molecule are small.[17] It is of interest in this connection to note the influence on *f*-values of the —N$(CH_3)_2$ group substituted at the 4-position in stilbene derivatives. Where comparison may be made between derivatives with and without this substituent, as in results reported in Table II, the Δf-values are independent of the presence of the —$N(CH_3)_2$ group. It follows, therefore, that this group also exerts a constant effect at the 4-position, in the presence or absence of a methyl substituent in ring B. (The effect of 4-$N(CH_3)_2$ in the presence of a methyl substituent in the same ring (A) cannot be evaluated without further data.)[18] The Δf_{av} value for 4-$N(CH_3)_2$, calculated excluding the small band discussed under Results, is +0.095 ($f_8 - f_1 = 0.100$; $f_{18} - f_6 = 0.090$; $f_{11} - f_4 = 0.090$; $f_{10} - f_3 = 0.095$). If this band is included the Δf_{av} value is +0.120, the difference being due to the greater intensity of the small band in basic stilbene derivatives, as noted before. It is apparent that even if this small band is excluded from consideration, the effect of the 4-$N(CH_3)_2$ group is much greater than that of a methyl group at the 4-position in stilbene, as would be expected on grounds of resonance theory.

Further experimental data are necessary before any conclusive rules could be made concerning the changes in *f*-values due to substitution in stilbene and its derivatives. Preliminary work on other alkyl derivatives of 4-dimethylaminostilbene suggests that an increasing *f*-decrement results from increase in bulk of an alkyl group substituted at the 2′-position. In addition, the substitution of an isopropyl group at the 4-position in stilbene or at the 4′-position in the basic stilbene causes a smaller *f*-increment than is the case with methyl substitution at these positions. This, together with a comparison of the effects in these compounds of methyl substitution at the 3-(or 3′-) position (no significant change in *f*), and the 4- (or 4′-) position (*f*-increment) indicates that the mesomeric effect of these groups is called into play to a greater extent than their inductive effect.

Thus, the results reported above suggest that careful measurement of *f*-values may prove a useful means of investigation of small degrees of steric hindrance to planarity and of other effects of substitution in these compounds.

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[17] See Note by J. R. Platt, THIS JOURNAL, **74**, 2376 (1952).

[18] NOTE ADDED TO PROOF.—The recently measured *f*-value for 2,2′-dimethylstilbene (0.645) allows this effect to be evaluated, *i.e.*, $f_{17} - 0.645 = +0.100$, which should be compared with the average value of +0.120 and indicates absence of interaction between 4-$N(CH_3)_2$ and a substituent in the same ring A.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Reaction of Methyl Radicals with Hydrogen and Deuterium[1,2]

BY SOL DAVISON[3] AND MILTON BURTON

Free methyl radicals produced by photolysis of acetone or acetaldehyde in presence of deuterium or mixtures of hydrogen and deuterium yield various ratios of CH_4 and CH_3D determined by competition for methyl radicals by the different compounds present. By this method the reaction between free methyl and molecular hydrogen is established as $CH_3 + H_2 \rightarrow CH_4 + H$. Separate studies with acetone and acetaldehyde combined with previous work by Trotman-Dickenson and Steacie, Rollefson and Grahame, and Dodd indicate an activation energy of the reaction of methyl with hydrogen >13 kcal. and a steric factor of the order of 10^{-2}. The similar reaction with deuterium has an activation energy ~1 kcal. greater.

1. Introduction

The reaction of free methyl radical and molecular hydrogen has been the subject of repeated experimental and theoretical investigation.[4] Activation energies given in the literature vary from an estimated low of 6–8 kcal. by Hartel and Polanyi[5] to an estimated high of 20 kcal. by F. O. Rice.[6] The tendency has been to favor a low activation energy, ~9 kcal., and a low steric factor,[7] $\sim 10^{-4}$. On the other hand, arguments have been offered that such a steric factor is much lower than that to be expected for simple free radical reactions.[8] The activation energy is not in good agreement with most recent information on bond strengths and activation energy of the reverse reaction. Calculations based on low values of activation energy led to the conclusion by Patat and Sachsse[9] that the Rice–Herzfeld free-radical chain theory[10] is unsatisfactory for the cases they examined.

The situation regarding this important elementary reaction has been so confusing that even the reality of the mechanism

$$CH_3 + H_2 \longrightarrow CH_4 + H \qquad (1)$$

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[1] Paper presented before Division of Petroleum Chemistry, American Chemical Society, Chicago, Ill., September, 1950.

[2] Abstract from a thesis submitted by Sol Davison to the Department of Chemistry of the University of Notre Dame in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Sinclair Research Fellow.

[4] *Cf.* R. D. Anderson, S. Davison and M. Burton, *Discussions Faraday Soc.*, **10**, 136 (1951), for a review of previous work.

[5] H. v. Hartel and M. Polanyi, *Z. physik. Chem.*, **B11**, 97 (1930).

[6] F. O. Rice, THIS JOURNAL, **56**, 488 (1934).

[7] *Cf.* E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946.

[8] M. G. Evans and M. Szwarc, *Trans. Faraday Soc.*, **45**, 940 (1949).

[9] D. Patat and H. Sachsse, *Z. physik Chem.*, **B31**, 105 (1936); F. Patat, *ibid.*, **B32**, 274, 294 (1936).

[10] F. O. Rice and K. F. Herzfeld, THIS JOURNAL, **56**, 284 (1934).

has been questioned and the suggestion has been made[11] that the mechanism is actually termolecular

$$CH_3 + H_2 + CH_3 \longrightarrow 2CH_4 \qquad (2)$$

and involves a persistent intermediate free radical complex CH_3–H_2, suggested by Gorin, Kauzman, Walter and Eyring.[12]

$$CH_3 + H_2 \longrightarrow CH_3\text{–}H_2 \qquad (3)$$

$$CH_3\text{–}H_2 + CH_3 \longrightarrow 2CH_4 \qquad (4)$$

New data reported herein confirm the reality of mechanism (1), lead to high activation energy and high steric factor, and indicate the applicability of the Rice–Herzfeld theory to the cases reported by Patat and Sachsse.

2. Theory of Experimental Approach

If reaction (1) is the correct mechanism of the reaction, free H atoms are produced. On the other hand, the termolecular mechanism does not involve production of hydrogen atoms.

If parent compound A is photolyzed (with resultant production of free methyl) in the presence of deuterium, mechanism (1) results in the sequence

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

$$D + A \longrightarrow HD + \text{residue} \qquad (6)$$

while no HD is produced if reactions

$$CH_3 + D_2 \longrightarrow CH_3\text{-}D_2 \qquad (7)$$

$$CH_3\text{-}D_2 + CH_3 \longrightarrow 2CH_3D \qquad (8)$$

occur. Thus, the ratio of products produced, $[HD]/[CH_3D]$, is a measure of the relative contributions of the two mechanisms. If the mechanism is (5), (6) exclusively, the ratio $[HD]/[CH_3D] = 1$.

According to this argument, the data presented later in this report indicate that (1) is the only important reaction between free methyl and hydrogen. The ensuant discussion consequently omits further consideration of the termolecular mechanism.

In addition to reactions (5) and (6) photolysis of A in presence of deuterium can result in the reaction

$$CH_3 + A \longrightarrow CH_4 + \text{residue} \qquad (9)$$

The rates of reactions (5) and (9) are

$$d[CH_3D]/dt = k_5[CH_3][D_2] \qquad 1$$

$$d[CH_4]/dt = k_9[CH_3][A] \qquad 2$$

Dividing *1* by *2* and integrating, noting that at zero time $[CH_3D] = [CH_4] = 0$, we obtain

$$\frac{[CH_3D]}{[CH_4]} = \frac{k_5}{k_9}\frac{[D_2]}{[A]} \qquad 3$$

provided $[D_2]$ and $[A]$ are substantially constant during the run. The ratio of specific rates is given by

$$\frac{k_5}{k_9} = \frac{[CH_3D]_t}{[CH_4]_t}\frac{[A]_i}{[D_2]_i} \qquad 4$$

where subscripts t and i refer to time t and initial condition, respectively.

If $a_{5,9}$ is the ratio of collision numbers for reactions (5) and (9), collision theory of reaction gives

$$\frac{k_5}{k_9} = a_{5,9}\frac{s_5}{s_9}\exp\left[-(E_5 - E_9)/RT\right] \qquad 5$$

where s and E terms are steric factors and activation energies, respectively. Substitution from *4* gives

$$\log\frac{[CH_3D]_t}{[CH_4]_t} = -\frac{E_5 - E_9}{2.303RT} + \log\frac{a_{5.9}s_5}{s_9}\frac{[D_2]_i}{[A]_i} \qquad 6$$

where, from collision theory

$$a_{5,9} = \left(\frac{\sigma_{D_2.\,CH_3}}{\sigma_{A,\,CH_3}}\right)^2\left(\frac{1/M_{D_2} + 1/M_{CH_3}}{1/M_A + 1/M_{CH_3}}\right)^{1/2} \qquad 7$$

the σ terms being the sums of the radii of the species indicated and the M terms the molecular weights. The factor $[D_2]/[A]$ is omitted from equation *7* because it equals unity, for k_5 and k_9 are specific rates.

If the ratio $[D_2]/[A]$ is kept constant, it follows from equation *6* that plot of $\log [CH_3D]_t/[CH_4]_t$ as a function of $1/T$ should yield a straight line whose slope and intercept can be used for calculation of $E_5 - E_9$ and estimation of s_5/s_9. Equation *6* is applicable, however, only if percentage decomposition of the parent compound be kept low: (a) to satisfy the restriction made in its derivation, (b) to reduce probability of exchange reactions involving deuterium atoms and product molecules. We shall see that disadvantages inherent in this restriction may be avoided by extrapolations to zero time.

For information on reaction (1), hydrogen in addition to deuterium must be introduced into the reaction vessel. The rate equations are *1* and

$$d[CH_4]/dt = k_1[CH_3][H_2] + k_9[CH_3][A] \qquad 8$$

As before, we obtain

$$\frac{[CH_4]_t}{[CH_3D]_t} = \frac{k_1[H_2]_i}{k_5[D_2]_i} + \frac{k_9[A]_i}{k_5[D_2]_i} \qquad 9$$

If [A], $[H_2]$ and $[D_2]$ are held sensibly constant, k_9/k_5 can be determined from equation *4* by runs involving deuterium alone. We may put

$$\frac{[CH_4]_{t,1}}{[CH_3D]_t} = \frac{[CH_4]_t}{[CH_3D]_t} - \frac{k_9[A]_i}{k_5[D_2]_i} \qquad 10$$

where $[CH_4]_{t,1}$ represents the total methane produced from reaction (1) alone. If a 1:1 mixture of H_2 and D_2 is used, combination of equations *9* and *10* gives

$$[CH_3D]_t/[CH_4]_{t,1} = k_5/k_1;\ ([H_2]_i = [D_2]_i) \qquad 11$$

The collisional theory equations give

$$\log\frac{[CH_3D]_t}{[CH_4]_{t,1}} = -\frac{E_5 - E_1}{2.303\ RT} + \log\frac{a_{5,1}\,s_5}{s_1} \qquad 12$$

Plot of values of $[CH_3D]t/[CH_4]_{t,1}$ against corresponding values of $1/T$ yields difference in activation energies and information bearing on ratio of steric factors for reactions (1) and (5).

An outstanding experimental advantage inherent in the procedures just outlined is that the reactions considered are all first order with respect to methyl radical concentration. This fact results in cancellation of methyl radical concentration terms in expressions of ratios of reaction rates. The intensity of radiation used to maintain production of methyl radicals need not be homogeneous in the reaction vessel or constant with time. Furthermore, no assumptions need be made about reactions involving chain-terminating steps, *e.g.*, the molecularity of the reaction producing ethane from combination of

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[11] H. A. Taylor and M. Burton, *J. Chem. Phys.*, **7**, 676 (1938).

[12] E. Gorin, W. Kauzman, J. Walter and H. Eyring, *ibid.*, **7**, 633 (1939).

methyl radicals. Szwarc[13] has shown that comparison of a reaction first order in methyl with a reaction second order in methyl may yield a calculated activation energy for the first order reaction somewhat less than the true value.

3. Experimental

Chemicals.—Acetone and acetaldehyde, *via* their photolysis, were used as sources of free methyl radical. Eimer and Amend T.P. grade acetone, b.p. 55.5–57.5°, was purified according to the method of Shipsey and Werner[14]; n^{20}D 1.3594; n^{20}D (lit.) 1.3591. Acetaldehyde, Eastman Kodak Co. White Label, b.p. 20–22°, was transferred to a container on the vacuum line without exposure to the atmosphere and purified and used the same day according to the method described by Zemany and Burton.[15]

Hydrogen, Matheson Co., specified purity 99.8% was purified by diffusion through a hot palladium thimble. The palladium thimble was baked out prior to each treatment and flushed prior to final collection of a pure sample of gas.

Deuterium,[16] Stuart Oxygen Co., specified purity 99.5% or greater was purified by diffusion through a hot palladium thimble. The palladium thimble was baked out prior to each treatment and flushed prior to final collection of a pure sample of gas. Mass spectrometric analyses showed a mass-three peak which corresponded to an average 1% HD impurity.

In addition, the following materials were used in calibration of the mass spectrometer.

Hydrogen deuteride was synthesized by reaction of lithium aluminum hydride with heavy water[16] according to the method of Wender, Friedel and Orchin.[17] The mass spectrometer was also calibrated for HD with a 1:2:1 mixture of H_2, HD and D_2 made by equilibration of a 1:1 mixture of H_2 and D_2.

Methane, Matheson tank gas, specified purity 99% was purified by pumping off the tank product condensed out at liquid air temperature and using the middle fraction.

Carbon monoxide was synthesized by reaction of sodium formate with concentrated sulfuric acid. The resultant gas was run through a liquid air trap.

Apparatus.—All analyses were done by mass spectrometer.[18]

The reaction cell was a cylindrical quartz vessel of ~ 50-cc. volume with a plane quartz window on one end. The furnace of an aluminum block type, was electrically heated and was temperature-controlled by a Brown regulating pyrometer. An air jacket in brass container surrounded the entire furnace. Temperature measurements with thermocouples embedded in wells in the metal of the furnace showed a variation of no more than 3° at the highest temperatures used. Light from a General Electric AH 6 high pressure mercury vapor lamp entered the window of the reaction vessel through two plane quartz disks inserted in one end of the furnace. This lamp is supposed to give complete self-reversal of the 2537 Å. line. Nevertheless, in all runs made, a filter, consisting of a sealed off quartz tube containing a drop of mercury and about 100 mm. of hydrogen, was used as a precautionary measure to eliminate the possibility of mercury-photosensitized reactions. Tests with hydrogen–deuterium mixtures and para-hydrogen showed that under these conditions equilibration did not occur and consequently that mercury-photosensitization could not be responsible for results in any of the runs herein reported.

Techniques.—Reactant materials were stored in vessels on the vacuum line after purification and thereafter mixtures of known ratio of partial pressures of reactants could be made up and similarly stored. Portions of a single such mixture were then used in a series of runs. A Toepler pump was used for mixing and for transfer of gases to various parts of the apparatus. After introduction of reactants into the reaction cell (which had previously been brought to a prescribed temperature) the pressure was adjusted and the cell was shut off before illumination. After the run the products were transferred through a liquid-air trap to a sample container with stopcock and standard-taper joint for introduction into the mass spectrometer.

Analysis of Products.—Gases determined were hydrogen, deuterium, hydrogen deuteride, methane, deuteromethane and carbon monoxide. Except in one case, purified gases were used for calibration of the mass spectrometer. For deuteromethane literature values[19] were assumed when analyses were made on the Consolidated 21–102 mass spectrometer with the sensitivity of deuteromethane assumed to be equal to that of methane. Corrections were made to the literature value for a voltage effect characteristic of the Notre Dame instrument when this instrument was used for analysis.

4. Results and Discussion

The tables list the various experimental conditions and pertinent product ratios for the different series of experiments. Tables I and II give results of photolyses of acetone in presence of deuterium.

TABLE I

PHOTOLYSIS OF ACETONE IN PRESENCE OF DEUTERIUM: RATIOS OF PRODUCTS AS FUNCTION OF INITIAL CONDITIONS, TIME AND TEMPERATURE

Run no.	Time, min.	Temp., °K.	Press., mm.	$\frac{[A]_i}{[D_2]_i}$	$\frac{[CH_3D]_t}{[CH_4]_t}$	$\frac{[CO]_t}{[D]_t}$	$\frac{]HD]_t}{[D_2]_t}$	$\frac{[HD]_t}{[CH_3D]_t}$
231	60.0	423	250	0.54	0.260	0.0911	0.0146	1.44
187	20.0	493	250	.54	.353	.0124	.0132	0.31
186	173.5	493	250	.54	.432	.113	.0260	.51
233	24.0	562	250	.54	.495	.0516	.0289	.99
232	60.0	562	250	.54	.535	.115	.0420	.74
190	10.0	588	250	.54	.530	.0165	.0136	.21
226	35.0	591	250	.54	.600	.144	.0546	.76
225	62.0	591	250	.54	.677	.223	.0540	.60
207	10.0	655	250	.54	.650	.005	.0241	1.16
227	8.0	660	250	.54	.688	.0479	.0417	1.19
228	20.0	660	250	.54	.739	.0968	.0634	0.95
229	40.2	660	250	.54	.930	.181	.0986	.73
155	10.0	655	180	.51	.714	.0082	.0209	.36
164	9.0	677	180	.51	.825	.0162	.0227	.68
158	10.0	697	180	.51	.957	.0114	.0256	.73
166	7.0	721	180	.51	.977	.0200	.0300	.71
157	12.0	731	180	.51	1.12	.0209	.0354	.75

TABLE II

PHOTOLYSIS OF ACETONE IN PRESENCE OF DEUTERIUM: PROLONGED RUNS: RATIOS OF PRODUCTS AS FUNCTION OF INITIAL CONDITIONS, TIME AND TEMPERATURE

Run no.	Time, min.	Temp., °K.	Press., mm.	$\frac{[A]_i}{[D_2]_i}$	$\frac{[CH_3C]_t}{[CH_4]_t}$	$\frac{[CO]_t}{[D_2]_t}$	$\frac{[HD]_t}{[D_2]_t}$	$\frac{[HD]_t}{[CH_3D]_t}$
145	136	472	200	0.077	1.70	0.0356	0.0169	0.45
153	101	489	200	.077	2.10	.0131	.0176	.49
148	83	529	200	.077	3.38	.0212	.0171	.28
147	112	573	200	.077	4.47	.0393	.0271	.39
150	82	645	200	.077	6.95	.0314	.0401	.95
154	222	684	200	.077	8.32	.0556	.0745	.55
112	146	455	80	.170	0.72	.167	.0241	.43
117	105	507	80	.170	1.07	.097	.0352	.63
115	126	530	80	.170	1.25	.0808	.0419	.66
116	100	548	80	.170	1.31	.158	.0422	.44
121	121	573	80	.170	1.49	.203	.0712	.44
109	132	613	80	.170	1.79	.166	.0930	.53
120	135	640	80	.170	1.92	.155	.0914	.59
119	59	674	80	.170	2.44	....	.104	.53
118	88	696	80	.170	2.50	.121	.138	.65

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[13] M. Szwarc, *J. Chem. Phys.*, **19**, 256 (1951).

[14] K. Shipsey and E. A. Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

[15] P. Zemany and M. Burton, *J. Phys. Colloid Chem.*, **55**, 949 (1951).

[16] Deuterium and heavy water employed in this investigation were portions of samples supplied to the Radiation Chemistry Project of the University of Notre Dame through the courtesy of the Atomic Energy Commission.

[17] I. Wender, R. A. Friedel and M. Orchin, THIS JOURNAL, **71**, 1140 (1949).

[18] The authors express their appreciation to the Sinclair Refining Company both for a grant which facilitated construction of a mass spectrometer on which the majority of analyses were made and for generously granted access to their own Consolidated 21-102 instrument at Harvey, Illinois, for numerous analyses. In the latter connection, the operating staff, notably Messrs. Richard Wertzler, John Kinder and John Gallagher, were especially helpful.

[19] J. Turkevich, L. Friedman, E. Solomon and F. M. Wrightson, THIS JOURNAL, **70**, 2638 (1948).

Table III shows results of photolysis of acetone in presence of an equimolar mixture of hydrogen and deuterium. Table IV summarizes results of photolysis of acetaldehyde in presence of deuterium. All runs listed in Table II involved considerable decomposition of parent compound.

TABLE III

PHOTOLYSIS OF ACETONE IN PRESENCE OF EQUIMOLAR MIXTURE OF HYDROGEN AND DEUTERIUM: RATIOS OF PRODUCTS AS FUNCTION OF INITIAL CONDITIONS, TIME AND TEMPERATURE

Run no.	Time, min.	Temp., °K.	Press., mm.	$\frac{[A]_i}{[D_2]_i}$	$\frac{[CH_3D]_t}{[CH_4]_{t,i}}$	$\frac{[CO]_t}{[D_2]_t}$	$\frac{[HD]_t}{[D_2]_t}$	$\frac{[HD]_t}{[CH_3D]_t}$
127	271	409	140	0.186	0.174	0.140	0.0492	11.0
126	156	426	140	.186	.188	.0388	.0936	27.3
128	191	439	140	.186	.228	.0388	.0819	14.4
130	154	464	140	.186	.261	.0202	.0749	15.2
131	190	484	140	.186	.255	.0235	.122	17.4
132	162	500	140	.186	.260	.0234	.142	21.4
214	20.2	466	400	.54	.250	.00755	.0240	18.0
215	20.0	502	400	.54	.290	.00956	.0412	19.3
216	20.0	550	400	.54	.340	.0118	.0701	22.4
217	24.5	591	400	.54	.270	.0106	.0978	33.8

TABLE IV

PHOTOLYSIS OF ACETALDEHYDE IN PRESENCE OF DEUTERIUM: RATIOS OF PRODUCTS AS FUNCTION OF INITIAL CONDITIONS, TIME AND TEMPERATURE

Run no.	Time, min.	Temp., °K.	Press., mm.	$\frac{[A]_i}{[D_2]_i}$	$\frac{[CH_3D]_t}{[CH_4]_t}$	$\frac{[CO]_t}{[D_2]_t}$	$\frac{[HD]_t}{[D_2]_t}$	$\frac{[HD]_t}{[CH_3D]_t}$
168	10.0	531	180	0.55	0.0470	0.125	0.0193	0.80
169	2.0	531	180	.55	.0400	.0252	.0131	..
172	2.0	558	180	.55	.0514	.0529	.0155	.47
167	3.0	586	180	.55	.0677	.0985	.0203	.69
174	5.0	622	180	.55	.122	.345	.0445	.66
176	2.0	655	180	.55	.118	.0885	.0206	.87
170	10.0	690	180	.55	.186	.208	.0652	.81
177	2.0	705	180	.55	.168	.0960	.0200	.43
171	10.0	724	180	.55	.269	.390	.0936	.75

In the interpretation of mass spectra for calculation of $[CH_3D]/[CH_4]$, the mass 18 peaks were assumed to be due to water residual peaks. In runs of low decomposition these were not significantly greater than background. However, in some runs involving considerable decomposition of the parent compound, the increase in mass 18 over background indicated possible production of CH_2D_2. Calculations for HD in the ratio $[HD]/[CH_3D]$ in Tables I, II and IV were corrected for HD impurity in the D_2 used.

Production of HD in all runs was evidence that the reaction between methyl radicals and hydrogen actually produces hydrogen atoms. The reasonable closeness of the ratio $[HD]/[CH_3D]$ to unity for runs listed in Tables I, II and IV indicates that (1) is the only important mechanism. Any significant contribution from the mechanism (7), (8) might not affect that ratio markedly at any one temperature but should affect it systematically over the large temperature range covered. The actual variations from a ratio of 1.0 are erratic and may be attributed to (a) difficulties in obtaining accurate analyses for small percentages of HD on the mass spectrometer and (b) uncertainties introduced by corrections made for presence of the HD impurity in D_2.

The log $[CH_3D]/[CH_4]$ values for runs at each temperature in Table I may be plotted against corresponding values of $[CO]/[D_2]$ and extrapolated to $[CO]/[D_2] = 0$ to obtain "zero-time" values.[20] Runs with $[CO]/[D_2] < 0.02$ give no significant change in log $[CH_3D]/[CH_4]$ on extrapolation to zero time. Hence, at the higher temperatures where such runs yielded adequate products for accurate analysis, no runs of greater decomposition were made. When only one run was made at a given temperature, extrapolation was made along a line of slope estimated from the slopes of lines at neighboring temperatures. The logarithms of these zero-time values of $[CH_3D]/[CH_4]$ are plotted against $1/T$ in Fig. 1. Adjustment of the $[A]/[D_2]$ ratio to a predetermined value in all runs was not convenient. Actually Fig. 1 contains two sets of values of $([CH_3D]_t/[CH_3]_t)_{ext.}$ (*i.e.*, extrapolated to approximately zero time), those based on a ratio of 0.51 and those based on a ratio of 0.54. The former have been adjusted to the 0.54 base by the multiplication factor 0.51/0.54. The figure shows two straight lines corresponding to best fits to the two sets of values as well as a single curved line passing through both sets. It is not known whether the different slopes at higher and lower temperature are the result of experimental differences in the two series of runs or represent some basic difference such as a hot radical effect. The inflection point at 350° is a rather high temperature for disappearance of such an effect. Application of equation *6* gives $E_5 - E_{10}$ and s_5/s_{10} where E_{10} and s_{10} are for the reaction

$$CH_3 + (CH_3)_2CO \longrightarrow CH_4 + CH_2COCH_3 \quad (10)$$

For collision diameters we use the values of Trotman-Dickenson and Steacie,[21] namely, 2.8, 3.5 and 5.5 Å. for D_2, CH_3 and $(CH_3)_2CO$, respectively. The points in the temperature range 350 to 450° give $E_5 - E_{10} = 4.6$ kcal. while in the range 150 to 350° the value is 3.0 kcal. The value 4.6 kcal. is preferred because (a) possible "hot radical" effects are minimized at higher temperatures and (b) longer times of photolysis at lower temperatures, to obtain adequate products for analysis, have resulted in less reproducible results in this work. The validity of this preference is supported by the good agreement of E_1 so calculated with the value found from the acetaldehyde studies. The value obtained for s_5/s_{10} is of the order of 10.

The log $[CH_3D]/[CH_4]$ values of single runs involving considerable decomposition, listed in Table II, may be plotted against $1/T$ without zero-time extrapolation. The conditions at termination of the experiments do not warrant strict application of equation *6*. Nevertheless, straight lines are obtained which give values of activation energy surprisingly close to results obtained from Fig. 1. For $[A]_i/[D_2]_i = 0.17$, $E_5 - E_{10} = 3.3$ kcal.; for $[A]_i/[D_2]_i = 0.077$, $E_5 - E_{10} = 4.5$ kcal.

The runs listed in Table III were employed for determination of $E_5 - E_1$. Values of k_{10}/k_5 necessary for calculation of $[CH_3D]_t/[CH_4]_{t,i}$ (*cf.* equation *10*) were obtained from Fig. 1 by application of

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[20] Great variations in intensity of the AH6 lamp prevent accurate representation of extent of decomposition by time of run. The yield $[CO]/[D_2]$ is considered to be more reliable in this respect.

[21] A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **18**, 1097 (1950), also report a value of $E_{10} = 9.7$ kcal.; *cf.* A. J. C. Nicholson, THIS JOURNAL, **73**, 3981 (1951), who gives the value 9.6 kcal.

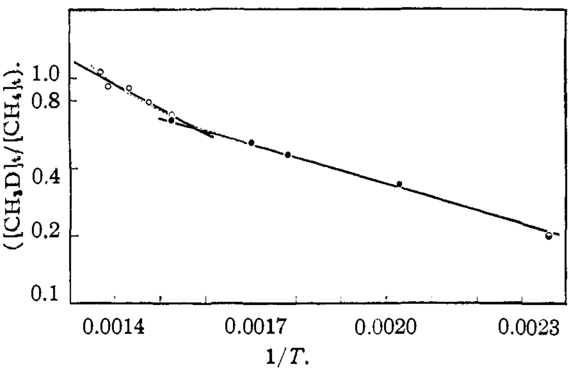

Fig. 1.—Photolysis of acetone in presence of deuterium: effect of temperature on competition for methyl radicals by the two components: ○, short single run; ●, extrapolated values from series of runs; ⊖, single long run.

equation *4*. Figure 2 shows the plot of $[CH_3D]_t/[CH_4]_{t,1}$ values against $1/T$. Application of expression *12* to the best straight line results in the value $E_5 - E_1 = 1.1$ kcal. for the condition $s_5/s_1 = 1.0$. This value for $E_5 - E_1$ appears reasonable in view of the difference in zero-point energies for the H_2 and D_2 molecules, *i.e.*, 1.8 kcal. In Fig. 2 the spread of points about the straight line is greater than in Fig. 1. Such greater spread is expected, for these points are each calculated from two independent experiments instead of one. Furthermore, the relatively large amounts of HD produced increase probability of reaction of methyl radicals with HD instead of with D_2 or acetone. The best straight line was drawn with an intercept which would make $s_5/s_1 = 1.0$. Assumption of equal steric factors appears reasonable, since the work of Farkas and Farkas[22] has indicated equal steric factors for the analogous reactions

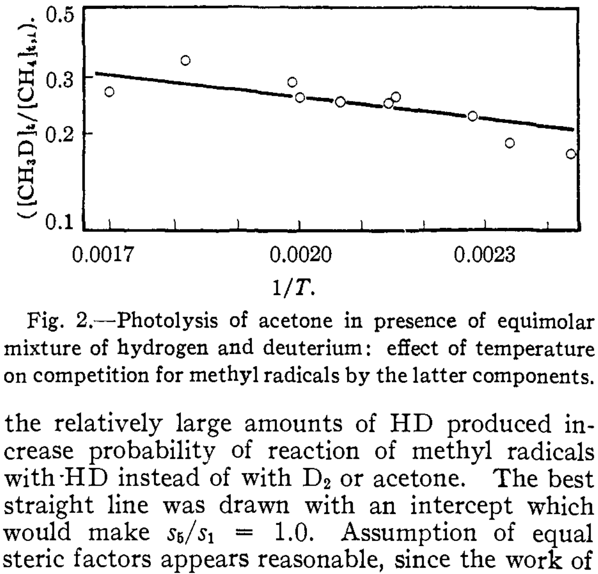

Fig. 2.—Photolysis of acetone in presence of equimolar mixture of hydrogen and deuterium: effect of temperature on competition for methyl radicals by the latter components.

$$H + D_2 \longrightarrow HD + D \quad (11)$$

$$H + p\text{-}H_2 \longrightarrow o\text{-}H_2 + H \quad (12)$$

For all runs listed in Table III, the $[HD]/[CH_3D]$ values are considerably greater than unity. This result is to be expected because the chain reactions (11) and

$$D + H_2 \longrightarrow HD + H \quad (13)$$

have lower activation energies than the chain-ending step

$$H + (CH_3)_2CO \longrightarrow H_2 + \text{residue} \quad (14)$$

$E_{11} = 6.5$ kcal.,[22] $E_{13} = 4.8$ kcal.[22] and $E_{14} = 9$ kcal.[7]

Some runs involving extensive decomposition of acetone were included in the plot of Fig. 2. Such usage is considered permissible since those particular runs involved about a fivefold excess of hydrogen and deuterium. Hence, the correction for presence of acetone was relatively small.

Table IV lists experimental conditions and product ratios of runs involving photolysis of acetaldehyde in presence of deuterium. The logarithms of the $[CH_3D]/[CH_4]$ ratios are plotted against $1/T$ in Fig. 3. The two-minute runs represent runs with lowest amount of decomposition necessary for good accuracy. Runs of longer duration were made to indicate change in the log $[CH_3D]/[CH_4]$ ratios. The best straight line through values of the two minute runs yields the results[23] $E_5 - E_{15} = 6.2$ kcal. and $s_5/s_{15} \sim 10$, where E_{15} and s_{15} are activation energy and steric factor for the reaction

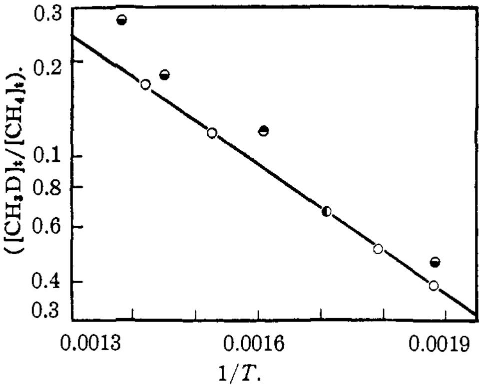

Fig. 3.—Photolysis of acetaldehyde in presence of deuterium: effect of temperature on competition for methyl radicals by two components: ○, 2 minute run; ◐, 3 minute run; ●, 5 minute run; ⊖, 10 minute run.

$$CH_3 + CH_3CHO \longrightarrow CH_4 + CH_3CO \quad (15)$$

The values thus far given involve only differences in activation energies and ratios of steric factors. For absolute values of activation energy and steric factor for the various reactions, one must assume certain values for these quantities for at least one of the reactions involved. Values for the other reactions are then automatically fixed. Results on the high temperature photolysis of acetone by Trotman-Dickenson and Steacie[21] have been chosen as reference points for the acetone experiments. These authors have measured values of $k_{10}/k_{16}^{1/2}$ at various temperatures and have obtained the values $E_{10} - {}^1/_2E_{16} = 9.7$ kcal. and $s_{10}/s_{16}^{1/2} = 10^{-3}$ where E_{16} and s_{16} are for the reaction

$$CH_3 + CH_3 \longrightarrow C_2H_6 \quad (16)$$

Values of E_{16} and s_{16} have been the subject of extensive discussion. Steacie and his co-workers[24,25] have estimated the collision yield of reaction (16) based on comparison with the rate of the reaction of

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

[23] A collisional diameter of 5.0 Å. was assumed for CH_3CHO. Collisional diameters for CH_3 and D_2 were those adopted for the acetone calculations.

[24] R. A. Marcus and E. W. R. Steacie, *Z. Naturforsch.*, **4a**, 332 (1949).

[25] D. M. Miller and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 73 (1951).

CH_3 with NO; they favor a yield of 4.4×10^{-5} within one power of 10. Thus, for an assumed E_{16} near zero, they would favor a value of s_{16} not much greater than 10^{-4}. Lucas and Rice[26] studied photolysis of acetaldehyde by a rotating sector technique at a variety of temperatures and calculated the specific rate of the chain-breaking step. On the assumption that this step is reaction (16) they found $s_{16} \sim 1$ for $E_{16} \sim 0$, which latter value they favored, since k_{16} was found to be close to the estimated collision number of 10^{14} cc. mole^{-1} sec.$^{-1}$ at 200°. Gomer and Kistiakowsky[27] made a similar study and concluded that the chain-ending step (contrary to Dodd[28]) is reaction (16) and found $k_{16} = 4.5 \times 10^{13}$ cc. mole^{-1} sec.$^{-1}$ at 125° and $E_{16} = 0 \pm 7$ kcal. We adopt the values $E_{16} \sim 0$ and $s_{16} \sim 1$. It has been shown[4] that the values of E_1 and s_1 based on these latter values give reaction rates in reasonable agreement with those estimated by Rice[5] from mirror experiments.

If E_{16} be taken equal to zero, work of Grahame and Rollefson[29] on high-temperature photolysis of acetaldehyde gives a value $E_{15} = 8.6$ kcal. This value has been re-examined by Dodd[30] with a rotating-sector technique. He concluded that $E_{15} = 10.7$ kcal. and that the earlier work was also consonant with that result.

Table V summarizes our conclusions regarding reactions (1) and (5). Low values of E_1 and E_5 are based on the results of Trotman-Dickenson and Steacie[21] on acetone and of Grahame and Rollefson[29] on acetaldehyde, respectively. They are in substantially good agreement. High values are based on the work of Dodd[30] on acetaldehyde. The photolysis of acetaldehyde is a chain reaction above 80° with a chain length of 300 at about 300°.[31] Hence, no significant fraction of radicals present at any one time is suprathermal and the acetaldehyde runs thus tend to be free from possible hot-radical effects. However, the difference between the values $E_1 = 13.2$ kcal. and $E_1 = 15.8$ kcal. are greater than we would expect on such a basis. Nevertheless, it may be said that $E_1 > 13$ kcal. and that $s_1 \sim 10^{-2}$.

TABLE V

CONCLUSIONS REGARDING ACTIVATION ENERGY AND STERIC FACTOR ON VARIOUS BASES

	E, kcal.			s
Base:	$E_{10} = 9.7$[21]	$E_{15} = 8.6$[29]	$E_{15} = 10.7$[30]	$s_{10} = 10^{-3}$
Reaction (1)	13.2	13.7	15.8	10^{-2}
Reaction (2)	14.3	14.8	16.9	10^{-2}

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(26) V. E. Lucas and O. K. Rice, *J. Chem. Phys.*, **18**, 992 (1950).

(27) R. Gomer and G. B. Kistiakowsky, *ibid.*, **19**, 85 (1951).

(28) R. E. Dodd, *ibid.*, **18**, 234 (1950).

(29) D. C. Grahame and G. K. Rollefson, *ibid.*, **8**, 98 (1940).

(30) R. E. Dodd, *Trans. Faraday Soc.*, **47**, 56 (1951).

(31) J. A. Leermakers, THIS JOURNAL, **56**, 1537 (1934).

NOTRE DAME, INDIANA RECEIVED OCTOBER 30, 1951

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Use of Heavy Oxygen in the Study of Reactions of Hydrogen Peroxide[1]

BY ALLEN E. CAHILL[2] AND HENRY TAUBE

In the oxidation of H_2O_2 in water solution by Ce(IV), MnO_4^-, Cl_2, HClO, $Cr_2O_7^=$, the O_2 formed is derived cleanly from the H_2O_2. The O_2 liberated in the decomposition of H_2O_2 by Fe(III), I^-–I_2, Br^-–Br_2, MnO_2 and Pt is also derived only from the H_2O_2. The isotope fractionation factors for the reduction of H_2O_2 by Ti(III), Fe(II), Sn(II), Cr(II) and Cu(I) at 25° are 0.994, 0.932, 0.943, <0.95, <0.945. The discrimination increases measurably when the temperature is lowered. For the reaction of the oxidizing agents Ce^{IV}, Cl_2, HOCl with H_2O_2, the factors are 0.987, 0.990 and 0.992, respectively. The fractionation factors characteristic of the oxidizing agent, and of the reducing agent which attack the molecules when Fe^{+++}, I^-–I_2, Br^-–Br_2 act catalytically have been determined. The slight discrimination exercised by Ti(III) in comparison with Fe(II), Sn(II), Cr(II) and Cu(I) has been interpreted as indicating a $1e^-$ reduction by it, but a $2e^-$ reduction of H_2O_2 by the other cationic reducing agents. The reducing intermediate present when Fe(III) acts catalytically has the same fractionation factor as Fe^{++}. It is concluded that the reducing intermediate is Fe(II) (and not HO_2). A mechanism for the catalysis of the decomposition of H_2O_2 and Fe(III) is proposed which incorporates this feature, and admits Fe(IV) as the usual product of the interaction of Fe(II) and H_2O_2. The $1e^-$ reduction of H_2O_2 by Fe(II) appears in the mechanism as a chain breaking step. Isotope fractionation by the heterogeneous catalysts MnO_2 and Pt was observed. The results to be expected for solids when diffusion limits the rate are outlined.

Significant information about the mechanisms by which hydrogen peroxide in water solution undergoes oxidation, reduction or catalytic decomposition can be gained by a study of the path of oxygen in these reactions. A number of investigations, with this as a goal have been carried out using O^{18} as a tracer.

Somewhat less obvious, but equally forceful in their implications as to mechanisms, are observations on the relative rates of reaction of oxidizing or reducing agents with isotopic species of hydrogen peroxide. The relative rate of reaction of a particular substance with isotopically distinct forms of another is a characteristic of the process, and has a value which varies only with temperature (or pressure). It can therefore be used to identify a particular process or reaction path, and to distinguish between processes. This application is particularly valuable in studying mechanisms by which catalysts act on hydrogen peroxide. The isotope fractionation exerted by catalysts can be analyzed into a fractionation factor for the production of oxygen, which is characteristic of the oxidation step in the catalysis, and the factor for the production of water, characteristic of the reducing agent present. The data are then useful in deciding whether the same intermediates act for different catalysts, and in comparing the unknown reducing

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(1) The tracer work described in this paper was presented at the A.C.S. Meeting, Detroit, Mich., April, 1950; the results on fractionation in New York, Sept., 1951.

(2) A.E.C. Predoctoral Fellow, 1950–1951.