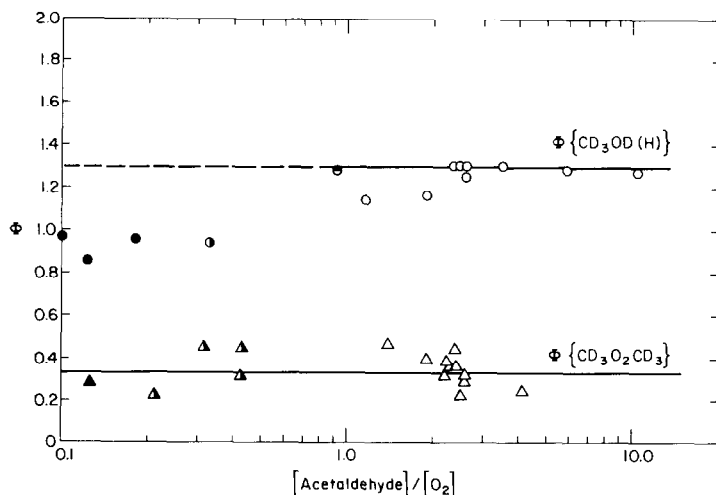
Fig. 1. Semilog plots of the quantum yields of methanol (from the $CD_3N_2CD_3$ + CH_3CHO system) and dimethylperoxide (from the $CD_3N_2CD_3$ + CD_3CDO system) $vs.$ [acetaldehyde]/[O_2]. [Acetaldehyde]/[O_2]: ●, ▲, <0.2; ◑, ◭, 0.2 - 0.5; ◓, 0.5 - 1.0; ○,△, >1.0.

$$+ \frac{k_{4b}k_5}{k_{4a}}\left(\frac{k_{1a}}{k_7(k_{1b}+k_{1c})}\right)^{1/2}\frac{[CH_3CHO]}{I_a^{1/2}} \qquad (VII)$$

$$\Phi\{CH_3CO_3H\} = \frac{k_5}{k_7^{1/2}}\left(\frac{k_{1a}}{k_{1b}+k_{1c}}\right)^{1/2}\frac{[CH_3CHO]}{I_a^{1/2}} \qquad (VIII)$$

As the lower plot in Fig. 1 shows, the quantum yield for dimethylperoxide is 0.33 ± 0.07 independent of acetaldehyde pressure, oxygen pressure and I_a. From the previous work on the photo-oxidation of $CD_3N_2CD_3$ [12], values for the branching ratios k_{1a}/k_1, k_{1b}/k_1 and k_{1c}/k_1 were obtained. However, these branching ratio values were in poor agreement with those from the photo-oxidation of $CH_3N_2CH_3$. These values can now be recomputed by utilizing the data from both the previous work and the present work. With no acetaldehyde present in the system, a steady state analysis leads to the following rate law based on the quantum yields of methanol and dimethylperoxide [12]:

$$\frac{\Phi_0\{CD_3O_2CD_3\}}{1 + \Phi_0\{CD_3OD(H)\} + \Phi_0\{CD_3O_2CD_3\}} = \frac{k_{1c}}{2k_1} \qquad (IX)$$

where the subscript zero refers to the results in the absence of acetaldehyde at high limiting values of [O_2]/$I_a^{1/2}$. The values reported earlier by us [12] are $\Phi_0\{CD_3O_2CD_3\}$ = 0.15 and $\Phi\{CD_3OD(H)\}$ = 0.49. From eqn. (V) and the results found here in the presence of acetaldehyde:

$$\Phi\{CD_3O_2CD_3\} = \frac{k_{1c}/k_1}{1 - k_{1a}/k_1} = 0.33 \qquad (X)$$
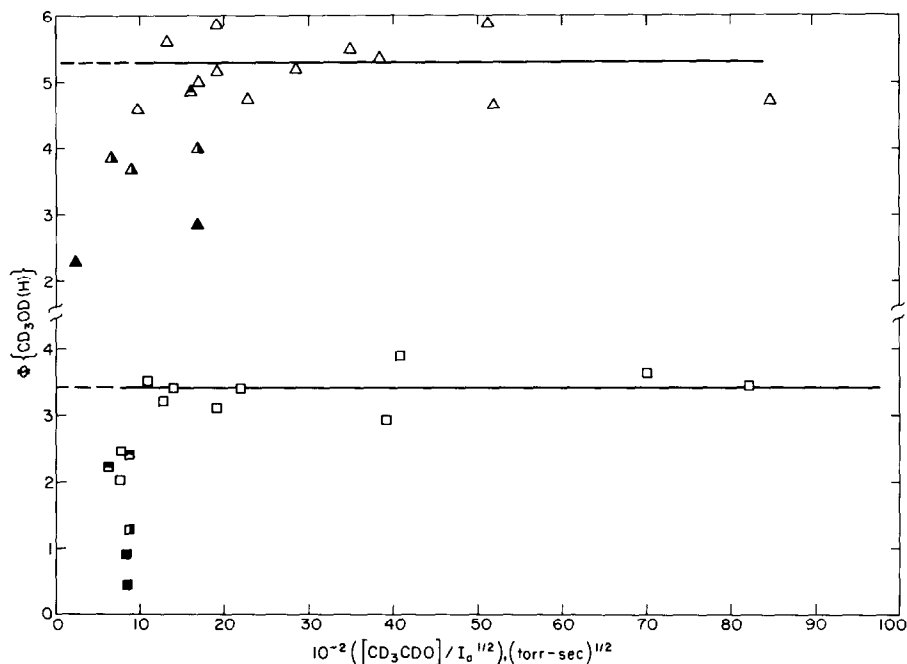
Fig. 2. Plots of $\Phi\{CD_3OD(H)\}$ vs. $[CD_3CDO]/I_a^{1/2}$. Upper plot: $CD_3OD(H)$ from the $(CD_3N_2CD_3 + CD_3CDO)$ system. Lower plot: $CD_3OD(H)$ from the $(CH_3N_2CH_3 + CD_3CDO)$ system. $[CD_3CDO]/[O_2]$: ▲, ■, <0.2; ▲,◨, 0.2 - 0.5; ◭,◪, 0.5 - 1.0; △,□, >1.0.

By dividing eqn. (IX) by eqn. (X) most of the inaccuracies in the mass spectral sensitivity for $CD_3O_2CD_3$ are eliminated, since $\Phi_0\{CD_3O_2CD_3\}$ is only a small correction in the denominator of the left-hand-side of eqn. (IX), and a value of $k_{1a}/k_1 = 0.45 \pm 0.15$ is obtained. This value agrees very well with the 0.43 value for k_{1a}/k_1 obtained in the $CH_3N_2CH_3$ photo-oxidation [12], but is much higher than the value of 0.22 found for $CD_3N_2CD_3$ photo-oxidation [12]. (See Appendix for a more detailed discussion.)

Also from the work on the photo-oxidation of pure $CD_3N_2CD_3$, the relationship between k_{1a}/k_1 and k_{1b}/k_1 is such that:

$$\frac{k_{1b}}{2k_1} + \frac{k_{1a}}{2k_1} = 0.43 \qquad \text{(XI)}$$

With the value of $k_{1a}/k_1 = 0.45$, $k_{1b}/k_1 = 0.41$, and thus $k_{1c}/k_1 = 0.14$.

Figure 2 shows plots of the quantum yields of $CD_3OD(H)$ vs. $[CD_3CDO]/I_a^{1/2}$. The upper plot is for $CD_3OD(H)$ from the $(CD_3N_2CD_3 + CD_3CDO)$ system and thus shows how the quantum yield for the methanol from all sources varies with $[CD_3CDO]/I_a^{1/2}$. The data for $[CD_3CDO]/[O_2] > 0.5$ show that $\Phi\{CD_3OD(H)\}$ is independent of $[CD_3CDO]/I_a^{1/2}$ as the ratio is varied by a factor of 10. An examination of eqn. (VI) shows that this can be true only if k_{4b}/k_4 is zero. The upper limiting value for $\Phi\{CD_3OD(H)\}$ for the upper plot in Fig. 2 has a value of 5.3 ± 0.5 which when equated to
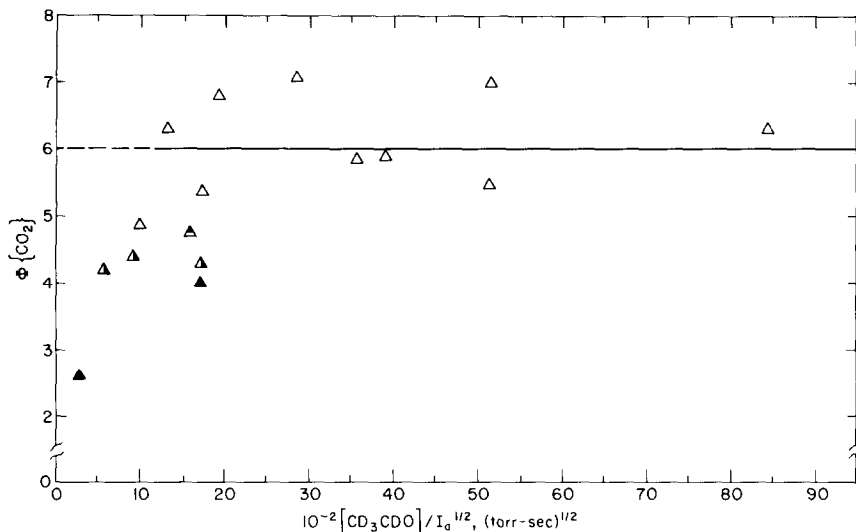
Fig. 3. Plot of $\Phi\{CO_2\}$ vs. $[CD_3CDO]/I_a^{1/2}$ for the $(CD_3N_2CD_3 + CD_3CDO)$ system. $[CD_3CDO]/[O_2]$: $\blacktriangle$, <0.2; $\blacktriangle$, $0.2 - 0.5$; $\triangle$, >1.0.

the sum of the first two terms of eqn. (VI) gives a value of 2.39 for $k_8/(k_1k_7)^{1/2}$, which is consistent with the statistically expected value of 2.0.

Figures 3, 4 and 5 show plots of the quantum yields of CO_2 vs. $[CH_3CHO]/I_a^{1/2}$ for all four isotopic combinations. Data for $[CH_3CHO]/[O_2]$ > 0.5 shows that $\Phi\{CO_2\}$ is also independent of $[CH_3CHO]/I_a^{1/2}$ in each case as this ratio was varied by a factor of 10. Equation (VII) predicts that $\Phi\{CO_2\}$ will show this behavior only if k_{4b}/k_4 is zero, thus confirming the conclusions from the methanol data. The upper limiting value for $\Phi\{CO_2\}$ of 6.0 ± 1.0, 5.0 ± 1.0, and 4.75 ± 0.75 for the plots in Figs. 3, 4 and 5, respectively, can be equated with the first term in eqn. (VII) to give values for $k_8/(k_1k_7)^{1/2}$ of 3.57 for the $(CD_3N_2CD_3 + CD_3CDO)$ system, 2.75 for the $(CH_3N_2CH_3 + CD_3CDO)$ system and 2.55 for the $(CH_3N_2CH_3 + CH_3CHO)$ and $(CD_3N_2CD_3 + CH_3CHO)$ systems. The average of these three numbers is 2.8 ± 0.4 which is in good agreement with the value of 2.4 obtained from the methanol data.

An analysis of the mechanism shows that the quantum yield for the methanol coming only from the azomethane is given by the expression:

$$\Phi\{CH_3OH(Az)\} = \frac{2(2R_{1a} + R_{1b} + R_8)}{2R_1 + R_8} \qquad \text{(XII)}$$

where R refers to the rate of the subscripted reaction. This becomes, upon substitution of the steady state radical concentrations:

$$\Phi\{CH_3OH(Az)\} = \frac{2\left[2k_{1a}/k_1 + k_{1b}/k_1 + \dfrac{k_8}{(k_1k_7)^{1/2}}\left(\dfrac{k_{1a}}{k_1}\right)^{1/2}\right]}{2 + \dfrac{k_8}{(k_1k_7)^{1/2}}\left(\dfrac{k_{1a}}{k_1}\right)^{1/2}} \qquad \text{(XIII)}$$
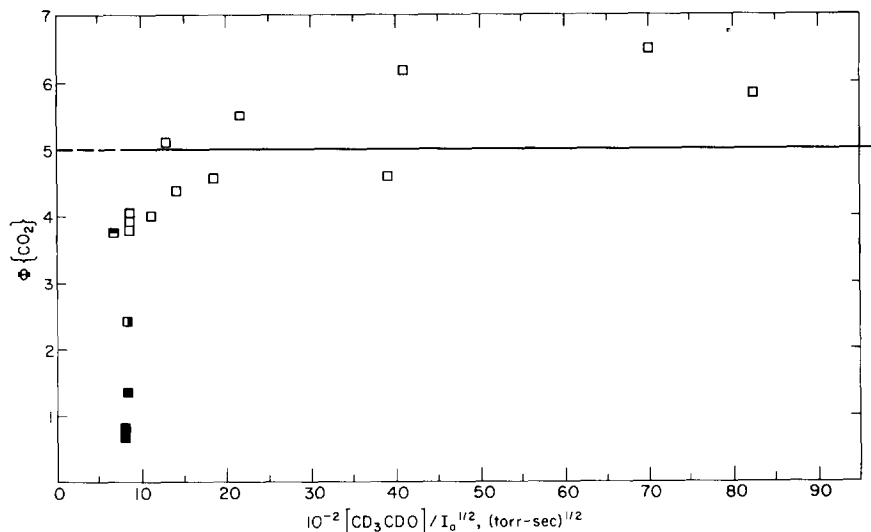
Fig. 4. Plot of $\Phi\{CO_2\}$ vs. $[CD_3CDO]/I_a^{1/2}$ for the $(CH_3N_2CH_3 + CD_3CDO)$ system. $[CD_3CDO]/[O_2]$: ■, <0.2; ◨, 0.2 - 0.5; ▤, 0.5 - 1.0; □, >1.0.
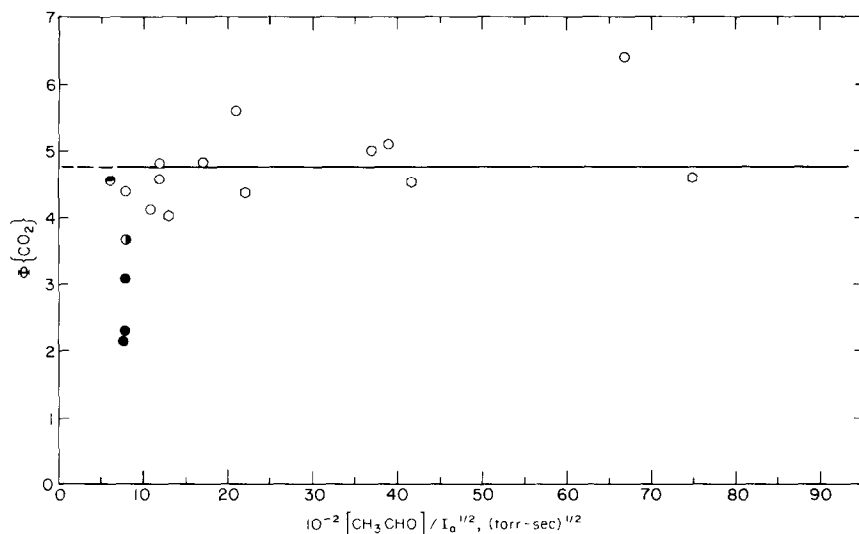
Fig. 5. Plot of $\Phi\{CO_2\}$ vs. $[CH_3CHO]/I_a^{1/2}$ for the $(CD_3N_2CD_3 + CH_3CHO)$ system (○), and for the $(CH_3N_2CH_3 + CH_3CHO)$ system (◯). $[CH_3CHO]/[O_2]$: ●, <0.2; ◐, 0.2 - 0.5; ◓, 0.5 - 1.0; ○, ◯ >1.0.

Using the average value of 2.8 for $k_8/(k_1k_7)^{1/2}$ and the branching ratio values for k_{1a}/k_1 and k_{1b}/k_1 obtained above, we calculate the value of $\Phi\{CH_3OH(Az)\}$ = 1.65. Figure 1 shows a plot of $\Phi\{CD_3OD(H)\}$ from the $(CD_3N_2CD_3 + CH_3CHO)$ system, that is, the methanol only from the azomethane. The data for $[CH_3CHO]/[O_2] > 0.5$ show that the quantum yield for methanol from this source is constant at $\sim$ 1.3, independent of acetaldehyde pressure and I_a.

The lower set of data in Fig. 2 shows a plot of $\Phi\{CD_3OD(H)\}$ vs. $[CD_3CDO]/I_a^{1/2}$ from the $(CH_3N_2CH_3 + CD_3CDO)$ system, that is, the methanol from all non-azomethane sources. Once again, the data for $[CD_3CDO]/[O_2] > 0.5$ show that methanol from these sources is independent of acetaldehyde pressure and I_a. The plot has an upper limiting value for $\Phi\{CD_3OD(H)\}$ of 3.40 which, when subtracted from the upper limiting value of the plot for methanol from all sources (upper plot, Fig. 2), yields a value of 1.90 for the quantum yield of methanol from azomethane sources. Thus, both the two experimental measurements for the $\Phi\{CD_3OD(H)\}$ from the $CD_3N_2CD_3$ are in reasonable accord with the calculated value.

Figure 6 is a log–log plot of the quantum yield of CH_3CO_3H and $CD_3CO_3D(H)$ vs. $[acetaldehyde]/I_a^{1/2}$. The data for $\Phi\{CH_3CO_3H\}$ ($[CH_3CHO]/[O_2] > 0.5$) can be fitted to a straight line of slope 1 indicating that $\Phi\{CH_3CO_3H\}$ is directly proportional to $[CH_3CHO]/I_a^{1/2}$, as indicated by eqn. (VIII). The constant of proportionality is $(k_5/k_7)^{1/2}[k_{1a}/(k_{1b} + k_{1c})]^{1/2}$ which has a value of 5.4×10^{-3} $(Torr-s)^{-1/2}$, and thus $k_5/k_7^{1/2} = 6.0 \times 10^{-3}$ $(Torr-s)^{-1/2}$ for the non-deuterated peracetic acid. The data for $\Phi\{CD_3CO_3D(H)\}$ ($[CD_3CDO]/[O_2] > 0.5$) can also be fitted to a straight line of slope one except at high values of the $[CD_3CDO]/I_a^{1/2}$ ratio. We have no explanation for the lower quantum yields obtained in this regime. Also, the value of $k_5/k_7^{1/2}$ $[k_{1a}/(k_{1b} + k_{1c})]^{1/2}$ obtained for the deuterated peracetic acid is 1.16×10^{-3} and thus $k_5/k_7^{1/2} = 1.29 \times 10^{-3}$ $(Torr-s)^{-1/2}$, a factor of 4.6 lower than the corresponding rate constant ratio for the non-deuterated peracetic acid. Since no isotope effect was observed in the other expressions involving k_7 obtained above, the isotope effect is attributed to reaction (5).

It is impossible to accurately predict the value for the kinetic isotope effect observed in reaction (5) without knowing the details of the potential energy surface on which it occurs. However, if we ignore the contributions from tunnelling, we can calculate the maximum value from known reactant parameters (mass effects and zero point energy of reactants). Using this technique we obtain a value for the ratio $k_5\{H\}/k_5\{D\}$ of 8.9. This number will be reduced by an amount related to the lowering of the zero point energy of the activated complex. Since the reaction is essentially thermoneutral and the two groups attached to the H atom in the activated complex are of similar mass, the experimentally observed ratio seems quite reasonable.

In the abstraction of H or D from CH_4 or CD_4 by Cl, the isotope effect at 25 °C was found to be $(k\{H\}/k\{D\}) \approx 11$ [22, 23]. This reaction is also essentially thermoneutral and the mass ratios in the activated complex are similar to those found in the present system. Russell [24] has reported an isotope effect of 5.5 for hydrogen abstractions by complex organic peroxy radicals in solution. Thus the isotope effect reported in this work is in accord with those studies in similar systems.

Conclusions

The product distribution found in the photolysis of azomethane in the presence of acetaldehyde and oxygen is strongly dependent on the ratio
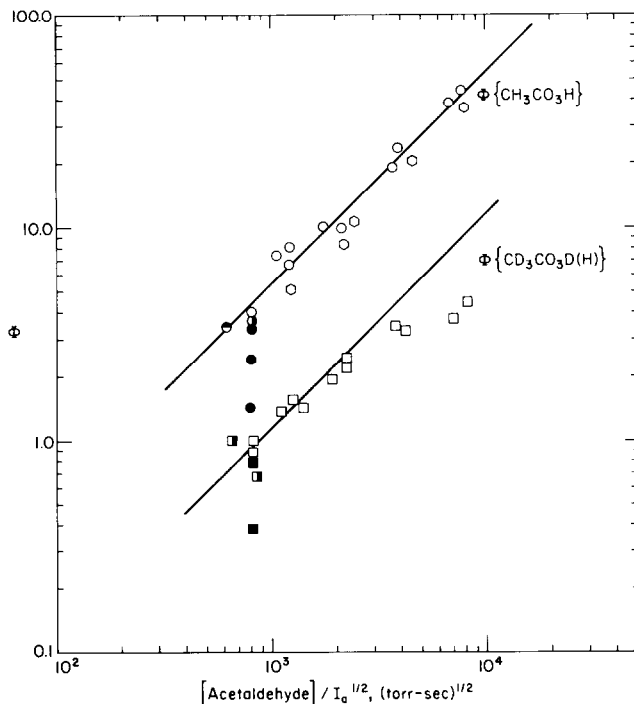
Fig. 6. Log–log plots of the quantum yield of peracetic acid *vs.* [acetaldehyde]/$I_a^{1/2}$.
(1) CH_3CO_3H from the ($CH_3N_2CH_3$ + CH_3CHO) (◊) and ($CD_3N_2CD_3$ + CH_3CHO) (○) systems. (2) $CD_3CO_3D(H)$ from the ($CH_3N_2CH_3$ + CD_3CDO) system (□).
[Acetaldehyde]/[O_2]: ●, ■, <0.2; ◐,◙, 0.2 - 0.5; ◓, 0.5 - 1.0; ○, □, ◇ >1.0.

[CH_3CHO]/[O_2]. At high values of this ratio ([CH_3CHO]/[O_2] > 0.5), the experimental results can be described by a mechanism in which essentially all the methoxy (CH_3O) radicals react with acetaldehyde to produce methanol and acetyl radicals (reaction 2). At intermediate values of the ratio, ~ 10^{-3} < [CH_3CHO]/[O_2] < 0.5, there exists a competition between acetaldehyde and oxygen for the methoxy radicals (reactions 2 and 3). From the decrease in product quantum yields as [CH_3CHO]/[O_2] goes from 0.5 to 0.1, k_2/k_3 can be estimated to be between 10 and 20. Using a reported value for k_3 at 300 K of $1.7 \times 10^5 M^{-1} s^{-1}$ [25], k_2 can be estimated to be between 1.7×10^6 and $3.4 \times 10^6 M^{-1} s^{-1}$.

At low values of the ratio, [CH_3CHO]/[O_2] < 10^{-3}, essentially all the methoxy radicals react with oxygen to form CH_2O and HO_2 which goes on to produce methylhydroperoxide — the product observed in the photo-oxidation of azomethane [12]. It is in this regime that Subbaratnam and Calvert [11] photolyzed azomethane in the presence of acetaldehyde and oxygen and thus observed methylhydroperoxide and not peracetic acid as a major product.

At values of the [CH_3CHO]/[O_2] ratio greater than 0.5, the experimental product quantum yields are consistent with the mechanism given by

TABLE 5

Summary of rate coefficient ratios at 25 °C

Ratio	Units	$CH_3N_2CH_3$ + CH_3CHO	$CH_3N_2CH_3$ + CD_3CDO	$CD_3N_2CD_3$ + CH_3CHO	$CD_3N_2CD_3$ + CD_3CDO
k_{1a}/k_1	None	0.43	—	—	0.45
k_{1b}/k_1	None	0.50	—	—	0.41
k_{1c}/k_1	None	0.07	—	—	0.14
k_{4a}/k_4	None	1.0	1.0	1.0	1.0
k_{4b}/k_4	None	0.0	0.0	0.0	0.0
$k_8/(k_1k_7)^{1/2}$	None	2.8	2.8	2.8	2.8
k_5/k_7	$(Torr \cdot s)^{-1/2}$	6.0×10^{-3}	1.29×10^{-3}	6.0×10^{-3}	—

eqns. (1) - (8). On the basis of this mechanism, the rate coefficient ratios obtained are summarized in Table 5. As presented in the discussion, the occurrence of the isotope effect in the rate constant for reaction (5) is both expected on theoretical grounds and is of the same order of magnitude as reported isotope effects for similar systems.

Acknowledgements

References

1 S. L. Kopczynski, A. P. Altshuller and F. D. Sutterfield, Environ. Sci. Technol., 8 (1974) 909.
2 G. J. Minkoff and C. F. H. Tipper, Chemistry of Combustion Reactions, Butterworths, London, 1962.
3 E. J. Bowen and E. L. Tietz, J. Chem. Soc., (1930) 234.
4 J. E. Carruthers and R. G. W. Norrish, J. Chem. Soc., (1936) 1036.
5 J. Mignolet, Bull. Soc. Roy. Sci. Liège, 10 (1941) 343.
6 C. A. McDowell and L. K. Sharples, Can. J. Chem., 36 (1958) 251.
7 C. A. McDowell and L. K. Sharples, Can. J. Chem., 36 (1958) 268.
8 C. A. McDowell and S. Sifoniades, Can. J. Chem., 41 (1963) 300.
9 J. G. Calvert and P. L. Hanst, Can. J. Chem., 37 (1959) 1671.
10 H. S. Johnston and J. Heicklen, J. Am. Chem. Soc., 86 (1964) 4254.
11 N. R. Subbaratnam and J. G. Calvert, J. Am. Chem. Soc., 84 (1961) 1113.
12 J. Weaver, R. Shortridge, J. Meagher and J. Heicklen, Center for Air Environment Studies publication No. 363-74, The Pennsylvania State University (1974); J. Photochem., 4 (1975) 109.
13 H. A. Wiebe, A. Villa, T. M. Hellman and J. Heicklen, J. Am. Chem. Soc., 95 (1973) 7.
14 R. Renaud and L. C. Leitch, Can. J. Chem., 32 (1954) 549.
15 P. A. Giguere and A. W. Olmos, Can. J. Chem., 30 (1952) 821.
16 F. H. MacDougall, J. Am. Chem. Soc., 58 (1936) 2585.
17 C. Jaffe, E. J. Prosen and M. Szwarc, J. Chem. Phys., 27 (1957) 416.
18 P. Gray and J. C. J. Thynne, Nature, 191 (1961) 1357.
19 M. Szwarc and L. Herk, J. Chem. Phys., 29 (1958) 438.
20 A. Rembaum and M. Szwarc, J. Am. Chem. Soc., 76 (1954) 5975.
21 L. Herk and M. Szwarc, J. Am. Chem. Soc., 82 (1960) 3558.
22 K. B. Wiberg and E. L. Motell, Tetrahedron, 19 (1963) 2009.
23 G. Chiltz et al., J. Chem. Phys., 38 (1963) 1053.
24 G. A. Russell, J. Am. Chem. Soc., 79 (1957) 3871.
25 S. Benson, personal communication (1975)
26 D. A. Parkes, Presented at 15th Symposium (International) on Combustion, Japan (1974).

Appendix

In the photo-oxidation of $CD_3N_2CD_3$ [12], k_{1a}/k_1 was determined to be 0.22 ± 0.06, the error being based on the experimental precision of the methanol product quantum yields. However, in the photo-oxidation of

$CH_3N_2CH_3$, the 0.43 value for k_{1a}/k_1 was determined from measurements of the methylhydroperoxide product quantum yields. Since the experimental mass spectral sensitivity for this product was very imprecise, the calculated value for k_{1a}/k_1 could have been anywhere from 0.18 to 0.75. Thus the value of 0.22 ± 0.06 for k_{1a}/k_1 obtained from the $CD_3N_2CD_3$ photo-oxidation study is better from the standpoint of experimental uncertainty. For the light system, Parkes [26] has obtained $k_{1a}/k_{1b} = 0.59$ which gives $k_{1a}/k_1 = 0.35$, assuming $k_{1c}/k_1 = 0.07$. This value is intermediate to our two values for the deuterated system.

If the 0.22 value for k_{1a}/k_1 is used to calculate the ratio of rate constants $k_8/(k_1k_7)^{1/2}$ from eqns. (VI) and (VII), this ratio is found to be 7.49 ± 0.78, a number much larger than the maximum value of 2 expected from statistical considerations. For this reason, the value for k_{1a}/k_1 of 0.45 ± 0.15 obtained in this work was used in the calculations despite the larger experimental uncertainty associated with it.