

THE REACTION OF METHYL RADICALS WITH CH₃CHO AND CH₃CDO¹

By P. Ausloos² and E. W. R. Steacie

ABSTRACT

Azomethane has been photolyzed in the presence of CH₂CHO and CH₃CDO, and the results compared with the direct photolysis of the aldehydes. The activa-tion energies found were 6.8 and 7.8 kcal./mole, respectively, for the reactions $CH_3+CH_3CHO \rightarrow CH_4+CH_3CO$ $CH_3+CH_3CDO \rightarrow CH_4+CH_3CO$. The results furnich aridones that only an acrel hydrogen is constructed. Evidence

[1] [2]

The results furnish evidence that only an acyl hydrogen is captured. Evidence has also been found for the occurrence of wall reactions and the disproportionation reaction

$CH_3 + CH_3CO \rightarrow CH_4 + CH_2CO.$

INTRODUCTION

By decomposing di-t-butyl peroxide in the presence of CH₃CHO, Volman and Brinton (6) obtained a value of 7.5 ± 0.3 kcal. for the activation energy for hydrogen abstraction by methyl from CH₃CHO. This value lies well below most previous estimates. Its acceptance has explained a number of anomalies in the acetaldehyde photolysis, and the value is therefore of considerable importance.

Up to the present no value has been obtained for the activation energy of the companion reaction

$$CH_3 + CH_3CDO \rightarrow CH_3D + CH_3CO.$$

Also, there has been no definite proof whether it is an acyl or a methyl hydrogen which is captured in the reaction (4), although the acyl hydrogen is far more probable on general grounds.

The purpose of the present work was to compare the rates of abstraction from CH₃CHO and CH₃CDO, to obtain a check on the activation energy of the abstraction reaction using a different source of methyl radicals, and to determine whether an acyl or a methyl hydrogen is captured in the abstraction reaction. Azomethane has been used as a source of methyl radicals, since it can be photolyzed at wave lengths greater than 3400 Å where acetaldehyde is transparent. It can thus be photolyzed without complications due to the simultaneous photolysis of the aldehyde. The photolysis of CH₃CHO and CH₃CDO has also been investigated very briefly at 3130 Å in order to compare the results with those obtained with azomethane-acetaldehyde mixtures at longer wave lengths. By using relatively low pressures of acetaldehyde and higher intensities $(1-5 \times 10^{13} \text{ quanta per cc. per sec.})$ than have usually been used in the past, it is possible to obtain measurable amounts of ethane and thus to determine values of $R_{CH_4}/R_{C_2H_6}^2$ in the photolysis of acetaldehyde itself.

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EXPERIMENTAL

Acetaldehyde-d was prepared by Dr. L. C. Leitch (5) of this laboratory by the reaction sequence

$$\begin{array}{c} D_2O\\ CH_3CH_2NO_2 \rightleftharpoons CH_3CD_2NO_2\\ CH_3CD_2NO_2 \xrightarrow{H_2SO_4(6M)} CH_3CDO+HDO+N_2O. \end{array}$$

Mass-spectrometer analysis indicated that the CH_3CDO contained about one per cent CH_2DCDO and less than five per cent CH_3CHO .

The light source was a Hanovia S-500 medium pressure mercury arc. The cylindrical quartz reaction cell, 10 cm. long, 5 cm. diameter, was completely filled by a nearly parallel light beam. Four types of filter were used to limit the incident radiation to longer wave lengths:

Corning clear chemical glass 774 (0-53),

Corning 586 (7–37),

Corning 738 (0-52), and

Corning 970 (9-53).

The apparatus was essentially similar to that used in previous investigations. The methane, N₂, CO fractions were taken off at liquid nitrogen temperature and CO determined by passing over hot CuO. Further analysis was done with a mass spectrometer. The ethane fraction was separated at -170° C., and occasionally checked by mass-spectrometer analysis.

RESULTS AND DISCUSSION

(A) The Reaction of CH_3 with CH_3CHO

When azomethane is photolyzed in the presence of CH_3CHO the following reactions may be considered:

$CH_3NNCH_3 + h\nu \rightarrow 2CH_3 + N_2$	[3]
$CH_3 + CH_3 \rightarrow C_2H_6$	[4]
$CH_3 + CH_3NNCH_3 \rightarrow CH_4 + CH_2NNCH_3$	[5]
$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$	[1]
$CH_{3}CO \rightarrow CH_{3} + CO$	[6]

$$CH_2 + CH_2CO \rightarrow CH_2COCH_2$$
 [7]

 $2CH_3CO \rightarrow CH_3COCOCH_3$ [8]

$$CH_3 + CH_3CO \rightarrow CH_4 + CH_2CO$$
 [9]

 $2CH_3CO \rightarrow CH_2CO + CH_3CHO$ [10]

If reaction [9] is neglected for the moment, then

$$\frac{k_1}{k_4^{\frac{1}{2}}} = \left(\frac{R_{\text{CH}_4}}{R_{\text{C}_2\text{H}_6}^{\frac{1}{2}}} - \frac{k_5}{k_4^{\frac{1}{2}}} \left[\text{CH}_3\text{NNCH}_3\right]\right) / \text{[CH}_3\text{CHO]}.$$

The values of $k_5/k_4^{\frac{1}{2}}$ which are required in the calculations have been taken from an experimental Arrhenius plot for azomethane alone (1).

The results of runs at different temperatures, intensities, and concentrations are given in Table I. As can be seen from Fig. 1 (Curve *B*), a plot of $\log R_{CH_4}/R_{C_{2H_6}}^{\frac{1}{2}}$ [Ald] against 1/T gives a straight line, except at temperatures below

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AUSLOOS AND STEACIE: METHYL RADICALS TABLE I

THE PHOTOLYSIS OF AZOMETHANE IN THE PRESENCE OF CH₃CHO Temp., °C. Time, Pressure, cm. CH₃NNCH₃ CH₃CHO Rate, cc./min. $\times 10^4$ $_2$ CH₄ C₂H₆ k_1 $imes 10^{13}$ $\frac{1}{k_{4^{\frac{1}{2}}}}$ CO N_2 min. $\begin{array}{c} 27\\ 27\\ 27\\ 27\\ 51\\ 51\\ 73\\ 72\\ 91 \end{array}$ 8.5 $\begin{array}{c} 713\\73\\20\\28\\20\\35\\61\\35\\75\\25\\30\\60\\220\\20\\25\end{array}$ 5.500.4350.57 0.80 1.16 $6.48 \\ 4.39$ $10.5 \\ 17.7$ 1.772.3 9.1 9.7 0.827.680.8014.4 $\begin{array}{r} 2.3 \\ 4.25 \\ 8.40 \\ 8.95 \\ 12.4 \\ 3.9 \\ 5.4 \end{array}$ $5.20 \\ 2.60$ 0.7254.043.511.01.524.1018.710.79.7 $5.29 \\ 1.8$ $\begin{array}{c} 0.855 \\ 2.10 \end{array}$ $\bar{3}\bar{9}$ 1.2328.2519.4 14.38.6 17.6 22.3 27.8 25.1 27.0 5.80 4.419.6 $6.10 \\ 5.12$ 0.90 3.11 0.7330.7 1.35 0.759.30 29.58.8017.4 23.7 8.90 $3.89 \\ 5.28$ $1.29 \\ 1.52$ 12.12.1029.3 9.45 5.3552.03.56 5.33 93 2.628.40 9.70 55.0 0.80 1103.60 81.0 4.66 $4.88 \\ 5.41$ $1.83 \\ 1.37$ 26.7 28.5 $22.5 \\ 22.7$ $115 \\ 132$ 12.20 5.6090.04.1711.40 135.0 28.536.433.840.230.6 $26.8 \\ 45.7$ 5.454.353.63.20 $1.08 \\ 2.50$ $14.6 \\ 29.0$ 146 4.92175.04.324.455.504.07146172.0 $\begin{array}{r} 2.30 \\ 0.98 \\ 2.70 \end{array}$ 29.053.0 $12.8 \\ 35.5$ 165250.0165 230.0



FIG. 1. Arrhenius plot of $R_{CH_4}/R_{C_2H_6}^{\frac{1}{2}}$ [Aldehyde]. Curve A-CH₃CHO photolysis.

Curve B—Photolysis of azomethane in the presence of CH₃CHO. Curve C—Photolysis of azomethane in the presence of CH₃CDO, containing 5% CH₃CHO.

75°C. where curvature is evident. (The units of k throughout are cm.³, molecules, sec.)

From the first four runs at 27°C., it may be concluded that $R_{CH_4}/R_{C_{2H_6}}^{\frac{1}{2}}$ [Ald] decreases with decreasing intensity as shown by Fig. 2. This can be explained by the occurrence of the disproportionation reaction [9]. Evidence for the

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FIG. 2. The effect of intensity at 27°C. on the photolysis of azomethane in the presence of CH_3CHO.

occurrence of this reaction has been found in the photolysis of acetone (2) and biacetyl (3) as well. When the curve in Fig. 2 is extrapolated to zero intensity, a value of 8.4×10^{-13} is obtained for $k_1/k_4^{\frac{1}{2}}$. This is still higher than the value obtained by extrapolation of the linear portion of curve *B* in Fig. 1. This is therefore not due to reaction [9], and it is suggested that wall effects occur as well at low temperatures, as is the case with acetone and biacetyl.

From the slope of curve B in Fig. 1 at temperatures above 75°C. an activation energy difference $E_1 - \frac{1}{2}E_4$ of 6.8 kcal. is obtained. Since $E_4 = 0$, $E_1 = 6.8$ kcal. This is in excellent agreement with the value found by Volman and Brinton, whose results are also given in Fig. 1. The lower value for E_1 may therefore be considered to be established.

(B) The Photolysis of CH₃CHO

A few experiments were also made on the direct photolysis of CH₃CHO. A Corning Filter No. 970 (opaque at wave lengths below 2900 Å) was used, so that the light absorbed by acetaldehyde consisted mainly of the 3130 Å group of lines. The results are given in Table II. The rate of hydrogen formation has not been included since it was always too small to measure with any great accuracy. An Arrhenius plot of $R_{CH_4}/R_{2H_5}^2$ [CH₃CHO] is given in Fig. 1 (Curve

TABLE II Photolysis of CH₃CHO

Temp.,	Time,	Pressure,	Rate i	n cc./min	$1. \times 10^4$	$\frac{R_{\rm CH_4}}{R_{\rm C_2H_6}^{\frac{1}{2}}[\rm CH_3CHO]} \times 10^{13}$
°C.	min.	cm.	CH₄	C2H6	CO	
275092143146165	$30 \\ 20 \\ 15 \\ 20 \\ 13 \\ 6$	$\begin{array}{r} 3.78\\ 3.75\\ 3.45\\ 3.13\\ 3.45\\ 3.53\end{array}$	$ \begin{array}{c} 11.0\\ 19.8\\ 33.0\\ 79.5\\ 101.0\\ 148.0 \end{array} $	$\begin{array}{r} 4.65 \\ 6.20 \\ 6.42 \\ 7.75 \\ 8.85 \\ 10.8 \end{array}$	$ \begin{array}{r} 17.0 \\ 24.5 \\ 38.0 \\ 90.0 \\ 120.0 \\ 160.0 \\ \end{array} $	21.634.573.2202.0217.0297.0

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A). A curved line is obtained which at higher temperatures appears to become parallel to the line obtained by photolyzing azomethane in the presence of CH_3CHO . The curvature may largely be explained by the direct formation of some methane in the primary step. However, in the light of the azomethane results it is probable that the curvature also results in part from reaction [9] and from wall reactions. In spite of these complications the results indicate that at higher temperatures methane mainly results from reaction [1].

(C) The Reaction of CH_3 with CH_3CDO

When azomethane is photolyzed in the presence of CH_3CDO the same reaction scheme holds as for CH_3CHO , except that in place of [1] we have $CH_3+CH_3CDO \rightarrow CH_3D+CH_3CO$. [2]

Also we may consider the possible reaction

 $CH_3+CH_3CDO \rightarrow CH_4+CH_2CDO.$ [11] If it is assumed that only an acyl hydrogen is captured, then

$$\frac{R_{\rm CH_{3D}}}{R_{\rm C_{2H_{6}}}^{\frac{1}{2}}[\rm CH_{3}CDO]} = \frac{k_{2}}{k_{4}^{\frac{1}{2}}}$$

$$\frac{R_{\rm CH_4}}{R_{\rm C_{2H_6}}^{\frac{1}{2}}[\rm CH_3NNCH_3]} = \frac{k_5}{k_4^{\frac{1}{2}}}$$

The values of $k_2/k_4^{\frac{1}{2}}$ and $k_5/k_4^{\frac{1}{2}}$ given in columns 9 and 10 of Table III have been calculated in this way. In Fig. 3 curve *F*, the triangles represent the values of log $k_5/k_4^{\frac{1}{2}}$, while the line drawn through them represents the results from the photolysis of azomethane alone. It is evident, therefore, that reaction [11] does not occur to an appreciable extent (i.e. not over five per cent of [2]) since all the CH₄ found can be accounted for by abstraction from azomethane. The small amount of CH₃CHO present in the CH₃CDO is not sufficient to alter the results appreciably.

The fact that no C_2H_5D or $C_2H_4D_2$ could be detected in the ethane fraction is further proof that no hydrogen atoms are captured from the methyl group of CH₃CDO. Also no CH₂D₂ was found in the methane fraction, which, as Blacet and Brinton point out (4) excludes a mixed mechanism.

An Arrhenius plot of $k_2/k_4^{\frac{1}{2}}$ (curve *E*) gives an activation energy of 7.9 kcal. for reaction [2], as compared with 6.8 kcal. for [1].

A very small amount of curvature is present in the $\log k_2/k_4^{\frac{1}{2}}$ plot at low temperatures. Since this plot involves CH₃D, the curvature cannot result from the disproportionation of methyl with acetyl, since all the acetyl radicals are CH₃CO. It is therefore probably to be explained by wall reactions.

No curvature was found in the $k_5/k_4^{\frac{1}{2}}$ plot (curve F). In this case the reaction $CH_3+CH_3CO \rightarrow CH_4+CH_2CO$ [9] would cause such curvature. Its absence is presumably due to the much smaller rate of abstraction from CH_3CDO as compared with CH_3CHO (a factor of 20). This results in a much smaller concentration of acetyl, and the effect of reaction [9] is apparently negligible.

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	TABLE III							
Тне	PHOTOLYSIS	OF	AZOMETHANE	IN	THE	PRESENCE	OF	CH₃CD0

Temp., °C.	Time, min.	Pressur CH₃CDO	e, cm. CH₃NNCH₃	CH₃D	Rate, cc./1 CH4	nin. $\times 10^4$ C ₂ H ₆	СО	$rac{k_5}{k_4^{rac{1}{2}}} imes 10^{13}$	$\frac{k_2}{k_4^{\frac{1}{2}}} imes 10^{13}$	
$27 \\ 27 \\ 61 \\ 62 \\ 85 \\ 86 \\ 126 \\ 127 \\ 158$	$125 \\ 125 \\ 60 \\ 126 \\ 60 \\ 100 \\ 50 \\ 100 \\ 55$	$1.08 \\ 0.74 \\ 1.20 \\ 1.00 \\ 0.72 \\ 1.06 \\ 0.84 \\ 1.65 \\ 0.83$	5.26 5.38 4.88 5.14 5.70 4.29 5.30 5.50 5.58	$\begin{array}{c} 0.115\\ 0.08\\ 0.460\\ 0.385\\ 0.52\\ 0.49\\ 1.14\\ 1.29\\ 1.52 \end{array}$	$\begin{array}{c} 0.465\\ 0.495\\ 1.55\\ 1.17\\ 3.36\\ 1.52\\ 5.50\\ 2.90\\ 6.82 \end{array}$	$10.2 \\ 10.0 \\ 16.3 \\ 6.9 \\ 12.9 \\ 4.4 \\ 5.4 \\ 1.62 \\ 2.60$	$\begin{matrix} 0.02 \\ 0.02 \\ 0.15 \\ 0.16 \\ 0.40 \\ 0.34 \\ 1.24 \\ 1.27 \\ \end{matrix}$	$\begin{array}{c} 0.435\\ 0.463\\ 1.40\\ 1.50\\ 3.12\\ 3.24\\ 9.00\\ 9.40\\ 17.30\\ \end{array}$	$\begin{array}{c} 0.530\\ 0.54\\ 1.70\\ 1.80\\ 3.90\\ 4.20\\ 12.30\\ 13.00\\ 26.00\\ \end{array}$	CANADIAN JOURNAL OF CI
				TAB Photolysis	LE IV of CH3CI	00				HEMISTR
Temp., °C.	Time, min.	Pressure, cm.	CH₃D	Rate, cc./min. CH4 Et	× 104 hane (20	$R_{ m CH_3I}$ $R_{ m Ethane}^{rac{1}{2}}[m CH_3$	$\frac{1}{CDO} \times 10^{13} \frac{1}{R_{Eth}^{\frac{1}{2}}}$	$\frac{R_{\rm CH_4}}{R_{\rm LBDe}[\rm CH_3CDO]} \times 10^{10}$	ч. vol. 33

TABLE IV PHOTOLYSIS OF CH3CDO

Temp., °C.	Time, min.	Pressure, cm.	CH₃D	Rate, cc.∕ CH₄	min. × 104 Ethane	СО	$\frac{R_{\rm CH_3D}}{R_{\rm Ethane}^{\frac{1}{2}}[\rm CH_3CDO]} \times 10^4$	$\frac{R_{\rm CH_4}}{R_{\rm Ethane}^{\frac{1}{2}}[\rm CH_3CDO]} \times 10^{13}$
$26 \\ 43 \\ 86 \\ 108 \\ 151 \\ 196$	62 45 90 85 90 60	$\begin{array}{r} 4.90\\ 3.95\\ 3.75\\ 3.72\\ 3.83\\ 3.24 \end{array}$	$\begin{array}{c} 0.77 \\ 0.95 \\ 1.90 \\ 2.47 \\ 6.08 \\ 9.95 \end{array}$	$\begin{array}{c} 0.175 \\ 0.215 \\ 0.495 \\ 0.652 \\ 1.70 \\ 2.85 \end{array}$	1.481.681.561.682.221.92	$\begin{array}{c} 2.85\\ 3.00\\ 4.92\\ 5.30\\ 10.6\\ 16.4 \end{array}$	$\begin{array}{r} 2.05\\ 3.05\\ 7.45\\ 10.4\\ 23.5\\ 52.2 \end{array}$	$\begin{array}{c} 0.46 \\ 0.70 \\ 1.94 \\ 3.25 \\ 6.65 \\ 15.0 \end{array}$

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Curve D—Arrhenius plot of $R_{CH_3D}/R_{Ethane}^{\frac{1}{2}}$ [Aldehyde] for the direct photolysis of CH₃CDO.

- Curve *E*—Arrhenius plot of $R_{CH_{3D}}/R_{Ethane}^{\frac{1}{2}}$ [Aldehyde] for the photolysis of azomethane in the presence of CH₃CDO.
- Curve *F*—Arrhenius plot of $R_{CH_4}/R_{C_2H_6}^{\frac{1}{2}}$ [Azomethane] for the photolysis of azomethane in the presence of CH₃CDO.

(D) The Photolysis of CH_3CDO

The photolysis of CH₃CDO was briefly investigated. A Corning 970 filter was used so that absorption was mainly of the 3130 Å group of lines. The results are given in Table IV. The fraction coming off at -195° C. consisted of CO, CH₄, and CH₃D. No CH₂D₂, D₂, or H₂ was found by mass-spectrometer analysis, so that they amounted to less than one per cent of the products. The ethane fraction consisted mainly of C₂H₆ (\sim 60%); considerable amounts of deuterated ethanes were also present. Only the total ethane has been given in Table IV.

In Fig. 3 (curve *D*) an Arrhenius plot of $R_{CH_{3D}}/R_{Lthane}^{\pm}[CH_{3}CDO]$ is given. A large curvature is present at low temperatures, while at higher temperatures the plot becomes parallel to the one found when azomethane is photolyzed in the presence of CH₃CDO. This appears to indicate that at high temperatures CH₃D is mainly formed by reaction [2], while at low temperatures the occurrence of the primary step

$$CH_3CDO + h\nu \rightarrow CH_3D + CO$$
 [12]

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explains largely the excess of CH₃D responsible for the curvature in the Arrhenius plot.

Considerable CH₄ is formed in addition to CH₃D. This may be accounted for by the presence of about five per cent CH_3CHO in the CH_3CDO sample. Since abstraction by methyl is about 20 times faster from CH₃CHO than from CH₃CDO, even five per cent of CH₃CHO has a large effect. In Fig. 1 (curve C) an Arrhenius plot is given for this methane, i.e. a plot of $R_{CH_4}/R_{Ethane}^{\frac{1}{2}}$ [Aldehyde]. Since the exact amount of CH₃CHO present is somewhat uncertain, but its percentage is constant, we have used the total aldehyde concentration. The actual value of the ratio $R_{CH_4}/R_{Ethane}^{\frac{5}{2}}$ [CH₃CHO] will therefore be approximately 20 to 25 times higher than the figures plotted in Fig. 1, and the results will therefore coincide approximately with the linear portion of curve A as they should. From the slope of curve C a value of 6.4 kcal. is obtained for $E_{\rm I}$, in excellent agreement with the value of 6.8 kcal. obtained by photolyzing azomethane in the presence of CH₃CHO.

It may be noted that the deviation from linearity is much less for curve C than for curve A. This is to be expected since the relatively fast abstraction by methyl from CH₃CHO as compared with CH₃CDO, causes a small amount of $CH_{3}CHO$ to have an important effect on the abstraction reaction. There is, however, no reason to suppose that reaction [11] will be more important for CH₃CHO than for CH₃CDO.

If CH₄ was also produced by abstraction from the methyl group

 $CH_3 + CH_3CDO \rightarrow CH_4 + CH_2CDO$,

[13]

a higher activation energy than 6.8 kcal. would be expected, and CH_2D_2 should also be produced. It may therefore be concluded that reaction [13] does not occur to an appreciable extent. However, no explanation can be given for the production of a considerable amount of C_2H_5D and $C_2H_4D_2$.

Since there is no appreciable abstraction from the methyl group in CH₃CDO, in spite of the higher acyl C-D bond strength, it is evident that no appreciable abstraction from the methyl group in CH₃CHO will occur.

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