THE PREËXPONENTIAL FACTOR FOR SOME REACTIONS OF METHYL RADICALS[1, 2]

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I. INTRODUCTION

The present state of reaction rate theory makes it important to have experimental evidence with which to check theory. In the past, emphasis has largely been placed on the evaluation of activation energies rather than of the preëxponential factor in the rate constant expression. It is readily seen that a knowledge of this factor is of importance experimentally as well as theoretically.

Although few, if any, bimolecular elementary reaction rates are known absolutely, much information can be gained from relative reaction rates. The reactions of methyl radicals in the gas phase seem among the best understood. A number of photochemical reactions in which methyl radicals play a significant role have been studied in this laboratory. These investigations have furnished data which permit an evaluation of the activation energies and preëxponential factors for hydrogen abstraction reactions of the type

$$CH_3 + RH = CH_4 + R$$

relative to those for the association reaction of methyl radicals:

$$CH_3 + CH_3 = C_2H_6$$

Evaluation of the relative steric factors is possible upon the assumption of arbitrary collision cross-sections for these reactions.

A previous estimate of steric factors from experimental data has been made by Steacie *et al.* (12). These authors have reviewed the reactions of methyl radicals with some hydrocarbons to form methane and have concluded that steric factors of the order of 10^{-4} or lower must be assumed. A recent Eyring-type calculation by Hill (8) has predicted a steric factor of 2×10^{-4} for methane formation in the photolysis of acetone.

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The reactions of methyl radicals with the following compounds have been considered.

II. ACETONE

It has been shown (3, 10) that reactions 1 and 2 (see table 1) account for the formation of ethane and methane in the photolysis of acetone. A plot of

$$\Phi_{CH_4}/\Phi^{1/2}_{C_2H_6} \quad vs. \quad (Ac)/I_a^{1/2}$$

where Φ is the quantum yield of product and (Ac) the concentration of acetone, showed that the equation

$$\frac{\Phi_{CH_4}}{\Phi^{1/2}_{C_2H_6}} = \frac{k_2}{k_1^{1/2}} \frac{(Ac)}{I_a^{1/2}} \tag{I}$$

represents a straight line through the origin as required by reactions 1 and 2. At 122°C. the value of $k_2/k_1^{1/2}$ obtained from the slope of this line was found to be 3.19×10^{-13} (molecules/cc.)$^{-1/2}$ sec.$^{-1/2}$ At 26°C. $k_2/k_1^{1/2} = 2.70 \times 10^{-14}$. The activation energy difference, determined from the temperature coefficient of $k_2/k_1^{1/2}$, was $E_2 - \frac{1}{2}E_1 = 5.7$ kcal./mole.

TABLE 1*

Preëxponential factors for reactions of methyl radicals

REACTION	$E_n - \frac{1}{2}E_1$	$p_n a_n$	$\alpha_n^2 = p_n \sigma_n^2$	σ	p_n
	kcal./mole			Å.	
(1) $CH_3 + CH_3 = C_2H_6$	—	$p_1 a_1$	α_1^2	1.54	p_1
(2) $CH_3 + CH_3COCH_3 = CH_4 + CH_2COCH_3$	5.7	$1.1 \times 10^{-10}(p_1 a_1)^{1/2}$	$0.1 \times 10^{-11}\alpha_1$	3.7	$0.1 \times 10^{-4} p_1^{1/2}$
(3) $CH_3 + CH_3HgCH_3 = CH_4 + CH_2HgCH_3$	8.7	$3.6 \times 10^{-9}(p_1 a_1)^{1/2}$	$2.7 \times 10^{-11}\alpha_1$	4.4	$2 \times 10^{-4} p_1^{1/2}$
(4) $CH_3 + (CH_2)_2O = CH_4 + C_2H_3O$	8.7	$1.2 \times 10^{-9}(p_1 a_1)^{1/2}$	$0.8 \times 10^{-11}\alpha_1$	3.1	$1 \times 10^{-4} p_1^{1/2}$
(5) $CH_3 + C_4H_{10} = CH_4 + C_4H_9$	8.0	$2.5 \times 10^{-9}(p_1 a_1)^{1/2}$	$1.7 \times 10^{-11}\alpha_1$	2.7	$4 \times 10^{-4} p_1^{1/2}$
(6) $CH_3 + CH_3HgCH_3 = C_2H_6 +$ —	—	—	$3.6 \times 10^{-4}\alpha_3^2$	2.2	$30 \times 10^{-8} p_1^{1/2}$

* *Note added in proof:* The values of the activation energy difference $E_n - \frac{1}{2}E_1 = 8.7$ kcal./mole for reactions 3 and 4 are from the Ph.D. Thesis of Robert Gomer. In the published reports (6, 7) these values have been rounded off to 9 kcal./mole.

A brief consideration of evidence pertaining to the question of a three-body requirement in the association of methyl radicals is in order. Davis (2) has investigated the formation of methane in the photolysis of acetone over a pressure range from 95 to 233 mm. The experimentally determined methane quantum yields are shown in table 2. The quantum yield of ethane may be determined from the relationship:

$$2\Phi_{C_2H_6} + \Phi_{CH_4} = 2\Phi_{CO}$$

This relationship is valid if the quantum yield of formation of methyl ethyl ketone is small. The last column of table 2 lists the values of $k_2/k_1^{1/2}$ over the 2.5-fold pressure change, as calculated from equation I. As may be seen, there is no significant trend in $k_2/k_1^{1/2}$ with increase in pressure. Further evidence favoring a bimolecular recombination of methyl radicals without a third-body requirement is also present in the following photochemical investigations.

TABLE 2

Quantum yields of methane in photolysis of acetone

TEMPERATURE	ABSORBED INTENSITY	ACETONE PRESSURE	Φ_{CH_4}	$\Phi_{C_2H_4}$ (CALCULATED)	$k_2/k_1^{1/2}$ (FROM EQUATION I)
°C.	*quanta/cc./sec.* $\times 10^{13}$	*mm.*			
122	2.7	95	0.62	0.69	4.5×10^{-13}
126.5	2.1	109	0.63	0.69	4.2
127	2.4	152	0.6	0.7	3.0
126	16.4	194	0.40	0.80	3.9
120	2.2	205	0.91	0.55	3.6
120	2.3	233	0.97	0.52	3.6
136	0.27	101.3	1.15	0.42	3.8
137	2.3	111.1	0.56	0.72	3.7
136	0.39	137.6	1.14	0.43	3.2
134.5	2.1	145.2	0.93	0.54	3.6
138	2.9	148.2	0.73	0.64	4.3
138	1.4	184.4	1.06	0.57	3.8
137	1.7	191	1.04	0.48	4.3
131.5	1.4	199.6	0.99	0.51	3.4

III. DIMETHYLMERCURY

Gomer and Noyes (6) measured the rates of formation of ethane and methane over a several hundred-fold range of light intensities in the photochemical decomposition of dimethylmercury and were able to obtain linear plots with positive intercepts of $R_{C_2H_6}/R_{CH_4}$ *vs.* R_{CH_4}, where R represents the rate of formation of product. These were explained on the basis of reactions 1, 3, and 6, from which the following expression was derived:

$$\frac{R_{C_2H_6}}{R_{CH_4}} = \frac{k_1}{k_3^2}\,\frac{R_{CH_4}}{(\text{DM})^2} + \frac{k_6}{k_3} \qquad \text{(II)}$$

The authors verified the pressure independence of the intercept and the dependence of the slope of equation II on $(\text{DM})^{-2}$, where (DM) is the concentration of dimethylmercury. At very low light intensities deviation from linearity occurred, suggesting that reaction 6 represented the high-intensity limiting case of a more complex series of steps. Reactions 1 and 3 seem established, however, and are not affected by reaction 6, which shows up only in the intercept and not the slope of equation II. The latter yielded values of 1.2×10^{24} (molecules/cc.) sec. at 175°C. and 0.19×10^{24} (molecules/cc.) sec. at 220°C. for k_1/k_3^2. From the intercepts k_6/k_3 was found to be 8.0 at 175°C. and 3.2 at 220°C. The activation energy difference $E_3 - \frac{1}{2}E_1 = 8.7$ kcal./mole was also determined separately from the temperature coefficient of methane formation at constant and high light intensity where

$$\ln R_{\mathrm{CH_4}} \cong (E_3 - \tfrac{1}{2}E_1)/RT$$

IV. ETHYLENE OXIDE

The rates of formation of methane during the photolysis of dimethylmercury in the presence and absence of ethylene oxide have been determined (7). It was shown that k_4/k_3 could be obtained from the following:

$$\frac{R_{\mathrm{CH_4}}}{R'_{\mathrm{CH_4}}} = \left(1 + \frac{k_4}{k_3}\frac{E}{(\mathrm{DM})}\right)\left(\frac{R_{\mathrm{C_2H_6}}}{R'_{\mathrm{C_2H_6}}}\right)^{1/2} \qquad \text{(III)}$$

where R and R' represent the rates of formation of product in the presence and absence, respectively, of ethylene oxide. The factor $(R_{\mathrm{C_2H_6}}/R'_{\mathrm{C_2H_6}})^{1/2}$ in equation III is a correction for the differences in $\mathrm{CH_3}$ steady-state concentration in the presence and absence of ethylene oxide and assumes that reaction 1 predominates over reaction 6, an assumption which seems justified except at very low light intensities.

The authors also measured the rates of formation of methane and ethane for mixtures of 5 mm. of dimethylmercury and 100 mm. of ethylene oxide over *ca.* a 1000-fold range of light intensity. From their value of k_3/k_4 they were able to show that k_1/k_3^2 was identical with the value obtained at total pressures of 5, 13, and 20 mm. in the photolysis of dimethylmercury alone.

V. BUTANE

The ratio k_5/k_3 has been determined (5) as in the case of ethylene oxide, by comparing the amounts of methane formed in the presence and absence of butane in the photolysis of dimethylmercury. The equation used was obtained from equation III by replacing (E) with the concentration of butane, and also by substituting in place of $(R_{\mathrm{C_2H_6}}/R'_{\mathrm{C_2H_6}})^{1/2}$ the following more precise expression to correct for the differences in $\mathrm{CH_3}$ steady-state concentration in the presence and absence of butane:

$$\frac{(\mathrm{CH_3})}{(\mathrm{CH_3'})} = \frac{\sqrt{\dfrac{k_6^2(\mathrm{DM})^2}{k_1} + 4R_{\mathrm{C_2H_6}}} - \dfrac{k_6(\mathrm{DM})}{k_1^{1/2}}}{\sqrt{\dfrac{k_6^2(\mathrm{DM})^2}{k_1} + 4R'_{\mathrm{C_2H_6}}} - \dfrac{k_6(\mathrm{DM})}{k_1^{1/2}}} \qquad \text{(IV)}$$

A temperature interval from 130°C. to 220°C. was covered in these experiments. The following average values for k_5/k_3 were found: at 130°C., 4.20; at 150°C., 4.03; at 187°C., 3.8; at 220°C., 3.65. The activation energy difference $E_3 - E_5$ obtained by plotting ln k_3/k_5 *vs.* $1/T$ was 0.64 kcal./mole. This, with the value of $E_3 - \frac{1}{2}E_1 = 8.7$ kcal./mole, yields a value of $E_5 - \frac{1}{2}E_1 = 8.0$ kcal./mole. This value is somewhat higher than that obtained by previous workers (11). It has been pointed out (5) that reaction 5 probably involves chiefly secondary hydrogens below 600°C. if the difference in activation energies between primary and secondary hydrogen abstraction is as small as 0.5 kcal./mole.

VI. DISCUSSION

The rate constants k_1 for the association reaction and k_n for the hydrogen abstraction reactions are related by the equation:

$$\frac{k_n}{k_1^{1/2}} = \frac{p_n Z_n}{p_1^{1/2} Z_1^{1/2}} e^{-(E_n - 1/2 E_1)/RT} \tag{V}$$

Since $k_n/k_1^{1/2}$ and $E_n - \frac{1}{2}E_1$ are known experimentally, the relative values of the preëxponential factor may be determined:

$$\frac{p_n Z_n}{p_1^{1/2} Z_1^{1/2}} = \frac{k_n}{k_1^{1/2}} e^{(E_n - 1/2 E_1)/RT} \tag{VI}$$

or

$$\frac{p_n a_n}{p_1^{1/2} a_1^{1/2}} = \frac{k_n}{k_1^{1/2}} \frac{e^{(E_n - 1/2 E_1)/RT}}{T^{1/4}} \tag{VII}$$

where

$$a_n = 2\sigma_n^2 \left(2\pi R \frac{M_{CH_3} + M_n}{M_{CH_3} M_n}\right)^{1/2}$$

and

$$a_1 = 2\sigma_1^2(\pi R/M_{CH_3})^{1/2}$$

The data are summarized in table 1.

The assignment of values for the collision cross-section σ^2 is a matter of considerable uncertainty. The values of σ listed in table 1 were taken somewhat arbitrarily by computing the distance of the hydrogen to be abstracted from the center of gravity of the molecule and adding to this the value 1.1 Å. The latter figure is the normal C—H bond distance. It is obvious that this procedure does not give the "true" collision cross-section, since the distance of interaction is undoubtedly larger than the normal distances used. However, this assignment seems as good as any other one, since the concept of collision diameter is at best an artificial one. It may be pointed out that a recent paper by T. L. Hill (8) employs collision diameters of 4.23 Å. for methyl plus acetone and 3.50 Å. for the association of methyl radicals. A variation of 100 per cent in the choice of values for the collision cross-sections does not effect a profound change in the relative steric factors obtained using these values.

Because of the artificiality of collision diameters and hence of steric factors, the quantity $\alpha^2 = p\sigma^2$ has been listed in column 4 of table 1. α^2 represents a reaction cross-section and has in a sense more significance than p and σ^2 considered as separate entities.

It is seen from the values of p or α^2 in table 1 that the steric factors or reaction cross-sections for all of the hydrogen abstraction reactions considered are of the same order of magnitude. Although no absolute values can be assigned to any of these steric factors at the present time, it is clear that a value of unity for the steric factor of the association reaction (reaction 1) places an upper limit of $p_n \cong 10^{-4}$ on the steric factors for the hydrogen abstraction reactions.

p_1 may be less than unity. The Eyring-type calculation (8) has given $p_1 = 1.4\kappa$, where κ is the transmission coefficient. In this calculation the three-body restriction has been accepted and κ should therefore be pressure dependent and will have a value of unity if every molecule of ethane formed becomes deactivated before redissociation can occur. Ignoring all degrees of freedom except the C—C vibrations (considered classically and corrected for anharmonicity), Hill found that roughly one in 10^3 molecules would be deactivated at a pressure of 100 mm., thus making $\kappa = 10^{-3}$. In view of this it is significant that $k_n/k_1^{1/2}$ seems invariant over a pressure range of 5 to 100 mm. in the experiments on dimethylmercury and ethylene oxide and 95 to 233 mm. in the experiments on acetone. This could be taken to mean that the energy of recombination can become distributed among some of the internal degrees of freedom of the ethane molecule, thus prolonging the lifetime of the excited state sufficiently to make reaction 1 appear independent of third-body requirements at the pressures indicated. It must be added, however, that the validity of an Eyring-type calculation for reactions of low activation energy is very much open to question, since the steady state actually existing between reactants and activated complex may be substantially different from the true thermodynamic equilibrium assumed.

An earlier estimate by Bawn (1) of the steric factor for the association reaction has given $p_1 = 8 \times 10^{-6}$, assuming zero activation energy for the reaction. While it is impossible, at the present time, to establish the validity of any of these absolute values, it is clear that the values $p_1 = 8 \times 10^{-6}$ and $p_2 = 2 \times 10^{-4}$ are together incompatible with the experimental relationship obtained.

Evans and Szwarc (4) have recently proposed that metathesis reactions have "normal" probability factors of the order of 10^{-2} or greater. The experimental data they considered were mainly for atomic reactions. On the basis of the data for the reactions of methyl radicals considered in the present review, an upper limit of $p_n \cong 10^{-4}$ must be assigned to the probability factors of the hydrogen abstraction reactions.

Although it is dangerous to link bond strengths too closely with activation energies, a rough correlation probably does exist. It is interesting to compare the activation energies listed here from this point of view. The activation energy for acetone is lowest which probably corresponds to a weakening of the C—H bond because of the inductive effect of the carbonyl group. The highest activation energy is encountered in dimethylmercury. Since mercury has a much greater tendency to lose than to gain electrons, the C—H bond in this compound may be very strong. In the case of ethylene oxide the structure is not perfectly understood, and the high activation energy found may be an indication of the proposed (9) ethylene-like structure resulting in a "saturation" of the oxygen atom. In the reaction of methyl radicals with butane at the temperatures studied the likelihood that secondary hydrogens are chiefly involved may account for an activation energy intermediate between dimethylmercury and acetone.

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