

THERMOCHEMISTRY OF METALLIC ALKYLs

IV. MERCURY DIETHYL AND MERCURY DIPHENYL

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From measurements of the heats of reaction at 20° C, of HgEt_2 with Br_2 , I_2 and the mercuric halides, the heats of formation Q_f of HgEt_2 and HgEtX are obtained, viz.:

$$\begin{aligned} Q_f(\text{HgEt}_2, \text{liq.}) &= -9.9 \pm 1.7 \text{ kcal. mole}^{-1}, \\ Q_f(\text{HgEtCl, cryst.}) &= 32.3 \pm 1.5 \text{ kcal. mole}^{-1}, \\ Q_f(\text{HgEtBr, cryst.}) &= 24.2 \pm 1.5 \text{ kcal. mole}^{-1}, \\ Q_f(\text{HgEtI, cryst.}) &= 14.2 \pm 1.6 \text{ kcal. mole}^{-1}. \end{aligned}$$

Similar experiments using $\text{Hg}\phi_2$ provide equations relating the heats of formation of $\text{Hg}\phi_2$ and $\text{Hg}\phi\text{X}$ to the heats of formation of phenyl bromide and of phenyl iodide. Values of $Q_f(\text{Hg}\phi_2, \text{cryst.})$ and $Q_f(\text{Hg}\phi\text{X, cryst.})$ are listed based on two alternative values for $Q_f(\phi\text{Br})$.

The energy of removal of *both* ethyl groups from HgEt_2 is derived as 45.1 ± 6 kcal. mole⁻¹, and evidence is quoted that the removal of the first ethyl group requires some 40 kcal. of this total. The dissociation energies in the HgEtX compounds are derived as follows:

$$\begin{aligned} D(\text{Et—HgCl}) &= 58.0 \pm 3.8 \text{ kcal. mole}^{-1}, \\ D(\text{Et—HgBr}) &= 55.5 \pm 4.5 \text{ kcal. mole}^{-1}, \\ D(\text{Et—HgI}) &= 54.2 \pm 5.6 \text{ kcal. mole}^{-1}. \end{aligned}$$

Using the experimental result of Ghosh and Szwarc of $69 (\pm 3)$ kcal. mole⁻¹ for the dissociation energy in phenyl bromide, the energy of removal of *both* phenyl groups from $\text{Hg}\phi_2$ is calculated to be 55.4 ± 9 kcal. mole⁻¹.

In Part III of this series,¹ we reported some measurements of the heats of bromination and iodination of mercury dimethyl. The present paper extends these studies to cover the reactions of mercury diethyl and mercury diphenyl, and values are now given for the heats of reaction (in alcohol solution) of these compounds with bromine, iodine and with the mercuric halides. The *heats of formation* Q_f of HgEt_2 , $\text{Hg}\phi_2$, HgEtX and $\text{Hg}\phi\text{X}$ ($\text{X} = \text{Cl, Br, I, Et} = \text{C}_2\text{H}_5$, $\phi = \text{C}_6\text{H}_5$) are obtained from the reaction heats, and values for the heats of dissociation of the Hg—C bonds in this set of compounds are derived. All heat quantities are given in terms of the thermochemical calorie, defined² by the equation:

$$1 \text{ calorie} = 4.1840 \text{ abs. joule.}$$

¹ Hartley, Pritchard and Skinner, *Trans. Faraday Soc.*, 1950, **46**, 1019.

² Mueller and Rossini, *Amer. J. Physics*, 1944, **12**, 1.

Experimental

Preparation of Compounds.— HgEt_2 was prepared by the method of Gilman and Brown³ by interacting HgCl_2 with the Grignard reagent. The crude product was dried and then purified by fractional distillation under reduced pressure using a gauze-packed column.

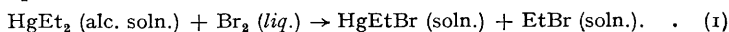
$\text{Hg}\phi_2$ was prepared by the method of Bachmann⁴ by interacting HgBr_2 with ϕMgBr in an ether-benzene solvent. The crude product was purified by fractional crystallization from hot methanol solvent.

The iodine, bromine, and mercuric halides used were A.R. reagents, and the methanol a high-grade synthetic product.

Calorimeters.—The calorimeters have been described previously,¹ the larger one by Pritchard and Skinner,⁵ and the smaller one by Hartley and Skinner.⁶

Results

Mercury Diethyl and Bromine.—The reaction between bromine and HgEt_2 occurs readily in methyl alcohol solution at room temperature. If the HgEt_2 is present in excess, the reaction follows the equation:

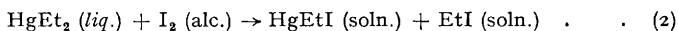


The experiments were performed by breaking glass phials containing known weights of bromine into dilute solutions of (excess) HgEt_2 in methyl alcohol, and the temperature changes measured in terms of the resistance change of a thermistor element (R_i = initial, R_f = final resistance (in ohms) of the thermistor). The results are summarized in Table I.

TABLE I.—REACTION OF HgEt_2 WITH BROMINE

Expt.	Wt. of Br_2 (g.)	R_i	R_f	Q (kcal. mole ⁻¹)
1	1.4645	1740.65	1662.5	50.95
2	1.5502	1740.05	1657.3	51.05
3	1.5592	1740.4	1657.3	50.97
4	1.5056	1740.0	1659.6	51.04
			Mean	51.00 \pm 0.05

Mercury Diethyl and Iodine.—Owing to the relative slowness of the reaction of iodine with mercury diethyl, we have found it best to add the HgEt_2 to an excess of iodine dissolved in methanol. The reaction



occurs under these conditions with moderate speed (reaction times of 20-30 min.), and the secondary reaction which might be anticipated between the excess I_2 and HgEtI is fortunately sufficiently slow to be of almost negligible importance. The measured heats of reaction (2) are listed in Table II.

TABLE II.—REACTION OF HgEt_2 WITH IODINE

Expt.	Wt. HgEt_2 (g.)	R_i	R_f	Q (kcal. mole ⁻¹)
1	2.5847	1721.5	1673.05	29.04
2	2.5636	1739.85	1691.15	29.12
3	2.8275	1736.75	1683.25	29.10
4	2.6862	1735.55	1684.6	29.16
			Mean	29.10 \pm 0.06

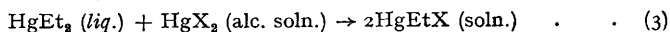
³ Gilman and Brown, *J. Amer. Chem. Soc.*, 1930, **52**, 3314.

⁴ Bachmann, *J. Amer. Chem. Soc.*, 1933, **55**, 2827.

⁵ Pritchard and Skinner, *J. Chem. Soc.*, 1950, 272.

⁶ Hartley and Skinner, *Trans. Faraday Soc.*, 1950, **46**, 621.

Mercury Diethyl and the Mercuric Halides.— HgEt_2 reacts readily with methanol solutions of the mercuric halides (HgCl_2 , HgBr_2 , HgI_2) at room temperature. The experiments were performed by adding weighed amounts of the dialkyl to excess of the mercuric halide, dissolved in 750 ml. methanol. The heats of the reactions

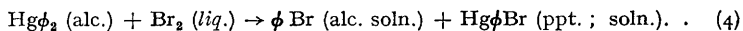


are listed in Table III.

TABLE III.—REACTIONS OF HgEt_2 WITH HgX_2

Reaction	Expt.	Wt. HgEt_2 (g.)	R_i	R_f	Q	Mean Q
$\text{HgEt}_2 + \text{HgCl}_2$	(i)	1.7422	1764.7	1753.2	9.87	9.85
	(ii)	1.7547	1721.85	1710.6	9.83	
$\text{HgEt}_2 + \text{HgBr}_2$	(i)	1.7609	1713.1	1703.8	8.13	8.16
	(ii)	1.7691	1644.3	1635.25	8.20	
	(iii)	1.6302	1725.85	1717.15	8.15	
$\text{HgEt}_2 + \text{HgI}_2$	(i)	1.0010	1749.2	1745.6	5.41	5.45
	(ii)	0.9540	1709.0	1705.6	5.49	

Mercury Diphenyl and Bromine.—The reaction of mercury diphenyl and bromine was carried out in methanol solution, by adding the bromine to a solution containing an excess of mercury diphenyl:

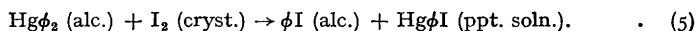


The reaction occurs almost instantaneously, with precipitation of the crystalline mercury phenyl bromide, which is only sparingly soluble in methanol at room temperature. The experimental results are summarized in Table IV.

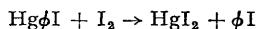
TABLE IV.—REACTION OF $\text{Hg}\phi_2$ WITH BROMINE

Expt.	Wt. of Br_2 (g.)	R_i	R_f	Q (kcal. mole ⁻¹)
1	0.6775	1758.3	1722.8	48.90
2	0.7244	1758.5	1720.5	48.98
3	0.6961	1762.65	1726.0	49.03
			Mean	48.97 (± 0.07)

Mercury Diphenyl and Iodine.—The reaction of mercury diphenyl with iodine was carried out by adding crystalline iodine to a solution containing an excess of mercury diphenyl dissolved in methanol:

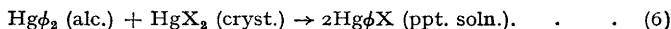


The reaction occurs readily, and the mercury phenyl iodide is formed as a crystalline precipitate. In this reaction (contrast the corresponding reactions using HgMe_2 and HgEt_2), we have observed that the addition of $\text{Hg}\phi_2$ to a solution containing an excess of iodine results in the complete iodination of the mercury diphenyl—i.e. the second step



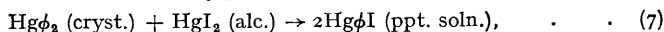
occurs with moderate ease at room temperature. The measured heats of reaction (5) are given in Table V.

Mercury Diphenyl and the Mercuric Halides.—The reactions of mercury diphenyl with HgCl_2 and HgBr_2 were studied by adding the crystalline halides to the mercury diphenyl dissolved in 750 ml. methanol:



With HgCl_2 , the $\text{Hg}\phi\text{Cl}$ formed remained in solution; with HgBr_2 , the greater portion of the $\text{Hg}\phi\text{Br}$ was formed as a crystalline precipitate. The reaction with

HgI_2 was carried out in a slightly different manner, by adding the crystalline $\text{Hg}\phi_2$ to a saturated solution of HgI_2 in methanol:



the mercury phenyl iodide precipitating out as a crystalline solid. We should perhaps stress that the heats measured in Table VI refer to the formation of $\text{Hg}\phi\text{Cl}$ in solution and to $\text{Hg}\phi\text{Br}$ and $\text{Hg}\phi\text{I}$ mainly as solid but part in solution.

TABLE V.—REACTION OF $\text{Hg}\phi_2$ WITH IODINE

Expt.	Wt. of I_2 (g.)	R_i	R_f	Q (kcal. mole ⁻¹)
1	0.9929	1716.4	1698.7	26.93
2	1.0535	1750.75	1731.5	27.07
3	1.0037	1729.2	1711.15	26.97
			Mean	26.99 (± 0.07)

The quantities of reactants were so chosen as to give approximately the same amounts of mercury phenyl halides as obtained in the halogenation experiments, in this way ensuring that the heat effects due to the partial solubilities of $\text{Hg}\phi\text{Br}$ and $\text{Hg}\phi\text{I}$ in methanol were of the same thermal importance in each set of experiments. The measured heats of reactions (6) and (7) are given in Table VI.

TABLE VI.—REACTIONS OF $\text{Hg}\phi_2$ WITH MERCURIC HALIDES

Reaction	Expt.	Wt. $\text{Hg}\phi_2$ (g.)	Wt. HgX_2 (g.)	R_i	R_f	Q (kcal.)	Mean Q (kcal.)
$\text{Hg}\phi_2 + \text{HgCl}_2$	(i)	1.0538	0.6345	1760.4	1756.95	8.53	8.42
	(ii)	1.1096	0.6427	1756.2	1752.8	8.32	
$\text{Hg}\phi_2 + \text{HgBr}_2$	(i)	0.9990	0.8398	1733.05	1727.65	13.61	13.64
	(ii)	1.0350	0.7887	1751.5	1746.4	13.54	
	(iii)	1.0491	0.8209	1758.95	1753.55	13.77	
$\text{Hg}\phi_2 + \text{HgI}_2$	(i)	0.7256	large excess	1726.85	1724.4	7.05	7.07
	(ii)	0.8421	large excess	1721.55	1718.7	7.10	

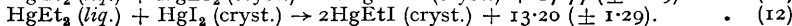
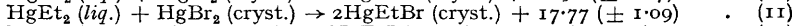
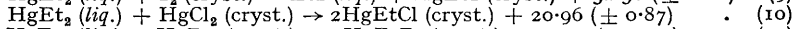
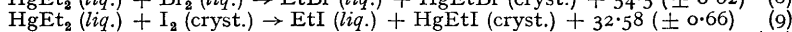
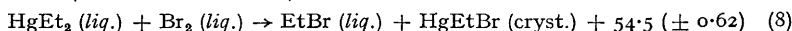
Heats of Solution.—The interpretation of the experimental results as Q_f values requires the heats of solution of the various reactants and products; some of these were measured previously,¹ and the remainder were measured as required in a smaller calorimeter (cf. Hartley and Skinner⁶). The results are summarized in Table VII; the relatively large limits of error attached to the values quoted for the heats of solution of HgRX crystals are due to the slowness of the solution process with these compounds.

TABLE VII.—HEATS OF SOLUTION IN METHANOL

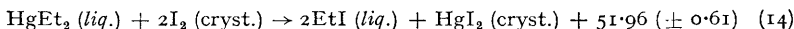
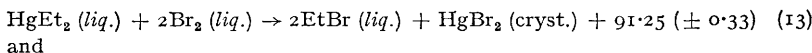
Solute	Heat of Solution (kcal. mole ⁻¹)	Solute	Heat of Solution (kcal. mole ⁻¹)
HgCl_2 (cryst.)	$+ 0.71 \pm 0.05$	EtBr (liq.)	$- 0.28 \pm 0.02$
HgBr_2 (cryst.)	$+ 0.41 \pm 0.05$	EtI (liq.)	$- 0.75 \pm 0.05$
HgI_2 (cryst.)	$- 1.85 \pm 0.15$	HgEt_2 (liq.)	$- 1.37 \pm 0.05$
I_2 (cryst.)	$- 2.07 \pm 0.05$	$\text{Hg}\phi_2$ (cryst.)	$- 5.15 \pm 0.15$
EtHgCl (cryst.)	$- 5.2 \pm 0.4$	ϕBr (liq.)	$- 0.20 \pm 0.03$
EtHgBr (cryst.)	$- 4.6 \pm 0.5$	ϕI (liq.)	$- 0.40 \pm 0.04$
EtHgI (cryst.)	$- 4.8 \pm 0.5$	$\text{Hg}\phi\text{Cl}$ (cryst.)	$- 3.0 \pm 0.3$

Calculation of Heats of Formation.—(a) HgEt_2 , (liq.)

From the heats of reaction given in Tables I, II, III and the relevant heats of solution in Table VII, the following set of thermochemical equations can be written (heats in kcal. mole⁻¹):



Two further equations are obtained by subtracting eqn. (11) from twice eqn. (8), and by the subtraction of eqn. (12) from twice eqn. (9), viz.,



The error limits quoted for the eqn. (8) to (12) include the uncertainties in the heats of solution of the HgEtX in methanol; these same uncertainties do not enter into the errors associated with eqn. (13) and (14), as the solution heat errors cancel out in deriving these latter.

The heat of formation of $\text{HgEt}_2(\text{liq.})$ can be obtained either from eqn. (13), assuming values for $Q_f(\text{HgBr}_2, \text{cryst.})$ and $Q_f(\text{EtBr}, \text{liq.})$, or from eqn. (14), assuming values for $Q_f(\text{HgI}_2, \text{cryst.})$ and $Q_f(\text{EtI}, \text{liq.})$. Probable values for the heats of formation of the mercuric halides were discussed in Part III of this series,¹ and we adopt the same values as previously used, viz.:

$$Q_f(\text{HgBr}_2, \text{cryst.}) = 40.64 \pm 0.24 \text{ kcal. mole}^{-1},$$

$$Q_f(\text{HgI}_2, \text{cryst.}) = 25.2 \pm 0.2 \text{ kcal. mole}^{-1}.$$

For the heat of formation of liquid EtBr , the recommended value in the *Tables of Selected Values of Chemical Thermodynamic Constants* (Nat. Bureau Standards, Washington, 1949) is $Q_f(\text{EtBr}, \text{liq.}) = 20.4 \text{ kcal. mole}^{-1}$; this presumably derives from the heat of combustion data of Thomsen,⁷ and may involve an uncertainty of the order $\pm 0.5 \text{ kcal. mole}^{-1}$. A recent determination of the heat of combustion of liquid EtI by Springall and White⁸ gave $Q_f(\text{EtI}, \text{liq.}) = 8.4 \pm 0.5 \text{ kcal. mole}^{-1}$; this is in fair agreement with the value $8.9 \pm 1.1 \text{ kcal. mole}^{-1}$ obtained by Carson, Hartley and Skinner⁹ from measurements of the heat of iodination of cadmium diethyl.*

The value for $Q_f(\text{HgEt}_2, \text{liq.})$ obtained from eqn. (13), and the above values for $Q_f(\text{HgBr}_2)$ and $Q_f(\text{EtBr}, \text{liq.})$ is $-9.81 (\pm 1.55) \text{ kcal. mole}^{-1}$; from eqn. (14), the quoted value for $Q_f(\text{HgI}_2)$, and the value of Springall and White for $Q_f(\text{EtI}, \text{liq.})$, the derived value for $Q_f(\text{HgEt}_2, \text{liq.})$ is $-9.96 (\pm 1.81) \text{ kcal. mole}^{-1}$. The close agreement of these separate determinations of the heat of formation of HgEt_2 may be due to a fortuitously good choice of values for $Q_f(\text{EtBr})$ and $Q_f(\text{EtI})$, but since the probable errors in these are allowed for in the estimated error quoted for $Q_f(\text{HgEt}_2)$, the final value

$$Q_f(\text{HgEt}_2, \text{liq.}) = -9.9 \pm 1.7 \text{ kcal. mole}^{-1}$$

can be recommended with confidence.

(b) HgEtCl , cryst.:

From the heat of reaction (10), the heat of formation of mercuric chloride ($Q_f(\text{HgCl}_2, \text{cryst.}) = 53.5 \pm 0.5 \text{ kcal. mole}^{-1}$), and our value for $Q_f(\text{HgEt}_2, \text{liq.})$, we obtain

$$Q_f(\text{HgEtCl}, \text{cryst.}) = 32.3 \pm 1.5 \text{ kcal. mole}^{-1}.$$

(c) HgEtBr , cryst.

In similar manner we may derive the heat of formation of crystalline HgEtBr from the heat of reaction (11), using our values for $Q_f(\text{HgBr}_2, \text{cryst.})$ and $Q_f(\text{HgEt}_2, \text{liq.})$, whence

$$Q_f(\text{HgEtBr}, \text{cryst.}) = 24.25 \pm 1.5 \text{ kcal. mole}^{-1}.$$

⁷ Thomsen, *Thermochemische Untersuchungen*, 1-4 (Barth, Leipzig).

⁸ Springall and White, *Research*, 1949, **2**, 296.

⁹ Carson, Hartley and Skinner, *Trans. Faraday Soc.*, 1949, **45**, 1159.

* This value differs slightly from that published in ref. (9). The amendment corresponds to a similar change made in the value for $Q_f(\text{MeI})$ discussed in Part III of this series.

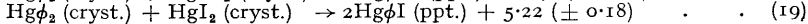
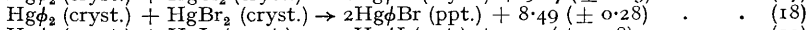
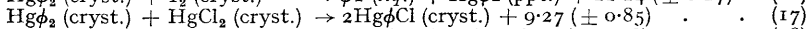
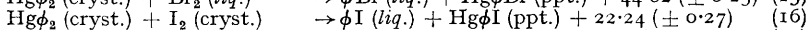
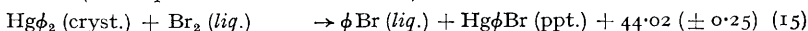
(d) HgEtI, cryst.

Using the heat of reaction (12), and our values for $Q_f(\text{HgEt}_2, \text{liq.})$ and $Q_f(\text{HgI}_2, \text{cryst.})$, the heat of formation of crystalline HgEtI is calculated as

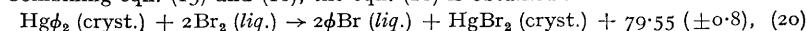
$$Q_f(\text{HgEtI, cryst.}) = 14.25 \pm 1.6 \text{ kcal. mole}^{-1}.$$

(e) Hg ϕ_2 , cryst.

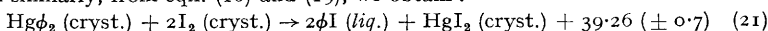
From the heats of the reactions given in Tables IV, V, and VI, and heats of solution in Table VII, we can obtain the following set of thermochemical equations * (heats quoted are in kcal. mole⁻¹) :



Combining eqn. (15) and (18), the eqn. (20) is obtained :



and similarly, from eqn. (16) and (19), we obtain :



The value of $Q_f(\text{Hg}\phi_2, \text{cryst.})$ is obtainable *either* from eqn. (20), given a knowledge of $Q_f(\phi\text{Br}, \text{liq.})$, or from eqn. (21), given the value of $Q_f(\phi\text{I}, \text{liq.})$. Unfortunately, we are not satisfied that reliable values for the heats of formation of phenyl bromide and iodide can be quoted at the present time.

Values for the heat of combustion of liquid phenyl bromide have been reported by Kablukow and Perelman,¹⁰ and more recently by Smith and Bjellerup.¹¹ The data of the former lead to $Q_f(\phi\text{Br}, \text{liq.}) = -12.5$ kcal. mole⁻¹, and we have been informed by Smith and Bjellerup¹² that their results yield the value $Q_f(\phi\text{Br}, \text{liq.}) = -8.8$ kcal. mole⁻¹. From the experimental viewpoint, the combustion of bromides presents difficulties, and the corrections are not easy to make ; in consequence the derived Q_f values cannot yet be quoted with complete certainty.

It is possible to make an *estimate* of the value of $Q_f(\phi\text{Br})$, starting from the recently determined value of the heat of formation of liquid phenyl chloride, $Q_f(\phi\text{Cl}, \text{liq.}) = -2.6 \pm 0.3$ kcal. mole⁻¹, obtained by Hubbard, Knowlton and Huffman.¹³ The estimate is based on the fact that the difference ΔQ_f between the heats of formation of gaseous RCl and RBr compounds lies in the range 11.0 to 12.4 kcal. mole⁻¹, in cases where this difference is known (i.e. R = Me, Et, *tert.*-Bu, acetyl) ; accordingly if we assume that $\Delta Q_f = 11.7 \pm 0.7$ in the case of ϕCl and ϕBr , we arrive at the figure, $Q_f(\phi\text{Br}, g) = -23.2 \pm 1$ kcal. mole⁻¹, which corresponds to $Q_f(\phi\text{Br}, \text{liq.}) = -14.1 \pm 1$ kcal. mole⁻¹ ($\lambda_{\text{vap.}}(\phi\text{Br})^{14} = 9.1$ kcal. mole⁻¹). Since the estimated value differs significantly from the most recent experimental value (obtained by Smith and Bjellerup), we have used both the alternative values of $Q_f(\phi\text{Br}, \text{liq.})$ in deriving $Q_f(\text{Hg}\phi_2, \text{cryst.})$.

The value of $Q_f(\text{Hg}\phi_2, \text{cryst.})$ is obtained from the heat of the reaction in eqn. (20), and is related to $Q_f(\phi\text{Br}, \text{liq.})$ by

$$Q_f(\text{Hg}\phi_2, \text{cryst.}) = 2Q_f(\phi\text{Br}, \text{liq.}) - 38.9 (\pm 1.0). \quad (22)$$

Using the value of Smith and Bjellerup for $Q_f(\phi\text{Br}, \text{liq.})$, eqn. (22) gives $-56.5 (\pm 3)$ kcal. mole⁻¹ for $Q_f(\text{Hg}\phi_2, \text{cryst.})$, whereas the alternative estimate of $Q_f(\phi\text{Br}, \text{liq.})$ yields $-67.1 (\pm 3)$ kcal. mole⁻¹.

The derivation of $Q_f(\text{Hg}\phi_2, \text{cryst.})$ from the iodination data is contained in eqn. (21), and may be expressed in the form :

$$Q_f(\text{Hg}\phi_2, \text{cryst.}) = 2Q_f(\phi\text{I}, \text{liq.}) - 14.06 (\pm 0.9). \quad (23)$$

* In the reactions producing Hg ϕBr (ppt.) and Hg ϕI (ppt.), the designation (ppt.) refers strictly to crystalline precipitate plus saturated solution : the relative concentrations of Hg ϕX and MeOH are obtainable from the preceding Tables.

¹⁰ Kablukow and Perelman, *Compt. rend. (U.R.S.S.) A*, 1930, 519.

¹¹ Smith and Bjellerup, *Acta Chim. Scand.*, 1947, I, 566.

¹² Private communication from Prof. Lennart-Smith and Lars Bjellerup.

¹³ Hubbard, Knowlton and Huffman, *Abstracts of the Chicago Meeting, A.C.S. (March)*, 1948 ; and corrected value in a private communication from Ward N. Hubbard.

¹⁴ Zil'berman-Granovskaya and Shugam, *J. Physic. Chem. (U.R.S.S.)*, 1940, 14, 1004.

Eqn. (23) becomes compatible with eqn. (22) if

$$Q_f(\phi\text{Br}, \text{liq.}) - Q_f(\phi\text{I}, \text{liq.}) = 12.42 \pm 0.95, \quad (24)$$

which gives $Q_f(\phi\text{I}, \text{liq.}) = -21.2 \pm 2$ kcal. mole⁻¹ if Smith's value for $Q_f(\phi\text{Br}, \text{liq.})$ is used, or -26.5 ± 2 kcal. mole⁻¹, if our estimated value of $Q_f(\phi\text{Br}, \text{liq.})$ is used. At present, a reliable independent value for $Q_f(\phi\text{I}, \text{liq.})$ is not available, so that the direct determination of $Q_f(\text{Hg}\phi_2, \text{cryst.})$ from eqn. (23) cannot yet be made.

The difference ΔQ_f expressed by eqn. (24) corresponds to a difference in the heats of formation of *gaseous* ϕBr and ϕI (λ_{vap} , of $\phi\text{I}^{14} = 9.6$ kcal. mole⁻¹) of 13.0 ± 1 kcal. mole⁻¹. This agrees well with the average ΔQ_f for the differences between $Q_f(\text{RBr})$ and $Q_f(\text{RI})$, when $\text{R} = \text{Me}$, Et , *tert.*-Bu, acetyl, which range from 13.1 to 14.8 kcal., with the mean ΔQ_f as 14.0 ± 0.9 kcal. mole⁻¹.

Further evidence of the reliability of eqn. (24) may be got from the studies of Butler and Polanyi¹⁵ on the pyrolytic decomposition of phenyl iodide, and Ghosh and Szwarc¹⁶ on the pyrolysis of phenyl bromide. Butler and Polanyi obtained a value of *ca.* 55 kcal. mole⁻¹ for the dissociation energy of the C—I bond in phenyl iodide, and Ghosh and Szwarc found the C—Br dissociation energy in phenyl bromide to be of the order 69 kcal. mole⁻¹. These dissociation energies are related to the heats of formation of the phenyl halides by the equations:

$$-D(\phi-\text{Br}) = -69 \text{ kcal.} = Q_f(\phi) + Q_f(\text{Br}) - Q_f(\phi\text{Br}), \quad (25)$$

$$-D(\phi-\text{I}) = -55 \text{ kcal.} = Q_f(\phi) + Q_f(\text{I}) - Q_f(\phi\text{I}), \quad (26)$$

from which by subtraction,

$$Q_f(\phi\text{Br}) - Q_f(\phi\text{I}) = \Delta Q_f = 12.8 \text{ kcal.},$$

since the values $Q_f(\text{Br}) = -26.7$ kcal. mole⁻¹, and $Q_f(\text{I}) = -25.5$ kcal. mole⁻¹ are known quantities. This value of ΔQ_f from pyrolysis studies agrees closely both with our experimental value of 13.0 ± 2 kcal., and our extrapolation value of 14.0 ± 1 kcal.

(f) $\text{Hg}\phi\text{Cl}$, *cryst.*

The value of $Q_f(\text{Hg}\phi\text{Cl}, \text{cryst.})$ derives from eqn. (17), and is related to $Q_f(\text{Hg}\phi_2, \text{cryst.})$ by

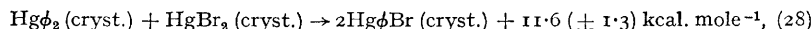
$$Q_f(\text{Hg}\phi\text{Cl}, \text{cryst.}) = 31.4 (\pm 0.7) + \frac{1}{2}Q_f(\text{Hg}\phi_2, \text{cryst.}). \quad (27)$$

Using the two alternative values for $Q_f(\text{Hg}\phi_2, \text{cryst.})$ of -56.5 ± 3 kcal. mole⁻¹ (alternative A) and -67.1 ± 3 kcal. mole⁻¹ (alternative B), eqn. (27) yields:

$$Q_f(\text{Hg}\phi\text{Cl}, \text{cryst.}) = \begin{cases} 3.15 \pm 2.2 \text{ kcal. mole}^{-1} & \text{(A)} \\ -2.17 \pm 2.2 \text{ kcal. mole}^{-1} & \text{(B)} \end{cases}$$

(g) $\text{Hg}\phi\text{Br}$, *cryst.*

The heat of reaction (18) corresponds to the formation of $\text{Hg}\phi\text{Br}$ (*cryst.* + *sat. soln.*), and on making allowance for the heat effect due to the partial solubility of the $\text{Hg}\phi\text{Br}$ in methanol, the equation becomes



from which we may write

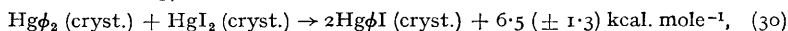
$$Q_f(\text{Hg}\phi\text{Br}, \text{cryst.}) = 26.12 (\pm 0.77) + \frac{1}{2}Q_f(\text{Hg}\phi_2, \text{cryst.}) \quad (29)$$

leading to

$$Q_f(\text{Hg}\phi\text{Br}, \text{cryst.}) = \begin{cases} -2.13 \pm 2.3 \text{ kcal. mole}^{-1} & \text{(A)} \\ -7.43 \pm 2.3 \text{ kcal. mole}^{-1} & \text{(B)} \end{cases}$$

(h) $\text{Hg}\phi\text{I}$, *cryst.*

In similar manner, eqn. (19) after correction for the heat due to partial solution of the $\text{Hg}\phi\text{I}$ becomes



from which we may write

$$Q_f(\text{Hg}\phi\text{I}, \text{cryst.}) = 15.85 (\pm 0.75) + \frac{1}{2}Q_f(\text{Hg}\phi_2, \text{cryst.}), \quad (31)$$

and obtain

$$Q_f(\text{Hg}\phi\text{I}, \text{cryst.}) = \begin{cases} -12.4 \pm 2.3 \text{ kcal. mole}^{-1} & \text{(A)} \\ -17.7 \pm 2.3 \text{ kcal. mole}^{-1} & \text{(B)} \end{cases}$$

¹⁵ Butler and Polanyi, *Trans. Faraday Soc.*, 1943, **39**, 19.

¹⁶ Ghosh, *Thesis* (University of Manchester, 1949).

Discussion

The values we find for the heats of formation of HgEt_2 and $\text{Hg}\phi_2$ differ markedly from the values that are derived from the heats of combustion by Berthelot.¹⁷ It was concluded in Part III of this series that Berthelot's combustion data on mercury dimethyl are misleading, and it is our view that new investigations on the heats of combustion of the mercury dialkyls are needed.

The combustion of a mercury alkyl should yield CO_2 , H_2O , HgO and/or Hg as products, and presuming an analysis of the products is made, an accurate value of the heat of formation could be derived from the combustion data. The accuracy of the thermochemical method we have used (excluding experimental errors), depends on the validity of the equations (1) to (6) which we have assumed. There is independent evidence that these equations are substantially correct. Steinkopf^{17a} has shown that the reactions of $\text{Hg}\phi_2$ and HgX_2 occur quantitatively in alcohol solution, and Whitmore^{17b} states "there are practically no complications" in the reactions between HgR_2 and HgX_2 . Rice and Rice^{17c} make a similar statement. Whitmore provides confirmation for the equations used to describe the halogenation experiments.

From the Q_f values of the gaseous states of HgR_2 and HgRX , it is possible to derive the $\text{Hg}-\text{R}$ bond dissociation energies, given that $Q_f(\text{R})$ and $Q_f(\text{HgX})$ are known quantities. The method has been fully described elsewhere.^{1, 18} For the HgR_2 compounds, the thermochemical method gives only the sum, $D_1 + D_2$, of the two $\text{Hg}-\text{R}$ bond dissociation energies. The values of $(D_1 + D_2)$ are listed in Table VIII. The data on HgMe_2 are from Part III.¹

TABLE VIII.—BOND DISSOCIATION ENERGIES IN HgR_2

Molecule	Q_f (obs.) (kcal.)	λ_{vap} (kcal.)	Q_f (g) (kcal.)	Q_f (R) (kcal.)	$(D_1 + D_2)$ (kcal.)
HgMe_2 (liq.) .	-14.3 ± 2	8.1	-22.4 ± 2	-32.6 ± 1	57.3 ± 4
HgEt_2 (liq.) .	-9.9 ± 2	10.1 (a)	-20.0 ± 2	-25.3 ± 2 (b)	45.1 ± 6
$\text{Hg}\phi_2$ (cryst.) .	$\begin{cases} -67.1 \pm 3 \\ -56.5 \pm 3 \end{cases}$	$\begin{cases} 23 \pm 2$ (c) \\ 23 ± 2 (c) \end{cases}	$\begin{cases} -90.1 \pm 5 \\ -79.5 \pm 5 \end{cases}$	$\begin{cases} -65.6 \pm 2 \\ -60.3 \pm 2 \end{cases}$	$\begin{cases} 55.4 \pm 9 \\ 55.4 \pm 9 \end{cases}$

(a) Linnett and Thompson.¹⁹

(b) Roberts and Skinner.¹⁸

(c) Sidgwick : ²⁰ (the error limits are arbitrary).

The magnitudes of the error limits are determined mainly by the uncertainties in $Q_f(\text{R})$, and also for $\text{Hg}\phi_2$ by the uncertain value for the heat of sublimation.* The figures in the final column of Table VIII

¹⁷ Berthelot, *Compt. rend.*, 1899, **139**, 918.

^{17a} Whitmore, *Organic Compounds of Mercury* (Chemical Catalog Company, New York, 1921), p. 40.

^{17b} Steinkopf, *Annalen*, 1917, **413**, 310.

^{17c} Rice and Rice, *The Aliphatic Free Radicals* (Johns Hopkins Press, Baltimore, 1935), p. 34.

¹⁸ Roberts and Skinner, *Trans. Faraday Soc.*, 1949, **45**, 339.

¹⁹ Linnett and Thompson, *Trans. Faraday Soc.*, 1936, **32**, 681.

²⁰ Sidgwick, *The Chemical Elements and their Compounds* (O.U.P.), 1950.

* The $(D_1 + D_2)$ value in $\text{Hg}\phi_2$ is derived from the set of equations :

$$(a) -(D_1 + D_2) = 2Q_f(\phi) - 14.5 - Q_f(\text{Hg}\phi_2, g),$$

$$(b) Q_f(\text{Hg}\phi_2, g) = (Q_f(\phi\text{Br}, g) - 43.7 (\pm 3),$$

$$(c) -D(\phi\text{Br}) = Q_f(\phi) - 26.7 - Q_f(\phi\text{Br}),$$

of which (b) is a transcription of eqn. (22). Combining (a), (b), (c), one obtains

$$-(D_1 + D_2) = 82.6 (\pm 3) - 2D(\phi\text{Br}).$$

The uncertainty in the value $D(\phi-\text{Br}) \sim 69$ kcal. is not quoted by Ghosh and Szwarc, and we have allowed a spread of ± 3 kcal. in their value, to give an overall error of ± 9 kcal. in the final value of $(D_1 + D_2)$. Note that if $D(\phi-\text{Br})$ is given, $(D_1 + D_2)$ is independent of $Q_f(\phi\text{Br})$.

are important in considerations of the relative stability of the HgR_2 compounds. From the viewpoint of thermal stability, it would be most useful to know the D_1 values alone, but as we have previously pointed out,¹ it is probable that generally $D_1 \gg D_2$, so that the smaller the sum, $(D_1 + D_2)$, correspondingly the smaller is D_1 likely to be. The large fall in $(D_1 + D_2)$ in passing from HgMe_2 to HgEt_2 is, in this sense, borne out by the preliminary measurements of Warhurst and Gowenlock²¹ on D_1 , who found values of $D_1 \sim 51$ kcal. in HgMe_2 , and $D_1 \sim 40$ kcal. in HgEt_2 . The error limits associated with $(D_1 + D_2)$ in $\text{Hg}\phi_2$ are too large at present to allow of much more than speculation; nevertheless, Sidgwick²⁰ has commented on the fact that HgMe_2 is markedly more stable than other HgR_2 compounds—that $\text{Hg}\phi_2$, for example, begins to decompose slowly at 200°C , whereas HgMe_2 is stable up to 300°C —so that it appears probable that D_1 is smaller in $\text{Hg}\phi_2$ than in HgMe_2 . If this is so, our results on $\text{Hg}\phi_2$ would require D_2 in the radical $\cdot\text{Hg}\phi$ to be as large as, or preferably larger than, D_2 in the radical $\cdot\text{HgMe}$. Theoretically, one might anticipate this as a result of a resonance stabilization in the radical $\cdot\text{Hg}\phi$, in which there is the possibility of conjugation between the π -electrons of the phenyl radical with the (vacant) 6 p -orbitals of the Hg atom.

It is of interest at this point to remark on a consequence of the determination by Ghosh and Szwarc of the bond dissociation energy in phenyl bromide. By combining the value $D(\phi - \text{Br}) = 69$ kcal. mole⁻¹ with the value obtained by Smith and Bjellerup for $Q_f(\phi\text{Br})$, the heat of formation of the phenyl radical is obtained as $Q_f(\phi) = -60.3$ kcal. mole⁻¹; the alternative value based on our estimate of $Q_f(\phi\text{Br})$ is $Q_f(\phi) = -65.6$ kcal. mole⁻¹. This latter corresponds to a heat of dissociation of the C—H bond in benzene of 97.8 kcal. mole⁻¹, and the value $Q_f(\phi) = -60.3$ yields 92.5 kcal. mole⁻¹ for $D(\phi - \text{H})$. Both these figures are smaller than has previously been assumed for the strength of the benzene C—H bonds.¹⁸

In Table IX, we have listed values for the bond dissociation energies $D(\text{R—HgX})$, in the methyl and ethyl mercuric halides. The values

TABLE IX.—BOND DISSOCIATION ENERGIES IN R—HgX

Molecule	Q_f (cryst.) (kcal.)	λ_{sub} (kcal.)	$Q_f(\text{HgX})$ (kcal.)	$D(\text{R—HgX})$ (kcal.)
HgMeCl . .	27.7 ± 1.5	$15.6(a)$	-18.7	63.4 ± 2.5
HgMeBr . .	20.5 ± 1.4	$16.3(a)$	-24.0	60.7 ± 2.5
HgMeI . .	10.2 ± 1.2	$15.8(a)$	-32.1 ± 1	59.2 ± 3.5
HgEtCl . .	32.3 ± 1.5	$18.3 \pm 0.3(a)$	-18.7	58.0 ± 3.8
HgEtBr . .	24.2 ± 1.5	$18 \pm 1(b)$	-24.0	55.5 ± 4.5
HgEtI . .	14.2 ± 1.6	$17.5 \pm 1(b)$	-32.2 ± 1	54.2 ± 5.6

(a) Charnley and Skinner.²²

(b) Estimated values.

are to be considered as preliminary for $D(\text{Et—HgX})$, as we have not yet got accurate values for the heats of sublimation of the crystalline HgEtX compounds. Values for $D(\phi\text{—HgX})$ are omitted pending the determination of the sublimation heats of these compounds.

Three points of interest emerging from the $D(\text{R—HgX})$ values of Table IX are:

(i) The values $D(\text{R—HgX})$ are *larger* than the values $D(\text{R—HgR})$: thus, $D(\text{Me—HgCl})$ is larger by some 13 kcal. than $D(\text{Me—HgMe})$, and $D(\text{Et—HgCl})$ is larger than $D(\text{Et—HgEt})$ by approximately 18 kcal.

²¹ Gowenlock, *Thesis* (University of Manchester, 1949).²² Charnley and Skinner (unpublished).

(ii) The values $D(\text{R—HgCl})$ are larger than $D(\text{R—HgBr})$ and $D(\text{R—HgI})$, although in this sequence the differences do not exceed the present limits of error, and it remains to be established with certainty that the order $D(\text{R—HgCl}) > D(\text{R—HgBr}) > D(\text{R—HgI})$ is a genuine feature.

(iii) The fall in $D(\text{Et—HgX})$ compared with $D(\text{Me—HgX})$ is of the same order of magnitude as the difference between $D(\text{Me—H})$ and $D(\text{Et—H})$; but, for $D(\text{Et—HgEt})$ compared with $D(\text{Me—HgMe})$ (cf. Gowenlock and Warhurst), the fall is twice as large.

A fuller discussion of these points will be taken up in a later publication, by which time we hope to have reduced the limits of error that are attached to some of the present values.

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