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. :

$$Q_f(\mathrm{HgEt_2},\ liq.) = -9{\cdot}9 \pm 1{\cdot}7\ \mathrm{kcal.\ mole^{-1}},$$
$$Q_f(\mathrm{HgEtCl,\ cryst.}) = 32{\cdot}3 \pm 1{\cdot}5\ \mathrm{kcal.\ mole^{-1}},$$
$$Q_f(\mathrm{HgEtBr,\ cryst.}) = 24{\cdot}2 \pm 1{\cdot}5\ \mathrm{kcal.\ mole^{-1}},$$
$$Q_f(\mathrm{HgEtI,\ cryst.}) = 14{\cdot}2 \pm 1{\cdot}6\ \mathrm{kcal.\ mole^{-1}}.$$

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

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 :

$$D(\mathrm{Et{-}HgCl}) = 58{\cdot}0 \pm 3{\cdot}8\ \mathrm{kcal.\ mole^{-1}},$$
$$D(\mathrm{Et{-}HgBr}) = 55{\cdot}5 \pm 4{\cdot}5\ \mathrm{kcal.\ mole^{-1}},$$
$$D(\mathrm{Et{-}HgI}) = 54{\cdot}2 \pm 5{\cdot}6\ \mathrm{kcal.\ mole^{-1}}.$$

Using the experimental result of Ghosh and Szwarc of 69 (± 3) kcal. mole^{-1} for the dissociation energy in phenyl bromide, the energy of removal of *both* phenyl groups from $Hg\phi_2$ 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 $HgEt_2$, $Hg\phi_2$, HgEtX and $Hg\phi X$ (X = Cl, Br, I, Et = C_2H_5, $\phi = C_6H_5$) 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, defined [2] by the equation :

$$1\ \text{calorie} = 4{\cdot}1840\ \text{abs. joule.}$$

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[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 Brown[3] 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.

$Hg\phi_2$ was prepared by the method of Bachmann[4] by interacting $HgBr_2$ with $\phi MgBr$ 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 :

$$HgEt_2\ (\text{alc. soln.}) + Br_2\ (\textit{liq.}) \rightarrow HgEtBr\ (\text{soln.}) + EtBr\ (\text{soln.}) \quad . \quad (1)$$

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** ± 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

$$HgEt_2\ (\textit{liq.}) + I_2\ (\text{alc.}) \rightarrow HgEtI\ (\text{soln.}) + EtI\ (\text{soln.}) \quad . \quad . \quad (2)$$

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** ± 0·06

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[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

$$HgEt_2\ (liq.) + HgX_2\ (\text{alc. soln.}) \rightarrow 2HgEtX\ (\text{soln.}) \quad . \quad . \quad (3)$$

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
$HgEt_2 + HgCl_2$ . .	(i)	1·7422	1764·7	1753·2	9·87	**9·85**
	(ii)	1·7547	1721·85	1710·6	9·83	
$HgEt_2 + HgBr_2$.	(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	
$HgEt_2 + HgI_2$ . .	(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 :

$$Hg\phi_2\ (\text{alc.}) + Br_2\ (liq.) \rightarrow \phi\,Br\ (\text{alc. soln.}) + Hg\phi Br\ (\text{ppt. ; soln.}) . \quad . \quad (4)$$

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 $Hg\phi_2$ 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 :

$$Hg\phi_2\ (\text{alc.}) + I_2\ (\text{cryst.}) \rightarrow \phi I\ (\text{alc.}) + Hg\phi I\ (\text{ppt. soln.}). \quad . \quad (5)$$

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 $Hg\phi_2$ to a solution containing an excess of iodine results in the complete iodination of the mercury diphenyl—i.e. the second step

$$Hg\phi I + I_2 \rightarrow HgI_2 + \phi I$$

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 :

$$Hg\phi_2\ (\text{alc.}) + HgX_2\ (\text{cryst.}) \rightarrow 2Hg\phi X\ (\text{ppt. soln.}). \quad . \quad . \quad (6)$$

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

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

$$Hg\phi_2 \text{ (cryst.)} + HgI_2 \text{ (alc.)} \rightarrow 2Hg\phi I \text{ (ppt. soln.)}, \quad . \quad . \quad (7)$$

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 $Hg\phi Cl$ in *solution* and to $Hg\phi Br$ and $Hg\phi I$ mainly as solid but part in solution.

TABLE V.—REACTION OF $Hg\phi_2$ 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 $Hg\phi Br$ and $Hg\phi I$ 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 $Hg\phi_2$ WITH MERCURIC HALIDES

Reaction	Expt.	Wt. $Hg\phi_2$ (g.)	Wt. HgX_2 (g.)	R_i	R_f	Q (kcal.)	Mean Q (kcal.)
$Hg\phi_2 + HgCl_2$.	(i)	1·0538	0·6345	1760·4	1756·95	8·53	**8·42**
	(ii)	1·1096	0·6427	1756·2	1752·8	8·32	
$Hg\phi_2 + HgBr_2$	(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	
$Hg\phi_2 + HgI_2$.	(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 Skinner [6]). 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 ± 0·05	EtBr (*liq.*) . .	− 0·28 ± 0·02
$HgBr_2$ (cryst.) .	+ 0·41 ± 0·05	EtI (*liq.*) . .	− 0·75 ± 0·05
HgI_2 (cryst.) .	− 1·85 ± 0·15	$HgEt_2$ (*liq.*) .	− 1·37 ± 0·05
I_2 (cryst.) . .	− 2·07 ± 0·05	$Hg\phi_2$ (cryst.) .	− 5·15 ± 0·15
EtHgCl (cryst.) .	− 5·2 ± 0·4	ϕBr (*liq.*) . .	− 0·20 ± 0·03
EtHgBr (cryst.) .	− 4·6 ± 0·5	ϕI (*liq.*) . .	− 0·40 ± 0·04
EtHgI (cryst.) .	− 4·8 ± 0·5	$Hg\phi Cl$ (cryst.) .	− 3·0 ± 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}):

$$HgEt_2\ (liq.) + Br_2\ (liq.) \rightarrow EtBr\ (liq.) + HgEtBr\ (cryst.) + 54{\cdot}5\ (\pm\ 0{\cdot}62) \quad (8)$$
$$HgEt_2\ (liq.) + I_2\ (cryst.) \rightarrow EtI\ (liq.) + HgEtI\ (cryst.) + 32{\cdot}58\ (\pm\ 0{\cdot}66) \quad (9)$$
$$HgEt_2\ (liq.) + HgCl_2\ (cryst.) \rightarrow 2HgEtCl\ (cryst.) + 20{\cdot}96\ (\pm\ 0{\cdot}87) \quad (10)$$
$$HgEt_2\ (liq.) + HgBr_2\ (cryst.) \rightarrow 2HgEtBr\ (cryst.) + 17{\cdot}77\ (\pm\ 1{\cdot}09) \quad (11)$$
$$HgEt_2\ (liq.) + HgI_2\ (cryst.) \rightarrow 2HgEtI\ (cryst.) + 13{\cdot}20\ (\pm\ 1{\cdot}29). \quad (12)$$

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.,

$$HgEt_2\ (liq.) + 2Br_2\ (liq.) \rightarrow 2EtBr\ (liq.) + HgBr_2\ (cryst.) + 91{\cdot}25\ (\pm\ 0{\cdot}33) \quad (13)$$

and

$$HgEt_2\ (liq.) + 2I_2\ (cryst.) \rightarrow 2EtI\ (liq.) + HgI_2\ (cryst.) + 51{\cdot}96\ (\pm\ 0{\cdot}61) \quad (14)$$

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 $HgEt_2$ (*liq.*) can be obtained either from eqn. (13), assuming values for $Q_f(HgBr_2$, cryst.) and Q_f(EtBr, *liq.*), or from eqn. (14), assuming values for $Q_f(HgI_2$, cryst.) and Q_f(EtI, *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.:

$$Q_f(HgBr_2,\ cryst.) = 40{\cdot}64 \pm 0{\cdot}24\ kcal.\ mole^{-1},$$
$$Q_f(HgI_2,\ cryst.) = 25{\cdot}2 \pm 0{\cdot}2\ kcal.\ mole^{-1}.$$

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(EtBr, *liq.*) = 20·4 kcal. mole^{-1}; this presumably derives from the heat of combustion data of Thomsen,[7] and may involve an uncertainty of the order ± 0·5 kcal. mole^{-1}. A recent determination of the heat of combustion of liquid EtI by Springall and White [8] gave Q_f(EtI, *liq.*) = 8·4 ± 0·5 kcal. mole^{-1}; this is in fair agreement with the value 8·9 ± 1·1 kcal. mole^{-1} obtained by Carson, Hartley and Skinner [9] from measurements of the heat of iodination of cadmium diethyl.*

The value for $Q_f(HgEt_2$, *liq.*) obtained from eqn. (13), and the above values for $Q_f(HgBr_2)$ and Q_f(EtBr, *liq.*) is − 9·81 (± 1·55) kcal. mole^{-1}; from eqn. (14), the quoted value for $Q_f(HgI_2)$, and the value of Springall and White for Q_f(EtI, *liq.*), the derived value for $Q_f(HgEt_2$, *liq.*) is − 9·96 (± 1·81) 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(EtBr) and Q_f(EtI), but since the probable errors in these are allowed for in the estimated error quoted for $Q_f(HgEt_2)$, the final value

$$Q_f(HgEt_2,\ liq.) = -\ 9{\cdot}9 \pm 1{\cdot}7\ kcal.\ mole^{-1}$$

can be recommended with confidence.

***(b)* HgEtCl, cryst.:**

From the heat of reaction (10), the heat of formation of mercuric chloride ($Q_f(HgCl_2$, cryst.) = 53·5 ± 0·5 kcal. mole^{-1}), and our value for $Q_f(HgEt_2$, *liq.*), we obtain

$$Q_f(HgEtCl,\ cryst.) = 32{\cdot}3 \pm 1{\cdot}5\ kcal.\ mole^{-1}.$$

***(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 $Q_f(HgBr_2$, cryst.) and $Q_f(HgEt_2$, *liq.*), whence

$$Q_f(HgEtBr,\ cryst.) = 24{\cdot}25 \pm 1{\cdot}5\ kcal.\ mole^{-1}.$$

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[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(MeI) discussed in Part III of this series.

(*d*) HgEtI, cryst.

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

$$Q_f(\text{HgEtI, cryst.}) = 14{\cdot}25 \pm 1{\cdot}6 \text{ kcal. mole}^{-1}.$$

(*e*) Hgϕ_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}) :

$$\text{Hg}\phi_2\ (\text{cryst.}) + \text{Br}_2\ (\textit{liq.}) \rightarrow \phi\text{Br}\ (\textit{liq.}) + \text{Hg}\phi\text{Br (ppt.)} + 44{\cdot}02\ (\pm 0{\cdot}25) \quad (15)$$

$$\text{Hg}\phi_2\ (\text{cryst.}) + \text{I}_2\ (\text{cryst.}) \rightarrow \phi\text{I}\ (\textit{liq.}) + \text{Hg}\phi\text{I (ppt.)} + 22{\cdot}24\ (\pm 0{\cdot}27) \quad (16)$$

$$\text{Hg}\phi_2\ (\text{cryst.}) + \text{HgCl}_2\ (\text{cryst.}) \rightarrow 2\text{Hg}\phi\text{Cl (cryst.)} + 9{\cdot}27\ (\pm 0{\cdot}85) \quad (17)$$

$$\text{Hg}\phi_2\ (\text{cryst.}) + \text{HgBr}_2\ (\text{cryst.}) \rightarrow 2\text{Hg}\phi\text{Br (ppt.)} + 8{\cdot}49\ (\pm 0{\cdot}28) \quad (18)$$

$$\text{Hg}\phi_2\ (\text{cryst.}) + \text{HgI}_2\ (\text{cryst.}) \rightarrow 2\text{Hg}\phi\text{I (ppt.)} + 5{\cdot}22\ (\pm 0{\cdot}18) \quad (19)$$

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

$$\text{Hg}\phi_2\ (\text{cryst.}) + 2\text{Br}_2\ (\textit{liq.}) \rightarrow 2\phi\text{Br}\ (\textit{liq.}) + \text{HgBr}_2\ (\text{cryst.}) + 79{\cdot}55\ (\pm 0{\cdot}8), \quad (20)$$

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

$$\text{Hg}\phi_2\ (\text{cryst.}) + 2\text{I}_2\ (\text{cryst.}) \rightarrow 2\phi\text{I}\ (\textit{liq.}) + \text{HgI}_2\ (\text{cryst.}) + 39{\cdot}26\ (\pm 0{\cdot}7) \quad (21)$$

The value of Q_f(Hgϕ_2, cryst.) is obtainable *either* from eqn. (20), given a knowledge of Q_f(ϕBr, *liq.*), *or* from eqn. (21), given the value of Q_f(ϕI, *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(ϕBr, *liq.*) $= -$ 12·5 kcal. mole^{-1}, and we have been informed by Smith and Bjellerup [12] that their results yield the value Q_f(ϕBr, *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(ϕBr), starting from the recently determined value of the heat of formation of liquid phenyl chloride, Q_f(ϕCl, *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 $\Delta Q_f = 11{\cdot}7 \pm 0{\cdot}7$ in the case of ϕCl and ϕBr, we arrive at the figure, Q_f(ϕBr, *g*) $= -$ 23·2 $\pm$ 1 kcal. mole^{-1}, which corresponds to Q_f(ϕBr, *liq.*) $= -$ 14·1 $\pm$ 1 kcal. mole^{-1} ($\lambda_{\text{vap.}}$ (ϕBr) [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(ϕBr, *liq.*) in deriving Q_f(Hgϕ_2, cryst.).

The value of Q_f(Hgϕ_2, cryst.) is obtained from the heat of the reaction in eqn. (20), and is related to Q_f(ϕBr, *liq.*) by

$$Q_f(\text{Hg}\phi_2, \text{cryst.}) = 2Q_f(\phi\text{Br}, \textit{liq.}) - 38{\cdot}9\ (\pm 1{\cdot}0). \quad (22)$$

Using the value of Smith and Bjellerup for Q_f(ϕBr, *liq.*), eqn. (22) gives $-$ 56·5 ($\pm$ 3) kcal. mole^{-1} for Q_f(Hgϕ_2, cryst.), whereas the alternative estimate of Q_f(ϕBr, *liq.*) yields $-$ 67·1 ($\pm$ 3) kcal. mole^{-1}.

The derivation of Q_f(Hgϕ_2, cryst.) from the iodination data is contained in eqn. (21), and may be expressed in the form :

$$Q_f(\text{Hg}\phi_2, \text{cryst.}) = 2Q_f(\phi\text{I}, \textit{liq.}) - 14{\cdot}06\ (\pm 0{\cdot}9). \quad (23)$$

* In the reactions producing HgϕBr (ppt.) and HgϕI (ppt.), the designation (ppt.) refers strictly to crystalline precipitate plus saturated solution : the relative concentrations of HgϕX 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, **1**, 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

$$Q_f(\phi\mathrm{Br},\ \mathit{liq.}) - Q_f(\phi\mathrm{I},\ \mathit{liq.}) = 12{\cdot}42 \pm 0{\cdot}95, \qquad (24)$$

which gives $Q_f(\phi\mathrm{I},\ \mathit{liq.}) = -\,21{\cdot}2 \pm 2$ kcal. mole^{-1} if Smith's value for $Q_f(\phi\mathrm{Br},\ \mathit{liq.})$ is used, or $-\ 26{\cdot}5 \pm 2$ kcal. mole^{-1}, if our estimated value of $Q_f(\phi\mathrm{Br},\ \mathit{liq.})$ is used. At present, a reliable independent value for $Q_f(\phi\mathrm{I},\ \mathit{liq.})$ is not available, so that the direct determination of $Q_f(\mathrm{Hg}\phi_2$, 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 ($\lambda_{\mathrm{vap.}}$ of ϕI [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(RBr) and Q_f(RI), when R = 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 Polanyi [15] on the pyrolytic decomposition of phenyl iodide, and Ghosh and Szwarc [16] 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 :

$$-D(\phi\text{—}\mathrm{Br}) = -\ 69\ \text{kcal.} = Q_f(\phi) + Q_f(\mathrm{Br}) - Q_f(\phi\mathrm{Br}), \qquad (25)$$
$$-D(\phi\text{—}\mathrm{I}) = -\ 55\ \text{kcal.} = Q_f(\phi) + Q_f(\mathrm{I}) - Q_f(\phi\mathrm{I}), \qquad (26)$$

from which by subtraction,

$$Q_f(\phi\mathrm{Br}) - Q_f(\phi\mathrm{I}) = \Delta Q_f = 12{\cdot}8\ \text{kcal.},$$

since the values $Q_f(\mathrm{Br}) = -\ 26{\cdot}7$ kcal. mole^{-1}, and $Q_f(\mathrm{I}) = -\ 25{\cdot}5$ 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*) HgϕCl, cryst.

The value of Q_f(HgϕCl, cryst.) derives from eqn. (17), and is related to Q_f(Hgϕ_2, cryst.) by

$$Q_f(\mathrm{Hg}\phi\mathrm{Cl},\ \text{cryst.}) = 31{\cdot}4\ (\pm\ 0{\cdot}7) + \tfrac{1}{2}Q_f(\mathrm{Hg}\phi_2,\ \text{cryst.}). \qquad (27)$$

Using the two alternative values for Q_f(Hgϕ_2, cryst.) of − 56·5 ± 3 kcal. mole^{-1} (alternative A) and − 67·1 ± 3 kcal. mole^{-1} (alternative B), eqn. (27) yields :

$$Q_f(\mathrm{Hg}\phi\mathrm{Cl},\ \text{cryst.}) = \left\{\begin{array}{ll} 3{\cdot}15 \pm 2{\cdot}2\ \text{kcal. mole}^{-1} & (\mathrm{A}) \\ -\ 2{\cdot}17 \pm 2{\cdot}2\ \text{kcal. mole}^{-1} & (\mathrm{B}) \end{array}\right.$$

(*g*) HgϕBr, cryst.

The heat of reaction (18) corresponds to the formation of HgϕBr (cryst. + sat. soln.), and on making allowance for the heat effect due to the partial solubility of the HgϕBr in methanol, the equation becomes

$$\mathrm{Hg}\phi_2\ (\text{cryst.}) + \mathrm{HgBr}_2\ (\text{cryst.}) \rightarrow 2\mathrm{Hg}\phi\mathrm{Br}\ (\text{cryst.}) + 11{\cdot}6\ (\pm\ 1{\cdot}3)\ \text{kcal. mole}^{-1}, \quad (28)$$

from which we may write

$$Q_f(\mathrm{Hg}\phi\mathrm{Br},\ \text{cryst.}) = 26{\cdot}12\ (\pm\ 0{\cdot}77) + \tfrac{1}{2}Q_f(\mathrm{Hg}\phi_2,\ \text{cryst.}) \qquad (29)$$

leading to

$$Q_f(\mathrm{Hg}\phi\mathrm{Br},\ \text{cryst.}) = \left\{\begin{array}{ll} -\ 2{\cdot}13 \pm 2{\cdot}3\ \text{kcal. mole}^{-1} & (\mathrm{A}) \\ -\ 7{\cdot}43 \pm 2{\cdot}3\ \text{kcal. mole}^{-1} & (\mathrm{B}) \end{array}\right.$$

(*h*) HgϕI, cryst.

In similar manner, eqn. (19) after correction for the heat due to partial solution of the HgϕI becomes

$$\mathrm{Hg}\phi_2\ (\text{cryst.}) + \mathrm{HgI}_2\ (\text{cryst.}) \rightarrow 2\mathrm{Hg}\phi\mathrm{I}\ (\text{cryst.}) + 6{\cdot}5\ (\pm\ 1{\cdot}3)\ \text{kcal. mole}^{-1}, \quad (30)$$

from which we may write

$$Q_f(\mathrm{Hg}\phi\mathrm{I},\ \text{cryst.}) = 15{\cdot}85\ (\pm\ 0{\cdot}75) + \tfrac{1}{2}Q_f(\mathrm{Hg}\phi_2,\ \text{cryst.}), \qquad (31)$$

and obtain

$$Q_f(\mathrm{Hg}\phi\mathrm{I},\ \text{cryst.}) = \left\{\begin{array}{ll} -\ 12{\cdot}4 \pm 2{\cdot}3\ \text{kcal. mole}^{-1} & (\mathrm{A}) \\ -\ 17{\cdot}7 \pm 2{\cdot}3\ \text{kcal. mole}^{-1} & (\mathrm{B}) \end{array}\right.$$

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[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 $Hg\phi_2$ 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 $Hg\phi_2$ 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 Hg—R bond dissociation energies, given that Q_f(R) and Q_f(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 Hg—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.)	$\lambda_{vap.}$ (kcal.)	Q_f (g) (kcal.)	Q_f (R) (kcal.)	$(D_1 + D_2)$ (kcal.)
$HgMe_2$ (*liq.*) .	$-14{\cdot}3 \pm 2$	$8{\cdot}1$	$-22{\cdot}4 \pm 2$	$-32{\cdot}6 \pm 1$	$57{\cdot}3 \pm 4$
$HgEt_2$ (*liq.*) .	$-9{\cdot}9 \pm 2$	$10{\cdot}1$ (*a*)	$-20{\cdot}0 \pm 2$	$-25{\cdot}3 \pm 2$ (*b*)	$45{\cdot}1 \pm 6$
$Hg\phi_2$ (cryst.) .	$-67{\cdot}1 \pm 3$	23 ± 2 (*c*)	$-90{\cdot}1 \pm 5$	$-65{\cdot}6 \pm 2$	$55{\cdot}4 \pm 9$
	$-56{\cdot}5 \pm 3$	23 ± 2 (*c*)	$-79{\cdot}5 \pm 5$	$-60{\cdot}3 \pm 2$	$55{\cdot}4 \pm 9$

(*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(R), and also for $Hg\phi_2$ by the uncertain value for the heat of sublimation.* The figures in the final column of Table VIII

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[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 $Hg\phi_2$ is derived from the set of equations :

$$(a) \quad -(D_1 + D_2) = 2Q_f(\phi) - 14{\cdot}5 - Q_f(Hg\phi_2, g),$$
$$(b) \quad Q_f(Hg\phi_2, g) = (Q_f(\phi Br, g) - 43{\cdot}7\ (\pm 3),$$
$$(c) \quad -D(\phi Br) = Q_f(\phi) - 26{\cdot}7 - Q_f(\phi Br),$$

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

$$-(D_1 + D_2) = 82{\cdot}6\ (\pm 3) - 2D(\phi Br).$$

The uncertainty in the value $D(\phi-Br) \sim 69$ 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 $D(\phi-Br)$ is given, $(D_1 + D_2)$ is *independent of* $Q_f(\phi Br)$.

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 Gowenlock[21] 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 $Hg\phi_2$ are too large at present to allow of much more than speculation; nevertheless, Sidgwick[20] has commented on the fact that $HgMe_2$ is markedly more stable than other HgR_2 compounds—that $Hg\phi_2$ 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 $Hg\phi_2$ than in $HgMe_2$. If this is so, our results on $Hg\phi_2$ would require D_2 in the radical $^{\bullet}Hg\phi$ to be as large as, or preferably larger than, D_2 in the radical $^{\bullet}HgMe$. Theoretically, one might anticipate this as a result of a resonance stabilization in the radical $^{\bullet}Hg\phi$, 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 $D(\phi - Br) = 69$ kcal. mole^{-1} with the value obtained by Smith and Bjellerup for $Q_f(\phi Br)$, the heat of formation of the phenyl radical is obtained as $Q_f(\phi) = -60{\cdot}3$ kcal. mole^{-1}; the alternative value based on our estimate of $Q_f(\phi Br)$ is $Q_f(\phi) = -65{\cdot}6$ 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 $Q_f(\phi) = -60{\cdot}3$ yields 92·5 kcal. mole^{-1} for $D(\phi - H)$. 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(R—HgX), in the methyl and ethyl mercuric halides. The values are to be considered as preliminary for D(Et—HgX), as we have not yet got accurate values for the heats of sublimation of the crystalline HgEtX compounds. Values for $D(\phi$—HgX) are omitted pending the determination of the sublimation heats of these compounds.

TABLE IX.—BOND DISSOCIATION ENERGIES IN R—HgX

Molecule	Q_f (cryst.) (kcal.)	$\lambda_{sub.}$ (kcal.)	Q_f(HgX) (kcal.)	D(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 ± 0·3(*a*)	− 18·7	58·0 ± 3·8
HgEtBr . .	24·2 ± 1·5	18 ± 1(*b*)	− 24·0	55·5 ± 4·5
HgEtI . .	14·2 ± 1·6	17·5 ± 1(*b*)	− 32·2 ± 1	54·2 ± 5·6

(*a*) Charnley and Skinner.[22] (*b*) Estimated values.

Three points of interest emerging from the D(R—HgX) values of Table IX are:

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

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[21] Gowenlock, *Thesis* (University of Manchester, 1949).

[22] Charnley and Skinner (unpublished).

(ii) The values *D*(R—HgCl) are larger than *D*(R—HgBr) and *D*(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*(R—HgCl) > *D*(R—HgBr) > *D*(R—HgI) is a genuine feature.

(iii) The fall in *D*(Et—HgX) compared with *D*(Me—HgX) is of the same order of magnitude as the difference between *D*(Me—H) and *D*(Et—H) ; but, for *D*(Et—HgEt) compared with *D*(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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