[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Reaction of Methyl Radicals with *n*-Butane

BY ROBERT GOMER*[1,2]

Previous attempts to study the reaction of methyl radicals with various hydrocarbons seem confined to the work of Smith and Taylor[3] who measured the total rate of methane formation as a function of temperature in the photolysis of mixtures of mercury dimethyl and deuterium, ethane, butane, isobutane and neopentane. A plot of log R_{CH_4} *vs.* $1/T$ gave a nearly straight line, allowing them to calculate an activation energy of 5.5 kcal. for the formation of methane from butane.

Recent work on the photochemistry of mercury dimethyl[4] makes it possible to compare the rate constants for hydrogen abstraction by methyl radicals for butane and mercury dimethyl, and thus to obtain a value for the activation energy of the former reaction. It was desired to study the hydrogen abstraction from a simple hydrocarbon by methyl radicals in order to compare this with similar reactions involving different types of compounds.

Experimental

The apparatus used and the general procedure have been described previously.[4] The butane was C. P. grade, obtained from the Matheson Company. It was stored in a 2-liter bulb and could be withdrawn by means of a sintered-glass, mercury valve. It was degassed several times at −120 to −130° before use. Blank runs showed no thermal or photosensitized decomposition. Unsaturates were shown to be absent by means of the Blacet–Leighton apparatus.[4] Runs carried out in the presence and absence of butane were closely consecutive, to minimize changes in light intensity. Runs were so adjusted that no more than 5 to 10% of the mercury dimethyl and no more than 0.5% of the butane present were decomposed.

TABLE I

RATES OF FORMATION OF ETHANE AND METHANE, AND STOICHIOMETRIC BALANCE IN THE PHOTOLYSIS OF MERCURY DIMETHYL IN THE PRESENCE OF *n*-BUTANE

Cell: quartz cylindrical, 20 cm. long, 2.4 cm. diameter, volume 90.4 cc. Light source: Hanovia S-353 Hg arc. Mercury dimethyl pressure 20.0 mm. at 300° K. in cell. Butane pressure in mm. at 300° K. in cell. Product rates of formation (R_x) in microns per hour at 300° K. in a volume of 590 cc. Rates must be multiplied by 9.70×10^{-14} to convert to moles/cc./second. Barred quantities refer to runs in the absence of butane.

Run	Temp., °C.	Butane pres., mm.	$\bar{R}_{CH_4}$	$\bar{R}_{C_2H_6}$	R_{CH_4}	$R_{C_2H_6}$	$\bar{R}_{C_2H_6} + \bar{R}_{CH_4}$	$R_{C_2H_6} + R_{CH_4}$
Bu-11	130	5.0	?	?	8.28	180	?	188
Bu-10	130	20.0	4.13	188	19.7	169	192	189
Bu-7	150	5.0	17.5	726	32.0	738	744	770
Bu-6	150	20.0	16.1	700	79.0	?	716	?
Bu-5	150	10.0	16.3	717	45.4	658	733	703
Bu-12	150	6.0	14.9	650	31.4	614	665	645
Bu-9	187	5.0	43.2	794	79.5	788	837	868
Bu-8	187	20.0	44.2	803	186	632	844	818
Bu-4	220	6.0	102	795	196	709	897	905
Bu-3	220	20.0	96.4	789	350	542	885	892

Results

The results obtained are shown in Table I. The incident intensity was held constant over the temperature range from 150 to 220° (runs Bu-3, 4, 5, 6, 7, 8, 9). At 130° the intensity was lowered to approximately 30% of this by means of a screen between lens and arc (runs Bu-10, 11).

Discussion

The following mechanism will be assumed for the photolysis of mercury dimethyl in the presence of butane.

$$CH_3 + CH_3 = C_2H_6 \qquad k_1(CH_3)^2 \quad (1)$$

$$CH_3 + (CH_3)_2Hg = C_2H_6 + Hg + CH_3 \qquad k_2(CH_3)(D) \quad (2)$$

$$CH_3 + (CH_3)_2Hg = CH_4 + CH_2HgCH_3 \qquad k_3(CH_3)(D) \quad (3)$$

$$CH_3 + CH_2HgCH_3 = C_2H_5HgCH_3 \qquad k_4(CH_3)(CH_2HgCH_3) \quad (4)$$

$$CH_3 + C_4H_{10} = CH_4 + C_4H_9 \qquad k_5(CH_3)(B) \quad (5)$$

$$CH_3 + C_4H_9 = C_5H_{12} \qquad k_6(CH_3)(C_4H_9) \quad (6)$$

(D) and (B) refer to the concentrations of mercury dimethyl and butane, respectively. The nature of the primary process is of no effect as long as CH_3 radicals are produced and its nature does not change over the temperature interval covered.

Evidence for reactions (1) to (4) has been given elsewhere. Reactions (5) and (6) have been assumed by Smith and Taylor.[3] Most of the conclusions to be drawn depend only on the validity of reactions (1), (3), (5) and (2). The above mechanism leads to the following stoichiometric relation if the amount of ethane formed by reaction (2) is essentially the same in the presence and absence of butane

$$R_{C_2H_6} + R_{CH_4} = \bar{R}_{C_2H_6} + \bar{R}_{CH_4} \qquad (7)$$

where barred quantities refer to conditions in the absence of butane. Table I shows that equation (7) is well obeyed.

Reactions (3) and (5) lead to the relation

$$\frac{R_{CH_4}}{\bar{R}_{CH_4}} = \left(1 + \frac{k_5}{k_3} \cdot \frac{(B)}{(D)}\right) \frac{CH_3}{\overline{CH_3}} \qquad (8)$$

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(3) J. O. Smith and H. S. Taylor, *J. Chem. Phys.*, **7**, 390 (1939).

(4) R. Gomer and W. A. Noyes, Jr., THIS JOURNAL, **71**, 3390 (1949).

The quantity $CH_3/\overline{CH}_3$ can be obtained by considering equations (1) and (2) and solving the resulting quadratic expression in CH_3.

$$\frac{CH_3}{\overline{CH}_3} = \frac{(k_2^2(D)^2/k_1 + 4R_{C_2H_6})^{1/2} - k_2(D)/k_1^{1/2}}{(k_2^2(D)^2/k_1 + 4\overline{R}_{C_2H_6})^{1/2} - k_2(D)/k_1^{1/2}} \qquad (9)$$

The quantity k_2^2/k_1 can be found from the ratios k_2/k_3 and k_1/k_3^2 determined in a previous investigation.[4] It is found that $k_2^2/k_1 = 0.187 \times 10^{24}$ (molecules/cc.) × seconds, practically independent of temperature, since the quantity $2E_2 - E_1 \approx 0$. It is therefore possible to determine k_5/k_3 from equations (8) and (9).

Equation (9) makes use of a quantity which depends largely on the correctness of the assumed mechanism for the photolysis of mercury dimethyl.[4] It is interesting to note that there is a more direct check on its accuracy. If ethane formation depended only on equation (1), the ratio of methyl steady-state concentrations would be given by

$$\frac{CH_3}{\overline{CH}_3} = \left(\frac{R_{C_2H_6}}{\overline{R}_{C_2H_6}}\right)^{1/2} \qquad (10)$$

If reaction (2) were solely responsible for ethane formation, $CH_3/\overline{CH}_3$ would be given by

$$\frac{CH_3}{\overline{CH}_3} = \frac{R_{C_2H_6}}{\overline{R}_{C_2H_6}} \qquad (11)$$

The true value of $CH_3/\overline{CH}_3$ should lie between these limits. Table II shows this to be the case. It is interesting to note that the amount of butane added was so small that $R_{C_2H_6}$ and $\overline{R}_{C_2H_6}$ did not differ much in most runs. Hence $CH_3/\overline{CH}_3$ calculated on the basis of equation (10) differs by not more than 10% from that calculated on the basis of equation (11). No large error can be introduced into the calculation of k_5/k_3, no matter how the quantity $CH_3/\overline{CH}_3$ is evaluated, or even if it is taken as unity to a first approximation. The values of k_5/k_3 listed in Table II are based on equations (8) and (9).

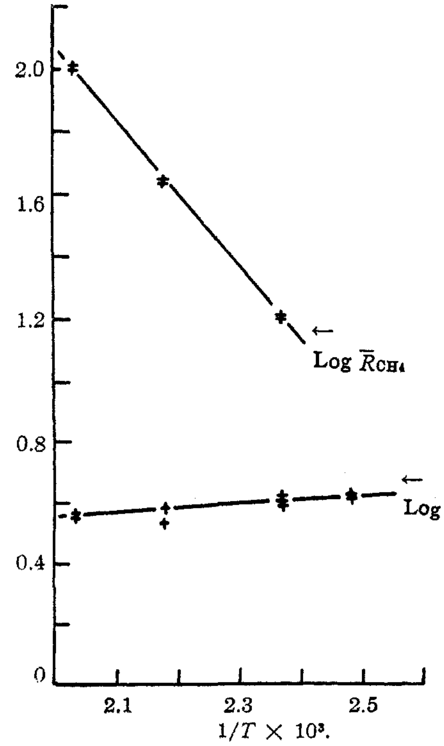

Fig. 1.

In run Bu-11 values of $\overline{R}_{CH_4}$ and $\overline{R}_{C_2H_6}$ were taken from run Bu-10, which was made immediately prior to run Bu-11. No value of $R_{C_2H_6}$ was obtained in run Bu-6. In this case $R_{C_2H_6}$ was obtained from equation (7). Run Bu-7 is to be taken as unreliable, since the temperature in the absence of butane rose to 155°.

Figure 1 shows a plot of log k_5/k_3 *vs.* $1/T$. It is seen that a good straight line results. The activation energy difference $E_5 - E_3$ is calculated from the plot

$$E_5 - E_3 = 640 \text{ cal.} \qquad (12)$$

The value of E_3 has been previously determined[4] as $9000 + {}^1/_2 E_1$ cal. This value is based on the comparison at 175 and 220° of the slopes of the plots of $\overline{R}_{C_2H_6}/\overline{R}_{CH_4}$ *vs.* $\overline{R}_{CH_4}$ in the photolysis of mercury dimethyl. This method avoids the errors inherent in the calculation of activation energies from rates of formation as functions of temperature.

TABLE II

RATIO OF METHYL STEADY STATE CONCENTRATIONS AND THE RATIO k_5/k_3 IN THE PHOTOLYSIS OF MERCURY DIMETHYL WITH *n*-BUTANE

The quantity $CH_3/\overline{CH}_3$ has been computed from equation (9) and a value $k_2^2/k_1 = 0.187 \times 10^{24}$ (molecules/cc.) × secs.

Run	$\frac{R_{C_2H_6}}{\overline{R}_{C_2H_6}}$	$\left(\frac{R_{C_2H_6}}{\overline{R}_{C_2H_6}}\right)^{1/2}$	$\frac{CH_3}{\overline{CH}_3}$	$\frac{k_5}{k_3}$	Temp., °C.
Bu-11	0.95	0.98	0.97	4.3	130
Bu-10	0.90	0.95	0.93	4.1	130
Bu-7	1.0	1.0	1.0	3.2	150
Bu-6	0.91	0.96	0.94	4.2	150
Bu-5	.92	0.96	0.95	3.9	150
Bu-12	.94	0.97	0.96	4.0	150
Bu-9	.99	1.0	1.0	3.4	187
Bu-8	.79	0.89	0.86	3.8	187
Bu-4	.89	0.95	0.93	3.6	220
Bu-3	.69	0.83	0.78	3.7	220

It will be seen from Fig. 1 that a plot of $\overline{R}_{CH_4}$ *vs.* $1/T$ also gives a good straight line, from which E_3 can be calculated to be 9000 to 10,000 cal. A similar value can be found from the data of Cunningham and Taylor[5] and others.[4] The calculation of E_3 on the latter basis hinges on the condition that the CH_3 steady-state concentration remain sensibly invariant with temperature. If the *absorbed* light intensity is constant, this

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[5] J. P. Cunningham and H. S. Taylor, *J. Chem. Phys.*, **6**, 359 (1938).

condition can be shown approximately equivalent to

$$(\bar{R}_{C_2H_6}/\bar{R}_{CH_4})^2 \gg 4 \qquad (13)$$

a condition which is amply met by the present experiments. However, the absorption of mercury dimethyl has been shown to increase when a medium pressure mercury arc was used as light source. Although no quantitative measurements were made, it is not improbable that this increase should vary in an exponential manner and give rise to a somewhat higher activation energy than the true one. The agreement between the two methods must therefore be regarded as somewhat fortuitous and the value of $E_3 = 9000 + {}^1/_2\, E_1$ cal. will be considered the correct one. This gives for E_5 the value

$$E_5 = 8400 + {}^1/_2 E_1 \text{ cal.} \qquad (14)$$

This value is considerably higher than the one obtained by Smith and Taylor.[3] This discrepancy may be due to the fact that these authors used concentrations of butane so large that methane formation exceeded ethane formation. Under these conditions the CH_3 steady-state concentration must have decreased by a factor of 2 or 3 over the temperature interval in question. If the lowest two temperatures given are used to calculate E_5, a value of 6400 cal. is obtained, in contrast to the over-all value of 5500 cal. Here the rate of ethane formation decreased by a factor of 2.25 as the temperature *increased* from 369 to 404°K. Since concentrations of mercury dimethyl high enough to be completely absorbing were used, these data probably were free from the compensating error of increased light absorption. These arguments probably apply to other cases where the activation energy of hydrogen abstraction was calculated on the basis of increase in methane formation as a function of temperature.

The question arises whether the present work deals with the abstraction of primary or secondary hydrogens. It has been pointed out by Hinshelwood[6] that compound reactions yielding the same measurable product should give rise to bent curves in the plots of ln rate *vs.* $1/T$. It can be shown that the asymptotes to the high and low temperature branches of the curve (corresponding to the high and low activation energy steps) intersect at a temperature given by

$$(E_2 - E_1)/R \ln a_2/a_1 = T_{\text{intersection}} \qquad (15)$$

where a_1 and a_2 are the pre-exponential factors corresponding to the activation energies E_1 and E_2. A real intersection can occur only when $a_2 > a_1$, for $E_2 > E_1$.

If the difference in pre-exponential factors for primary and secondary hydrogen abstraction in butane is small, $T_{\text{intersection}}$ will be quite high, even if $E_{\text{prim.}} - E_{\text{sec.}}$ is small. If the pre-exponential factors may be assumed proportional to the number of primary and secondary hydrogens, this temperature will be 600°K, if $E_{\text{prim.}} - E_{\text{sec.}}$ is only 500 cal., which is unlikely. Any *linear* portion of the ln rate *vs.* $1/T$ curve below $T_{\text{intersection}}$ must be ascribed to the low activation energy reaction. It is therefore likely that the present work deals with the abstraction of secondary hydrogens.

Summary

1. The reaction of methyl radicals produced from mercury dimethyl with butane has been studied.

2. The activation energy difference between the reactions of methyl radicals with mercury dimethyl and butane (to give methane in each case) is 640 cal. leading to an activation energy of about $8400 + {}^1/_2\, E_1$ cal. for the reaction of CH_3 radicals with butane.

3. The reaction with butane may involve mostly secondary hydrogens.

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[6] C. N. Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," The Clarendon Press, Oxford, 1933, p. 67.

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The Fluorescence of Cyanine and Related Dyes in the Monomeric State[1]

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A great deal of work has been done on the correlation of the position of the principal absorption maxima of cyanine and related dyes in the monomeric state and the structure of these dyes.[4-9] No data for the corresponding fluorescence maxima have been published except some

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[1] This article is based on portions of theses by L. J. E. Hofer and R. J. Grabenstetter submitted to the Graduate School of the University of Rochester in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Now at the Bureau of Mines, Central Experiment Station, Pittsburgh, Pa.

[3] Now at Proctor and Gamble Co., Ivorydale, Ohio.

[4] L. G. S. Brooker, "Nuclear and Theoretical Organic Chemistry," Vol. III, Frontiers in Chemistry, Interscience Publishers, Inc., New York, N. Y., 1945.

[5] L. G. S. Brooker, F. L. White, R. H. Sprague, S. G. Dent, Jr., and G. van Zandt, *Chem. Rev.*, **41**, 325 (1947).

[6] N. I. Fisher and F. M. Hamer, *Proc. Roy. Soc.* (*London*), **A154**, 703 (1936).

[7] Beilensen, N. I. Fisher and F. M. Hamer, *ibid.*, **A163**, 138 (1937).

[8] Herzfeld and Sklar, *Rev. Modern Phys.*, **14**, 294 (1942).

[9] H. Kuhn, *J. Chem. Phys.*, **16**, 840 (1948).