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

Photochemical Studies. XLI. The Photochemistry of Dimethyl Mercury[1]

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It was found during an investigation to be reported later that methyl radicals are almost certainly intermediates in the direct photochemical decomposition of ethylene oxide. The study of the reactions of CH_3 radicals with that molecule was, therefore, advisable and for this purpose the photochemical decomposition of $Hg(CH_3)_2$ was found to be convenient. Certain aspects of the decomposition of the latter molecule need further clarification.[3]

Experimental

Dimethyl mercury was prepared by the method of Gilman and Brown.[4] It was purified by fractional distillation in a column and then by bulb to bulb distillation at low temperatures. Vapor pressures agreed with the values of Linnett and Thompson.[5] The compound was degassed repeatedly after condensation by dry ice.

Two quartz reaction vessels were used: (a) 20 cm. length, 2.4 cm. inside diameter; (b) 3.5 cm. length, 2.0 cm. inside diameter. They were attached by quartz to Pyrex graded seals through mercury cut-offs to a line without stopcocks. The dead space during illumination was about 3 cc. In the case of the short cell it was necessary to replenish the $Hg(CH_3)_2$ periodically to prevent more than 10% decomposition.

The cells were placed in a brass cylinder about 10 cm. in diameter which could be heated electrically. Temperatures were read on thermometers placed in holes in the brass cylinder and by a thermocouple placed in a well in the vessel near the rear window. Extreme variations did not exceed three degrees.

Two different light sources were used: (a) a Hanovia medium pressure arc, S353; (b) a General Electric Company AH-6 high pressure arc. Filters were not used and radiation passing through a hole in a diaphragm next to the arc was made approximately parallel by a quartz lens, so that the cells were filled as completely and as uniformly as possible with radiation.

The absorption spectum of $Hg(CH_3)_2$ has been investigated by several authors, particularly Thompson and Linnett[6] and Terenin and Prileshayewa.[7] These authors agree that the spectrum is continuous in the neighborhood of 2500 Å., but long wave limits are placed at 2550 and 2800 Å., respectively.

The products uncondensed by liquid nitrogen (CH_4 with some C_2H_6) were separated from the $Hg(CH_3)_2$ by Toepler pumps. The remaining C_2H_6 and C_2H_4 (if any) were separated from $Hg(CH_3)_2$ by use of a modified Ward apparatus.[8] Combustions with oxygen over a heated platinum wire were usually used, but unsaturates were determined by fuming sulfuric acid, using a Blacet–Leighton apparatus.[9]

Light intensities with a given arc were varied by neutral density filters. These consisted of quartz plates, 1 mm.

TABLE I

RATES OF FORMATION OF METHANE AND OF ETHANE DURING PHOTOCHEMICAL DECOMPOSITION OF $Hg(HC_3)_2$

V = 590 cc. (for measurement of gas pressures of products); cell, 20 cm. long, 2.4 cm. diameter (V = 90.4 cc.); pressure of $Hg(CH_3)_2$ = 5 mm. (at 300°K.); rates in microns/hr. (at 300°K.).

Run	Temp., °C.	R_{CH_4}	$R_{C_2H_6}$	$R_{C_2H_6}/R_{CH_4}$
DM-8	175	20.1	1298	64.6
E-5		13.8	631	45.7
DM-9		11.0	422	38.4
E-1		3.22	55.7	17.3
2		1.77	22.5	12.7
3		0.742	4.84	6.52
8		.794	5.50	6.93
4		.544	2.16	3.97
Blank		.04	.....	...
DM-11	220	41.0	836	20.4
10		29.1	450	15.5
12		9.46	67.2	7.10
13		9.04	60.3	6.67
15		5.49	23.7	4.32
14		2.37	3.78	1.59
Blank		0.658	2.84	...

TABLE II

RATES OF FORMATION OF METHANE AND OF ETHANE DURING PHOTOCHEMICAL DECOMPOSITION OF $Hg(CH_3)_2$

V = 590 cc. (for measurement of gas pressures of products); cell, 3.5 cm. long, 2.0 cm. diameter (V = 11.0 cc.); rates in microns/hr. (at 300°K.); T = 175°C.

Run	R_{CH_4}	$R_{C_2H_6}$	$Hg(CH_3)_2$ Pressure, mm.	$R_{C_2H_6}/R_{CH_4}$
F-11	12.4	508.5	20 (at 175°)	41.0
9	10.2	395.6		38.8
1	10.0	355.9		35.6
6	7.21	233.8		32.4
2	5.84	130.1		22.3
5	5.13	118.9		23.1
14	3.42	50.6		14.8
3	2.55	29.1		11.4
4	1.98	20.3		10.3
12	20.1	700.5	30 (at 175°)	34.9
16	11.7	287.8		24.6
7	10.5	223.6		21.3
10	9.78	224.3		22.9
8	6.03	107.4		17.8
13	4.98	55.2		11.1
15	3.21	24.3		7.58

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(2) E. I. du Pont de Nemours and Company Fellow during 1948–1949.

(3) See W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," The Reinhold Publishing Corporation, New York, N. Y., 1941, for a review of work through 1939. Later references will be given in the present article.

(4) H. Gilman and R. E. Brown, THIS JOURNAL, **52**, 3314 (1930).

(5) J. W. Linnett and H. W. Thompson, *Trans. Faraday Soc.*, **32**, 681 (1936).

(6) H. W. Thompson and J. W. Linnett, *Proc. Roy. Soc.* (*London*), **A156**, 108 (1936).

(7) A. Terenin and N. Prileshayewa, *Acta Physicochimica, U. S. S. R.*, **1**, 759 (1935).

(8) E. C. Ward, *Ind. Eng. Chem.*, *Anal. Ed.*, **10**, 169 (1938); see W. Davis, Jr., and W. A. Noyes, Jr., THIS JOURNAL, **69**, 2155 (1947).

(9) F. E. Blacet and P. A. Leighton, *Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 266 (1931); for list of references see R. N. Smith and P. A. Leighton, *ibid.*, **14**, 758 (1942).

in thickness, coated with a Cr–Al alloy by evaporation.[10] These filters were placed in such a way as to minimize local variations in density, although their uniformity was such as to render this precaution probably unnecessary.

Results

Table I shows data on rates of formation of CH_4 and of C_2H_6 in the large cell at 175° and at 220°. Table II shows similar data at 175° obtained in the small cell. Since the rate of C_2H_6 production is roughly proportional to the intensity, it can be seen that the intensity has been varied about 600-fold.

Table III shows data obtained in the large cell and over a range of temperature from 25 to 250° at approximately constant intensity.

TABLE III

RATES OF FORMATION OF METHANE AND OF ETHANE DURING PHOTOCHEMICAL DECOMPOSITION OF $Hg(CH_3)_2$

V = 590 cc. (for measurement of gas pressures of products); cell, 20 cm. long, 2.4 cm. diameter (V = 90.4 cc.); intensity constant; pressure of $Hg(CH_3)_2$ = 20.0 mm. (at 300 °K.); arc – S 353; rates in microns/hr. (at 300 °K.).

Run	Temp., °C.	R_{CH_4}	$R_{C_2H_6}$	$R_{C_2H_6}/R_{CH_4}$
DM-0	25	0	56.1	....
1	100	1.28	81.7	63.8
2	125	2.62	83.2	31.8
3	150	5.15	88.6	17.2
4	175	9.81	89.9	9.2
B-1	175	9.95	97.4	9.8
5	175	10.4	95.4	9.2
DM-5	200	19.4	97.9	5.04
B-4	200	19.5	100.8	5.17
3	220	33.9	102.4	3.02
7	220	35.4	104.0	2.94
8	218	30.3	94.1	3.10
DM-6	225	47.5	113.4	2.39
7	250	75.2	116.5[a]	(1.55)
B-2	248	72.0	129.3[a]	(1.79)
6	250	71.0	121.6[b]	1.71

[a] Total C_2 hydrocarbons, C_2H_4 not determined. [b] 1.8 × 10^{-2} mm. C_2H_4 formed in addition.

Discussion

The data in Table III show that at constant intensity the rate of C_2H_6 formation increases markedly between 25 and 100° but that the change is very gradual as the temperature is increased further. This is in general agreement with the quantum yields determined by Linnett and Thompson[11] and the results of Cunningham and Taylor.[12] These facts may be connected with a decrease in stability of the $HgCH_3$ radical with increasing temperature. Thus if the primary process were $Hg(CH_3)_2 + h\nu = CH_3 + HgCH_3$ followed by a thermal decomposition of $HgCH_3$, $HgCH_3 = Hg + CH_3$, a recombination reaction could acccount for a low quantum yield of $Hg(CH_3)_2$ disappearance at low temperatures. The solid compound mercury methyl is, however, known not to be very stable even at room temperature.[13] The situation may resemble in important respects that found in acetone.[14] There is, however, evidence pointing to a reaction between CH_3 radicals and $Hg(CH_3)_2$ to give C_2H_6[15,19] and this may account for the gradual increase in $R_{C_2H_6}$ at higher temperatures.

The chief conclusions to be drawn in this paper are independent of the nature of the primary process provided, of course, CH_3 radicals are produced.[6,12]

For the sake of clarity of presentation it may be best to list at once the various steps in the mechanism and to follow them with evidence in their favor. It will be assumed in agreement with all other authors who have studied this molecule that CH_3 radicals are formed.[12]

$$CH_3 + CH_3 = C_2H_6;\ R_{C_2H_6}(1) = k_1(CH_3)^2 \quad (1)$$

$$CH_3 + Hg(CH_3)_2 = A;\ R_A = k_2(CH_3)(D) \quad (2)$$

$$A = CH_3 + Hg(CH_3)_2;\ -R'_A = k_3\,(A) \quad (3)$$

$$CH_3 + A = C_2H_6 + Hg + 2CH_3 \text{ (or } CH_3 + HgCH_3 \text{ or } Hg(CH_3)_2);\ -R''_A = k_4(CH_3)(A) \quad (4)$$

$$CH_3 + Hg(CH_3)_2 = CH_4 + H_2CHgCH_3;\ R_{CH_4} = k_5(CH_3)\,(D) \quad (5)$$

$$CH_3 + H_2CHgCH_3 = C_2H_5HgCH_3;\ R(6) = k_6(CH_3)(H_2CHgCH_3) \quad (6)$$

(D) = concentration of $Hg(CH_3)_2$.

The rate of CH_4 formation will be the rate of (5) and the rate of C_2H_6 formation will be the rate of (1) plus the rate of (4). If $R_{C_2H_6}(T)$ is the total rate of C_2H_6 formation, the following equation can be derived by assumption of the steady state for the intermediate A

$$\frac{R_{C_2H_6}(T)}{R_{CH_4}} = \frac{k_1R_{CH_4}}{k_5^2(D)^2} + \frac{k_2R_{CH_4}}{k_5}\,\frac{1}{(k_3k_5(D)/k_4 + R_{CH_4}} \quad (7)$$

Equation (7) should be valid regardless of the units chosen for the various rates, but if comparison between constants for $Hg(CH_3)_2$ and for other molecules is desired, the rates should be expressed in standard units. For this purpose the rates have been converted to molecules cc.$^{-3}$ sec.$^{-1}$ with the assumption that CH_4 and C_2H_6 are produced uniformly throughout the reaction vessel. The validity of this assumption will be examined in a later paragraph.

It can be seen from the data in Tables I and II (Figs. 1 and 2) that a plot of $R_{C_2H_6}(T)/R_{CH_4}$ *vs.* R_{CH_4} gives a straight line except for low values of R_{CH_4} and that this straight line does not pass through the origin. The data for the short cell (Fig. 2) show more scatter than those for the long cell. This is due, undoubtedly, to the necessity for replenishing $Hg(CH_3)_2$ to prevent excessive decomposition during a run.

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[10] The authors wish to express their appreciation to Dr. Harry Polster, Department of Optics, University of Rochester, for preparing these filters.

[11] J. W. Linnett and H. W. Thompson, *Trans. Faraday Soc.*, **33**, 501, 874 (1937).

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

[13] F. O. Rice and B. L. Evering, THIS JOURNAL, **56**, 2405 (1934)

[14] See W. A. Noyes, Jr., and L. M. Dorfman, *J. Chem. Phys.*, **16** 788 (1948).

[15] See K. W. Saunders and H. A. Taylor, *ibid.*, **9**, 616 (1941).

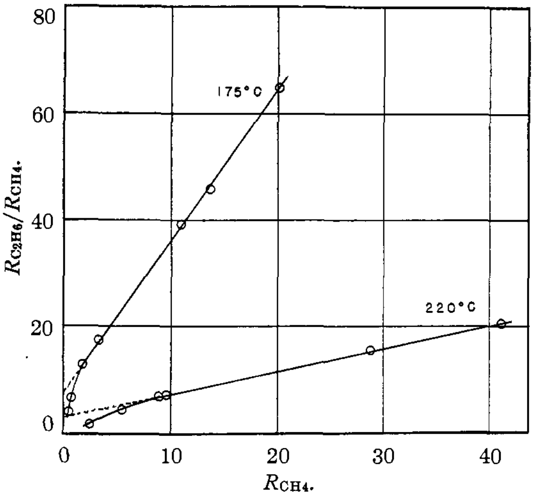

Fig. 1.—$R_{C_2H_6}/R_{CH_4}$ vs. R_{CH_4} in quartz cell 20.0 cm. long and 2.4 cm. internal diameter at 175° and at 220°C. The pressure of $Hg(CH_3)_2$ is 5.0 mm. (measured at 300°K.). Rates are in microns/hr. measured in a volume of 590 cc. at 300°K. Rates should be multiplied by 5.83×10^{10} to convert them to molecules/cc./sec. in the reaction vessel.

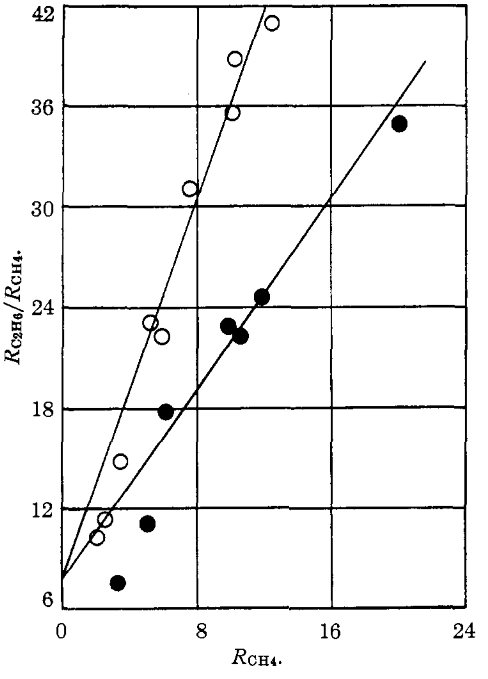

Fig. 2.—$R_{C_2H_6}/R_{CH_4}$ vs. R_{CH_4} in quartz cell 3.5 cm. long and 2.0 cm. internal diameter. Pressures of $Hg(CH_3)_2$ are 13.4 mm. (empty circles) and 20.1 mm. (solid circles) both measured at 300°K., $T = 175°$. The points are experimental and the lines are calculated from rate constants determined in the long cell at 175°C. (Fig. 1.). Rates are in micron/hr. and should be multiplied by 4.79×10^{11} to convert them to molecules/cc./sec.

A linear plot with positive intercept is obtained from equation (7) when $R_{CH_4} \gg k_3k_5(D)/k_4$. This situation would be obtained when the CH_3 concentration is sufficiently high to make (4) rapid compared to (3). The rate of formation of C_2H_6 by action of CH_3 on $Hg(CH_3)_2$ would be controlled by the rate of (2). The intercept would be k_2/k_5 and should be independent of (D) at constant temperature. This is seen to be true within experimental error (Fig. 2).

The slope of the linear plot would be $k_1/k_5^2(D)^2$ and hence should vary with $1/(D)$.[2] This is also found to be true within experimental error for the data in Tables I and II at 175°.

For this linear portion of the plot equations (2), (3) and (4) could be replaced simply by $CH_3 + Hg(CH_3)_2 = C_2H_6 + Hg + CH_3$, but the data necessitate a variable slope for low values of R_{CH_4} and the curve apparently tends toward the origin. This is satisfactorily accounted for by the complete mechanism embodied in equations (1) to (6) inclusive. While the authors have been unable to suggest any other mechanism which accounts for all of the facts, it should be emphasized that this does not constitute a proof that the proposed mechanism is a unique solution of the problem.

Equation (7) is, therefore, of the right form to fit the data in Tables I and II (Figs. 1 and 2). The smooth curves in Fig. 2 are calculated with the aid of rate constants obtained from the data in Table I and the fit to the experimental points adds strong support to the belief that the data are self-consistent.

It is not desired at the present time to enter into any detailed discussion of the theory of reaction rates, but a standard form of equation must be used for intercomparisons of various types of data. Hence the various rate constants are expressed in the form $aT^{1/2}e^{-E/RT}$ where $a = 2\sigma^2(\pi k/m)^{1/2}$ when the two colliding particles are identical (equation (1)) and $a = 2\sigma^2(2\pi k(m_1 + m_2)/m_1m_2))^{1/2}$ when the two colliding particles are different (equations (2), (4), (5), and (6)). k is the Boltzmann constant and σ^2 may be referred to as the "effective cross section" for the reaction.

If k_1 and k_5 are written in the above form it is seen that

$$\ln (k_1/k_5^2) = \ln (a_1/a_5^2) - {}^1/_2 \ln T - (E_1 - 2E_5)/RT \quad (8)$$

and $E_1 - 2E_5$ can be obtained from the slopes in Fig. 1 at two different temperatures. In this way it is found that $E_5 = 9000 + {}^1/_2 E_1$. This may be contrasted with approximately $5700 + {}^1/_2 E_1$ for the corresponding reaction of CH_4 formation in acetone.[16] The value of E_1 is not known precisely but is undoubtedly low.[17]

It is next possible to calculate a_1/a_5^2 and hence a relationship between the cross sections for C_2H_6 formation from radicals and for methane forma-

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[16] L. M. Dorfman and W. A. Noyes, Jr., *J. Chem. Phys.*, **16**, 557 (1948).

[17] See ref. 12 and also S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Company, Inc., New York, N. Y., 1941, p. 260.

tion. The results are: $a_5 = a_1^{1/2} \times 4.6 \times 10^{-9}$ (molecules^{-1} sec.$^{-1}$ cc.)$^{1/2}$; $\sigma_5^2 = 3.5 \times 10^{-11}\ \sigma_1$. In other words if $CH_3 + CH_3$ is a very fast reaction with a "normal" collision diameter of about 5×10^{-8} cm., the "effective cross section" for CH_4 formation is very low, roughly 10^{-3} times that which would be expected on a simple collision picture with 100% efficiency for each collision providing enough energy. It is interesting to note that the cross section obtained in this way is almost exactly the same as for the similar reaction in acetone[14,16] after suitable correction for the volume of the vessel.

The intercept of the straight line portion of the curves in Figs. 1 and 2 gives directly the ratio of $R_{C_2H_6}$ (4)/R_{CH_4}, *i. e.*, the ratio of the rate of C_2H_6 formation to that of CH_4 formation when CH_3 radicals react with $Hg(CH_3)_2$. By use of the intercepts at two different temperatures one finds $E_5 - E_2$ to be approximately 9000 calories, *i. e.*, the energies of activation for C_2H_6 formation by the two different processes are about the same.

This result is somewhat surprising because reactions (2), (3) and (4) together could give rise to a chain reaction. Reaction (4) could be sufficiently exothermic to produce two CH_3 radicals.[18] The answer must be found in the very low a term for reaction (2), *i. e.*, it is found that $a_2 = 3.5 \times 10^{-4}\ a_5$. Since the same particles are involved the "cross section" for ethane formation from $CH_3 + Hg(CH_3)_2$ is also 3.5×10^{-4} times that for CH_4 formation. Thus in spite of a low activation energy the chain propagating step would be so slow as to be unimportant under most conditions.

Reference may now be made to the data in Table III to obtain a rough check on the energy of activation of the step leading to CH_4 formation. The CH_3 steady state concentration as obtained from the complete mechanism is

$$(CH_3) = -(k_5/2k_1)(D)(1 - (1 + 4I_a\, k_1/(k_5^2(D)^2)^{1/2}) \quad (9)$$

where I_a = number of quanta absorbed per cm.^{3} per second and two CH_3 radicals are assumed to be formed per quantum absorbed. From the rate of C_2H_6 formation a rough estimate can be made of I_a and this combined with the value determined above for k_1/k_5^2 indicates that $4I_ak_1/k_5^2(D) \gg 1$. Even the square root of this quantity is probably 10 to 100. Since $R_{CH_4} = k_5(CH_3)(D)$, one may write to a first approximation

$$R_{CH_4} = k_5 I_a^{1/2}(D)/k_1^{1/2} \quad (10)$$

At constant intensity and constant (D) a plot of $\ln R_{CH_4}$ *vs.* $1/T$ should give a straight line with slope $-(E_5 - {}^1/_2\,E_1)/R$. The assumptions made are probably least valid at high temperatures, but $E_5 - {}^1/_2\,E_1$ is found from the data in Table III to be approximately 10,000 cal., about as good a check as could be expected with the 9000 calories previously calculated from the data in Table I.

The mechanism postulated fits all of the data described in this article and as far as can be ascertained agrees well with data in the literature. A reaction between CH_3 radicals and $Hg(CH_3)_2$ to give C_2H_6 has been postulated frequently but the work of Harris and Steacie[19] affords the best proof for its occurrence. These authors studied the reaction of H atoms with $Hg(CH_3)_2$ and found that the ratio CH_4/C_2H_6 in the products was even less than unity under some conditions. If C_2H_6 were produced solely by combination of CH_3 radicals this ratio would have a minimum value of 2. It is necessary, therefore, to postulate a second method of formation of C_2H_6. Since the work just described seems to necessitate reactions (2), (3) and (4) for this method, it may or may not correspond to a simple inversion. Little more can be said about this matter at the present time.

The calculations which have been made are based on a uniform distribution of CH_3 radicals throughout the vessel, although they would be approximately valid (with minor changes in numerical values) if the distributions were similar from one run to another. Dr. T. L. Hill[20] has made approximate calculations of CH_3 distribution in a cell in the case of acetone where a situation similar to that in $Hg(CH_3)_2$ is encountered. The character of the distribution is very markedly dependent on the fate of radicals when they reach the walls, *i. e.*, under the conditions used in most of these experiments gas phase reactions will not be fast enough to prevent diffusion of many radicals to the walls. If the radicals are totally reflected a reasonably uniform distribution in a given cross section of the vessel is to be expected, although there will be a progressive decrease in concentration as the distance from the window through which the radiation is incident on the vessel increases.

Very little quantitative information is available on the fate of CH_3 radicals when they encounter walls under conditions obtaining in experiments of the type herein described. It appears probable, although the data are not exact enough to warrant a definite conclusion, that a very large fraction of encounters between CH_3 radicals and walls must lead to reflection. Otherwise the data would not be as consistent as they seem to be. More positive information on this point would certainly be of great value. The self-consistency of data in two different cells and the further fact that the addition of several hundred millimeters of carbon dioxide in one experiment did not affect the results, offer evidence that the methods of calculation used are justified.

In conclusion it should be reëmphasized that the pre-exponential factors in the rate constants for reactions (5) and (2) are very low. For many bimolecular reactions $aT^{1/2}$ is of the order of magnitude of 10^{13} to 10^{14} if concentrations are expressed in moles/cc. For reaction (5) (CH_4 forma-

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[18] See N. V. Sidgwick and H. D. Springall, *Nature*, **156**, 599 (1945), and H. S. Gutowsky, *J. Chem. Phys.*, **17**, 128 (1949).

[19] G. M. Harris and E. W. R. Steacie, *J. Chem. Phys.*, **13**, 559 (1945).

[20] Private communication.

tion) $aT^{1/2}$ is about 2×10^{11} in these units and low values of this magnitude are found for other similar reactions if the assumption is made that the association reaction for CH_3 radicals is "normal." If the latter is low the constant for CH_4 formation will be reduced even further. For reaction (2) (the rate determining step for C_2H_6 formation from CH_3 and $Hg(CH_3)_2$), $aT^{1/2}$ is about 7×10^6, a very low value compared to most other bimolecular reactions.

Summary

1. The rates of formation of C_2H_6 and of CH_4 during irradiation of $Hg(CH_3)_2$ have been studied as functions of intensity, pressure, and temperature.
2. At temperatures below 250° CH_4 seems to be formed solely by the reaction $CH_3 + Hg(CH_3)_2 = CH_4 + CH_2HgCH_3$.
3. Ethane must be formed by at least two processes, one of which is the combination of CH_3 radicals and the other of which is a reaction of CH_3 radicals with $Hg(CH_3)_2$ which apparently proceeds through an unstable intermediate addition complex.
4. The pre-exponential factor in the rate constant for CH_4 formation is very much smaller than for ethane formation by radical combination.
5. The activation energy for reaction of CH_3 radicals with $Hg(CH_3)_2$ to form C_2H_6 is very low, about the same as for C_2H_6 formation by radical combination, but the pre-exponential factor is so low that the rate is small and a chain reaction is of relatively minor importance.
6. A mechanism consistent with the facts has been proposed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BOSTON UNIVERSITY]

The Heats of Reaction of Lithium, Sodium, Potassium and Cesium with Ammonium Ion in Liquid Ammonia at $-33°$

BY LOWELL V. COULTER AND ROBERT H. MAYBURY

The thermochemistry of oxidation–reduction reactions involving the alkali metals in liquid ammonia is of twofold interest. From a long range view the heats of reaction of the metals with ammonium ion in liquid ammonia, for example

$$M + NH_4^+ = M^+ + NH_3 + {}^1/_2H_2 \qquad (1)$$

may provide basic thermal values which when combined with corresponding free energy changes permit evaluation of relative partial molal ionic entropies in this solvent. In addition to the use of ionic entropies in the calculation of oxidation–reduction potentials not measurable directly, these ionic properties also permit evaluation of relative entropies of solvation of ions in liquid ammonia in a manner developed by Latimer[1] for water solutions. The existing scarcity of accurate free energy data for reactions occurring in liquid ammonia imposes temporary restrictions on the development of a set of reliable ionic entropies for this medium. However, the presumably simpler nature of liquid ammonia as compared with water arising from weaker hydrogen bonding would appear to simplify somewhat the theoretical treatment of the solvation process in this medium and therefore justify the exploration of this solvent.

Of immediate interest is the utilization of thermal data for the above reaction for the comparison of the nature of liquid ammonia solutions of the ammonia soluble metals. Prevailing concepts of these systems, while differing with regard to the equilibria involved in the more concentrated solutions and though incomplete as to the exact nature of the ammoniated electron, agree that the dilute solutions consist of solvated metal ions and single electrons resulting from essentially complete ionization in the dilute range of concentration. An exact similarity for these solutions has been observed by Gibson and Argo,[2] who have reported identical absorption spectra for dilute solutions of lithium, sodium, potassium and cesium. It is to be expected that these systems would likewise possess identical thermochemical properties for reactions involving the solvated electron of these solutions with a common oxidizing agent, as for example

$$e^-_{(am)} + NH_4^+{}_{(am)} = {}^1/_2H_{2(g)} + NH_{3(l)}$$

Direct measurement of the thermal effect associated with this reaction has not seemed experimentally feasible. It may be obtained indirectly, however, as the difference between the heat of solution of the metal in pure liquid ammonia and the heat of reaction of the metal with ammonium ion in liquid ammonia. The latter heat of reaction for solid lithium, sodium, potassium and cesium determined in this research combined with the literature values for the heats of solution of the metals has made possible the evaluation of the heat of this reaction. For dilute solutions of each of these metals we have obtained heats of reaction ranging from 39.7 kcal. for potassium to 41.6 kcal. for cesium with a mean of 40.4 kcal. This we regard as indicative of a common reaction for these solutions involving the solvated electron which energetically appears identical within experimental error in all cases.

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[1] Latimer, *Chem. Rev.*, **18**, 349 (1936).

[2] Gibson and Argo, THIS JOURNAL, **40**, 1327 (1918).