

		Acid		
		Homoterephthalic	Homophthalic	<i>p</i> -Phenylbenzoic
M.p., °C.	Found	234-236	175-177	215-218
	Liter.	237-238	175-177	216-218
Neut. equiv.	Found	97	89	214
	Calcd.	90	90	198
Carbon, %	Found	60.5	60.6	78.7
	Calcd.	60.0	60.0	78.4
Hydrogen, %	Found	4.7	4.5	5.45
	Calcd.	4.5	4.5	5.43
Oxidation		Terephthalic acid <sup>a</sup>	Phthalic acid <sup>b</sup>	Methyl ester <sup>c</sup>

<sup>a</sup> Shown by m.p. of dimethyl ester and mixed m.p.'s with authentic sample. <sup>b</sup> Formed anhydride by heat, m.p. 139-140°. <sup>c</sup> M.p. 110-113°, lit. m.p. 117°.

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### The Quantum Yields during Mercury Dimethyl Decomposition

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The photochemical decomposition of mercury dimethyl has been used as a source of methyl radicals during several recent investigations. Some disagreement exists, however, between various authors as to the steps in the decomposition of this molecule in the absence of foreign gas. This work reports quantum yields of ethane and of methane formation; the data provide evidence concerning certain steps which have been suggested by various authors for the mechanism.

#### Experimental

The mercury dimethyl was prepared by the method of Gilman and Brown<sup>2</sup> and purified by the method previously described.<sup>3</sup>

Acetone vapor at a temperature of 150° and diethyl ketone vapor at a temperature of 100° were used as actinometers. The quantum yields of carbon monoxide formation from both of these substances are unity under these conditions.<sup>4,5</sup> Radiation from an Hanovia Alpine burner was collimated by a quartz lens and passed through both a chlorine filter and a solution of iodine dissolved in potassium iodide. The effective radiation consisted of wave lengths at  $2600 \pm 200 \text{ \AA}$ .

One run was made at 30° by use of two cells in series. By use of the following series of experiments data could be obtained for a quantum yield calculation: (a) cell I empty, cell II filled with acetone; (b) cell I and cell II filled with acetone (this and the previous run give data for window corrections); (c) cell I filled with mercury dimethyl and cell II with acetone. From the three runs one can calculate the fraction of the radiation absorbed by the mercury dimethyl and the amount of radiation entering cell I. With mercury dimethyl at a pressure of 21.6 mm.,  $2.1 \times 10^{12}$  quanta absorbed per cc. per second (about 25% of the incident radiation was absorbed, light beam filled the cell), and temperature 30°,  $\Phi_{C_2H_6}$  was 1.14 and  $\Phi_{CH_4}$  was too small to be measured with any accuracy.

For most of the runs the percentage of radiation absorbed was determined by the malachite green leucocyanide actinometer.<sup>6</sup> It was not feasible to meet all of the conditions for use of this actinometer and hence corrections were made by use of acetone and of diethyl ketone used as inter-

nal actinometers. Results with the two ketones agreed to better than 5%.

Rates (in molecules per cubic centimeter per second) are calculated on the assumption that they are uniform throughout the vessel. This assumption may be approximately valid at 30° where about 25% of the incident radiation was absorbed, but the validity at 175° where the absorption was more than twice as great is doubtful.

The results are given in Table I.

TABLE I

QUANTUM YIELDS DURING MERCURY DIMETHYL DECOMPOSITION

Concentration,  $6.9 \times 10^{17}$  molecules/cc.; cell length, 200 mm.; cell diameter, 18 mm.; light beam fills vessel, wave length  $2600 \pm 200 \text{ \AA}$ .

$T = 30^\circ$

Quanta absorbed/ cc./sec. $\times$ $10^{-10}$	31.7	17.3	16.9	6.7	6.3	3.8	1.6
$\Phi_{C_2H_6}$	0.9	0.9	1.0	1.3	1.2	1.4	1.3
$\Phi_{CH_4}$	(Negligible)						

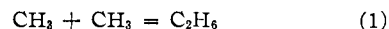
$T = 175^\circ$

Quanta absorbed/ cc./sec. $\times$ $10^{-10}$	119	66.8	39.8	20.6	10.1
$\Phi_{C_2H_6}$	1.0	1.2	1.1	0.9	1.3
$\Phi_{CH_4}$	0.35	0.47	0.54	0.7	1.0
$R_{CH_4}/(R_{C_2H_6})^{1/2}$ molecules <sup>1/2</sup> /cc. <sup>1/2</sup> / sec. <sup>1/2</sup> $\times 10^{-5}$	3.8	3.5	3.3	3.3	2.8

The average values of  $\Phi_{C_2H_6}$  are  $1.14 \pm 0.16$  at 30° and  $1.10 \pm 0.12$  at 175°. There seems to be, therefore, little or no change with temperature. The trend with intensity at 30° is probably not real but might possibly be due to a small amount of back reaction, such as  $CH_3 + HgCH_3 = Hg(CH_3)_2$ . The trends of  $\Phi_{CH_4}$ , both with temperature and with intensity are undoubtedly real.

#### Discussion

It is not necessary at this point to enter upon a detailed discussion of reaction mechanism. Rebert and Steacie,<sup>7</sup> in a series of articles have shown that to all intents and purposes ethane may be considered to be formed by the reaction



and methane by the reaction



We will discuss only two points: (a) the possibility of a second ethane producing reaction; (b) the question of "hot" radicals.

Failure to obtain a linear plot of  $R_{C_2H_6}/R_{CH_4}$  vs.  $R_{CH_4}$  at constant pressure and temperature but variable intensity<sup>8</sup> should lead also to failure to obtain a linear plot for  $R_{CH_4}/R_{C_2H_6}^{1/2}$  vs. (DM) where (DM) is the concentration of mercury dimethyl. Reasons for failure to obtain correct values of  $k_2/k_1^{1/2}$  have been discussed.<sup>8</sup> Due to the high absorption coefficient of mercury dimethyl and the fact that its vapor pressure at room temperature precludes the use of high enough pressures to ensure the absence of wall effects, it is difficult to be sure that the effective "volume" for the reaction is constant and independent of conditions.

The trend in  $R_{CH_4}/R_{C_2H_6}^{1/2}$  at 175° in Table I is

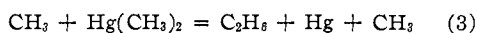
(7) R. E. Rebert and E. W. R. Steacie, *Can. J. Chem.*, **31**, 631 (1953); **32**, 40 (1954); *J. Chem. Phys.*, **21**, 1723 (1953).

(8) W. A. Noyes, Jr., *J. Phys. Colloid Chem.*, **55**, 925 (1951).

(1) National Science Foundation Predoctoral Fellow, 1953-1954.  
(2) H. Gilman and R. E. Brown, *This Journal*, **52**, 3314 (1930).  
(3) R. Gomer and W. A. Noyes, Jr., *ibid.*, **71**, 3390 (1949).  
(4) D. S. Herr and W. A. Noyes, Jr., *ibid.*, **62**, 2052 (1940).  
(5) W. Davis, Jr., *ibid.*, **70**, 1868 (1948).  
(6) J. G. Calvert and H. J. L. Rechen, *ibid.*, **74**, 2101 (1952).

undoubtedly real. These values if divided by the concentration of mercury dimethyl in molecules/cc. should give  $k_2/k_1^{1/2}$ . The results are as follows: 5.5, 5.0, 4.8, 4.8, 4.1 all times  $10^{-13}$  molecules $^{-1/2}$  cc. $^{1/2}$  sec. $^{-1/2}$ . The average value is  $4.8 \times 10^{-13}$  in this respect in good agreement with the Rebbert and Steacie value of  $4.6 \times 10^{-13}$  at the same temperature. The trend in the results in Table I could be due to several causes, such as "volume effect," walls, or possibly a method of ethane formation in addition to 1.

There are reasons for suspecting that a second ethane forming step may not be real,<sup>9</sup> but one argument in favor of such a step needs to be examined. Evidently at 175° (Table I) more than two methyls appear as methane and ethane per quantum absorbed. This might be due to some reaction which could be written either as the single step



or as a sequence of steps<sup>3</sup> with the same over-all result. However, the quantum yield of ethane formation is nearly independent of the amount of methane formed. This makes one suspect that formation of methane is accompanied by regeneration of methyl radicals at 175°, possibly by decomposition of  $\text{CH}_2\text{HgCH}_3$ . Ethylene is observed at temperatures over 200° so that  $\text{CH}_2\text{HgCH}_3$  may decompose to give  $\text{CH}_3$ ,  $\text{CH}_2$  and Hg. At 175° the fate of  $\text{HgCH}_2$  is unknown. Further speculation about the mechanism is not warranted. Suffice to say that short chains evidently occur, in agreement with the work of Linnett and Thompson.<sup>10</sup>

The formation of "hot" methyls has been postulated for this reaction by several authors.<sup>11</sup> If the steric factor for reaction 2 for "hot" methyls is the same as for "cold" methyls, it would be exceedingly difficult to obtain evidence either for or against them. At most 1% of the initially formed methyls would form methane because they are "hot," i.e., the quantum yield of methane from this source would be not over 0.01 to 0.02 and would escape notice under most experimental conditions. At 175° where some of the methyls are formed from a chain propagating step an even smaller fraction would appear to be "hot" and the conclusion of Rebbert and Steacie<sup>7</sup> that "hot" methyls can be neglected in obtaining activation energies for the methane forming steps is undoubtedly correct under most experimental conditions.

It may be stated, therefore, that there is no conclusive evidence for an ethane forming step other than 1 and that evidence either for or against "hot" methyls could be obtained in this system only under exceptional circumstances and with data of very high precision.

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(9) R. B. Martin and W. A. Noyes, Jr., *THIS JOURNAL*, **75**, 4183 (1953).

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

(11) See ref. 9 for references.

## On the Theory of the Polarographic Diffusion Current. II. Diffusion of Small Amount of Thallium Ion in Aqueous Potassium Chloride Solutions<sup>1</sup>

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Previous results on the tracer-diffusion coefficients of Pb(II) and Zn(II) ions in solution of various supporting electrolytes show that there is considerable disagreement between the observed "diffusion current constant" and the theoretical values computed from the Ilkovič and Lingane-Loveridge equations, respectively.<sup>1</sup> Values of the "diffusion current constant" calculated from the Strehlow-von Stackelberg equation lie closer to the experimental values for Pb(II) ion in 0.1 *F* HCl + 0.1 *F* KCl solution and for Zn(II) ion in 1.0 *F*  $\text{NH}_4\text{OH}$  + 1.0 *F*  $\text{NH}_4\text{Cl}$  solution, respectively, but the agreement is not satisfactory enough for us to conclude definitely that the Strehlow-von Stackelberg equation is correct.

In the present work the tracer-diffusion coefficients of Tl(I) ion in aqueous potassium chloride solutions were determined. The results were discussed in the light of Onsager's theory for tracer-diffusion in dilute solutions. The "diffusion current constant" of Tl(I) ion in 0.1 *F* KCl solution was then calculated from the present data by means of the Ilkovič, Strehlow-von Stackelberg and Lingane-Loveridge equations, respectively, and compared with experimental data.

### Experimental

**Tracer Solution.**— $\text{Tl}^{201}$  was used as tracer for Tl(I) ion. This was obtained from the Isotopes Division of the U. S. Atomic Energy Commission at Oak Ridge, Tennessee. In order to eliminate possible adsorption errors,<sup>1</sup> all solutions used in the present work were made from 0.0005 to 0.002 in  $\text{TlCl}$ .

**Diffusion Measurement.**—The experimental method of tracer-diffusion measurement has been described previously.<sup>2</sup> All measurements were carried out at  $25.00 \pm 0.01^\circ$ .

### Results and Discussion

The tracer-diffusion coefficients of Tl(I) ion in aqueous potassium chloride solutions at 25° as determined in the present work are summarized in Table I. Each value of *D* listed in Table I is the average result of six measurements.

TABLE I  
TRACER-DIFFUSION COEFFICIENTS OF Tl(I) ION IN AQUEOUS  
KCl + TlCl SOLUTIONS AT 25°

Concn. of KCl, formula wt./l.	Concn. of TlCl, formula wt./l.	<i>D</i> × 10 <sup>5</sup> , cm. <sup>2</sup> /sec.
0.005	0.0005	1.92 ± 0.02
.02	.002	1.90 ± .03
.05	.002	1.86 ± .02
.10	.002	1.84 ± .02
.20	.002	1.79 ± .02

Using appropriate units the Onsager equation<sup>3</sup> can be written as

(1) Paper I, *THIS JOURNAL*, **76**, 1528 (1954).

(2) J. H. Wang, C. V. Robinson and I. S. Edelman, *THIS JOURNAL*, **75**, 466 (1953).

(3) L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).