THERMOCHEMISTRY OF METALLIC ALKYLS

III.—MERCURY DIMETHYL AND MERCURY METHYL HALIDES

By K. Hartley, H. O. Pritchard and H. A. Skinner

Received 1st *June*, 1950

Measurements of the heats of reaction of mercury dimethyl with alcoholic solutions of bromine, iodine, mercuric chloride, mercuric bromide, and mercuric iodide (at 20° C) are reported. These data are combined with existing thermochemical values to give the relations :

(i) $Q_f(\text{HgMe}_2, \textit{liq.}) = 2Q_f(\text{MeBr}, g) - 31{\cdot}5\ (\pm 0{\cdot}85)$ kcal. mole.$^{-1}$.
(ii) $Q_f(\text{HgMe}_2, \textit{liq.}) = 2Q_f(\text{MeI}, g) - 18{\cdot}9\ (\pm 0{\cdot}64)$ kcal. mole^{-1}.

Accepting the value $Q_f(\text{MeBr}, g) = 8{\cdot}6 \pm 0{\cdot}5$ kcal. mole^{-1} as correct, (i) leads to $-14{\cdot}3 \pm 1{\cdot}85$ kcal. mole^{-1} for the heat of formation of liquid HgMe_2, and (ii) gives $2{\cdot}3 \pm 1{\cdot}2$ kcal. mole^{-1} for the heat of formation of liquid methyl iodide. The heats of formation of the crystalline mercury methyl halides are measured as follows : HgMeCl, $27{\cdot}68 \pm 1{\cdot}45$; HgMeBr, $20{\cdot}46 \pm 1{\cdot}42$; HgMeI, $10{\cdot}20 \pm 1{\cdot}21$, all in kcal. mole^{-1}.

The dissociation-energies of the two CH_3—Hg bonds in HgMe_2 add up to $57{\cdot}4 \pm 4$ kcal., and the first and second CH_3—Hg bonds have unequal heats of dissociation, viz. $D(\text{CH}_3\text{—HgCH}_3) \approx 51$ kcal., $D(\text{CH}_3\text{—Hg}) \approx 6$ kcal. The CH_3—HgX bonds in the methyl mercuric halides have the following dissociation energies ; $D(\text{CH}_3\text{—HgCl})$, $63{\cdot}4 \pm 2{\cdot}5$ kcal. ; $D(\text{CH}_3\text{—HgBr})$, $60{\cdot}7 \pm 2{\cdot}6$ kcal. ; $D(\text{CH}_3\text{—HgI})$, $59{\cdot}0 \pm 3{\cdot}3$ kcal.

Although mercury possesses an extensive organic chemistry,[1] little is known of the thermochemistry of organo-mercury compounds. It may be that the dialkyls of mercury are unsatisfactory compounds for study by the methods of combustion calorimetry, for in fact few data are available on this class of compounds, and it is our view that the limited published data are not reliable. For dimethyl mercury, in particular, there is a large discrepancy between the values for the heat of formation Q_f derived from the present research and from the heat of combustion given by Berthelot.[2] Nevertheless we consider the mercury dialkyls as suitable compounds for thermochemical study, since they undergo several simple reactions cleanly and easily at room temperature with halogens, halogen acids, and the mercuric halides.[3] In this paper we report some measurements of the heats of reaction of mercury dimethyl with iodine, bromine, and the halides of mercury, from which the values $Q_f(\text{HgMe}_2)$ and $Q_f(\text{HgMeX})$ are obtained, and the dissociation energies of some Hg—CH_3 bonds can be derived.

Experimental

Preparation of Compounds.—HgMe_2 was prepared by the method of Gilman [4] from the interaction of HgCl_2 with the Grignard reagent. The crude product was carefully dried and purified by fractional distillation using a gauze-packed column : b.p. 92·3° C at 768 mm. Hg. The iodine, bromine and mercuric halides used were A.R. reagents ; the solvents were clinical ethyl alcohol and high-grade synthetic methanol.

Calorimeters.—The reactions with the halogens were studied in the calorimeter described previously by Pritchard and Skinner [5] but modified from the

[1] See, e.g., Whitmore, *Organic Compounds of Mercury* (Chem. Catalog Co., New York, 1921).
[2] Berthelot, *Compt. rend.*, 1899, **129**, 918.
[3] Kharasch and Flenner, *J. Amer. Chem. Soc.*, 1932, **54**, 674.
[4] Gilman and Brown, *ibid.*, 1929, **51**, 928 ; 1930, **52**, 3314.
[5] Pritchard and Skinner, *J. Chem. Soc.*, 1950, 272.

original by the replacement of all the rhodium-plated internal fittings by their glass equivalents. Reactions involving the mercuric halides, and various determinations of the heats of solution and mixing, were carried out in a similar, but smaller, calorimeter described by Hartley and Skinner.[6] The procedure in both sets of experiments involved the measurement of the change in resistance of a thermistor element (R_i = initial, and R_f = final resistance in ohms) occasioned by the breakage of a phial containing one of the reactants into a solution (in ethanol or methanol) of the second reactant. The calorimetric systems were calibrated electrically. The heats are given in units of the kcal. mole^{-1} ≡ $4{\cdot}1833 \times 10^3$ int. joules mole^{-1}.

Results

Mercury Dimethyl and Bromine.—Bromine reacts almost instantaneously at room temperature with an excess of $HgMe_2$ in alcohol solution, according to the equation :

$$HgMe_2 \text{ (alcohol soln.)} + Br_2 \text{ (}liq.\text{)} \rightarrow HgMeBr \text{ (soln.)} + MeBr \text{ (soln.)} \quad . \quad (1)$$

The reaction was carried out by breaking thin glass phials containing known weights of bromine into dilute solutions of $HgMe_2$ in alcohol. Both ethyl and methyl alcohol were used as solvent, giving identical (± 0·2 kcal.) results. The $HgMe_2$ was present in excess in all experiments to eliminate the occurrence of a secondary reaction between the Br_2 and the HgMeBr, and the solutions were sufficiently dilute to keep to HgMeBr completely in solution. The results are summarized in Table I.

TABLE I.—REACTIONS OF $HgMe_2$ WITH BROMINE

Expt.	Wt. of Br_2 (g.)	R_i	R_f	Q (kcal. mole^{-1})
1	1·6665	1745·1	1663·4^5	44·81
2	1·8152	1734·4	1646·7	44·55
3	1·7332	1749·2	1664·3^5	44·71
4	1·7210	1704·6^5	1622·8^5	44·53
			Mean	44·65 ± 0·15

Mercury Dimethyl and Iodine.—The reaction of iodine in alcoholic solution with mercury dimethyl at room-temperature occurs less speedily than the similar reaction using bromine. We have found it most convenient to study this reaction by adding the mercury dimethyl to a solution of excess iodine in methanol—usually adding about 2 g. $HgMe_2$ to about 6 g. I_2 dissolved in 750 ml. alcohol. Under these conditions the reaction was completed in periods of less than ½ hr. Although these conditions correspond to a considerable I_2 excess, we have checked by independent studies that they do not lead to any significant occurrence of the secondary reaction between HgMeI and I_2, and that all the products of reaction remain completely in solution. The measured heats of the reaction

$$HgMe_2 \text{ (}liq.\text{)} + I_2\text{(methanol)} \rightarrow \{MeI + HgMeI\} \text{ (soln.)} \quad . \quad . \quad (2)$$

are summarized in Table II.

TABLE II.—REACTION OF $HgMe_2$ WITH IODINE

Expt.	Wt. $HgMe_2$ (g.)	R_i	R_f	Q (kcal. mole^{-1})
1	1·8120	1741·7	1709·1	24·45
2	1·9250	1735·6	1701·0	24·49
3	1·9914	1739·8	1704·0	24·48
				Mean= 24·47

---

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

Mercury Dimethyl and the Mercuric Halides.—The reactions between $HgMe_2$ and solutions of the mercuric halides in alcohol occur readily at room temperature. With $HgCl_2$ and $HgBr_2$ the reactions are reasonably fast if the mercuric halides are used in two or three-fold excess; the reaction with HgI_2 is rather sluggish and is better carried out in methanol than in ethanol as solvent.

The reactions were performed by breaking thin phials containing weighed amounts of mercury dimethyl into solutions of $HgCl_2$ in ethanol, $HgBr_2$ in ethanol, and HgI_2 in methanol. The measured heats of the reactions:

$HgMe_2$ (*liq.*) + HgX_2 (soln.) → 2HgMeX (soln.) . . (3)

are summarized in Table III.

TABLE III.—REACTION OF $HgMe_2$ WITH MERCURIC HALIDES

Reaction	Expt.	Wt. $HgMe_2$ (g.)	Wt. HgX_2 (g.)	Ml. of Solvent	R_i (ohms)	R_f (ohms)	Q (kcal. mole^{-1})	Mean Q (kcal. mole^{-1})
$HgMe_2$ + $HgCl_2$	(i)	1·300	3·129	300	2132·0	2112·7	7·72	—
	(ii)	1·996	2·423	300	2121·4	2091·6	7·82	—
	(iii)	1·475	7·10	300	2166·0	2143·2	7·92	—
	(iv)	6·2652	11·0	750	1737·4	1699·0	8·02	**7·87 ±0·15**
$HgMe_2$ + $HgBr_2$	(i)	1·268	9·033	300	2212·2	2196·6	6·16	—
		1·928			2214·0	2190·2	6·19	—
	(ii)	1·368	8·987	300	2213·9	2196·5	6·37	—
	(iii)	6·4017	25·0	750	1744·1	1713·6	6·21	**6·24 ±0·10**
$HgMe_2$ + HgI_2	(i)	3·6482	—	750	1741·7	1732·2	3·51	—
	(ii)	4·0065	—	750	1730·7	1720·5	3·46	**3·48 ±0·03**

Heats of Solution.—The interpretation of the heats of reaction given above requires additional data on the heats of solution of both reactants and products in alcohol. These solution heats were measured in our smaller calorimeter, and the results are briefly summarized in Table IV.

TABLE IV.—HEATS OF SOLUTION

Solute	Solvent	Heat of Solution (kcal. mole^{-1})
$HgCl_2$ (cryst.)	EtOH	+0·04(±0·01)
$HgBr_2$ (cryst.)	EtOH	+0·35(±0·05)
HgI_2 (cryst.)	MeOH	−1·85(±0·15)
HgMeCl (cryst.)	EtOH	−4·15(±0·2)
HgMeBr (cryst.)	EtOH	−4·0(±0·3)
HgMeI (cryst.)	MeOH	−3·94(±0·1)
$HgMe_2$ (*liq.*)	EtOH	−0·6(±0·05)
I_2 (cryst.)	MeOH	−2·07(±0·05)
MeBr(*g*)	EtOH	+4·68 (±0·03)
MeI (*liq.*)	MeOH+HgMeI	−0·47(±0·05)

Calculation of Heats of Formation.—By combining the heats of reaction given in Tables I, II and III with the relevant heats of solution in Table IV, we can write the following set of thermochemical equations:—

$HgMe_2$ (*liq.*)+Br_2 (*liq.*) → MeBr (*g*)+HgMeBr (cryst.) + 43·37±0·53 kcal. (4)

$HgMe_2$ (*liq.*)+I_2 (cryst.) → MeI (*liq.*)+HgMeI (cryst.)+26·81±0·23 kcal. (5)

$HgMe_2$ (*liq.*)+$HgCl_2$ (cryst.) → 2HgMeCl (cryst.) + 16·17 ± 0·55 kcal. . (6)

$HgMe_2$ (*liq.*)+$HgBr_2$ (cryst.) → 2HgMeBr (cryst.) + 14·59 ± 0·75 kcal. . (7)

$HgMe_2$ (*liq.*)+ HgI_2 (cryst.) → 2HgMeI (cryst.) + 9·51 ± 0·38 kcal. . (8)

By subtracting eqn. (7) from twice eqn. (4), the additional equation

$$\text{HgMe}_2\ (\textit{liq.}) + 2\text{Br}_2\ (\textit{liq.}) \rightarrow \text{HgBr}_2\ (\text{cryst.}) + 2\text{MeBr}\ (g) + 72{\cdot}15 \pm 0{\cdot}61\ \text{kcal.} \qquad (9)$$

is obtained. Similarly, subtraction of eqn. (8) from twice eqn. (5) gives

$$\text{HgMe}_2\ (\textit{liq.}) + 2\text{I}_2\ (\text{cryst.}) \rightarrow \text{HgI}_2\ (\text{cryst.}) + 2\text{MeI}\ (\textit{liq.}) + 44{\cdot}11 \pm 0{\cdot}44\ \text{kcal.} \qquad (10)$$

The heat of formation of HgMe_2 can be obtained either from eqn. (9), assuming values for $Q_f(\text{HgBr}_2,\ \text{cryst.})$ and $Q_f(\text{MeBr},\ g)$; or alternatively from eqn. (10), assuming values for $Q_f(\text{HgI}_2,\ \text{cryst.})$ and $Q_f(\text{MeI},\ \textit{liq.})$. Considering the bromination data first, we have

$$Q_f(\text{HgBr}_2,\ \text{cryst.}) = 40{\cdot}64 \pm 0{\cdot}24\ \text{kcal./mole}^{-1}\ (\text{Varet}^7)$$

and $$Q_f(\text{MeBr},\ g) = 8{\cdot}6 \pm 0{\cdot}5\ \text{kcal. mole}^{-1}.$$

The value for Q_f (MeBr, g) is based on the recommended value for Q_f (MeCl, g) given in the *Selected Values of Chemical Thermodynamic Properties* (Nat. Bur. Stand., Tables 23-7, 1949) and on measurements of the heat of the reaction $\text{CH}_3\text{Br} + \text{HCl} \rightarrow \text{CH}_3\text{Cl} + \text{HBr}$, reported by Bak.[8] Our estimate of $\pm$ 0·5 kcal. for the probable error in Q_f (MeBr) is perhaps optimistic; the combustion data of Thomsen [9] on MeBr correspond to $Q_f = 8{\cdot}2$ kcal., but Kharasch and Brown [10] suggest a correction to Thomsen's result which then gives $Q_f = 8{\cdot}8$ kcal.

Using the general thermochemical equation relating the heat of a reaction to the difference in the sums of the heats of formation of products and reactants, and eqn. (9), then

$$72{\cdot}15 \pm 0{\cdot}61 = Q_f(\text{HgBr}_2,\ \text{cryst.}) + 2Q_f\ (\text{MeBr},\ g) - Q_f\ (\text{HgMe}_2,\ \textit{liq.}). \qquad (11)$$

Substituting the values for $Q_f(\text{HgBr}_2)$ and $Q_f(\text{MeBr})$ discussed above into eqn. (11) gives

$$Q_f(\text{HgMe}_2,\ \textit{liq.}) = -\ 14{\cdot}31 \pm 1{\cdot}85\ \text{kcal.}$$

Turning to the iodination data, it is fortunate that one of the quantities we need is known with reasonably high accuracy, i.e. the heat of formation of HgI_2 (cryst. red), determined by Varet [7] by seven independent methods as $Q_f(\text{HgI}_2,\ \text{cryst.}) = 25{\cdot}2 \pm 0{\cdot}2$ kcal. The corresponding equation to (11) for the iodination of HgMe_2 is

$$44{\cdot}11 \pm 0{\cdot}44 = Q_f(\text{HgI}_2,\ \text{cryst.}) + 2Q_f(\text{MeI},\ \textit{liq.}) - Q_f(\text{HgMe}_2,\ \textit{liq.}) \qquad (12)$$

which, by substituting Varet's value for $Q_f(\text{HgI}_2,\ \text{cryst.})$ becomes

$$18{\cdot}91 \pm 0{\cdot}64 = 2Q_f(\text{MeI},\ \textit{liq.}) - Q_f(\text{HgMe}_2,\ \textit{liq.}). \qquad (13)$$

If we now replace $Q_f(\text{HgMe}_2,\ \textit{liq.})$ by the value obtained from our bromination experiments, eqn. (13) then yields

$$Q_f(\text{MeI},\ \textit{liq.}) = 2{\cdot}3 \pm 1{\cdot}2\ \text{kcal. mole}^{-1}.$$

The heat of combustion data of Thomsen [9] on MeI correspond to the value $Q_f(\text{MeI},\ \textit{liq.}) = 2{\cdot}0$ kcal. mole^{-1},* agreeing well with the value now obtained: the corrected Thomsen data of Kharasch and Brown [10] gave $Q_f = 3{\cdot}0$ kcal. Recently, however, Carson, Hartley and Skinner [11] reported $Q_f = 3{\cdot}85$ kcal., from studies of the heats of acid hydrolysis and iodination of cadmium dimethyl. As this latter value lies outside the estimated limits of error of the figure now recommended, we have re-examined the assumptions [5] implicit in the $Q_f = 3{\cdot}8$ determination, and are satisfied that it requires some amendment.

The results of Carson *et al.* may be expressed by the thermochemical equation:

$$\begin{aligned}(Q_3 - M - Q_2) = {} & 2Q_f(\text{CH}_4,\ g) + 2Q_f(\text{I}_2,\ \text{ether}) + Q_f(\text{CdSO}_4,\ 100) \\ & -Q_f(\text{H}_2\text{SO}_4,\ 100) - Q_f(\text{CdI}_2,\ \text{ppt.}) - 2Q_f(\text{MeI},\ \text{ether}),\end{aligned} \qquad (14)$$

where Q_3, M and Q_2 have the meanings given previously.[11] The experimental results of Carson, Hartley and Skinner gave for the term $(Q_3 - M - Q_2)$ the

[7] Varet, *Ann. chim. phys.*, 1896, **8,** 79.

[8] Bak, *Det Kgl. Danske Videns. Selskab*, 1948, **24,** 9.

[9] Thomsen, *Thermochemische Untersuchungen*, vol. 1-4 (Barth, Leipzig, 1882-1886).

[10] Kharasch and Brown, quoted by Wheland, *The Theory of Resonance* (John Wiley, New York, 1944).

* See *Selected Values of Chemical Thermodynamic Properties*, Table 23-11.

[11] Carson, Hartley and Skinner, *Proc. Roy Soc. A*, 1949, **195,** 500.

value − 2·3 ± 0·7 kcal. For the terms in Q_f on the right-hand side of eqn. (14), we have chosen the values recommended by the National Bureau of Standards [12] for $Q_f(CH_4)$, $Q_f(CdSO_4, 100)$ and $Q_f(H_2SO_4, 100)$, and the value $Q_f(I_2, \text{ether}) = -1{\cdot}80 \pm 0{\cdot}2$ kcal. determined by Hartley and Skinner.[6] With these substitutions, eqn. (14) becomes

$$2Q_f(\text{MeI}) = 55{\cdot}3 \pm 1{\cdot}1 - Q_f(CdI_2) \qquad . \quad . \quad . \quad (15)$$

The heat of formation of crystalline CdI_2 has been determined by various investigators and methods, and a selection of these is summarized below: 48·44 (Taylor and Perrott [13]), 48·22 (from Thomsen's [9] data), 48·86 (from Vosburgh's [14] data). The determination by Taylor and Perrott is the most direct, and for this reason we are inclined to give it the greatest weight. We adopt the value 48·5 ± 0·4 kcal. as one that covers the range in the various experimental data so far reported, and which lies close to the Taylor-Perrott value. With this substitution, eqn. (15) yields 3·4 ± 0·8 kcal. for the amended value of Q_f(MeI, *liq.*). Although within the limits of error of the present investigation, the amended value of Carson, Hartley and Skinner is subject to some uncertainty in that the precipitated CdI_2 obtained from the iodination of $CdMe_2$ was obtained as a fine microcrystalline powder, the heat content of which may well be influenced by the high surface area per unit weight.

The range in the published values for Q_f (MeI, *liq.*) corresponds to a range in the values of $Q_f(HgMe_2$, *liq.*) from − 14·9 to − 12·1 kcal. mole^{-1}; we accept the value of − 14·3 kcal. obtained from the bromination data as the best in the light of present information on the heats of formation of the methyl halides. With this starting-point, the heats of formation of the crystalline methyl mercuric halides are obtained from the heats of the reactions given by eqn. (6), (7) and (8) as follows:

$$Q_f(\text{MeHgCl, cryst.}) = 27{\cdot}68^{*} \pm 1{\cdot}45 \text{ kcal. mole}^{-1}$$
$$Q_f(\text{MeHgBr, cryst.}) = 20{\cdot}46 \pm 1{\cdot}42 \text{ kcal. mole}^{-1}$$
$$Q_f(\text{MeHgI, cryst.}) = 10{\cdot}20 \pm 1{\cdot}21 \text{ kcal. mole}^{-1}.$$

Discussion

We have given details of the assumptions implicit in the present determination of $Q_f(HgMe_2$, *liq.*) in order to assess the limits of error fairly and, we believe, generously. This is necessary in view of the serious divergence between the present value (− 14·3 ± 1·85) and the value of − 37·8 kcal. (quoted by Bichowsky and Rossini [15]) derived from the heat of combustion by Berthelot.[2] We understand that a re-examination of the combustion heats of the mercury alkyls is being undertaken by Springall and Carson,[16] and that the preliminary results confirm our conclusion of inaccuracies in Berthelot's data.

In previous papers of this series [11, 17] we have made use of the heats of formation of metal alkyls in order to derive values for the dissociation energies of metal-carbon bonds. In the present instance, we may derive the *sum* of the heats of dissociation of the first and second Hg—CH_3 bonds in $HgMe_2$ from the equation:

$$(D_1 + D_2) = Q_f(HgMe_2, g) - Q_f(Hg, g) - 2Q_f(CH_3, g), \quad . \quad (16)$$

and also the heats of dissociation of the bonds CH_3—HgX in the methyl mercuric halides from the equation:

$$D(CH_3 - HgX) = Q_f(MeHgX, g) - Q_f(HgX, g) - Q_f(CH_3\, g). \quad (17)$$

---

[12] *Selected Values of Chemical Thermodynamic Properties* (Nat. Bur. Stand. Washington, Tables 23–3, 32–5, 14–8).

[13] Taylor and Perrott, *J. Amer. Chem. Soc.*, 1921, **43**, 484.

[14] Vosburgh, *ibid.*, 1927, **49**, 2222.

* The value $Q_f(HgCl_2, \text{cryst.}) = 53{\cdot}5 \pm 0{\cdot}5$ kcal. (derived from Thomsen's [9] data) was assumed.

[15] Bichowsky and Rossini, *Thermochemistry of Chemical Substances* (Reinhold, New York, 1936).

[16] Springall and Carson (private communication).

[17] Carson, Hartley and Skinner, *Trans. Faraday Soc.*, 1949, **45**, 1159.

The terms in Q_f on the right-hand of eqn. (16) and (17) are now available, within relatively small limits of error, and are considered separately below.

(*a*) $Q_f(\mathrm{HgMe_2}, g)$.

This is obtainable directly from the measurement of the heat of formation of liquid $\mathrm{HgMe_2}$ reported here, and the heat of vaporization of $\mathrm{HgMe_2}$, $\lambda_{\mathrm{vap.}} = 8{\cdot}1$ kcal.,[18] whence $Q_f(\mathrm{HgMe_2}, g) = -22{\cdot}4 \pm 1{\cdot}9$ kcal.

(*b*) $Q_f(\mathrm{Hg}, g)$.

This is a well-established quantity. The National Bureau of Standards [18] recommends the value $Q_f(\mathrm{Hg}, g) = -14{\cdot}54$ kcal.

(*c*) $Q_f(\mathrm{CH_3}, g)$.

In earlier papers [11, 17] we have used the value $Q_f(\mathrm{CH_3}, g) = -32{\cdot}1$ kcal., based on the assumed value of 102·0 kcal. for $D(\mathrm{CH_3} - \mathrm{H})$ at room temperature. Long [19] has recently revised the estimate by Kistiakowsky and van Artsdalen [20] of $D(\mathrm{CH_3} - \mathrm{H})$, upgrading their value slightly. Accepting Long's amendment, we have used $Q_f(\mathrm{CH_3}, g) = -32{\cdot}6 \pm 1$ kcal., corresponding to $D(\mathrm{CH_3} - \mathrm{H}) = 102{\cdot}5 \pm 1$ kcal. at room temperature.

(*d*) $Q_f(\mathrm{HgCl}, g)$.

This may be derived from the spectroscopically determined value for the dissociation-energy of the HgCl molecule (Wieland ; [21] $D°(\mathrm{Hg} - \mathrm{Cl}) = 24{\cdot}0$ kcal.) ; $Q_f(\mathrm{HgCl}, g) = -18{\cdot}7$ kcal.

(*e*) $Q_f(\mathrm{HgBr}, g)$.

This may similarly be derived from Wieland's [22] determination of $D°(\mathrm{Hg} - \mathrm{Br})$ at 16·4 kcal. ; $Q_f(\mathrm{HgBr}, g) = -24{\cdot}0$ kcal.

(*f*) $Q_f(\mathrm{HgI}, g)$.

Gaydon [23] quotes $D°(\mathrm{Hg} - I) = 7 \pm 1$ kcal. ; whence $Q_f(\mathrm{HgI}, g) = -32{\cdot}1 \pm 1$ kcal.

(*g*) $Q_f(\mathrm{HgMeCl}, g)$.

Charnley and Skinner [24] have obtained the preliminary value $\lambda_{\mathrm{sub}}(\mathrm{HgMeCl}) = 15{\cdot}6 \pm 0{\cdot}1$ kcal. for the heat of sublimation of room temperature, whence $Q_f(\mathrm{HgMeCl}, g) = 12{\cdot}08 \pm 1{\cdot}55$ kcal.

(*h*) $Q_f(\mathrm{HgMeBr}, g)$.

Charnley and Skinner have measured $\lambda_{\mathrm{sub}}(\mathrm{HgMeBr})$ at $16{\cdot}35 \pm 0{\cdot}15$ kcal., whence $Q_f(\mathrm{HgMeBr}, g) = 4{\cdot}11 \pm 1{\cdot}57$ kcal.

(*i*) $Q_f(\mathrm{HgMeI}, g)$.

Charnley and Skinner have measured $\lambda_{\mathrm{sub}}(\mathrm{HgMeI})$ at $15{\cdot}85 \pm 0{\cdot}15$ kcal., whence $Q_f(\mathrm{HgMeI}, g) = -5{\cdot}65 \pm 1{\cdot}36$ kcal.

By substituting these values of the appropriate Q_f terms in eqn. (16) and (17), the following dissociation energies of Hg—$\mathrm{CH_3}$ bonds are derived :

(i) $D(\mathrm{CH_3{-}HgCH_3}) + D(\mathrm{CH_3{-}Hg}) = (D_1 + D_2)$ in $\mathrm{HgMe_2}$
$= 57{\cdot}3 \pm 4$ kcal.

(ii) $D(\mathrm{CH_3{-}HgCl}) = 63{\cdot}4 \pm 2{\cdot}5$ kcal.

(iii) $D(\mathrm{CH_3{-}HgBr}) = 60{\cdot}7 \pm 2{\cdot}6$ kcal.

(iv) $D(\mathrm{CH_3{-}HgI}) = 59{\cdot}0 \pm 3{\cdot}3$ kcal.

---

[18] *Selected Values of Chemical Thermodynamic Properties* (Table 33-1, 33-2).

[19] Long, *Proc. Roy. Soc. A*, 1949, **198,** 62.

[20] Kistiakowsky and v. Artsdalen, *J. Chem. Physics*, 1944, **12,** 469.

[21] Wieland, *Helv. physic. Acta*, 1939, **12,** 295 ; 1941, **14,** 549 ; *Helv. chim. Acta*, 1941, **24,** 1285.

[22] Wieland ; quoted by Werhli and Milazzo, *ibid.*, 1943, **26,** 1025.

[23] Gaydon, *Dissociation Energies* (Chapman and Hall, 1947).

[24] Charnley and Skinner (unpublished).

The thermochemical data on $HgMe_2$ are insufficient in themselves to give the individual values of the first and second bond dissociation energies, D_1 and D_2. The value of D_1 has, however, been obtained recently from kinetic studies on the pyrolytic decomposition of $HgMe_2$ by Warhurst and Gowenlock,[25] and by Szwarc. These experimenters have found $D_1 \approx 51$ kcal., which implies that the second bond dissociation energy is small, i.e. $D_2 \approx 6$ kcal., and that the radical $\cdot HgCH_3$ must be highly unstable, except in the circumstance that the reaction $Hg(^1S_0) + CH_3 \rightarrow \cdot HgCH_3$ requires a high activation energy.

The large difference between D_1 and D_2 in $HgMe_2$ follows the general trend in the D_1, D_2 values of HgX_2 molecules ; one of us (Skinner [26]) has previously discussed this point in terms of the valence bonding in HgX, HgX_2 compounds. The values now reported for $D(CH_3—HgX)$, which show that the CH_3—Hg bonds in the mercury methyl halides are more firmly held than the similar bonds in mercury dimethyl itself, raise several interesting questions on the character of metal-carbon bonds, but we reserve comment at the present time on these observations.

The authors wish to express thanks to Prof. M. G. Evans, F.R.S., for his interest and advice during the course of this research, and to Prof. H. D. Springall, Dr. E. Warhurst, and Dr. M. Szwarc for permission to quote their work prior to publication. We would also thank Prof. R. E. Lane of the Department of Occupational Health of Manchester University for the medical supervision of the experimenters handling the toxic materials. One of us (H. O. P.) thanks the D.S.I.R. for a maintenance grant.

Chemistry Department,
Manchester University.

[25] Warhurst and Gowenlock ; Szwarc (private communications).

[26] Skinner, *Trans. Faraday Soc.*, 1949, **45**, 20.