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The Reactions of Methyl Radicals with the Hydrogen Isotopes

E. Whittle* and E. W. R. Steacie
Division of Pure Chemistry, National Research Council, Ottawa, Canada

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The photolysis of acetone has been studied in the temperature range 130–420°C. Measurements have been made of the rates of most of the possible reactions of CH_3 and CD_3 radicals with hydrogen, deuterium, and deuterium hydride. The following activation energies for the abstraction of a hydrogen or deuterium atom have been found: CH_3+acetone, 9.7; CD_3+*d* acetone, 11.6; CH_3+D_2, 11.8; CD_3+H_2, 11.1; $CH_3+HD\rightarrow CH_4$, 10.0; $CH_3+HD\rightarrow CH_3D$, 11.3; $CD_3+HD\rightarrow CD_3H$, 10.7; $CD_3+HD\rightarrow CD_4$, 10.7 kcal. The steric factors are all of the order of 10^{-3}. The results are discussed in terms of isotope effects with particular reference to the deuterium hydride reactions.

INTRODUCTION

It is now well established that in the photolysis of acetone between 125°C and 300°C the formation of methane and ethane occurs in the following manner:

$$CH_3COCH_3\rightarrow 2CH_3+CO \quad (1)$$

$$CH_3+CH_3\rightarrow C_2H_6 \quad (2)$$

$$CH_3+CH_3COCH_3\rightarrow CH_4+CH_2COCH_3. \quad (3)$$

If the concentration of methyl radicals does not change during the reaction, it can be shown that

$$\frac{k_3}{k_2^{\frac{1}{2}}}=\frac{(R_{CH_4})_3}{R_{C_2H_6}{}^{\frac{1}{2}}[Ac]},$$

where $(R_{CH_4})_3$ is the rate of production of methane by reaction (3) and [Ac] is the concentration of acetone.

If the photolysis is carried out in the presence of hydrogen, methane is also produced by the reaction

$$CH_3+H_2\rightarrow CH_4+H \quad (4)$$

so that

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

$(R_{CH_4})_4$ is found from the equation

$$R_{CH_4}(\text{total})=(R_{CH_4})_4+(R_{CH_4})_3.$$

$(R_{CH_4})_3$ is calculated from data obtained for the photolysis of acetone alone. If deuterium is used we have, instead of reaction (4),

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

The rate of production of CH_3D can be found by subtracting $(R_{CH_4})_3$ from the total methane or can be estimated directly by means of mass spectrometric analysis, in which case

$$\frac{k_5}{k_2^{\frac{1}{2}}}=\frac{k_3}{k_2^{\frac{1}{2}}}\cdot\frac{R_{CH_3D}}{R_{CH_4}}\cdot\frac{[Ac]}{[D_2]}.$$

The two procedures will henceforth be called Method I and Method II, respectively, and should not be confused with the two methods referred to by Trotman-Dickenson and Steacie.[1] The Method I of these authors is identical with that used here, but their Method II refers to the use of heavy acetone instead of ordinary acetone. The reactions mentioned above have been studied by Majury and Steacie,[2] and we have extended their work and also studied the reactions of deuterium hydride. In this case the methyl radical may react in two ways,

$$CH_3+HD\rightarrow CH_4+D \quad (6)$$

$$CH_3+HD\rightarrow CH_3D+H. \quad (7)$$

$(R_{CH_3D})_7$ is found directly by mass spectrometric analysis and $(R_{CH_4})_6$ is obtained by Method I.

Materials

The purification of the acetone and preparation of the deuterated acetone have been described previously.[2] The composition of the latter was determined by the mass spectrometer with the following results:

93.7 percent C_2D_6CO, 3.5 percent C_2D_5HCO, 2.8 percent $C_2D_4H_2CO$.

Commercial cylinder hydrogen and deuterium were purified by passage through a palladium thimble. The deuterium contained 5 percent HD. The deuterium hydride was prepared from lithium aluminum hydride and heavy water as described by Fookson, Pomerantz,

Table I. The photolysis of acetone at high temperatures.

Run	Temp °K	Time (sec)	Molecules acetone/cc $\times 10^{-18}$	Products in molecules/cc/sec $\times 10^{-13}$ CO	CH_4	C_2 fraction	% C_2H_6	% C_2H_4
100	558	1200	1.78	7.40	8.75	1.04	100	0
101	600	1230	1.64	7.68	10.4	0.556	67	33
102	628	1200	1.52	8.61	12.0	0.530	···	···
103	662	1200	1.48	9.79	14.0	0.630	···	···
104	688	905	1.42	11.0	16.5	1.00	20	80

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* National Research Council of Canada Postdoctorate Fellow, 1951–1952.

[1] A. F. Trotman-Dickenson and E. W. R. Steacie, J. Chem. Phys. **19**, 163 (1951).

[2] T. G. Majury and E. W. R. Steacie, Disc. Faraday Soc. (to be published); Can. J. Chem. **30**, 800 (1952).

TABLE II. The photolysis of acetone in the presence of deuterium.

Run	Temp °K	Time (sec)	Molecules acetone/cc $\times 10^{-18}$	Molecules D_2/cc $\times 10^{-12}$	Molecules/cc/sec $\times 10^{-13}$ CO	Methane	C_2H_6	$\frac{CH_3D}{CH_4}$	$k_5/k_2^{\frac{1}{2}} \times 10^{13}$ Method I	Method II
	10 cm acetone		5 cm deuterium							
16	411	1800	2.33	1.16	5.62	1.19	4.41	0.0622		0.843
15	413	1800	2.28	1.16	5.86	1.27	4.63	0.0635		0.891
17	450	1800	2.15	1.09	5.55	2.48	3.33	0.0816		3.07
18	480	1800	2.04	1.16	5.62	3.95	2.40	0.108		7.09
19	522	1800	1.85	0.914	5.85	5.95	1.24	0.102		19.7
20	522	1800	1.95	0.972	5.96	6.49	1.16	0.104		17.8
21	563	1800	1.81	0.776	5.81	7.38	—	0.107		40.7
	10 cm acetone		20 cm deuterium							
27	410	1800	2.38	4.80	5.25	1.38	3.92	0.266	1.15	0.917
26	411	1800	2.35	4.80	7.46	1.40	4.00	0.231	1.10	0.812
25	462	1740	2.05	4.30	7.15	3.62	2.32	0.331	4.73	4.22
24	512	1800	1.89	3.65	6.92	5.92	0.985	0.411	13.7	15.6
22	564	1800	1.74	3.45	6.82	7.44	0.494	0.599	...	48.8
	5 cm acetone		10 cm deuterium							
32	408	1800	1.15	2.42	3.26	0.503	2.51	0.262	0.781	0.882
28	409	1800	1.17	2.38	3.22	0.513	2.61	0.239	0.892	0.852
29	456	1800	1.08	2.12	3.24	1.40	1.87	0.352	3.01	4.46
37	505	1800	0.984	1.96	3.38	2.81	0.978	0.383	11.2	13.3
30	508	1830	0.936	1.88	3.36	2.91	1.01	0.431	11.6	15.9
31	560	1800	0.886	1.74	3.29	4.22	0.378	0.515	33.4	46.9

and Rich.[3] Several samples were made and the average composition was found to be 94 percent HD, 4 percent H_2, and 2 percent D_2.

EXPERIMENTAL

Details of the apparatus and method of analysis have been given previously.[2] Most of the large excess of hydrogen was removed from the gaseous reaction products by compression of the mixture on to a palladium thimble at 370°C. In the experiments with acetone plus deuterium, one analysis (run 37) was made using liquid hydrogen to condense all the gases but deuterium, which was then pumped off. No change in the results was observed.

The mass spectrometer analyses were done under the direction of Dr. Lossing of these laboratories. The analyses for the $CD_4-CD_3H-CD_2H_2$ mixtures were computed assuming equal sensitivities for the isotopic molecules and using the spectra of the deuterated methanes given by Dibeler and Mohler.[4]

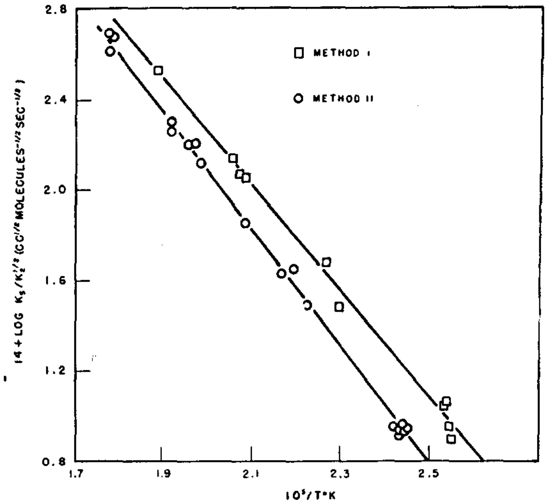

FIG. 1. Acetone plus deuterium. To avoid confusion the values of $10^3/T$ have been increased by 0.1 unit for the points marked □.

Nearly all the experiments were carried out to a 5 percent conversion of acetone or less. The activation energies were obtained directly by Arrhenius plots. The steric factors were then calculated by subtraction of $\frac{1}{2}RT$ from the activation energies, the mean temperature being taken as 490°K. The collision diameters used for the various molecules were acetone 5.5A, CH_3 3.5A, and H_2 2.8A.

The Photolysis of Acetone

The photolysis of acetone was examined in the temperature range 135–300°C and at pressures of 20 and 100 mm. The results obtained were in full agreement with those of previous workers; the value of $E_3-\frac{1}{2}E_2$ was found to be 9.7 kcal.

The photolysis was also studied in the temperature range 300–420°C, since very few experiments have been carried out in this region. The results are given in Table I. It was found that ethylene begins to form at temperatures higher than 300°C, and at 420°C it accounts for almost all the C_2 hydrocarbon produced. The ethylene could be formed by the photolysis of ketene, since the latter was found by Ferris and Haynes[5] in the high temperature photolysis of acetone. It seems clear that the photolysis becomes complicated above 300°C and that experiments which utilize acetone as a source of methyl radicals should preferably be carried out below this temperature.

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[3] Fookson, Pomerantz, and Rich, J. Research Natl. Bur. Standards **47**, 31 (1951).

[4] V. H. Dibeler and F. L. Mohler, J. Research Natl. Bur. Standards **45**, 441 (1950).

[5] R. C. Ferris and W. S. Haynes, J. Am. Chem. Soc. **72**, 893 (1950).

The Photolysis of *d* Acetone

The principal reactions occurring during the photolysis of *d*-acetone are

$$CD_3+CD_3\rightarrow C_2D_6 \qquad (8)$$

$$CD_3+CD_3\cdot CO\cdot CD_3\rightarrow CD_4+CD_2\cdot CO\cdot CD_3. \qquad (9)$$

The photolysis has been studied by Majury and Steacie[2] who found that $E_9-\frac{1}{2}E_8=10.6$ kcal. We have performed further experiments using a new sample of *d*-acetone and from an Arrhenius plot it is found that

$$13+\log\frac{k_9}{k_8^{\frac{1}{2}}}=6.20-\frac{2530}{T}.$$

It follows that $E_9-\frac{1}{2}E_8=11.6$ kcal and $P_9/P_8^{\frac{1}{2}}=3.3\times10^{-3}$, where P denotes the steric factor for a reaction.

The value of $E_9-\frac{1}{2}E_8=10.6$ kcal given by Majury and Steacie was based on an Arrhenius plot which tended to curve at lower temperatures. In the present work no such curvature was obtained, and so the higher value is felt to be somewhat more reliable. In the upper part of the temperature range, both sets of results agreed very well.

The Photolysis of Acetone with Deuterium

It was mentioned in the introduction that the rate of production of CH_3D by the reaction

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

can be determined by two methods. The results calculated by the two methods together with the experimental data obtained are given in Table II and are shown graphically in Fig. 1. A correction has been made for the presence of 5 percent HD in the deuterium. No CH_2D_2 could be detected. In the experiments in which 10 cm acetone and 5 cm D_2 were used, the calculation by Method I has not been given since the results are quite unreliable owing to the fact that the CH_4 produced by reaction (3) represents about 90 percent of the total methane.

The lines obtained from the Arrhenius plots have the following equations:

Method I

$$13+\log\frac{k_5}{k_2^{\frac{1}{2}}}=5.69-\frac{2340}{T}$$

$$E_5-\tfrac{1}{2}E_2=10.7\text{ kcal}$$

$$P_5/P_2^{\frac{1}{2}}=1.0\times10^{-3}$$

Method II

$$13+\log\frac{k_5}{k_2^{\frac{1}{2}}}=6.22-\frac{2570}{T}$$

$$E_5-\tfrac{1}{2}E_2=11.8\text{ kcal}$$

$$P_5/P_2^{\frac{1}{2}}=3.5\times10^{-3}$$

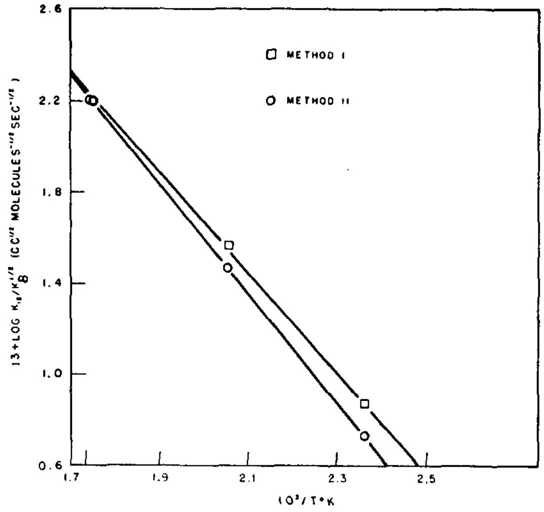

FIG. 2. *d*-acetone plus hydrogen.

The value of $E_5-\frac{1}{2}E_2$ found by Method II is identical with that found by Majury and Steacie.[2]

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

The methane formed in this system consists of CD_4 from reaction (9) and CD_3H from the reaction

$$CD_3+H_2\rightarrow CD_3H+H \qquad (10)$$

so that the rate constant can again be calculated in two ways. The results are given in Table III, and the Arrhenius plots are shown in Fig. 2. The equations of the lines are

Method I

$$13+\log\frac{k_{10}}{k_8^{\frac{1}{2}}}=6.10-\frac{2220}{T}$$

$$E_{10}-\tfrac{1}{2}E_8=10.1\text{ kcal}$$

$$P_{10}/P_8^{\frac{1}{2}}=1.84\times10^{-3}$$

Method II

$$13+\log\frac{k_{10}}{k_8^{\frac{1}{2}}}=6.44-\frac{2420}{T}$$

$$E_{10}-\tfrac{1}{2}E_8=11.1\text{ kcal}$$

$$P_{10}/P_8^{\frac{1}{2}}=4.10\times10^{-3}$$

We have described how the rate constants for the reactions CH_3+D_2 and CD_3+H_2 may be calculated by two methods. In both cases the use of Method I leads to lower steric factors and activation energies than Method II. It seems likely that Method II is the more reliable since it depends on a direct determination of the CH_3D/CH_4 ratio, whereas the ratio is calculated

TABLE III. The photolysis of *d*-acetone in the presence of hydrogen.

Run	Temp °K	Time sec	Molecules *d* acetone/cc $\times10^{-18}$	Molecules H_2/cc $\times10^{-18}$	Molecules/cc/sec $\times10^{-13}$ CO	methane	ethane	% CD_4	% CD_3H	% CD_2H_2	% C_2D_6 in ethane	$k_{10}/k_8^{\frac{1}{2}}\times10^{13}$ Method I	Method II
10 cm *d*-acetone, 10 cm H_2													
75	424	1800	2.27	2.37	3.48	1.18	2.59	21.1	69.9	9.1	96.3	7.22	5.34
76	487	1800	1.95	2.07	3.52	3.62	1.28	21.9	68.5	9.7	95.8	36.8	29.4
77	573	1890	1.60	1.77	3.73	···	0.294	23.4	67.4	9.2	···	···	159
78	570	1862	1.58	1.76	3.63	6.16	0.272	24.7	73.2	2.1	···	158	157

TABLE IV. The photolysis of acetone in the presence of deuterium hydride.

Run	Temp °K	Time sec	Molecules acetone/cc $\times 10^{-18}$	Molecules HD/cc $\times 10^{-18}$	Molecules/cc/sec $\times 10^{-13}$ CO	methane	C_2H_6	$\frac{CH_3D}{CH_4}$	$\frac{k_6}{k_2^{1/2}} \times 10^{13}$	$\frac{k_7}{k_2^{1/2}} \times 10^{13}$
	10 cm acetone, 10 cm HD									
43	408	1200	2.42	2.40	5.60	1.48	4.09	0.0624		0.531
86	418	1200	2.30	2.34	3.39	1.27	2.23	0.0718		0.812
47	424	1200	2.30	2.35	4.45	1.70	2.85	0.0722		0.988
45	454	1200	2.18	2.21	4.70	2.91	2.19	0.0805		2.13
51	469	1200	1.02	1.01	2.43	1.59	1.07	0.0816		3.93
50	472	1200	2.11	2.09	4.36	3.69	1.34	0.0906		4.33
52	474	1200	2.18	1.02	2.57	2.06	0.927	0.147		4.29
53	478	1200	2.03	2.03	4.11	3.66	1.17	0.0918		4.79
84	503	1214	1.94	1.92	3.51	4.07	0.626	0.0946		7.68
41	503	1200	1.95	1.83	5.77	5.49	1.20	0.0978		8.03
48	527	900	1.84	1.89	4.42	5.78	0.533	0.108		14.0
49	564	1200	1.71	1.66	4.33	6.58	0.268	0.130		30.2
42	569	1200	1.72	1.57	6.10	8.00	0.405	0.114		27.1
88	569	1200	1.73	1.70	3.64	5.56	0.178	0.113		26.2
	4 cm acetone 16 cm HD									
80	413	1800	0.942	3.67	1.81	0.572	1.24	0.183	1.51	0.714
87	414	2430	0.937	3.61	1.76	0.585	1.23	0.180	1.66	0.747
107	442	1800	0.860	3.50	3.63	1.56	2.27	0.226	3.21	1.82
90	471	1835	0.819	3.38	1.66	1.47	0.535	0.241	6.60	3.87
85	504	2400	0.756	3.06	1.78	2.17	0.315	0.254	15.2	8.54
96	506	2400	0.776	3.13	1.54	1.95	0.230	0.239	15.7	8.27
91	538	1800	0.730	2.89	1.94	2.62	0.166	0.270	23.9	16.0
89	569	2400	0.677	2.67	1.88	2.97	0.112	0.287	30.9	24.8

indirectly in Method I. The difference in the results of the two methods implies that the data obtained on the rate of reaction (3) from the photolysis of acetone alone are not strictly correct if other substances are present. It is known that the ratio $k_3/k_2^{1/2}$ varies slightly with pressure and this is one possible explanation of the discrepancy.

In the determination of the rate constant for the reaction

$$CH_3 + HD \rightarrow CH_4 + D \qquad (6)$$

we wish to know $(R_{CH_4})_3$ as accurately as possible in order to calculate the value of $(R_{CH_4})_6$. We therefore need to know the rate of reaction (3) in the presence of deuterium hydride. It is reasonable to suppose that, if the acetone photolysis is affected slightly by the presence of deuterium, it should be changed to about the same extent by the presence of deuterium hydride. From experiments on the photolysis of acetone with deuterium, we can find $(R_{CH_4})_3$ by mass spectrometric analysis and hence carry out an Arrhenius plot of $k_3/k_2^{1/2}$. Because of the discrepancy between Method I and Method II, the line obtained with a given pressure of acetone mixed with deuterium is not the same as the line obtained from acetone alone. Expressing the equations in the form $13 + \log k_3/k_2^{1/2} = A - B/T$, we have

	A	B
5 cm acetone	6.02	2120
5 cm acetone+10 cm D_2	5.92	2080
10 cm acetone	5.96	2110
10 cm acetone+20 cm D_2	5.72	1990

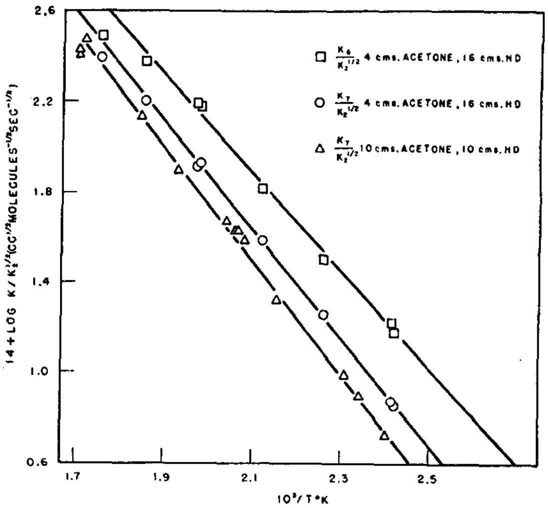

FIG. 3. Acetone plus deuterium hydride. The values of $10^3/T$ have been decreased by 0.05 unit for the points marked $\triangle$.

The same procedure has been used with *d*-acetone, but in this case the results obtained in the presence of hydrogen are used. The equations are

$$13 + \log \frac{k_9}{k_8^{1/2}} = 6.20 - \frac{2530}{T} \quad \text{10 cm } d\text{-acetone,}$$

$$13 + \log \frac{k_9}{k_8^{1/2}} = 5.88 - \frac{2350}{T} \quad \text{10 cm } d\text{-acetone} + \text{10 cm } H_2.$$

The corrected data given here have been used in the calculation of the results of the deuterium hydride experiments.

The Photolysis of Acetone in the Presence of Deuterium Hydride

In this case, methane is produced by reaction (3) and by two other processes which are

$$CH_3+HD \rightarrow CH_4+D \qquad (6)$$

$$CH_3+HD \rightarrow CH_3D+H. \qquad (7)$$

The results of the experiments are given in Table IV. No CH_2D_2 was found in the methane. The rate of production of CH_3D is determined unambiguously by mass spectrometer while $(R_{CH_4})_6$ is obtained by subtracting $(R_{CH_4})_3$ from the total CH_4 which is also found by mass spectrometer. The correction $(R_{CH_4})_3$ is quite large and, as expected, the values of $k_6/k_2^{\frac{1}{2}}$ show considerable scatter. Corrections have been applied for the products of the reaction of methyl radicals with the small amounts of H_2 and D_2 present in the HD.

Two series of experiments were carried out, one using 10 cm acetone and 10 cm HD, and the other with 4 cm acetone and 16 cm HD. From the first series only the rate constants for reaction (7) have been calculated, since $(R_{CH_4})_6$ is small and cannot be reliably estimated. The Arrhenius plots are shown in Fig. 3, and the equations of the lines are given below. Using 10 cm acetone +10 cm HD

$$13+\log\frac{k_7}{k_2^{\frac{1}{2}}}=5.92-\frac{2520}{T} \qquad E_7-\tfrac{1}{2}E_2=11.5\text{ kcal} \qquad \frac{P_7}{P_2^{\frac{1}{2}}}=1.53\times10^{-3}. \qquad (8)$$

Using 4 cm acetone and 16 cm HD,

$$13+\log\frac{k_6}{k_2^{\frac{1}{2}}}=5.48-\frac{2180}{T} \qquad E_6-\tfrac{1}{2}E_2=10.0\text{ kcal} \qquad P_6/P_2^{\frac{1}{2}}=0.55\times10^{-3} \qquad (9)$$

$$13+\log\frac{k_7}{k_2^{\frac{1}{2}}}=5.73-\frac{2430}{T} \qquad E_7-\tfrac{1}{2}E_2=11.1\text{ kcal} \qquad P_7/P_2^{\frac{1}{2}}=0.98\times10^{-3}. \qquad (10)$$

The Photolysis of *d*-Acetone in the Presence of Deuterium Hydride

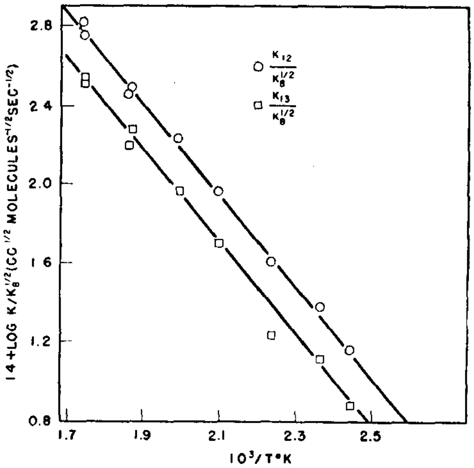

FIG. 4. *d*-acetone plus deuterium hydride.

The photolysis produces methane containing CD_4, CD_3H, and CD_2H_2. The reactions forming CD_4 and CD_3H are (9), and

$$CD_2H+CD_3\cdot CO\cdot CD_3 \rightarrow CD_3H+CD_2\cdot CO\cdot CD_3 \qquad (11)$$

$$CD_3+HD \rightarrow CD_3H+D \qquad (12)$$

$$CD_3+HD \rightarrow CD_4+H. \qquad (13)$$

$(R_{CD_4})_{13}$ is calculated in the usual way using Method I. $(R_{CD_3H})_{12}$ is found by subtracting from the total CD_3H the small amount formed by reaction (11) which can easily be estimated. The experimental results are given in Table V, and the Arrhenius plots for $k_{12}/k_8^{\frac{1}{2}}$ and $k_{13}/k_8^{\frac{1}{2}}$ are shown in Fig. 4. From the graphs it is found that

$$13+\log\frac{k_{12}}{k_8^{\frac{1}{2}}}=5.86-\frac{2340}{T} \qquad 13+\log\frac{k_{13}}{k_8^{\frac{1}{2}}}=5.63-\frac{2340}{T}$$

$$E_{12}-\tfrac{1}{2}E_8=10.7\text{ kcal} \qquad E_{13}-\tfrac{1}{2}E_8=10.7\text{ kcal}$$

$$P_{12}/P_8^{\frac{1}{2}}=1.26\times10^{-3} \qquad P_{13}/P_8^{\frac{1}{2}}=0.75\times10^{-3}.$$

The CD_2H_2 is produced by the reaction

$$CD_2H+HD \rightarrow CD_2H_2+D. \qquad (14)$$

The relative rates of reactions (12) and (14) are given by

$$\frac{(R_{CD_3H})_{12}}{(R_{CD_2H_2})_{14}}=\frac{k_{12}[CD_3][HD]}{k_{14}[CD_2H][HD]}.$$

TABLE V. The photolysis of *d*-acetone in the presence of deuterium hydride.

Run	Temp °K	Time sec	Molecules *d* acetone/cc $\times10^{-18}$	Molecules HD/cc $\times10^{-18}$	Molecules/cc/sec $\times10^{-13}$ CO	methane	ethane	% CD_4	% CD_3H	% CD_2H_2	% C_2D_6 in ethane	$\frac{k_{12}}{k_8^{\frac{1}{2}}}\times10^{13}$	$\frac{k_{13}}{k_8^{\frac{1}{2}}}\times10^{13}$
10 cm *d* acetone, 10 cm HD													
106	410	1205	2.33	2.45	6.99	0.783	6.28	50.0	43.3	6.7	—	1.44	0.757
74	423	1800	2.21	2.17	3.94	0.752	2.74	52.1	44.9	2.9	96.5	2.38	1.30
64	448	1200	2.14	2.21	3.76	1.35	2.94	50.9	42.2	6.9	96.6	4.02	1.70
65	477	1200	1.99	1.93	4.00	2.51	2.28	52.3	40.7	7.0	96.5	9.08	4.98
67	502	1229	1.88	1.90	3.89	3.53	1.52	51.5	41.7	6.8	96.2	17.1	9.20
69	534	1200	1.74	1.72	4.27	4.89	1.19	54.4	39.8	5.8	95.7	31.1	19.0
72	537	1860	1.71	1.73	3.97	4.22	0.830	54.9	40.0	5.1	95.0	28.7	15.7
71	572	1200	1.63	1.64	4.04	5.96	0.423	52.1	42.0	5.9	94.2	66.5	34.7
73	572	1800	1.65	1.61	4.00	5.43	0.416	55.4	39.2	5.5	93.0	56.7	32.7

TABLE VI.

		$k_A/k_B^{\frac{1}{2}}\times 10^{13}$			$P_A/P_B^{\frac{1}{2}}$	$E_A-\frac{1}{2}E_B$
	Reaction	130°C	210°C	290°C	$\times 10^3$	kcal
(3)	$CH_3+CH_3COCH_3$	5.35	39.4	164	1.8	9.7
(9)	$CD_3+CD_3COCD_3$	0.822	9.04	50.2	3.3	11.6
(5)	$CH_3+D_2\rightarrow CH_3D$	0.689	7.85	44.9	3.5	11.8
(4)[a]	CH_3+H_2	3.3	22	87	1.6	10.0
(10)	$CD_3+H_2\rightarrow CD_3H$	2.68	26.5	137	4.1	11.1
[b]	CD_3+D_2	0.9	8.9	46	2.0	10.9
(6)	$CH_3+HD\rightarrow CH_4$	1.16	9.12	40.0	0.55	10.0
(7)	$CH_3+HD\rightarrow CH_3D$	0.497	5.09	27.0	1.2	11.3
(12)	$CD_3+HD\rightarrow CD_3H$	1.15	10.4	51.2	1.3	10.7
(13)	$CD_3+HD\rightarrow CD_4$	0.655	6.00	29.3	0.75	10.7

[a] Majury and Steacie's value corrected as indicated below.
[b] Majury and Steacie's value.

From the ethane analysis we can estimate that $CD_3/CD_2H=95/5$ so that

$$\frac{k_{14}}{k_{12}}=\frac{6}{40}\times\frac{95}{5}\approx 2.5.$$

This result implies that CD_2H radicals abstract hydrogen from HD more readily than do CD_3 radicals provided that the rates of the recombination reactions

$$CD_3+CD_3\rightarrow C_2D_6$$

$$CD_3+CD_2H\rightarrow C_2D_5H$$

are not appreciably different. This enhanced reactivity of CD_2H radicals was also observed by Majury and Steacie, when hydrogen abstraction from the molecules H_2 and $CD_3\cdot CO\cdot CD_3$ was involved.

DISCUSSION

Before discussing the results which have been obtained, it is necessary to establish the validity of the reaction mechanism which has been assumed. In particular it is necessary to consider the possibility of exchange reactions. It is found that no exchange occurs if a mixture of D_2 and CH_4 is left in contact with a palladium thimble at 370°C for two hours or if the mixture is heated to 300°C in a furnace. Deuterium hydride rapidly equilibrates in contact with a hot palladium thimble but does not exchange with CH_4.

The fate of the hydrogen atoms produced by reactions such as (6) and (7) is of great importance. It is assumed that they are removed by the reactions

$$H+CH_3COCH_3\rightarrow H_2+CH_2COCH_3 \qquad (15)$$

$$D+CH_3COCH_3\rightarrow HD+CH_2COCH_3. \qquad (16)$$

The accumulation of H_2 from reaction (15) is prevented by the use of small conversions. The hydrogen atoms could also bring about equilibration of the HD if their stationary concentration were sufficiently high. This may actually occur to a small extent since the average composition of the gas before a run was 94 percent HD, 4 percent H_2, 2 percent D_2 and after a run was 90 percent HD, 8 percent H_2, and 2 percent D_2.

Serious complications would occur if the hydrogen atoms reacted with the radicals present; for example,

$$CH_3+D\rightarrow CH_2D+H \qquad (17)$$

$$CH_3+D\rightarrow CH_3D. \qquad (18)$$

If reaction (17) occurred, some of the CH_2D radicals produced would eventually form CH_3CH_2D, but no trace of this was found in experiments with acetone and D_2 or HD. The possibility of the occurrence of reaction (18) was considered by Majury and Steacie.[2] They suggested that the reaction would probably require a third body and demonstrated that no change occurred in the photolysis of *d* acetone with hydrogen if carbon dioxide were added. It is also possible to eliminate reaction (18) from considerations of the stationary concentrations of the species observed. We wish to prove that all the hydrogen atoms react with acetone rather than methyl radicals and therefore require the relative rates of the two processes. To take the most unfavorable case, it is assumed that reaction (18) occurs at every collision and does not require a third body. It is easily seen that

$$\frac{(R_{HD})_{16}}{(R_{CH_3D})_{18}}=\frac{k_{16}[Ac]}{k_{18}[CH_3]}.$$

The value of $[CH_3]$ can be roughly estimated from the fact that $R_{C_2H_6}=k_2[CH_3]^2$, and recent work indicates that k_2 is of the order of 2×10^{-11} cc/molecule/sec. k_{16} can be estimated from the data of Harris and Steacie[6] assuming a low steric factor, since this is least favorable to our argument. It is found that at 130°C, $R_{16}/R_{18}\approx 300$ and at 300°C the ratio is several thousand. Although this calculation is only approximate, it shows fairly conclusively that reaction (18) does not occur.

The results obtained for the various reactions are summarized in Table VI together with additional data obtained by Majury and Steacie. k_A, E_A, and P_A refer to the reaction between a methyl radical and the molecules concerned, while k_B, A_B, and P_B refer to the recombination of methyl radicals.

All the activation energies which have been measured are found to lie within the range 10–12 kcal, and the steric factors are of the order of 10^{-3}. There has recently been considerable discussion[7] as to whether the reaction of methyl radicals with hydrogen has an activation energy of about 14 kcal and a steric factor of 10^{-1} or an activation energy of about 10 kcal and a steric factor of about 10^{-3}. The latter value is favored by the present work. Majury and Steacie have measured the activation energy for the reaction $CH_3+H_2\rightarrow CH_4+H$ and obtained a value of 9.2 kcal. This is based on a Method I type of calculation, and consequently their results may perhaps be about 1 kcal low. A value of 10

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[6] G. M. Harris and E. W. R. Steacie, J. Chem. Phys. 13, 554 (1945).

[7] Discussions Faraday Soc. (to be published).

kcal would be more consistent with the present work, since it is unlikely that the two reactions CH_3+H_2 and CH_3+D_2 have a difference in activation energies which is greater than the difference between the zero-point energies of H_2 and D_2. If the activation energy of 10 kcal is accepted, then the value of $P_A/P_B^{\frac{1}{2}}$ becomes 1.6×10^{-3}.

Further evidence for an activation energy of 10 kcal is provided by the work of Phibbs and Darwent[8] on the photolysis of mercury dimethyl in the presence of hydrogen. From their results it is possible to plot $\log k_4/k_2^{\frac{1}{2}}$ against $1/T$ and thus correct for variations in the stationary concentration of methyl radicals. It is found that $E_4-\frac{1}{2}E_2=9.9$ kcal and $P_4/P_2^{\frac{1}{2}}=0.6\times 10^{-3}$, which are in excellent agreement with the data given in Table VI.

Majury and Steacie found that the rate constants for reactions involving methyl radicals and H_2 or D_2 were changed very little if CH_3 were replaced by CD_3. For example, the following ratios of rate constants at 210°C were found:

$$\frac{CH_3+H_2}{CD_3+H_2}=0.71 \qquad \frac{CH_3+D_2}{CD_3+D_2}=0.74.$$

We have observed a similar phenomenon in the case of deuterium hydride where the corresponding ratios are

$$\frac{CH_3+HD\rightarrow CH_4}{CD_3+HD\rightarrow CD_3H}=0.88 \qquad \frac{CH_3+HD\rightarrow CH_3D}{CD_3+HD\rightarrow CD_4}=0.85.$$

A comparison of the rates of the various deuterium hydride reactions reveals the interesting fact that hydrogen abstraction is about twice as rapid as deuterium abstraction. This is shown by the following ratios of rate constants at 210°C:

$$\frac{CH_3+HD\rightarrow CH_4}{CH_3+HD\rightarrow CH_3D}=1.73 \qquad \frac{CD_3+HD\rightarrow CD_3H}{CD_3+HD\rightarrow CD_4}=1.79.$$

A similar conclusion was reached by Farkas and Farkas[9] in their work on the reactions of hydrogen and deuterium atoms with the hydrogen isotopes.

In the case of CH_3 radicals this difference in rates of hydrogen and deuterium abstraction appears as a difference in the activation energies; if CD_3 radicals are used, we find different steric factors and identical activation energies. The discrepancy is probably due to experimental error, since it is unlikely that there is really such a difference in behavior of the two radicals. For this reason we have compared rate constants rather than activation energies or steric factors.

It is interesting to compare the rates of reactions (6) and (7) in terms of the transition state theory, since the treatment is simplified by the fact that the initial reactants are the same in each case. Some of the terms in the partition functions of the transition states CH_3-H-D and CH_3-D-H such as the translational contributions are also identical. In view of the large frequencies involved, the vibrational partition functions of the two complexes should be almost equal; if a difference does exist it should be in a direction favoring CH_3D formation. The rotational contributions of the two states, however, are not the same, since the moment of inertia of the structure $CH_3\cdots H\cdots D$ is obviously larger than that of $CH_3\cdots D\cdots H$. The ratio of the two moments can be calculated approximately by means of the transition state dimensions given by Glasstone, Laidler, and Eyring.[10] It is found that

$$\frac{I(CH_3\cdots H\cdots D)}{I(CH_3\cdots D\cdots H)}=1.5.$$

The ratio is surprisingly large and almost completely accounts for the preferential formation of CH_4.

These considerations suggest that the difference in rate constants for hydrogen and deuterium atom abstraction is mainly due to a difference in steric factor rather than activation energy. If this is so, it implies that the two transition states have almost identical zero-point energies.

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[8] M. K. Phibbs and B. de B. Darwent, Trans. Faraday Soc. **45**, 541 (1949).

[9] A. Farkas and L. Farkas, Proc. Roy. Soc. (London) **A152**, 124 (1935).

[10] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), p. 257.