

## The Decomposition of Mercury Dimethyl

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## The Decomposition of Mercury Dimethyl

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The thermal and photochemical decompositions of mercury dimethyl have been studied in presence and absence of hydrogen. The thermal process occurs measurably above 290° in absence of hydrogen and is complex, yielding ethane, methane and carbonaceous products. In presence of hydrogen there is no carbonaceous deposit and methane is predominantly formed with consumption of hydrogen, which accelerates the decomposition. The influence of surface effects has been noted. The photo-decomposition has been studied from 50–300°C. In absence of hydrogen, ethane is practically exclusively formed up to 200°. In presence of hydrogen, methane is formed at all temperatures, in increasing amounts with increase of temperature. A mechanism based on photo-decomposition to free methyl radicals with association to yield ethane and reaction with hydrogen to yield methane has been quantitatively determined. For the activation energy  $\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}$  a value of  $9 \pm 2$  kcal. has been deduced.

THE reaction  $\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}$  has recently been shown to be of importance as an intermediate process in exchange reactions involving the simpler saturated hydrocarbons,<sup>1, 2</sup> and any independently derived information regarding its energetics would be of value in explaining the results obtained. The present investigation was undertaken in an attempt to provide such information, the metal alkyl, mercury dimethyl, being used as a source of free methyl radicals. It was first necessary to establish the conditions under which the decomposition of mercury dimethyl proceeded at a measurable rate: then, from the effect of added hydrogen upon the kinetics of the decomposition, some conclusions were drawn regarding the process under consideration.

Direct evidence of the momentary existence of free organic radicals in the decomposition of metal alkyls was first obtained by Paneth and Hofeditz,<sup>3</sup> who passed lead tetramethyl vapor through a quartz tube heated at one point to about 700°, and detected free methyl radicals by causing them to combine with a number of metals deposited as mirrors in the cool parts of the tube. It was found<sup>4</sup> that free ethyl could be prepared from lead tetraethyl and identified in a similar manner, but the higher analogues were

apparently unstable at the temperatures necessary for the decomposition of the corresponding metal alkyls. Indirect evidence of the thermal liberation of free radicals from mercury dimethyl has been furnished by Taylor and Jones<sup>5</sup> who showed that such postulated radicals induced the polymerization of ethylene at reaction temperatures of 200–300°. Frey<sup>6</sup> also observed that the addition of 1 percent of the compound to butane brought about the decomposition of twenty equivalents at 525°, at which temperature the hydrocarbon itself would not have been affected in the time of the experiment; this result can only be explained as due to chain initiation by free methyl radicals. Rice, Rodowskas and Lewis<sup>7</sup> obtained similar results with acetone containing 1 percent of mercury dimethyl in the temperature range 350–400°: the relatively short chains observed were attributed to more effective chain-breaking processes than in the case of butane.

The photochemical decomposition of mercury dimethyl has been somewhat more extensively investigated, notably by Terenin and co-workers.<sup>8</sup> The absorption spectrum shows a continuum beginning at 2800Å and extending further into the ultraviolet, upon which is superimposed a group of diffuse bands in the

<sup>1</sup> Trenner, Morikawa and Taylor, *J. Chem. Phys.* **5**, 203 (1937).

<sup>2</sup> Morikawa, Benedict and Taylor, *J. Chem. Phys.* **5**, 212 (1937).

<sup>3</sup> Paneth and Hofeditz, *Ber.* **62**, 1335 (1929).

<sup>4</sup> Paneth and Lautsch, *Ber.* **64**, 2702 (1931).

<sup>5</sup> Taylor and Jones, *J. Am. Chem. Soc.* **52**, 1111 (1930).

<sup>6</sup> Frey, *Ind. Eng. Chem.* **26**, 200 (1934).

<sup>7</sup> Rice, Rodowskas and Lewis, *J. Am. Chem. Soc.* **56**, 2497 (1934).

<sup>8</sup> Terenin, *J. Chem. Phys.* **2**, 441 (1934); *Acta Physicochim. U. S. S. R.* **1**, 762 (1935); Terenin and Prileshajeva, *Trans. Faraday Soc.* **31**, 1483 (1935).

region 2100–1970Å. Terenin postulated a mechanism of decomposition involving free methyl radicals, and reported their identification by the metal mirror technique, the maximum concentration of radicals being observed when light in the 2100Å region was used. Linnett and Thompson,<sup>9</sup> using radiation of about 2537Å, reported rapid conversion of mercury dimethyl, largely to mercury and ethane, at room temperature, the quantum yield of the process being very nearly unity; these investigators first concluded that at least 90 percent of the metal alkyl decomposed directly to molecular ethane in the primary act, only a small fraction decomposing by way of free radicals. In their second paper they reversed their position and developed a mechanism of decomposition via free methyl radicals which leads to quantum yields higher than unity at elevated temperatures. In studying the analogous decomposition of lead tetramethyl, Leighton and Mortensen<sup>10</sup> held the radical view; in this case, free methyls were detected by the use of lead mirrors, the method being rendered much more sensitive than heretofore by the introduction of a radioactive indicator.

In several instances, the gaseous products resulting from the decomposition of metal alkyls have been analyzed, and the intermediate formation of free radicals has been suggested by the results obtained. Simons, McNamee and Hurd<sup>11</sup> and Paneth, Hofeditz and Wunsch,<sup>12</sup> postulate an initial dissociation of lead tetramethyl into free methyls in order to account for such products as methane, iso-butylene, and a solid carbonaceous deposit. Meinert<sup>13</sup> was led to a similar conclusion on examining the products from the thermal decomposition of lead tetraethyl.

The effect of added hydrogen in the decomposition of metal alkyls has received only brief consideration. It was disregarded by Paneth and Hofeditz in their original investigation,<sup>3</sup> in which hydrogen was used as a carrier gas, but in their later publication<sup>12</sup> interaction between free

methyls and molecular hydrogen was postulated to account for the removal as methane of a large fraction of the radicals produced at 900°, and subsequently passed through a tube at 20°. It is significant that the relative extent of methane production was greatly increased by raising the temperature of this tube to 350°. Simons, McNamee and Hurd<sup>11</sup> mention that the addition of hydrogen to lead tetramethyl in a single experiment at 700° increased the proportion of methane produced at the expense of the ethane, and suggest the same explanation.

Hartel and Polanyi<sup>14</sup> have studied the reaction  $\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}$  by the method of "highly dilute flames," free methyl radicals being liberated in the presence of hydrogen by the action of sodium atoms on methyl halides. From observations of the rate of reaction at two temperatures, they deduced an activation energy of approximately 8 kcal./mole for the reaction. Trenner, Morikawa and Taylor,<sup>1</sup> from their results on the reaction between ethane and atomic hydrogen produced by Wood's method, have suggested 11 kcal./mole as an upper limit.

## EXPERIMENTAL DETAILS

### Apparatus

Preliminary experiments showed that the decomposition of mercury dimethyl, alone or in the presence of hydrogen, did not involve any change in the total pressure, so the course of the reactions could only be followed by analysis of the products. For reasons outlined below, it was necessary to operate with small samples of gas or vapor, so a special apparatus was constructed. The essential parts are represented diagrammatically in Fig. 1.

Pyrex glass was used throughout, capillary tubing being inserted wherever possible to limit the dead space.  $V_1$  and  $V_2$  were all-metal valves with copper sylphon bellows, their use being necessitated by the readiness with which mercury dimethyl dissolves in grease of any kind, and the experimental procedure was so arranged that these were the only stopcocks with which the vapor came into more than fugitive contact. The mercury dimethyl was stored in *A*, and because a small amount of Picein was used in the ground

<sup>9</sup> Linnett and Thompson, *Trans. Faraday Soc.* **33**, 501, 874 (1937).

<sup>10</sup> Leighton and Mortensen, *J. Am. Chem. Soc.* **58**, 448 (1936).

<sup>11</sup> Simons, McNamee and Hurd, *J. Phys. Chem.* **36**, 939 (1932).

<sup>12</sup> Paneth, Hofeditz and Wunsch, *J. Chem. Soc.* 372 (1935).

<sup>13</sup> Meinert, *J. Am. Chem. Soc.* **55**, 979 (1933).

<sup>14</sup> Hartel and Polyani, *Zeits. f. physik. Chemie* **B11**, 97 (1930).

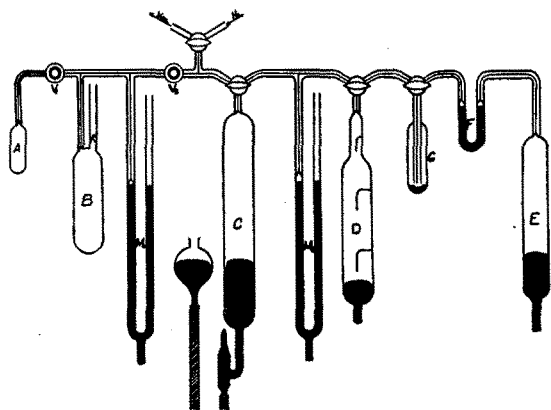


FIG. 1. Apparatus for study of decomposition of mercury dimethyl.

glass joints between the valves and the tubing, it was kept frozen out by means of a carbon dioxide-toluene mixture except for short intervals of time when the samples were being taken. The reaction vessel *B* was of Pyrex for the thermal experiments, and of quartz with quartz-to-Pyrex graded seals for the photochemical; a number of independently calibrated vessels were used, those of Pyrex ranging from 220 to 250 cc, and those of quartz from 115 to 150 cc in volume.

Attempts were first made to heat the sample in vessel *B* *in situ*, but this was soon found to be impracticable due to the readiness with which the mercury dimethyl distilled into the cooler parts of the connecting tubing and manometer, even with a small temperature gradient. In all the later runs, consequently, the reaction vessel was sealed off after introduction of the sample. After heating or irradiating for a definite length of time, the vessel could then be sealed in place by means of the 10 mm tube shown to the right of the vessel in the diagram. After evacuation, the small glass tip could be broken at will electromagnetically with an iron plunger, and the reaction products thus readmitted to the apparatus.

In the thermal runs, vapor baths containing the following substances were used: aniline, naphthalene, diphenyl, alpha-naphthol, diphenylamine, and anthracene. For the photochemical experiments, a furnace was constructed out of a cylindrical block of aluminum about twice the length of the reaction vessel, and of such diameter that a hole drilled to fit the reaction vessel left walls of 1" thickness. An aperture the length of

the quartz vessel and  $\frac{1}{2}$ " in width was cut in one side, covered by a quartz window, and the furnace was wound in such a fashion that the heating element did not cross this window. The furnace was then well covered with asbestos paste, and it was found that, at the highest temperatures used, the temperature did not vary by more than 5° throughout.

The arc used was of the mercury-in-quartz type, operated "hot" at 50 volts and 4 amp. d.c., under which conditions no resonance radiation could be detected; it was operated for fifteen minutes preceding every run in order to attain reproducible intensity, and then placed in a vertical position against the quartz window in the furnace for the duration of the experiment.

Hand Töpler pumps *C* and *E* of approximately 400 and 250 cc capacity, respectively, were used to transfer gas samples from one portion of the apparatus to another. Into a similar vessel *D* were sealed at different levels three glass pointers; by raising the confining liquid to any of these tips, and at the same time setting the level in the connecting arm of manometer *M*<sub>2</sub> at a standard reading, it was possible to confine a gas sample in a definite volume; these volumes were calibrated with mercury and found to be 33.6, 104.6, and 204.6 cc. Mercury was also used as the confining and manometric fluid throughout.

The bulb *G* of about 50 cc capacity, contained between 1.5 and 2 g of an active copper hydrogenation catalyst, and the U-tube at *F* contained about 5 g of partially-reduced Kahlbaum copper oxide.

The open arms of the manometers were actually connected to the vacuum line (not shown), thereby eliminating the effect of barometric variations; each manometer and hand Töpler pump was provided with a leveling bulb connected through an air-trap as shown for *C*, so that all gas pressures could be read at constant volume.

## Materials

The mercury dimethyl used was prepared by the method of Marvel and Gould,<sup>15</sup> and further purified by repeated fractionation at low pressures and in the presence of freshly fused calcium

<sup>15</sup> Marvel and Gould, J. Am. Chem. Soc. **44**, 153 (1922).

chloride. The hydrogen was obtained by the electrolysis at 2–3 amp. of 10 percent potassium hydroxide solution, and passed in succession through calcium chloride, activated charcoal, platinized asbestos at about 250°, and a trap chilled in liquid air. It was not considered necessary to purify the tank helium used to increase the total pressure in a few experiments. The active copper was prepared from Kahlbaum copper oxide by reduction and oxidation at successively lower temperatures, the last reduction being made below 150°; tests on tank ethylene showed rapid hydrogenation below 100°.

#### EXPERIMENTAL PROCEDURE

Before each experiment, the volume of the particular reaction vessel used, together with the connecting tubing to a set level of the mercury in manometer  $M_1$  was determined by measuring the pressure of a sample of air and then transferring it, by means of  $C$ , to the burette  $D$ , where its pressure was again measured in a previously calibrated volume. This was usually repeated at the close of the experiment, to determine the increase in volume due to the introduction of the 10 mm tubing containing the "inner seal."

After the sample of air had been pumped out of  $B$ , a sample of mercury dimethyl was admitted from  $A$ . Due to the readiness with which the material distills and condenses, it was considered advisable to set as an upper limit of mercury dimethyl pressure its vapor pressure at room temperature, which is in the vicinity of 50 mm; in very few cases did the pressure of the metal alkyl significantly exceed 40 mm. With valve  $V_2$  closed and  $V_1$  opened very slightly, the temperature of the vessel  $A$  was carefully raised to within a few degrees of that of the room, and the vapor thus allowed to diffuse slowly into  $B$ . After standing for some time in a water bath at room temperature, the pressure and temperature of the sample in  $B$  were recorded. A sample of hydrogen could similarly be admitted through  $V_2$ , the pressure of the hydrogen being maintained high enough to prevent back diffusion of the mercury dimethyl.

To avoid loss or decomposition of the mercury dimethyl while sealing the reaction vessel, it was first immersed in liquid air; this expedient did not prevent a small loss of hydrogen, but this could

be estimated by comparing the total pressures before and after the run, as the reaction proceeds without change in the total pressure: moreover, as the hydrogen was always in large excess, the importance of such an error would be minor. The disconnected vessel was then transferred to the vapor bath or furnace, depending on the experiment. In the former, the time of heating was measured from the introduction of the vessel, the time required for it to reach the bath temperature being considered to be offset by that necessary for cooling after its withdrawal; in the photochemical runs, however, the vessel was placed in the furnace for fifteen minutes prior to illumination; it will be seen that the thermal reaction during that period of time at the temperatures used is negligible.

After heating or illumination, the reaction vessel was again connected to the apparatus and the product gases readmitted.

#### Analysis

The vessel  $B$  was immersed in liquid air, and the fraction gaseous at that temperature pumped over, by repeated use of the hand Töpler pump  $C$ , into  $D$  where its pressure and temperature at known volume were recorded. This gas fraction could consist only of the so-called "permanent gases" methane and hydrogen. The possibility of imperfect fractionation due to solution of these gases in other products in  $B$  was investigated by closing  $V_2$ , melting and refreezing these products, and again pumping any residual gas over into  $D$ : in no case, however, was there observed to be any gas evolved. The hydrogen was removed from the mixture by passing the gases repeatedly over the copper oxide in  $F$  at 270–300°, with the mercury leveling bulbs attached to  $D$  and  $E$ ; the residual gas after this operation was measured as methane.

A second gas fraction was transferred from  $B$  to  $D$  in the same manner, the vessel  $B$  being immersed in a carbon dioxide-toluene mixture. This could consist of ethane, propane, and possibly butane, together with the lower members of the unsaturated series. Numerous attempts were made to detect unsaturated hydrocarbons by passing this second gas fraction, together with added hydrogen, over the active copper in vessel  $G$  maintained at 100°, but in no case was there any evidence of the pressure decrease which

would attend hydrogenation. Moreover, the observed stoichiometry of the decomposition in the majority of the experiments indicated that propane and butane, if present at all, appeared in negligible amounts, so that the second gas fraction might well be designated as ethane.

The residue in *B*, which probably consisted entirely of undecomposed mercury dimethyl in the majority of the runs, was not transferred from the reaction vessel, but was estimated by its pressure measured on manometer  $M_1$  while the vessel was immersed in a water bath at room temperature. By using this value in conjunction with the directly determined quantities of gaseous products, a satisfactory carbon and hydrogen balance could normally be obtained.

### EXPERIMENTAL RESULTS

#### Thermal decomposition of mercury dimethyl

No measurable decomposition of the metal alkyl alone could be detected after long heating at 184, 215 and 255°. At 290°, gaseous products corresponding to about 2 percent decomposition were observed after five hours heating; at 302°, the rate had increased only very slightly, but when the temperature was raised to 348°, it was relatively rapid.

The course of the decomposition at 348° was followed by heating separate samples for definite periods of time, and the results have been tabulated in Table I. All the pressures given have been calculated to 0°, only a short extrapolation being involved, as all the actual measurements

TABLE I. Thermal decomposition of  $\text{Hg}(\text{CH}_3)_2$  in absence of  $\text{H}_2$ .

TEMP. °C	RUN	TIME HR.	INITIAL $\text{Hg}(\text{CH}_3)_2$ MM	$\text{CH}_4$ MM	$\text{C}_2\text{H}_6$ MM
302	25	2½	21.3	—	1.0
		8	21.6	1.0	1.4
		21½	22.2	2.4	3.2
		30	22.8	5.1	2.9
		41½	23.3	7.7	2.9
348	106	2	37.0	14.2	4.8
	107	4	38.6	22.5	4.0
	105	6	43.3	29.0	5.1
	102	11	47.7	39.1	8.3
	103	21	47.1	39.8	7.3
	108	4	14.8	4.5	2.9
	109 <sup>1</sup>	4	46.7	44.3	8.4

<sup>1</sup> Surface increased 8-fold by packing with Pyrex tubing.

were made at room temperature. The pressures for the products listed in the last two columns have been recalculated to the volume of the original reaction vessel in each case, for comparison with the values in the fourth column. Appended to the table are two additional runs at 348°, which serve to throw some light on the nature of the decomposition: run 108 shows the effect of decreasing the initial mercury dimethyl pressure, run 109 that of increasing the total surface.

A single run at 302° is also reported for comparison, although the accuracy of the data is relatively low. This experiment was performed without detaching the reaction vessel from the apparatus; rough analyses were performed by interrupting the heating, and measuring the total pressure when the vessel was immersed in a water bath, a  $\text{CO}_2$  ether mixture, and liquid air. The pressures given, therefore, are obtained by fairly long temperature extrapolations, and serve only as a rough indication of the effect of temperature. It is definitely apparent that the process producing methane shows much greater dependence upon the temperature than does that forming ethane.

In every case in which measurable decomposition took place, it was observed that a dark brown deposit formed on the walls of the reaction vessel. This could be removed to a greater or less extent by washing out with cold water, on the surface of which it formed an oily scum. On gentle heating in the presence of air, the deposit darkened in color, and became definitely carbonaceous. Reference to runs 102 and 103 in Table 1 shows that although decomposition is undoubtedly complete, less than 60 percent of the carbon has been found in the product gases; it would appear that for every carbon atom appearing as methane there is one lost in the solid deposit on the walls. Added evidence for the belief that the deposit might well be a  $\text{CH}_2$  polymer is supplied by the experimental fact that no free hydrogen was detected in any run.

#### Thermal decomposition of mercury dimethyl in presence of hydrogen

In the runs listed in Table II, the initial mercury dimethyl pressures were  $40.0 \pm 0.2$  mm, and those of hydrogen (corrected for loss in

sealing the reaction vessel)  $200 \pm 4$  mm. As in Table I, all pressures are given for  $0^\circ$  and the volume of the reaction vessel. The values in the fourth and fifth columns were obtained by a method of difference, and so are less accurate than those for methane and ethane, which have been measured directly and in smaller volumes. However, the stoichiometry of the reaction producing methane is apparent, one mole of mercury dimethyl and one of hydrogen disappearing in the production of two moles of methane. This indicates that, with the introduction of hydrogen, a new methane-producing process occurs. The absence of any dark deposit at the conclusion of an experiment when hydrogen is present is corroborative evidence.

The presence of hydrogen markedly accelerates the decomposition, which is complete in one hour at  $348^\circ$  instead of eleven, as in the absence of hydrogen. That this effect is not due merely to the increase in the total pressure is shown by the runs using helium. In addition, the methane-producing process in the presence of hydrogen is much less strongly temperature-dependent than that in the case of mercury dimethyl alone, indicating a much lower energy of activation.

#### Effect of initial pressure

The data of Table III show the influence of reactant pressures at two temperatures. They yield the rate expressions:

$$\text{at } 302^\circ: d(\text{CH}_4)/dt = k(\text{Hg}(\text{CH}_3)_2)^{0.2}(\text{H}_2)^{0.7},$$

$$\text{at } 348^\circ: d(\text{CH}_4)/dt = k(\text{Hg}(\text{CH}_3)_2)^{0.7}(\text{H}_2)^{0.7}.$$

TABLE II. Thermal decomposition of  $\text{Hg}(\text{CH}_3)_2$  in presence of  $\text{H}_2$ .

TEMP. °C	RUN	TIME HR.	Hg(CH <sub>3</sub> ) <sub>2</sub> USED MM	H <sub>2</sub> USED MM	CH <sub>4</sub> MM	C <sub>2</sub> H <sub>6</sub> MM
302	125	$\frac{1}{2}$	9.3	8.8	13.2	—
	126	$\frac{1}{2}$	8.1	6.4	12.0	—
	124	1	13.8	11.2	22.0	—
	122	2	23.2	23.6	42.8	—
	123	4	40.1	44.8	80.2	0.7
	130 <sup>1</sup>	$4\frac{1}{2}$	40.0	—	2.4	—
348	115	$\frac{1}{2}$	35.3	31.2	65.0	1.2
	114	1	39.8	39.8	79.3	2.4
	119	1	39.6	38.4	74.9	2.7
	112	2	37.8	37.2	72.0	1.6
	110	4	40.0	40.0	77.6	2.4
	118 <sup>1</sup>	$\frac{1}{2}$	40.0	—	18.3	1.2

<sup>1</sup> 200 mm helium substituted for hydrogen.

TABLE III. Variation of initial pressures.

TEMP. °C	RUN	TIME HR.	INITIAL Hg(CH <sub>3</sub> ) <sub>2</sub> MM	INITIAL H <sub>2</sub> MM	CH <sub>4</sub> MM
302	122	2	40.1	199.5	42.8
	127		40.4	100.6	26.9
	129		18.7	185.5	36.6
	128		19.6	98.4	22.2
348	115	$\frac{1}{2}$	39.9	198.2	65.0
	120		40.0	100.4	40.1
	121		19.7	195.5	38.6
	117		19.7	98.4	24.0

There is a strong temperature dependence with respect to mercury dimethyl but none with respect to hydrogen.

Experiments at lower temperatures showed erratic behavior indicating surface effects, methane formation increasing with increase of mercury dimethyl, the effect of hydrogen remaining unchanged.

#### Photochemical decomposition of mercury dimethyl

The data of Table IV record the results of photodecomposition by the unfiltered radiation of a hot mercury arc from 50 to  $300^\circ$ , with an initial pressure of 40 mm of mercury dimethyl. In no photochemical experiment, with or without hydrogen, was any deposit observed to form on the walls of the reaction vessel, with the possible exception of a thin gray film of mercury. No methane was observed in the decomposition of mercury dimethyl below  $160^\circ$ , and it seemed probable that the reaction was free of the undesirable heterogeneous characteristics of the thermal decomposition.

TABLE IV. Photochemical decomposition of  $\text{Hg}(\text{CH}_3)_2$  in absence of  $\text{H}_2$ .

TEMP. °C	RUN	TIME MIN.	Hg(CH <sub>3</sub> ) <sub>2</sub> DECOMP. MM	CH <sub>4</sub> MM	C <sub>2</sub> H <sub>6</sub> MM	C <sub>2</sub> H <sub>6</sub> /MIN. MM
50	142	30	11.2	—	10.4	0.35
	144	60	20.4	—	19.7	0.33
	146	90	28.7	—	28.0	0.31
90	152	60	23.2	—	24.6	0.41
	160	154	30	0.1	20.8	0.69
200	168	10	9.3	0.3	7.9	0.79
250	173	6	6.4	0.6	6.2	1.03
275	182	5	5.7	—	4.1	0.82
300	184	3	5.1	1.2	3.4	1.13
	185	3	—	—	2.8	0.93

TABLE V. Photochemical decomposition of  $\text{Hg}(\text{CH}_3)_2$  in presence of  $\text{H}_2$ .

TEMP. °C	RUN	TIME MIN.	$\text{Hg}(\text{CH}_3)_2$ DECOMP. MM	$\text{CH}_4$ MM	$\text{C}_2\text{H}_6$ MM	$\frac{1}{2} \text{CH}_4$ + $\text{C}_2\text{H}_6$ MM	$\text{CH}_4/\text{MIN.}$ MM	$\text{C}_2\text{H}_6/\text{MIN.}$ MM
50	143	30	13.8	4.0	10.4	12.4	0.13	0.35
	145	60	23.2	6.8	19.5	22.9	0.11	0.33
	147	90	(28.7)	11.1	29.3	34.9	0.12	0.33
90	153	60	33.4	10.8	30.2	35.6	0.18	0.50
	155	30	21.3	8.9	16.1	20.6	0.30	0.54
	159		28.1	13.6	23.8	30.6	0.45	0.79
160	160		28.6	16.2	20.9	29.0	0.54	0.70
	169	10	14.2	10.9	7.8	13.3	1.09	0.78
	250	174	6	12.1	4.1	10.3	2.02	0.70
275	183	5	11.8	11.8	5.0	10.9	2.36	1.00
300	180	3	10.1	12.4	3.2	9.4	4.13	1.07
	181	3	9.9	12.2	2.8	8.9	4.07	0.93

### Photochemical decomposition of mercury dimethyl in presence of hydrogen

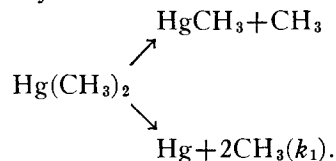
Addition of hydrogen to the mercury dimethyl was found to result in the production of measurable amounts of methane even at the lowest temperature employed. It was observed, moreover, that the process producing methane showed a much greater dependence upon temperature than that forming ethane, indicating a process of higher activation energy. The rate of ethane production was not affected by the presence of the hydrogen, indicating that the processes producing methane and ethane proceed quite independently of each other. This observation must be given due importance in postulating a mechanism for the decomposition.

In all runs reported in Table V very nearly 200 mm of hydrogen has been added to the mercury dimethyl. The values in the seventh column have been given for comparison with those of the fourth column, to indicate how satisfactory is the carbon balance throughout. It will be observed also from Table IV that the mercury dimethyl decomposed in each run is accounted for within the experimental error.

Special tests, using quartz vessels containing mercury and hydrogen as filters, showed that the effects produced were not due to mercury resonance radiation. It was also shown that a mixture of  $\text{H}_2 + \text{D}_2$  did not react to form 2HD under the experimental conditions. When a "cold" arc was used, the character of the decomposition changed, because of the resonance radiation, methane predominating even at room temperature, because of interaction of the mercury dimethyl and atomic hydrogen produced by photosensitisation with excited mercury.

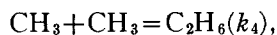
### DISCUSSION OF RESULTS

The primary photo-process, in agreement with Terenin<sup>8</sup> and the later conclusions of Linnett and Thompson,<sup>9</sup> must occur in either of the two following ways

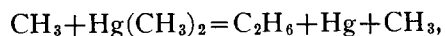


The preponderance of methane in presence of hydrogen at the highest temperatures is definite evidence that dissociation to yield mercury and molecular ethane is a minor or negligible result of the absorption act. A choice between the two radical mechanisms cannot be made from the kinetics of the over-all reaction. The complex  $\text{HgCH}_3$  will, in any case, be of relatively short life.

The ethane formation which preponderates in the low temperature range may be ascribed to the recombination process



the rate of production of ethane in absence of hydrogen increases by a factor of 3 in the range 50 to 300° (Table IV). There is no evidence that this can be ascribed to temperature dependence of light absorption, since this is very strong, even at room temperature. The temperature coefficient indicates, therefore, an increase of quantum yield and therefore a chain mechanism, for example,



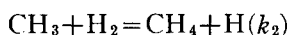
the chain-breaking mechanism being the recombination of two methyl groups. This latter reaction must have a small activation energy since it occurs less rapidly than the recombination of  $\text{CH}_3 + \text{I}$  in the photolysis of methyl iodide as indicated by the low quantum efficiency of the iodide decomposition and by the thermal stability of alkyl iodides.<sup>16</sup> The small temperature coefficient of ethane formation must be composite of these two processes.

The data of Tables IV and V show that the ethane producing reactions are not measurably affected by the presence of a large excess of

<sup>16</sup> Ogg, J. Am. Chem. Soc. **56**, 533 (1934).



hydrogen. However, the over-all rate of decomposition of mercury dimethyl is progressively increased, by a 5-fold addition of hydrogen, and approximately in the ratio 1 to 8 between 50 and 300°. An increasingly large proportion of methane appears in the products with increase of temperature. We ascribe this to the following new secondary steps



and



this chain being terminated by the recombination of two methyl radicals ( $k_4$ ).

For a photochemical stationary state

$$d[\text{CH}_3]/dt = 0 = k_1 I_{\text{abs}} - k_2 [\text{CH}_3][\text{H}_2] + k_3 [\text{H}][\text{Hg}(\text{CH}_3)_2] - k_4 [\text{CH}_3]^2$$

and

$$d[\text{H}]/dt = 0 = k_2 [\text{CH}_3][\text{H}_2] - k_3 [\text{H}][\text{Hg}(\text{CH}_3)_2].$$

By subtraction,

$$k_1 I_{\text{abs}} = k_4 [\text{CH}_3]^2$$

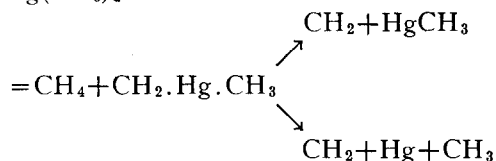
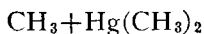
or 
$$[\text{CH}_3] = (k_1 I_{\text{abs}} / k_4)^{1/2}.$$

Substituting these values in the rate expression,

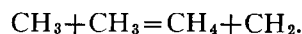
$$\begin{aligned} d[\text{CH}_4]/dt &= k_2 [\text{CH}_3][\text{H}_2] + k_3 [\text{H}][\text{Hg}(\text{CH}_3)_2] \\ &= 2k_2 [\text{CH}_3][\text{H}_2] \\ &= 2k_2 (k_1 I_{\text{abs}} / k_4)^{1/2} [\text{H}_2]. \end{aligned}$$

If the light absorption is constant, the rate of methane production is independent of mercury dimethyl concentration. The data at 50° in Table V are in agreement with this result. In this formulation of reaction mechanism it is seen that ethane formation is also independent of the hydrogen concentration as observed.

The production of methane in the absence of hydrogen must be ascribed to processes of the types



and



The large temperature coefficient of thermal reaction between 302 and 348° cannot be attributed to the reaction  $\text{CH}_3 + \text{H}_2$  since this has, as will be shown, a much smaller coefficient. The dark deposit on the reaction walls is evidence of the production of polymethylenic polymerization products. Evans and Lee<sup>17</sup> on studies of the electrolysis of methyl mercuric bromide and Shukla and Walker<sup>18</sup> in electrolysis of fatty acids and their salts postulate methane production by the second of the above processes.

### Activation energies of the reactions

If the logarithm of the rates of methane production from Table V be plotted against  $1/T$  in the range 160–300° a straight line is obtained whose slope is 8.1 kcal. per mole. As is evident from the expression

$$d[\text{CH}_4]/dt = 2k_2 [\text{CH}_3][\text{H}_2]$$

this value is a summation of the effect of temperature on the stationary state concentration of methyl radicals and the activation energy  $E_M$  of the process  $\text{CH}_3 + \text{H}_2 = \text{CH}_4 + \text{H}$ .

A plot of ethane production, in presence or absence of hydrogen, against  $1/T$  gives a single straight line over the entire temperature range the slope of which indicates an activation energy of 1.5 kcal. per mole. As suggested previously, this energy requirement may be attributable to the reaction between free methyl and mercury dimethyl. In such case the effect of temperature on the recombination of methyl radicals whether bimolecularly, or at the wall, must be very small indeed and  $E_M$  would be 8.1 kcal. per mole. This latter value would be reduced, if the value of  $E_E$  for ethane formation were to be attributed to an activation energy of the recombination process, by the whole amount, 1.5 kcal., in case of a wall recombination, or by 0.75 kcal. for a bimolecular association in the gas phase. These alternatives would set the value for  $E_M$  between 6.6 and 8.1 kcal. with the greater weight attaching to the upper figure.

The experimental figures of Hartel and Polanyi<sup>14</sup> led them to a value  $E_M = 8$  kcal., although a series at 10 mm hydrogen pressure

<sup>17</sup> Evans and Lee, J. Am. Chem. Soc. **56**, 654 (1934).

<sup>18</sup> Shukla and Walker, Trans. Faraday Soc. **27**, 35 (1931).

gave a value of  $\sim 6$  kcal. In a parallel investigation by Taylor and Rosenblum<sup>19</sup> on the photolysis of acetone in presence of hydrogen the value for  $E_M$  deduced on the basis of bimolecular

<sup>19</sup> H. S. Taylor and C. Rosenblum, *J. Chem. Phys.* **6**, 119 (1938).

recombination with negligible activation energy is 8.7 kcal., rising to 11 kcal. if the recombination process were unimolecular at the wall. Upon these bases therefore we must conclude that the most trustworthy value now available for the activation energy,  $E_M$ , is  $9 \pm 2$  kcal.

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## An Improved Calculation of the Energies of Metallic Li and Na

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The method of calculation used in the present work is a modification of that used by Wigner and Seitz in their original calculations of the energies of metallic Li and Na. The main difference lies in an improved method for the calculation of the Fermi energy. In each polyhedral cell, the wave function of an electron is taken to be of the form  $\psi_k = [u_0(r) + i(\mathbf{k} \cdot \mathbf{x})(v_1(r) - u_0(r))] \exp[i\mathbf{k} \cdot \mathbf{x}]$ , where  $u_0(r)$  and  $v_1(r)$  are radial  $s$  and  $p$  functions, respectively, which depend only on the distance from the ion in the center of

the cell. Both functions are determined explicitly from the differential equations, and the energy of the electron is expressed in terms of the boundary values of the wave function. Values of the Fermi energy, and of the total energy of each metal, are tabulated as a function of the lattice spacing. Calculated values of the lattice constants, heats of sublimation, and compressibilities are in fair agreement with experiment.

THE most accurate method for the calculation of metallic binding which has yet been suggested is that of Wigner and Seitz.<sup>1</sup> The method is especially suitable for the monovalent metals, and was first applied to the calculation of the binding energy and lattice constant of sodium. A rough value was also given for the compressibility. Lithium was considered in a later paper by Seitz.<sup>2</sup> His calculation of the energy did not extend to values of the lattice constant smaller than the observed, so that it was not possible to obtain the compressibility. The main object of the present work is to determine the energies of Li and Na and their dependence on volume with sufficient accuracy to obtain the compressibilities and their variation with pressure. A comparison of the results with recent experimental values of Bridgman, which

extend to pressures of the order of 45,000 kg/cm<sup>2</sup>, will be given in the following paper.<sup>3</sup>

The two main factors which determine the binding energy of a metal are the energy of an electron in its lowest state and the Fermi energy. Only two electrons can occupy the lowest state; the Fermi energy represents the average additional energy of electrons in higher states of the filled band. We will first give the general theory of the method used for the calculation of the electronic wave functions and energies, and then give the detailed numerical calculations of the binding energies.

### ELECTRONIC WAVE FUNCTIONS AND ENERGIES

The wave function of an electron in its lowest state is determined as follows. By passing planes perpendicular to and bisecting the lines joining near neighbors, the whole space of the crystal is broken up into a set of regular polyhedra, one surrounding each ion. It is a good approximation

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<sup>1</sup> E. Wigner and F. Seitz, **43**, 804 (1933); **46**, 509 (1934); E. Wigner, *Phys. Rev.* **46**, 1002 (1934). A survey of this work, together with references to applications of the method to other problems may be found in Mott and Jones, *Theory of the Properties of Metals and Alloys* (Oxford, 1936), Chapters II and IV.

<sup>2</sup> F. Seitz, *Phys. Rev.* **47**, 400 (1935).

<sup>3</sup> A discussion of an approximate method for the calculation of the energies of the alkali metals, due to Fröhlich, is also given in this paper.