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## The Reactions of Methyl Radicals in the Solid-, Liquid-, and Gas-Phase Photolysis of Dimethylmercury

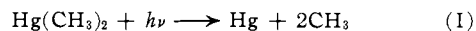
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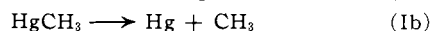
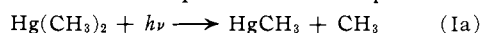
The gas-phase photolysis of  $\text{CD}_3\text{COCD}_3$  has been investigated in the presence of  $\text{CH}_3\text{HgCH}_3$  from 376 to 453°K. From the isotopic distributions of the methane and ethane fractions, evidence was obtained for the occurrence of the reaction:  $\text{CD}_3 + \text{CH}_3\text{HgCH}_3 \rightarrow \text{CD}_3\text{HgCH}_3 + \text{CH}_3$  ( $E_{\text{act}} = 12.6$  kcal./mole). This reaction is also postulated to occur in the liquid-phase photolysis of dimethylmercury. From the isotopic distribution of the ethane produced in the liquid- and solid-phase photolysis of  $\text{CH}_3\text{HgCH}_3\text{-CD}_3\text{HgCD}_3$  mixtures, it was concluded that cage recombination of methyl radicals does take place. Contrary to the conclusions reached in an earlier work by Derbyshire and Steacie, no evidence could be obtained for hot methyl radical effects in the liquid-phase photolysis of dimethylmercury.

### Introduction

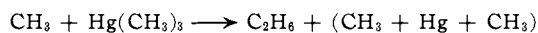
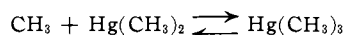
Earlier<sup>1</sup> work on the gas-phase photolysis of dimethylmercury had indicated that the primary process is essentially



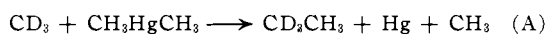
This may be written as a sequence of two steps



However, the methylmercury radical is known to be very unstable ( $\sim 6$  kcal.<sup>2</sup>) and may be expected to decompose readily. This is substantiated by the quantum yield close to unity reported for the photochemical decomposition at 30°.<sup>3</sup> Evidence was also presented<sup>1</sup> to show that methane is formed only by a hydrogen abstraction reaction and that ethane is formed only by a recombination of two methyl radicals. However, various experimentors have suggested a second ethane formation step in addition to the recombination of two methyl radicals. Gomer and Noyes<sup>4</sup> suggested the occurrence of the following steps, especially at high intensities



Oswin, *et al.*,<sup>5</sup> reported appreciable quantities of ethane- $d_3$  in the photolysis of acetone- $d_6$  at 3130 Å. with dimethylmercury added. A methyl abstraction process, such as



was proposed to explain these observations.

In order to obtain more detailed information concerning the reactions of methyl radicals with dimethylmercury, the photolysis of  $\text{CD}_3\text{COCD}_3$  in the presence of  $\text{CH}_3\text{HgCH}_3$  has been reinvestigated. Furthermore, the photolysis of  $\text{CH}_3\text{HgCH}_3\text{-CD}_3\text{HgCD}_3$  mixtures has been studied in the liquid and solid phases in order to obtain information about (a) hot methyl radical effects which have been proposed<sup>6</sup> to occur in the liquid-phase photolysis of dimethylmercury-*n*-heptane mixtures and (b) cage recombination of methyl radicals.

### Experimental

**Apparatus.**—The solid-phase photolysis experiments at 4 and 77°K. were performed in a stainless steel low-temperature dewar previously described.<sup>7</sup> The flow rate for deposition of the sample varied from about 1.3 cc. (STP) per minute for just dimethylmercury to about 10 cc. (STP) per minute for the carbon dioxide-

dimethylmercury mixture. In most experiments, about 26 cc. (STP) of gas was deposited. The unfiltered light from an Hanovia SH-100 lamp was used.

For the liquid-phase photolysis, a quartz cell (about 0.05 cm. in depth, 2.8 cm. diameter, and 0.4 cc. volume) was used. This cell, which was closed by means of a breakseal, was immersed in a Pyrex dewar flask with double-quartz windows. The light source was an Osram-100 lamp and, in a few cases, an Hanovia SH-100. In most experiments, either a diphenylbutadiene solution<sup>8</sup> or a 2537 Å. Baird-Atomic interference filter (Type A-31) was used. For the liquid-phase photolysis of azomethane in the presence of deuterated dimethylmercury, a Corning 3-75 filter was used.

In the gas-phase experiments, a cylindrical quartz cell (10 cm. long, 5 cm. diameter, and approximately 180 cc. volume) was used in conjunction with an Hanovia SH-100 lamp and a Corning 0-54 filter. The cell was situated in an aluminum-block furnace 30 cm. long with quartz windows. The maximum temperature variation during an experiment was  $\pm 1^\circ$ .

**Conversions.**—In the liquid-phase photolysis, conversions were kept below 0.1%. In the solid and gas phases, conversions were usually about 0.5%.

**Materials.**—Dimethylmercury, dimethylmercury- $d_6$ , azomethane, and acetone- $d_6$  were obtained from Merck Sharp and Dohme of Canada. Mass spectrometric analysis showed 3.8%  $\text{CD}_3\text{COCD}_2\text{H}$  in the acetone- $d_6$  and about 2%  $\text{CD}_3\text{HgCD}_2\text{H}$  in the dimethylmercury- $d_6$ . 2,3-Dimethylbutane was a standard sample from the National Bureau of Standards with  $0.11 \pm 0.06$  mole % impurity.

**Analysis.**—The analytical system consisted of a series of traps, a modified Ward still, and a Toepler pump-gas buret. Nitrogen, carbon monoxide, and methane were removed at  $-196^\circ$ , while ethane was removed at  $-175^\circ$ . These fractions were analyzed on the mass spectrometer. Standard mixtures of  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{D}_6$ , and  $\text{CH}_3\text{CD}_3$  were run on the same mass spectrometer for calibration.

### Results

**Solid and Liquid Phases.**—Table I gives the results for the photolysis of approximately equimolar mixtures of  $\text{CH}_3\text{HgCH}_3$  and  $\text{CD}_3\text{HgCD}_3$ . In the solid phase,  $\text{CH}_3\text{CD}_3$  is a minor product at both 4 and 77°K. Moreover, the addition of ethanol or carbon dioxide decreases the percentage of  $\text{CH}_3\text{CD}_3$  formed. Methane is present in surprisingly large amounts. In the liquid phase, the distribution of the ethanes does not seem to follow any pattern. In these experiments, the same mixture was reused in order to conserve dimethylmercury. The percentage of  $\text{CH}_3\text{CD}_3$  roughly follows the order in which the experiments were performed rather than the variation in temperature. Mass spectrographic analysis of the undecomposed dimethylmercury, after these experiments, showed essentially a statistical distribution of  $\text{CH}_3\text{HgCH}_3$ ,  $\text{CH}_3\text{HgCD}_3$ , and  $\text{CD}_3\text{HgCD}_3$  in the ratio of 1:2:1. The ratio  $\text{CD}_4/\text{CD}_3\text{H}$  is roughly equal to the ratio  $\text{CH}_3\text{D}/\text{CH}_4$  and both increase with an increase in temperature. It should be noted that the  $\text{CD}_4/\text{CD}_3\text{H}$  ratio could be determined with a better accuracy than the  $\text{CH}_3\text{D}/\text{CH}_4$  ratio. The Arrhenius plot of the  $\log \text{CD}_4/\text{CD}_3\text{H}$  vs.  $1/T$  gave an activation energy of  $1.4 \pm 0.4$  kcal./mole. The quantum yield (ethane plus 0.5 methane) for dimethylmercury decomposition in the equimolar

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 (2) B. G. Gowenlock, J. C. Polanyi, and E. Warhurst, *Proc. Roy. Soc. (London)*, **A218**, 269 (1953).  
 (3) R. A. Holroyd and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **76**, 1583 (1954).  
 (4) R. Gomer and W. A. Noyes, Jr., *ibid.*, **71**, 3390 (1949).  
 (5) H. G. Oswin, R. Rebbert, and E. W. R. Steacie, *Can. J. Chem.*, **33**, 472 (1955).  
 (6) D. H. Derbyshire and E. W. R. Steacie, *ibid.*, **32**, 457 (1954).  
 (7) R. E. Rebbert and P. Ausloos, *J. Phys. Chem.*, **66**, 2253 (1962).

TABLE I  
 SOLID- AND LIQUID-PHASE PHOTOLYSIS OF CH<sub>3</sub>HgCH<sub>3</sub>-CD<sub>3</sub>HgCD<sub>3</sub> MIXTURES (1:1)

| Temp.,<br>°K.   | R <sub>ethane</sub><br>moles sec. <sup>-1</sup> × 10 <sup>10</sup> | R <sub>methane</sub><br>moles sec. <sup>-1</sup> × 10 <sup>10</sup> | Distribution, %               |                                 |                               | Distribution, % |                   |                                |                   |                 |                                    |                                   |
|-----------------|--|---|-------------------------------|---------------------------------|-------------------------------|-----------------|-------------------|--------------------------------|-------------------|-----------------|------------------------------------|-----------------------------------|
|                 |  |   | C <sub>2</sub> D <sub>6</sub> | CH <sub>3</sub> CD <sub>3</sub> | C <sub>2</sub> H <sub>6</sub> | CD <sub>4</sub> | CD <sub>3</sub> H | CH <sub>2</sub> D <sub>2</sub> | CH <sub>3</sub> D | CH <sub>4</sub> | CD <sub>4</sub> /CD <sub>3</sub> H | CH <sub>3</sub> D/CH <sub>4</sub> |
| Solid phase     |  |   |                               |                                 |                               |                 |                   |                                |                   |                 |                                    |                                   |
| 4               | 12.1   | 6.09  | 36.7                          | 14.4                            | 48.9                          | 6.2             | 31.2              | ...                            | 18.8              | 43.8            | 0.20                               | 0.43                              |
| 77              | 6.68   | 5.23  | 39.5                          | 15.4                            | 45.0                          | 11.6            | 39.0              | 4.1                            | 12.4              | 32.9            | .30                                | .38                               |
| 77 <sup>a</sup> | 3.84   | 3.64  | 38.8                          | 7.6                             | 53.6                          | 1.3             | 32.3              | 1.7                            | 3.0               | 61.7            | .040                               | .049                              |
| 77 <sup>b</sup> | 7.60   | ..  | 42.2                          | 3.3                             | 54.4                          | ..              | ..                | ..                             | ..                | ..              | ..                                 | ..                                |
| Liquid phase    |  |   |                               |                                 |                               |                 |                   |                                |                   |                 |                                    |                                   |
| 273             | 1.91   | 1.96  | 25.3                          | 26.1                            | 48.6                          | 2.2             | 40.3              | 1.5                            | 2.8               | 53.1            | 0.055                              | 0.053                             |
| 309             | 1.63   | 6.41  | 21.6                          | 29.2                            | 49.3                          | 2.5             | 40.5              | 2.1                            | 3.1               | 51.6            | .063                               | 0.061                             |
| 338             | 0.37   | 3.91  | 22.3                          | 17.6                            | 60.1                          | 3.7             | 44.7              | ...                            | ..                | 51.5            | .083                               | ..                                |
| 338             | 5.91   | 15.3  | 30.6                          | 44.8                            | 24.7                          | 3.2             | 40.1              | 1.2                            | 3.7               | 51.9            | .080                               | 0.071                             |
| 338.5           | 0.76   | 7.13  | 27.7                          | 17.2                            | 55.1                          | 3.1             | 40.0              | 1.1                            | 3.9               | 51.9            | .078                               | .075                              |
| 364             | 1.00   | 21.8  | 30.2                          | 28.7                            | 41.2                          | 3.9             | 40.0              | 1.1                            | 4.2               | 50.7            | .097                               | .083                              |

<sup>a</sup> Ethanol-dimethylmercury (10:1). <sup>b</sup> Carbon dioxide-dimethylmercury (22:1).

 TABLE II  
 LIQUID-PHASE PHOTOLYSIS OF CH<sub>3</sub>HgCH<sub>3</sub>-CD<sub>3</sub>HgCD<sub>3</sub>-2,3-DI-  
 METHYLBUTANE (1:1:2)

| Run | Temp.,<br>°K. | R <sub>ethane</sub><br>moles sec. <sup>-1</sup> × 10 <sup>11</sup> | R <sub>methane</sub><br>moles sec. <sup>-1</sup> × 10 <sup>11</sup> | Distribution, %               |                                 |                               |                                    |
|-----|---------------|--|---|-------------------------------|---------------------------------|-------------------------------|------------------------------------|
|     |               |  |   | C <sub>2</sub> D <sub>6</sub> | CH <sub>3</sub> CD <sub>3</sub> | C <sub>2</sub> H <sub>6</sub> | CD <sub>4</sub> /CD <sub>3</sub> H |
| 3   | 226           | 5.21   | 23.8  | 33.2                          | 20.7                            | 46.1                          | 0.007                              |
| 1   | 273           | 8.49   | 35.8  | 48.3                          | 0.9                             | 50.8                          | .007                               |
| 2   | 325           | 7.82   | 46.7  | 35.8                          | 5.1                             | 59.1                          | .005                               |

wave length limit of ~2800 Å., while the Corning 3-75 filter has a short wave length limit of ~3600 Å.

**Gas Phase.**—The results for the photolysis of CD<sub>3</sub>-COCD<sub>3</sub> in the presence of CH<sub>3</sub>HgCH<sub>3</sub>, using a Corning 0-54 filter (short wave length limit ~3000 Å.), are given in Tables III and IV. Blank experiments (without CD<sub>3</sub>COCD<sub>3</sub>) showed that less than 3% of the total product could be accounted for by the thermal

 TABLE III  
 GAS-PHASE PHOTOLYSIS OF CD<sub>3</sub>COCD<sub>3</sub> IN THE PRESENCE OF CH<sub>3</sub>HgCH<sub>3</sub>

| Run | Temp.,<br>°K. | Pressure, mm.                          |  | R <sub>ethane</sub><br>moles liter <sup>-1</sup> sec. <sup>-1</sup> × 10 <sup>10</sup> | R <sub>methane</sub><br>moles liter <sup>-1</sup> sec. <sup>-1</sup> × 10 <sup>10</sup> | R <sub>CO</sub> | Distribution, %               |                                 |                               |                 |                   |                   |                 |
|-----|---------------|--|--|--|---|-----------------|-------------------------------|---------------------------------|-------------------------------|-----------------|-------------------|-------------------|-----------------|
|     |               | CD <sub>3</sub> -<br>COCD <sub>3</sub> | CH <sub>3</sub> -<br>HgCH <sub>3</sub> |  |   |                 | C <sub>2</sub> D <sub>6</sub> | CH <sub>3</sub> CD <sub>3</sub> | C <sub>2</sub> H <sub>6</sub> | CD <sub>4</sub> | CD <sub>3</sub> H | CH <sub>3</sub> D | CH <sub>4</sub> |
| 10  | 376.5         | 37.5                                   | 37.5                                   | 7.71   | 1.57  | 8.59            | 85.8                          | 14.0                            | 0.2                           | 35.4            | 56.1              | 4.5               | 4.0             |
| 11  | 399           | 39.5                                   | 40.0                                   | 7.67   | 3.33  | 9.37            | 75.3                          | 23.3                            | 1.4                           | 35.0            | 52.3              | 6.6               | 6.0             |
| 12  | 400           | 39.0                                   | 39.5                                   | 8.20   | 3.42  | 11.7            | 81.3                          | 18.0                            | 0.7                           | 40.1            | 49.7              | 6.6               | 3.6             |
| 13  | 415           | 40.0                                   | 41.5                                   | 7.75   | 5.58  | 11.0            | 67.8                          | 28.3                            | 3.9                           | 30.8            | 50.1              | 7.2               | 11.9            |
| 14  | 425           | 41.0                                   | 42.0                                   | 30.3   | 14.5  | 38.4            | 75.0                          | 23.2                            | 1.8                           | 37.5            | 47.0              | 8.1               | 7.4             |
| 15  | 425           | 41.5                                   | 42.5                                   | 7.68   | 7.00  | 10.7            | 60.9                          | 33.8                            | 5.4                           | 32.0            | 47.0              | 9.0               | 12.1            |
| 16  | 425           | 39.5                                   | 39.0                                   | 1.62   | 3.09  | 2.81            | 42.5                          | 41.0                            | 16.5                          | 29.0            | 40.0              | 13.5              | 17.5            |
| 17  | 425.5         | 41.5                                   | 42.5                                   | 1.14   | 2.53  | 2.06            | 40.9                          | 44.5                            | 14.6                          | 25.6            | 39.4              | 14.0              | 21.1            |
| 18  | 435.5         | 43.5                                   | 43.5                                   | 7.02   | 9.40  | 11.0            | 52.9                          | 38.5                            | 8.6                           | 30.5            | 43.4              | 10.8              | 15.3            |
| 19  | 440           | 87.5                                   | 43.5                                   | 10.1   | 16.4  | 17.1            | 61.1                          | 34.3                            | 4.7                           | 46.0            | 32.3              | 13.3              | 8.4             |
| 20  | 440           | 43.5                                   | 22.5                                   | 5.72   | 6.87  | 8.91            | 64.6                          | 31.8                            | 3.5                           | 46.3            | 34.3              | 11.9              | 7.4             |
| 21  | 440           | 23.0                                   | 43.5                                   | 3.63   | 5.93  | 5.39            | 36.5                          | 47.3                            | 16.2                          | 16.7            | 46.7              | 11.0              | 25.6            |
| 22  | 453           | 44.5                                   | 44.5                                   | 5.34   | 12.4  | 8.80            | 38.9                          | 45.4                            | 15.6                          | 27.2            | 36.7              | 15.5              | 20.5            |

mixture at 2537 Å. is about 1.1 at 364°K. and 0.3 at 273°K. The ethane quantum yield is 0.1 at 364°K. and 0.2 at 273°K. These quantum yield measurements are based on the assumption that the quantum yield for carbon monoxide formation from diethyl ketone in the liquid phase at 367°K. is 0.87.<sup>9</sup>

In Table II, the results are given for the photolysis of a mixture of CH<sub>3</sub>HgCH<sub>3</sub>, CD<sub>3</sub>HgCD<sub>3</sub>, and 2,3-dimethylbutane (1:1:2). Again the sample was re-used. It is even more obvious that the percentage of CH<sub>3</sub>CD<sub>3</sub> follows the order in which the experiments were performed rather than the temperature variation. The intensity ( $I_a \approx 10^{15}$  quanta per cc.-sec.) was kept essentially constant for these three runs. Thus, the relative quantum yield of decomposition (ethane plus 0.5 methane) increases with temperature.

The photolysis of CH<sub>3</sub>N<sub>2</sub>CH<sub>3</sub>, in the presence of CD<sub>3</sub>HgCD<sub>3</sub> in the liquid phase at 0° using a Corning 3-75 filter, showed the presence of 12.5% CD<sub>3</sub>H in the methane fraction but no detectable amount (<1%) of C<sub>2</sub>D<sub>6</sub> nor CH<sub>3</sub>CD<sub>3</sub> in the ethane fraction. For this experiment, the ratio CD<sub>3</sub>HgCD<sub>3</sub>/CH<sub>3</sub>N<sub>2</sub>CH<sub>3</sub> was about 7.6. Dimethylmercury absorbs only to a long

 TABLE IV  
 GAS-PHASE PHOTOLYSIS OF CD<sub>3</sub>COCD<sub>3</sub> IN THE PRESENCE OF  
 CH<sub>3</sub>HgCH<sub>3</sub>

| Run | CH <sub>4</sub> /<br>CD <sub>3</sub> H | CH <sub>3</sub> D/<br>CD <sub>4</sub> | CH <sub>3</sub> CD <sub>3</sub> /<br>2C <sub>2</sub> D <sub>6</sub> | 2C <sub>2</sub> H <sub>6</sub> /<br>CH <sub>3</sub> CD <sub>3</sub> | CH <sub>3</sub> CD <sub>3</sub> /<br>(C <sub>2</sub> H <sub>6</sub> ·<br>C <sub>2</sub> D <sub>6</sub> ) <sup>1/2</sup> | k <sub>1</sub> /k <sub>6</sub> <sup>1/2</sup><br>× 10 <sup>4</sup> ,<br>mole <sup>-1/2</sup><br>sec. <sup>-1/2</sup> |
|-----|--|---------------------------------------|---|---|---|--|
|     |  |                                       |   |   |   |  |
| 11  | .115                                   | .190                                  | .155  | 0.12  | 2.2   | 7.47   |
| 12  | .073                                   | .165                                  | .111  | ..  | ..  | 6.36   |
| 13  | .237                                   | .233                                  | .208  | 0.28  | 1.7   | 12.5   |
| 14  | .157                                   | .215                                  | .155  | .16   | 2.0   | 15.8   |
| 15  | .258                                   | .281                                  | .277  | .32   | 1.9   | 17.1   |
| 16  | .440                                   | .467                                  | .484  | .80   | 1.6   | 22.2   |
| 17  | .535                                   | .547                                  | .543  | .65   | 1.8   | 20.4   |
| 18  | .353                                   | .355                                  | .364  | .45   | 1.8   | 26.0   |
| 19  | .260                                   | .289                                  | .281  | .27   | 2.0   | 24.4   |
| 20  | .208                                   | .256                                  | .246  | .22   | 2.1   | 27.8   |
| 21  | .547                                   | .658                                  | .649  | .69   | 2.0   | 38.2   |
| 22  | .559                                   | .569                                  | .583  | .69   | 1.9   | 45.1   |

and photochemical decomposition of CH<sub>3</sub>HgCH<sub>3</sub> at 457°K. At lower temperatures, the thermal blank would be even smaller. Consequently, no corrections

(9) P. Austoos, *Can. J. Chem.*, **36**, 400 (1958).

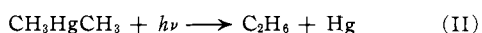
were made to obtain the final results. At higher temperatures, the thermal blank became quite large. The Arrhenius plot of  $\log k_1/k_2$  (Table IV) gives an activation energy of 12.6 kcal./mole. The ratio  $CD_4/CD_3H = 0.71 \pm 0.04$  for equal amounts of  $CD_3COCD_3$  and  $CH_3HgCH_3$  and is essentially independent of temperature.

In the photolysis of  $CH_3HgCH_3-CD_3HgCD_3$  mixtures with added oxygen, a small amount of ethane is still formed. However, about 25% of this is  $CH_3CD_3$ . The quantum yield of ethane formation at 45 mm. of dimethylmercury and 10 mm. of oxygen at 25° is about 0.005. This assumes a quantum yield of unity<sup>3</sup> in the absence of oxygen.

### Discussion

**I. Cage Recombination. (a) Liquid Phase.**—The presence of appreciable yields of  $CH_3CD_3$  in the liquid-phase photolysis of dimethylmercury was rather surprising. At the intensities used in the present study, recombination of methyl radicals originating from different molecules is not expected to compete with the hydrogen atom abstraction reaction to form methane. On the other side, the fact that the relative yield of  $CH_3CD_3$  increases with the order in which the experiments were performed indicated that some type of exchange reaction occurs resulting in the formation of  $CH_3HgCD_3$  which, upon subsequent photolysis, leads to the formation of  $CH_3CD_3$  by a cage recombination reaction. The detection of appreciable quantities of  $CH_3HgCD_3$  in the irradiated material supports this view.

More conclusive evidence for a cage recombination of methyl radicals was obtained by adding 2,3-dimethylbutane to an equimolar  $CH_3HgCH_3-CD_3HgCD_3$  mixture. Under these conditions, most methyl radicals were expected to react with the hydrocarbon,<sup>10</sup> thus preventing the formation of  $CH_3HgCD_3$ . The negligible yield of  $CH_3CD_3$ , at least in the first experiment, clearly shows that ethane is indeed mainly formed by a cage recombination reaction and that the  $CH_3CD_3$  produced in the previous experiments is most likely formed by a similar process involving  $CH_3HgCD_3$ . One still has to consider the possibility of the intramolecular formation of ethane as was noted in the



photolysis of azomethane.<sup>7</sup> However, the fact that, in the gas-phase photolysis of dimethylmercury carried out in the presence of oxygen, the quantum yield of ethane formation was only 0.005 or less as compared to a quantum yield of 0.1 to 0.2 for the formation of ethane in the liquid phase, indicates that process II is probably of minor importance.

**(b) Solid Phase.**—The small amount of ethane-*d*<sub>3</sub> in the ethane fraction suggests that cage recombination of methyl radicals does take place in the solid phase both at 4 and 77°K. The fact that dilution of dimethylmercury with ethanol or carbon dioxide diminishes the percentage of  $CH_3CD_3$  in the ethane fraction may be accounted for by (a) the longer path a methyl radical has to diffuse in the solid phase or during the warming-up of the irradiated sample in order to encounter a methyl radical originating from another molecule or (b) the lesser probability of a reaction between a hot methyl radical and a neighboring dimethylmercury molecule leading to the formation of  $CH_3CD_3$ . Hot methyl radical reactions will be discussed later in this paper.

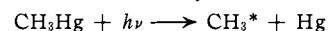
(10) A comparison of the ratio  $CD_4/CD_3H$  obtained for the diluted mixtures on one side with the same ratio for the undiluted dimethylmercury mixtures on the other side shows that the majority of the methyl radicals react with 2,3-dimethylbutane.

**II. Hot Methyl Radical Effects. (a) Liquid Phase.**—The relative high values for the ratios  $CH_4/CH_3D$  and  $CD_3H/CD_4$  obtained in the liquid-phase photolysis of  $CH_3HgCH_3-CD_3HgCD_3$  mixtures indicates that only thermal methyl radicals are taking part in the deuterium and hydrogen atom abstraction reactions. From a plot of  $\log CD_4/CD_3H$  vs.  $1/T$ , a value of 1.4 kcal. per mole can be deduced for the difference in activation energy for the abstraction of a deuterium atom and a hydrogen atom from dimethylmercury by a methyl radical. This value compares favorably with the value of 1.5 kcal./mole obtained by McNesby, *et al.*,<sup>11</sup> for the activation energy difference for deuterium and hydrogen atom abstraction from various hydrocarbons in the gas phase by methyl radicals.

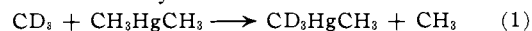
The increase in quantum yield of decomposition with temperature may be accounted for in one of two ways or both. The first possibility is the less efficient collisional deactivation of excited dimethylmercury at the higher temperatures because of its shorter lifetime. Although there is no evidence for this collisional deactivation in the gas-phase photolysis of dimethylmercury, it is a definite possibility in the liquid phase where the collisional yield is several orders of magnitude higher. A plot of the  $\log$  (ethane plus 0.5 methane) vs.  $1/T$  gives an apparent activation energy for the decomposition of dimethylmercury of  $1.0 \pm 0.2$  kcal./mole. The same value was obtained in the case of azomethane<sup>7</sup> for a plot of  $\log N_2$  as a function of  $1/T$ .

The second possibility is a cage recombination of a methyl radical with a methylmercury radical formed in the primary process. The methylmercury radical is reported to have a bond energy of about 6 kcal./mole.<sup>2</sup> Consequently, its lifetime may be long enough to undergo a cage recombination with a methyl radical in the liquid phase. If this is the case, the increase in quantum yield with temperature would be due to a higher rate of diffusion of the methyl radicals as well as a lower stability of the  $CH_3Hg$  radicals at the higher temperatures.

**(b) Solid Phase.**—The formation of such relatively large quantities of methane at 4 and 77°K., although surprising, is not unusual. Similar amounts of methane were also noted in the solid-phase photolysis of azomethane<sup>7</sup> and of ethyl acetate<sup>12</sup> at 4°K. In all cases, the results could be explained by assuming that, at these low temperatures, the free radicals formed are stable enough to undergo secondary photolysis leading to the production of hot methyl radicals as



**III. The Reaction  $CD_3 + Hg(CH_3)_2 \rightarrow CD_3HgCH_3 + CH_3$ .**—In agreement with the earlier observations by Oswin, *et al.*,<sup>5</sup>  $CH_3CD_3$  is formed when  $CD_3COCD_3$  is photolyzed in the presence of  $CH_3HgCH_3$  in the gas phase. In addition, it should be noted that  $C_2H_6$ , which has not been reported by these authors, is also a product. It is of interest that the values obtained for the ratio  $CH_3CD_3/(C_2H_6 \cdot CD_2D_6)^{1/2}$  are close to 2, independent of intensity or pressure especially in the higher temperature regions when the rates of  $C_2H_6$  could be determined most accurately. It may thus be concluded that  $CH_3CD_3$  and  $C_2H_6$  are mainly produced by methyl radical recombination reactions and that reaction A, which had been proposed earlier to account for the formation of  $CH_3CD_3$ , does not play an important role in this system. A reaction such as



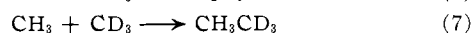
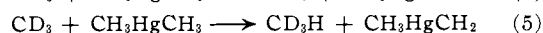
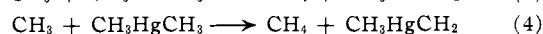
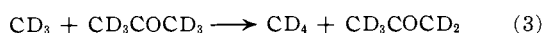
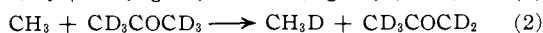
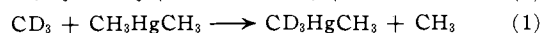
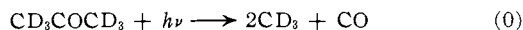
would, however, be consistent with the observed prod-

(11) W. M. Jackson, J. R. McNesby, and B. deB. Darwent, *J. Chem. Phys.*, **37**, 1610 (1962), and J. R. McNesby, *J. Phys. Chem.*, **64**, 1671 (1960).

(12) P. Ausloos and R. E. Rebbert, *ibid.*, **67**, 163 (1963).

uct distribution and will be tentatively considered as the most likely mechanism by which  $\text{CH}_3$  radicals are produced in this system. The occurrence of reaction 1 is substantiated by the results obtained in the liquid-phase photolysis of  $\text{CH}_3\text{N}_2\text{CH}_3$  in the presence of  $\text{CD}_3\text{HgCD}_3$ . The fact that, in these experiments, the ethane fraction consists exclusively of  $\text{C}_2\text{H}_6$  demonstrates that reaction A does not occur in this system. On the other side, the appearance of  $\text{CD}_3\text{H}$  as a product can reasonably be accounted for by the occurrence of reaction 1. Furthermore, the absence of  $\text{C}_2\text{D}_6$  in the ethane fraction indicates that the formation of  $\text{CD}_3\text{H}$  cannot be accounted for by a decomposition of an electronically excited dimethylmercury molecule because, in view of the existence of a cage effect, this should result in the formation of  $\text{C}_2\text{D}_6$  as well.

Accepting the occurrence of reaction 1, the following reaction mechanism may be proposed to account for the products formed during the photolysis of  $\text{CD}_3\text{COCD}_3$  carried out in the presence of  $\text{CH}_3\text{HgCH}_3$



If methane is formed only by reactions 2 to 5, then it follows that

$$\frac{R_{\text{CH}_4}}{R_{\text{CD}_3\text{H}}} = \frac{k_4}{k_5} \frac{[\text{CH}_3]}{[\text{CD}_3]} \text{ and } \frac{R_{\text{CH}_3\text{D}}}{R_{\text{CD}_4}} = \frac{k_2}{k_3} \frac{[\text{CH}_3]}{[\text{CD}_3]}$$

Also if ethane is formed only by reactions 6 to 8, then

$$\frac{R_{\text{CH}_3\text{CD}_3}}{R_{\text{C}_2\text{D}_6}} = \frac{k_7}{k_6} \frac{[\text{CH}_3]}{[\text{CD}_3]} \text{ and } \frac{R_{\text{C}_2\text{H}_6}}{R_{\text{CH}_3\text{CD}_3}} = \frac{k_8}{k_7} \frac{[\text{CH}_3]}{[\text{CD}_3]}$$

It has been shown in particular that  $k_2 = k_3^{13}$  and it

may be expected that  $k_4 = k_5$  and  $k_7 = 2k_6 = 2k_8$ . Thus, it follows that

$$\frac{R_{\text{CH}_4}}{R_{\text{CD}_3\text{H}}} = \frac{R_{\text{CH}_3\text{D}}}{R_{\text{CD}_4}} = \frac{R_{\text{CH}_3\text{CD}_3}}{2R_{\text{C}_2\text{D}_6}} = \frac{2R_{\text{C}_2\text{H}_6}}{R_{\text{CH}_3\text{CD}_3}} = \frac{[\text{CH}_3]}{[\text{CD}_3]}$$

Table IV substantiates the equality as well as the mechanism. Moreover, from the postulated mechanism, the rate of formation of  $\text{CD}_3$  and  $\text{CH}_3$  are given by the equations

$$R_{\text{CD}_3} = 2I_a\Phi + 2R_{\text{CO}}, \text{ and } R_{\text{CH}_3} = k_1[\text{CH}_3\text{HgCH}_3][\text{CD}_3]$$

Again, if  $\text{CD}_3$  and  $\text{CH}_3$  undergo the same reactions with the same rate constants, then the ratio of their rates of formation is equal to the ratio of their steady-state concentrations. Thus

$$\frac{R_{\text{CH}_3}}{R_{\text{CD}_3}} = \frac{[\text{CH}_3]}{[\text{CD}_3]} = \frac{k_1[\text{CH}_3\text{HgCH}_3][\text{CD}_3]}{2R_{\text{CO}}}$$

Any one of the four ratios, given before, can be used for  $[\text{CH}_3]/[\text{CD}_3]$ . However, the ratio  $R_{\text{CH}_3\text{CD}_3}/2R_{\text{C}_2\text{D}_6}$  should be the most accurate. Thus this equation can be rearranged to

$$\frac{k_1}{k_6^{1/2}} = \frac{R_{\text{CH}_3\text{CD}_3} R_{\text{CO}}}{R_{\text{C}_2\text{D}_6}^{1/2} [\text{CH}_3\text{HgCH}_3]}$$

The results (Table IV) show that  $k_1/k_6^{1/2}$  is essentially independent of intensity (see experiments 14–17) and also relatively independent of pressure (see experiments 19–21). The accumulation of evidence is in favor of the postulated type mechanism and the Arrhenius plot gives an activation energy of 12.6 kcal./mole which may be assigned to reaction 1.

Finally it is to be noted that the temperature independence of the ratio  $\text{CD}_4/\text{CD}_3\text{H}$  for equal amounts of  $\text{CD}_3\text{COCD}_3$  and  $\text{CH}_3\text{HgCH}_3$  means that the activation energy difference  $E_3 - E_5$  is  $0.0 \pm 0.4$  kcal./mole. This is in agreement with the reported values of  $E_3 = 11.2$  kcal./mole<sup>13</sup> and  $E_5 = 10.8$  kcal./mole.<sup>1</sup>

**Acknowledgment.**—This research was supported by a grant from the United States Public Health Service, Department of Health, Education and Welfare.

(13) J. R. McNesby and A. S. Gordon, *J. Am. Chem. Soc.*, **76**, 1416 (1954).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY, PITTSBURGH, PENNA.]

## Effects of Substituents on Acidities of Organic Acids in Water: Thermodynamic Theory of the Hammett Equation

BY LOREN G. HEPLER

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Qualitative discussion of  $\Delta H^\circ$  and  $\Delta S^\circ$  of ionization of some organic acids in aqueous solution is followed by development of thermodynamic equations for reactions of the type  $\text{HA}_s(\text{aq}) + \text{A}_u^-(\text{aq}) = \text{A}_s^-(\text{aq}) + \text{HA}_u(\text{aq})$ , where subscripts *s* and *u* indicate substituted and unsubstituted acids. The resulting thermodynamic equations, which are based on the idea that  $\Delta H^\circ$  and  $\Delta S^\circ$  can be expressed as sums of external and internal contributions, are used in determining values of  $\Delta H_{\text{int}}^\circ$  for various substituted acids transferring a proton to the anion of the unsubstituted acid. Combination of these thermodynamic equations with the Hammett equation leads to the prediction that the Hammett  $\sigma$ - and Taft  $\sigma^*$ -substituent constants should be proportional to  $\Delta H_{\text{int}}^\circ$ . The equations also predict correctly the observed linear dependence of  $\rho$  on  $1/T$ .

### Introduction

There are nearly as many theories and correlations of acid strengths as ionization data for organic acids. One of the reasons for developing another theory can be illustrated by considering the ionization of *p*-nitrophenol and *m*-nitrophenol in aqueous solution.

It has been stated many times that greater resonance stabilization of the anion of *p*-nitrophenol as compared to the anion of *m*-nitrophenol accounts for *p*-nitrophenol being a stronger acid than *m*-nitrophenol. If the resonance energy argument correctly describes the

only important factor contributing to a difference in ionization of these phenols, we should expect differences in  $\Delta F^\circ$  of ionization to be accounted for entirely by values of  $\Delta H^\circ$  of ionization. Earlier investigations<sup>1</sup> have yielded the data listed in Table I, which show that the difference in acidity of aqueous *p*-nitrophenol and *m*-nitrophenol is due to different  $\Delta S^\circ$  of ionization rather than different  $\Delta H^\circ$  of ionization. We conclude that interpretation of acid strengths solely in terms of

(1) L. P. Fernandez and L. G. Hepler, *J. Am. Chem. Soc.*, **81**, 1783 (1959).