THE REACTIONS OF CH_3 AND CD_3 RADICALS WITH HYDROGEN AND DEUTERIUM[1]

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ABSTRACT

The reaction of CH_3 and CD_3 radicals with hydrogen and deuterium have been investigated, acetone being used as a source of methyl radicals. The results indicate (1) that the substitution of D_2 for H_2 has a considerable effect, (2) the substitution of CD_3 for CH_3 has relatively little effect. (3) It is concluded that, contrary to the results of Burton *et al.*, the activation energy of the reaction

$$CH_3 + H_2 \rightarrow CH_4 + H$$

is 9.7 ± 0.6 kcal.

INTRODUCTION

It has been shown (12, 3) that in the photolysis of acetone between 130° and 300° the production of methyl radicals and the formation of methane and ethane are accounted for by the following reactions:

$$CH_3 . CO . CH_3 \rightarrow 2CH_3 + CO \tag{1}$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \tag{2}$$

$$CH_3 + CH_3 . CO . CH_3 \rightarrow CH_4 + CH_2 . CO . CH_3 . \tag{3}$$

Assuming a steady concentration of methyl radicals, it follows that

$$\frac{k_3}{k_2^{\frac{1}{2}}} = \frac{R_{CH_4}}{R^{\frac{1}{2}}_{C_2H_6}\,[Ac]} .$$

In the presence of hydrogen the methyl radicals also react as follows*

$$CH_3 + H_2 \rightarrow CH_4 + H \tag{4}$$

whence

$$\frac{k_4}{k_2^{\frac{1}{2}}} = \frac{(R_{CH_4})_4}{R^{\frac{1}{2}}_{C_2H_6}\,[H_2]}$$

where $(R_{CH_4})_4$ represents the rate of production of methane by reaction (4).

The fate of the H-atom produced in reaction (4) is presumed to be

$$H + CH_3 . CO . CH_3 \rightarrow H_2 + CH_2 . CO . CH_3 .$$

The alternative

$$H + CH_3 \rightarrow CH_4$$

appears to be ruled out as a significant process by evidence obtained in the course of the present work.

MATERIALS

Mallinckrodt Analytical Reagent Acetone was dried successively over sodium

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* *For a discussion of this reaction, see Reference (14).*

sulphate and calcium sulphate and distilled at 56.1–56.5°. The deuterated acetone was prepared by Dr. L. C. Leitch of these Laboratories by the following method.

A mixture of *d*-acetylene and heavy water vapor was passed over a Fe_3O_4–ZnO catalyst at 410° C. The crude product was purified by fractional distillation in a Stedman column at a reflux ratio of 10:1, collecting separately a portion which boiled at 55.5° C. This fraction was further enriched in deuterium by repeated exchanges with heavy water (99.8 mole %) at 60° C. in the presence of a trace of sodium carbonate. Samples taken both before and after enrichment were used in this work, though final quantitative results were based only on work done with the latter. Their compositions were determined by mass spectrometric analysis with the following results:

No. of D-atoms per molecule	Mole % composition I	II
6	86.4	93.2
5	10.2	3.7
4	3.0	3.1
3	0.4	0

The acetone samples were degassed before use to a vacuum of less than 10^{-4} mm. of permanent gas.

The hydrogen used was commercial cylinder gas purified by passage through a palladium thimble. The deuterium, also prepared by Dr. L. C. Leitch, was purified in the same way; mass spectrometric analysis showed the composition to be 95% D_2, 5% HD. The carbon dioxide was commercial cylinder gas which was found to have the composition 99.4% CO_2, 0.6% N_2.

EXPERIMENTAL

The apparatus and method of analysis were similar to those described in earlier papers from this laboratory (17, 16). The radiation from the mercury arc (a Hanovia S-500 lamp) was unfocused but defined by stops so as to fill the reaction cell, which was 4.8 cm. in diameter. In general, no filter was used, so that the absorbed radiation was chiefly at 2537Å; here the extinction coefficient of acetone is 6.7 (13), and, the reaction vessel depth being 10.35 cm. and the pressure of acetone not greater than 10 cm., the absorbed radiation did not exceed 60% of that incident on the cell. Variation of intensity was obtained by interposing a quartz neutral density screen of 27% transmission.

The 2537Å line in the lamp used is strongly reversed so that there was no risk of mercury sensitization. This was confirmed in one instance by a duplicate run using a Corning 9700 filter with a cutoff at 2600Å; no difference in the behavior of the reaction, other than diminished intensity, was detected.

The reactions were carried out to an acetone conversion of less than 10%.

The greater part of the hydrogen remaining after each experiment was removed by passage through a palladium thimble at 350° while the acetone was frozen out in a side-arm. Residual hydrogen was subsequently oxidized over copper oxide along with the carbon monoxide.

In runs involving isotopic mixtures of deuterated methane and ethane with hydrogen or deuterium it was shown by means of trial experiments that no isotope exchange took place photochemically or thermally in the reaction cell. Exchange at the palladium thimble was found to be negligible, affecting only 1–2% of the reaction products.

The separation of the ethane from the noncondensable gases was effected by means of a Ward–LeRoy still (8).

The mass spectrometric analyses of deuterated methanes and ethanes were made under the direction of Dr. F. P. Lossing of these Laboratories. The analyses for the CD_4–CD_3H mixtures were computed assuming equal sensitivities for the isotopic molecules. The analysis of CH_2D_2 was computed from the spectrum of CH_2D_2 prepared in these Laboratories by Dr. W. A. Bryce. The analysis of CH_3D was computed using C–H and C–D cracking ratios calculated from the spectrum of CH_3D supplied in a private communication by Dr. V. H. Dibeler of the National Bureau of Standards in Washington.

Arrhenius plots of the results were made by the method of least squares; this served also as the basis of calculation of the standard errors of the intercepts and slopes.

Six sets of experiments were performed in all, viz. the photolyses of the normal and deuterated acetones alone, and of each in the presence of hydrogen and deuterium. These will now be described in turn. All quantities of starting materials and products are expressed in molecules per cubic centimeter of reaction volume (190 cc.) and all reaction constants in terms of molecules, cubic centimeters, and seconds. Collision numbers were calculated at 490° K., which is approximately the mean temperature of the photolyses.

1. *The Photolysis of Acetone*

The dependence of this reaction on acetone pressure and light intensity was checked and found to be as predicted by the equation given above for $k_3/k_2^{\frac{1}{2}}$. The results are reported in Table I.

The Arrhenius plot of these results, which is shown in Fig. 1 (open circles), is given by

$$13 + \log \frac{k_3}{k_2^{\frac{1}{2}}} = 5.880 - 2.082 \frac{10^3}{T},$$

the standard errors of intercept and slope being ±0.062 and ±0.029, respectively. The slope gives $E_3 - \frac{1}{2}E_2$ as 9.5 ± 0.1 kcal. This agrees well with the values previously reported by Trotman-Dickenson and Steacie (17) (9.7 kcal.) and Nicholson (11) (9.6 kcal.). If the collision diameters of the acetone molecule and the methyl radical are taken as 5.5Å and 3.5Å, the ratio of the steric factors $P_3/P_2^{\frac{1}{2}}$ is found to be $1.9 \pm 0.3 \times 10^{-3}$.

2. *The Photolysis of Acetone in the Presence of Hydrogen*

These experiments were carried out at hydrogen pressures of 5 cm. and 20 cm. The ratio $k_4/k_2^{\frac{1}{2}}$ was found to be independent of hydrogen pressure except at the highest temperature and pressure where a falling-off was noted. The results are presented in Table II and plotted in Fig. 1 (open squares). If the obviously

TABLE I
THE PHOTOLYSIS OF ACETONE

Run	Temp., °K.	Intensity (arbitrary)	[Acetone] molecules per cc. × 10^{-18}	Time (sec.)	Products, molecules/cc./sec. × 10^{-13}			$\frac{k_3}{k_2^{\frac{1}{2}}} \times 10^{13}$
					CO	CH_4	C_2H_6	
A1	413	100	2.27	1800	4.33	0.93	3.42	7.01
A2	405	27	2.33	5400	0.81	0.30	0.53	5.62
B1	409	100	1.07	3600	2.36	0.30	2.05	6.17
C1	409	100	0.58	3600	1.34	0.12	1.19	6.09
D3	498	100	1.90	1200	4.46	3.57	1.50	48.5
D4	499	100	1.87	1200	4.63	3.57	1.49	49.4
D5	494	27	1.94	4800	0.87	0.95	0.13	43.3
F1	494	100	0.46	1200	1.42	0.65	0.79	50.3
G1	565	100	1.68	2400	4.80	5.65	0.52	147
I2	564	100	0.43	2400	1.52	1.29	0.33	168

TABLE II

THE PHOTOLYSIS OF ACETONE IN PRESENCE OF HYDROGEN

Run	Temp., °K.	Acetone concentration molecules/cc. × 10^{-18}	Hydrogen concentration molecules/cc. × 10^{-18}	Time (sec.)	Products, molecules/cc./sec. × 10^{-13}			$\frac{k_4}{k_2^{1/2}} \times 10^{13}$
					CO	CH_4	C_2D_6	
5 cm. hydrogen								
6	412	2.28	1.19	1800	4.10	1.11	3.04	4.12
4	454	2.07	1.03	1800	4.19	2.45	2.11	12.3
8	506	1.90	0.92	1800	4.25	4.41	0.94	35.4
11	523	1.85	0.89	1800	4.24	5.05	0.66	56.0
5	566	1.68	0.86	1800	4.31	6.12	0.33	82.8
10	571	1.70	0.86	1800	4.40	6.38	0.31	85.5
20 cm. hydrogen								
1	409	2.28	4.77	1800	4.24	1.67	2.79	3.68
3	453	2.12	4.41	1860	4.43	3.72	1.58	12.1
7	504	1.90	3.89	1800	4.41	5.90	0.58	35.4
2	567	1.69	3.55	1860	4.88	7.77	0.25	61.1
9	569	1.74	3.38	1800	4.73	7.56	0.26	53.6

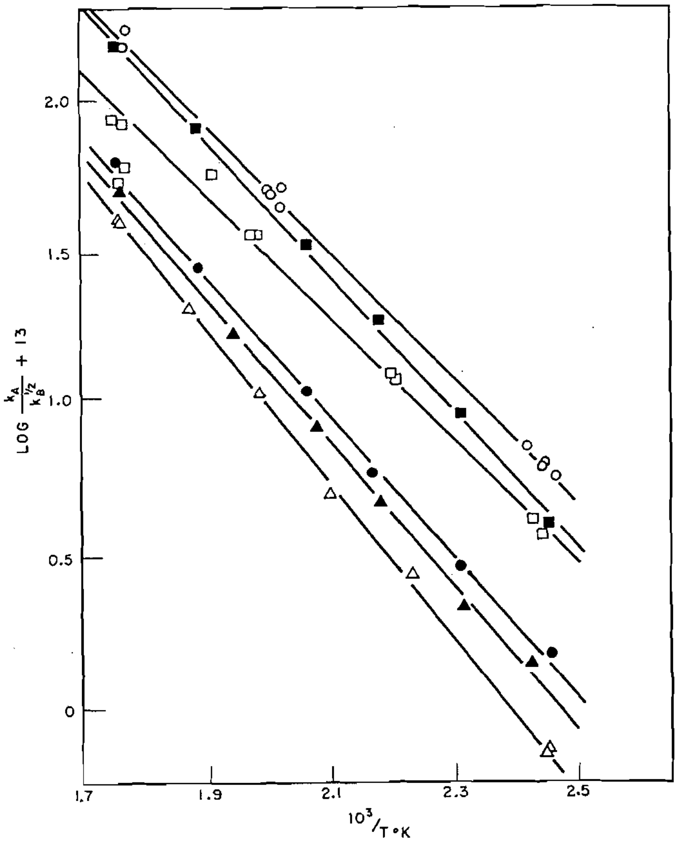

Fig. 1. Arrhenius plot of results.

○ = $CH_3 + CH_3COCH_3$
□ = $CH_3 + H_2$
△ = $CH_3 + D_2$
● = $CD_3 + CD_3COCD_3$
■ = $CD_3 + H_2$
▲ = $CD_3 + D_2$

low results of runs 2 and 9 are omitted, the remainder give the line

$$13 + \log \frac{k_4}{k_2^{\frac{1}{2}}} = 5.508 - 2.009 \frac{10^3}{T}$$

with standard errors of ±0.125 and ±0.060 for intercept and slope. The corresponding value for $E_4 - \frac{1}{2}E_2$ is 9.2 ± 0.3 kcal. If 2.8Å is taken as the collision diameter of the H_2 molecule the steric factor ratio $P_4/P_2^{\frac{1}{2}}$ is found to be $7 \pm 2 \times 10^{-4}$.

3. *The Photolysis of Acetone in the Presence of Deuterium*

In addition to the normal methane formed by reaction (3) we now have deuteromethane formed by

$$CH_3 + D_2 \rightarrow CH_3D + D\,. \qquad (5)$$

The products in this case can be dealt with by two methods. (1) The estimation of $(CH_3D)_5$ by subtracting $(CH_4)_3$ from the total methane; $(CH_4)_3$ is given by the expression $k_3/k_2^{\frac{1}{2}} \times \sqrt{(C_2D_6)} \times [Ac]$. This is the method already used in

Section 2 above. (II) Mass spectrometric analysis of the total methane formed will give the ratio $CH_3D/CH_4 = A$ and hence k_5/k_3 since

$$\frac{k_5}{k_3} = A \times \frac{[\mathrm{Ac}]}{[\mathrm{D_2}]}.$$

In both cases a small correction is necessary to allow for the presence of 5% HD in the deuterium used since this gives rise to two additional reactions:

$$CH_3 + HD \rightarrow CH_4 \quad + D, \tag{6}$$

$$CH_3 + HD \rightarrow CH_3D + H. \tag{7}$$

Assuming $k_6 = k_4$ and $k_7 = k_5$* it can easily be shown that for Method I the true value of $k_5/k_2^{\frac{1}{2}}$ is given by

$$\frac{R_{(CH_3D)_5} + R_{(CH_4)_6} + R_{(CH_3D)_7}}{R^{\frac{1}{2}}_{C_2H_6} \times \{[D_2] + [HD]\}} - \frac{[HD]}{[D_2] + [HD]} \cdot \frac{k_4}{k_2^{\frac{1}{2}}} = \frac{k_5}{k_2^{\frac{1}{2}}}\text{uncorrected} - \frac{1}{20} \cdot \frac{k_4}{k_2^{\frac{1}{2}}}.$$

For Method II,

$$\frac{k_5}{k_2^{\frac{1}{2}}} = A \cdot \frac{[Ac]}{[D_2] + [HD]} \cdot \frac{k_3}{k_2^{\frac{1}{2}}} + A \cdot \frac{[HD]}{[D_2] + [HD]} \cdot \frac{k_4}{k_2^{\frac{1}{2}}} = \frac{k_5}{k_2^{\frac{1}{2}}}\text{uncorrected} + \frac{A}{20} \cdot \frac{k_4}{k_2^{\frac{1}{2}}}.$$

The results obtained using both methods of analysis are presented in Table III and those obtained by Method II are plotted in Fig. 1 (open triangles). They show the expected independence of deuterium pressure. The wide scatter of the results obtained by Method I is due chiefly to the unfavorably low ratio of CH_3D to CH_4, particularly at the low temperatures where the total yield of methane is small, but partly also to the low ethane yield at high temperatures. The coefficients of the Arrhenius plots together with the corresponding ratios of steric factors and energies of activation are as follows:

	METHOD I	METHOD II
Intercept	5.60 ± 0.65	6.117 ± 0.064
$P_5/P_2^{\frac{1}{2}} \times 10^3$	0.2 — 4.6	3.5 ± 0.5
Slope	− 2.35 ± 0.31	− 2.559 ± 0.030
$E_5 - \frac{1}{2}E_2$, kcal.	10.7 ± 1.4	11.7 ± 0.1

4. *The Photolysis of d-Acetone*

The mass spectrometric analyses already quoted show that the percentage of fully-deuterated methyl groups was 92.35 in the first and 95.8 in the second sample of *d*-acetone used; the percentage of radicals containing one H-atom was 6.7 in the first and 3.4 in the second sample. Preliminary experiments only were made with the first sample; all final quantitative results are based on experiments made with the more highly deuterated acetone.

By basing our calculations on the fully-deuterated products only, as determined by the mass spectrometer, we can confine our considerations to the following reactions:

$$CD_3 + CD_3 \rightarrow C_2D_6 \tag{8}$$

$$CD_3 + CD_3.CO.CD_3 \rightarrow CD_4 + CD_2.CO.CD_3 \tag{9}$$

$$CD_3 + CD_2H.CO.CD_3 \rightarrow CD_4 + CDH.CO.CD_3 \tag{10}$$

Reaction (10) cannot contribute more than 4% of the CD_4 formed and will

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This assumption is somewhat in error, but since it is only involved in a minor correction it has no appreciable effect.

TABLE III
THE PHOTOLYSIS OF ACETONE IN PRESENCE OF DEUTERIUM

Run	Temp.,°K.	Acetone concentration molecules/cc. × 10^{-18}	Deuterium concentration molecules/cc. × 10^{-18}	Time (sec.)	Products, molecules/cc./sec. × 10^{-13}			$\frac{CH_3D}{CH_4}$	$\frac{k_5}{k_2^{\frac{1}{2}}} \times 10^{13}$	
					CO	CH_4+CH_3D	C_2H_6		Method I	Method II
5 cm. deuterium										
15	408	2.35	1.28	1800	4.15	0.90	3.22	0.064	1.2	0.72
12	448	2.16	1.11	1800	4.20	1.87	2.38	0.081	0.8	2.73
13	503	1.92	0.95	1800	4.15	3.86	1.11	0.097	8.5	11.0
16	534	1.79	0.92	1800	4.25	4.98	0.63	0.110	26.4	20.7
14	568	1.70	0.89	1800	4.31	5.81	0.36	0.130	25.3	41.5
20 cm. deuterium										
19	409	2.37	4.46	1800	3.96	1.04	3.00	0.202	0.8	0.70
18	476	2.04	3.86	1810	4.19	3.37	1.42	0.280	5.2	5.00
17	568	1.70	3.21	1800	4.21	6.52	0.30	0.447	26.5	40.8

TABLE IV
THE PHOTOLYSIS OF *d*-ACETONE

Run	Temp., °K.	[Acetone] molecules per cc. × 10^{-18}	Time (sec.)	%CD_4	%C_2D_6	Products, molecules/cc./sec. × 10^{-12}			$\frac{k_9}{k_8^{\frac{1}{2}}} \times 10^{13}$
						CO	CD_4	C_2D_6	
54	407	2.30	1800	89.6	95.8	54.1	2.33	46.7	1.48
64	433	2.19	1800	96.4	96.1	56.9	4.33	47.4	2.88
62	461	2.02	1200	92.7	96.0	56.9	7.55	41.9	5.78
60	485	1.92	1230	92.2	94.1	55.3	12.5	36.5	10.8
58	529	1.77	1200	93.5	95.3	54.0	24.5	24.9	27.9
56	569	1.63	1800	93.2	95.5	55.7	39.5	15.5	61.7

contribute less if, as seems likely, the abstraction of an H-atom is more probable than that of a D-atom. Consequently, this reaction has been ignored and the effective concentration of acetone taken as the percentage of CD_3 groups which it contains.

The results of this photolysis are presented in Table IV. The same pressure of acetone (10 cm.) and light intensity were used throughout.

The Arrhenius plot of these results, shown in Fig. 1 (closed circles), is given by

$$13 + \log \frac{k_9}{k_8^{\frac{1}{2}}} = 5.814 - 2.311 \frac{10^3}{T},$$

the standard errors for the coefficients being ±0.130 and ±0.059 respectively. The corresponding value for $P_9/P_8^{\frac{1}{2}}$ is $1.8 \pm 0.5.\ 10^{-3}$, and for $E_9 - \frac{1}{2}E_8$, 10.6 ± 0.3 kcal. This agrees with Trotman-Dickenson's value of 10.3 kcal. (17).

The analyses of the ethane produced in these runs showed it to consist of C_2D_6 and C_2D_5H, any $C_2D_4H_2$ present being below the limit of detectability ($\sim\frac{1}{2}\%$). Assigning k_{11} to the combination of CD_3 and CD_2H

$$CD_3 + CD_2H \rightarrow C_2D_5H \tag{11}$$

and taking the average percentage of C_2D_6 we have

$$\frac{k_{11}}{k_8} = \frac{R_{C_2D_5H}}{R_{C_2D_6}} \times \frac{[CD_3]}{[CD_2H]} = \frac{4.5}{95.5} \times \frac{95.8}{3.4} = 1.3\,.$$

This value is quite rough, and its difference from unity may not be significant.

A confirmatory calculation on the results obtained from the first sample of acetone gave the average percentage of C_2D_6 as 89.5, whence $k_{11}/k_8 = 1.6$.

5. *The Photolysis of d-Acetone in the Presence of Hydrogen*

This introduces the reaction

$$CD_3 + H_2 \rightarrow CD_3H + H. \tag{12}$$

The two independent methods of analysis described above are again applicable. For the first method, mass spectrometric analysis was used to estimate C_2D_6/total ethane and $(CD_4 + CD_3H)$/total methane, the latter ratio being required since an appreciable amount of CD_2H_2 was formed by

$$CD_2H + H_2 \rightarrow CD_2H_2 + H. \tag{13}$$

In both methods, the amount of CD_3H formed from the *d*-acetone itself was estimated from the data given in the preceding section. The results are presented in Table V and plotted in Fig. 1 (closed squares). The intercepts and slopes and the corresponding value of $P_{12}/P_8^{\frac{1}{2}}$ and $E_{12} - \frac{1}{2}E_8$ are as follows:

	METHOD I	METHOD II
Intercept	5.895 ± 0.090	6.106 ± 0.085
$P_{12}/P_8^{\frac{1}{2}} \times 10^3$	1.5 ± 0.4	2.5 ± 0.5
Slope	2.148 ± 0.044	− 2.230 ± 0.040
$E_{12} - \frac{1}{2}E_8$, kcal.	9.8 ± 0.2	10.2 ± 0.2

The results given by the two methods of analysis are in good agreement.

The amount of CD_2H_2 formed in these experiments, obtained by subtracting the total percentage of CD_4 and CD_3H from 100, is practically constant at 8.2%.

TABLE V
THE PHOTOLYSIS OF *d*-ACETONE IN PRESENCE OF HYDROGEN

Run	Temp., °K.	Acetone concentration molecules per cc. × 10^{-18}	Hydrogen concentration molecules per cc. × 10^{-18}	Time (sec.)	$\frac{\%CD_3H}{\%CD_4}$	$\frac{\%C_2D_6}{\text{Total ethane}}$	Products, molecules/cc./sec. × 10^{-12}				$\frac{k_{12}}{k_8^{1/2}} \times 10^{13}$	
							CO	CD_4	CD_3H	C_2D_6	Method I	Method II
55	407	2.33	1.21	1800	56.3/36.2	95.1	53.1	2.09	3.59	43.0	4.39	3.96
65	433	2.16	1.14	1800	56.8/33.8	95.8	—	4.14	6.16	40.9	8.17	9.16
63	459	2.03	1.07	1200	56.7/35.1	95.0	56.8	7.34	11.2	36.3	16.6	18.5
61	484	1.91	0.96	1200	56.3/36.5	95.1	56.5	11.3	14.3	29.1	26.4	32.7
59	530	1.72	0.89	1260	55.6/36.5	92.6	58.7	20.4	27.3	17.5	70.5	80.2
57	570	1.65	0.84	1830	52.6/38.6	88.5	57.7	28.6	36.9	9.0	139	148

TABLE VI
THE PHOTOLYSIS OF *d*-ACETONE IN PRESENCE OF HYDROGEN AND CARBON DIOXIDE

Run	Temp., °K.	Pressure, cm.			% CD_3H	% CD_4	$\frac{k_{12}}{k_8^{1/2}} \times 10^{13}$, Method II
		d-Ac	H_2	CO_2			
40	405	9.77	5.06	0	59.8	27.9	3.5
50	413	9.97	4.97	10.5	57.6	28.5	4.6
53	408	10.00	5.31	20.2	57.5	29.8	3.3
49	410	9.97	10.33	20.0	—	—	3.5
45	571	10.13	4.41	0	52.4	36.5	168
52	569	10.02	4.79	10.5	53.0	34.8	157

This is virtually all due to reaction (13), since the amount formed in the photolysis of *d*-acetone alone was undetectably small. We have now

$$\frac{k_{13}}{k_{12}} = \frac{R_{CD_2H_2}}{R_{CD_3H}} \times \frac{[CD_3]}{[CD_2H]} = \frac{8.2}{55.7} \times \frac{95.8}{3.4} = 4.1\,.$$

Averaged values for the percentages of methane have been used since the temperature coefficient is evidently too small to determine from these measurements. Using results obtained from the less highly deuterated acetone, the ratio $R_{CD_2H_2}/R_{CD_3H}$, again temperature-independent within the limits of accuracy, was found to be 15.0/71.8 for 20 cm. hydrogen pressure and 12.0/57.5 for 5 cm. hydrogen pressure. This gives k_{13}/k_{12} the value $0.21 \times 92.35/6.7 = 2.9$.

Preliminary experiments with the first sample of acetone yielded evidence on the problem, mentioned in the Introduction, of the fate of the H-atom resulting from the reaction under consideration. It has usually been assumed that this atom would be removed by reaction with an acetone molecule rather than by combination with a methyl radical since the latter reaction seems likely to require a third body. To check this, the photolysis was performed in the presence of carbon dioxide, and the methane composition determined by mass spectrometry. The results, which are given in Table VI, show no increase in the proportion of CD_3H or in the value of $k_{12}/k_8^{\frac{1}{2}}$, indicating that the combination of H-atoms with CD_3 radicals does not occur to any important extent.

6. *The Photolysis of d-Acetone in the Presence of Deuterium*

Since the deuterium used contained 5% HD, fully deuterated methane could be formed by the following two reactions:

$$CD_3 + D_2 \rightarrow CD_4 + D \tag{14}$$

$$CD_3 + HD \rightarrow CD_4 + H \tag{15}$$

as well as by reaction (9) above. Evidently the error will not be great if we assume $k_{15} = k_{14}$, giving

$$\frac{k_{14}}{k_8^{\frac{1}{2}}} = \frac{(R_{CD_4})\text{ total} - (R_{CD_4})_9}{R^{\frac{1}{2}}_{C_2D_6} \times \{[D_2] + [HD]\}}\,.$$

Mass spectrometric analysis was used to determine the percentages of fully deuterated material in the products. The results are presented in Table VII.

The Arrhenius plot of these results, which is shown in Fig. 1 (closed triangles), is given by

$$13 + \log\frac{k_{14}}{k_8^{\frac{1}{2}}} = 5.869 - 2.376\frac{10^3}{T}\,,$$

the standard errors for intercept and slope being ±0.130 and ±0.061 respectively. The corresponding value of $P_{14}/P_8^{\frac{1}{2}}$ is $2.0 \pm 0.6\,.\,10^{-3}$, and of $E_{14} - \frac{1}{2}E_8$, 10.9 ± 0.3 kcal.

The methane formed in these experiments was composed of CD_4 and CD_3H, the amount of CD_2H_2 being undetectably small. Assigning k_{16} to the reaction

$$CD_2H + D_2 \rightarrow CD_3H + D \tag{16}$$

and using the average value of the methane composition we have

TABLE VII

THE PHOTOLYSIS OF *d*-ACETONE IN PRESENCE OF DEUTERIUM

Run	Temp.,°K.	Acetone concentration molecules/cc. × 10^{-18}	Deuterium concentration molecules/cc. × 10^{-18}	Time (sec.)	% CD_4	% C_2D_6	Products, molecules/cc./sec. × 10^{12}			$\frac{k_{14}}{k_8^{1/2}} \times 10^{13}$
							CO	CD_4	C_2D_6	
66	412	2.30	2.30	1800	88.8	95.7	55.4	4.75	47.3	1.40
67	432	2.11	2.23	1800	92.0	95.6	—	7.10	42.4	2.13
68	458	1.98	2.16	1800	92.0	95.5	54.3	13.6	39.2	4.69
71	481	1.95	2.05	1200	92.6	95.0	58.3	21.7	34.1	8.40
70	514	1.79	1.93	1200	92.4	94.4	60.1	35.6	25.7	17.1
69	567	1.64	1.75	1200	92.2	92.4	59.2	61.2	11.9	50.2

TABLE VIII

THE REACTIONS OF CH_3 AND CD_3 RADICALS WITH HYDROGEN, DEUTERIUM, AND THE PARENT ACETONE

Reaction	$\frac{k_A}{k_B^{1/2}} \times 10^{13}$, cc.$^{1/2}$ molecules$^{-1/2}$ sec.$^{-1/2}$			$\frac{P_A}{P_B^{1/2}} \times 10^3$	$E_A - \frac{1}{2}E_B$, kcal.
	130°C.	210°C.	290°C.		
$CH_3 + CH_3.CO.CH_3$	5.2	37	151	1.9 ± 0.3	9.5 ± 0.1
$CH_3 + H_2$	3.3	22	87	0.7 ± 0.2	9.2 ± 0.3
$CH_3 + D_2$	0.6	6.6	37	3.5 ± 0.5	11.7 ± 0.1
$CD_3 + CD_3.CO.CD_3$	1.2	10.7	51	1.8 ± 0.5	10.6 ± 0.3
$CD_3 + H_2$	3.7	31	140	2.5 ± 0.5	10.2 ± 0.2
$CD_3 + D_2$	0.9	8.9	46	2.0 ± 0.6	10.9 ± 0.3

$$\frac{k_{16}}{k_{14}} = \frac{R_{CD_3H}}{R_{CD_4}} \times \frac{[CD_3]}{[CD_2H]} = \frac{8.0}{92.0} \times \frac{95.8}{3.4} = 2.5.$$

The values of the ratios k_{16}/k_{14} and k_{13}/k_{12} indicate that CD_2H radicals react somewhat faster than CD_3 radicals with H_2 and with D_2. This is surprising, since the ratios for CH_3/CD_3 have been accurately measured and are definitely slightly less than unity. This suggests that CD_2H radicals react somewhat faster than either CH_3 or CD_3. The ratios for CD_2H/CD_3 are, of course, very rough since they involve the values of R_{CD_3H} and of $[CD_2H]$, both of which are small and cannot be determined with high accuracy. It does, however, appear that the ratios are significantly greater than unity.

DISCUSSION

The results are summarized in Table VIII. k_A, E_A, and P_A refer to the reaction between the methyl radical and the molecule in question and k_B, E_B, and P_B to the combination of the two methyl radicals.

Recent work on the combination of CH_3 radicals (6, 4, 9, 10, 5) indicates that median values for P_B and E_B can be accepted as ≈ 0.3 and zero respectively, and these values are no doubt valid also for the combination of CD_3 radicals. The figures in the last column of Table VIII can therefore each be taken as the actual energy of activation of the reaction in question, and the absolute steric factors can be obtained from the figures in the preceding column by dividing throughout by ≈ 2.

The values of P_A and E_A for the reactions of CH_3 radicals with hydrogen and deuterium differ appreciably from those recently published by Anderson, Davison, and Burton (1). However, Wijnen (19) has shown that a recalculation of their data gives results in reasonable agreement with the present values.

Isotope Effects

The standard errors quoted for the activation energies indicate their experimental precision, but, having regard to small uncertainties of mechanism, their true physical significance is probably better expressed by a general variance of ± 0.3 kcal. or more. It is clear that this variance, being fairly large relative to the experimental differences, precludes any very precise interpretation of the results. However, it seems possible to draw two general conclusions regarding isotope effects. First, comparing the reactions of the CH_3 radical with those of the CD_3 radical, there is no consistent evidence of any significant difference in their behavior. Second, comparing the reactions of hydrogen with those of deuterium, it will be seen that the latter require the higher activation energies, the average value of the difference being 1.6 ± 0.6 kcal. This is roughly in agreement with theory (2) which predicts that at low temperatures the difference in activation energies for reactions of isotopic molecules should approach the difference in their zero-point energies, which in this case is 1.8 kcal.

The values of both P and E for the reaction of CH_3 with D_2 are somewhat out of line with the others. It is probable that in this case errors in E and P compensate one another, and that the real values of both may be somewhat lower. All that can be said for the moment is that for both CH_3 and CD_3 the results can be expressed by the average values

$$\begin{array}{ll} CH_3(\text{or } CD_3) + H_2 & E = 9.7 \pm 0.6 \text{ kcal.} \\ CH_3(\text{or } CD_3) + D_2 & E = 11.3 \pm 0.6 \text{ kcal.} \end{array}$$

It is also instructive to consider the relative values of the rate constants at a given temperature, since here the results are not affected by compensating errors in E and P, and such relative values should therefore be somewhat more precise. Thus at 210° C., for the ratios of values of $k_A/k_B^{\frac{1}{2}}$ we have

$$\left.\begin{array}{l} \dfrac{CH_3 + H_2}{CH_3 + D_2} = 3.3 \\ \\ \dfrac{CD_3 + H_2}{CD_3 + D_2} = 3.5 \end{array}\right\} \text{Average} = 3.4, \qquad \left.\begin{array}{l} \dfrac{CH_3 + H_2}{CD_3 + H_2} = 0.71 \\ \\ \dfrac{CH_3 + D_2}{CD_3 + D_2} = 0.74 \end{array}\right\} \text{Average} = 0.7.$$

This gives further confirmation of the considerable effect of the substitution of D_2 for H_2 and the relatively small effect of the substitution of CD_3 for CH_3.

In one case information is available on the corresponding reaction of ethyl radicals, since Wijnen and Steacie (18) have investigated the reaction

$$C_2H_5 + D_2 \rightarrow C_2H_5D + D. \qquad (17)$$

Comparing this with

$$CH_3 + D_2 \rightarrow CH_3D + D \qquad (5)$$

we have

	E, kcal.	$P/P_B^{\frac{1}{2}}$
$C_2H_5 + D_2$	13.3 ± 0.5	10^{-3}
$CH_3 + D_2$	11.7 ± 0.3	3.5×10^{-3}.

There thus appears to be little difference in the steric factors of the two reactions. The fact that E_{16} is somewhat higher than E_5 is in line with the lower value of the bond dissociation energy of C_2H_6, which makes reaction (17) 3 or 4 kcal. more endothermic than (5).

In view of the fact that the value of the bond dissociation energy $D(CH_3\text{–}H)$ is well established at 101 ± 1 kcal. (7) and that $D(H\text{–}H)$ is accurately known, we may write

$$CH_3 + H_2 \underset{E_R}{\overset{E = 9.7 \pm 0.6 \text{ kcal.}}{\rightleftarrows}} CH_4 + H \; -2.2 \pm 1 \text{ kcal.}$$

Hence, for the activation energy of the reverse reaction

$$E_R = 9.7 - 2.2 = 7.5 \pm 1.6 \text{ kcal.}$$

Considerable work* has been done on this reaction. The experimental results are consistent with a value of about 13 ± 2 kcal. for the reaction if a steric factor of 0.1 is assumed. It has been suggested that the results which lead to a value of the temperature coefficient should not be taken too seriously (15) and that perhaps the best value should be taken as $E = 10.9$ kcal., $P = 10^{-2}$. In

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See Reference (14) for a discussion of the experimental results.

view of the fact that methane does not react with H-atoms under conditions where other hydrocarbons do so, it is very difficult to reconcile the results with a lower value of E than this unless P is also low. If we take 9 kcal. as the extreme upper limit of E_R calculated from the present work, we are still left with a discrepancy of about 2 kcal. which must be taken care of by the steric factor. It may, therefore, be concluded that the present results can only be reconciled with the results on the reaction of H-atoms with methane if the latter reaction has a steric factor of the order of 10^{-4}.

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