424. *Measurements of the Vapour Pressures of Some Alkylmercury Halides. The Latent Heats of Sublimation of Methyl- and Ethyl-mercury Halides.*

By T. CHARNLEY and H. A. SKINNER.

The vapour pressures of six alkylmercury halides have been measured over a range of about 20° at " room " temperatures by means of a quartz fibre (viscosity) manometer. The values obtained fit expressions of the type $\log_{10} p = A - B/T$, from which the latent heats of sublimation have been calculated, as given in Table II (p. 1923). These values are combined with existing thermochemical data on the HgRX compounds, in order to derive the bond dissociation-energies $D(R\text{--}HgX)$ in these molecules.

THE present investigation was undertaken in connection with some studies on the thermo-chemistry of organo-mercury compounds, described by Hartley, Pritchard, and Skinner (*Trans. Faraday Soc.*, 1950, **46**, 1019; 1951, **47**, 254), who obtained values for the heats of formation (Q_f) of HgRX compounds (R = Me or Et; X = Cl, Br, or I) in the *crystalline* state at room temperature. In order to derive the bond dissociation energies $D(R\text{--}HgX)$ from these Q_f values, it is necessary to know the latent heats of sublimation, $\lambda_{sub.}$, of the various compounds, and to this end we have measured their vapour pressures over a range of temperature, from which the $\lambda_{sub.}$ values are derived indirectly by use of the Clausius–Clapeyron equation.

EXPERIMENTAL.

(a) *Preparation of Compounds.*—The crystalline chlorides and bromides were prepared by admixing pure samples of the mercury alkyls (provided by Mr. K. Hartley) with methanol solutions of mercuric chloride or bromide. The products were recrystallised from hot methanol. The iodides were made by adding iodine to excess of the mercury alkyl in methanol solution, and the crystalline precipitates were recrystallised from hot methanol.

(b) *Measurement of Vapour Pressures.*—Preliminary experiments demonstrated that the range of pressures it was necessary to cover lay between 10^{-2} and 10^{-4} mm. Hg. There are several methods suitable to this pressure range, and in choosing the viscosity (quartz fibre) gauge, we were attracted mainly by the relative simplicity of construction of this apparatus. As originally used by Langmuir (*J. Amer. Chem. Soc.*, 1913, **35**, 107), the gauge consisted of a flattened quartz fibre, 5 cm. long and 50 microns thick, which was set vibrating in a bulb containing gas at low pressure. The rate of decrease in amplitude of the vibrations with time can be related (under suitable conditions) to the pressure of the system. The single-fibre vibrating element calls for considerable manipulative skill in order to restrain the vibrations to a plane at right angles to the field of view. The bifilar gauge devised by Coolidge (*ibid.*, 1923, **45**, 1637)—in which two quartz fibres are fastened to a support about 1 cm. apart, and fused together at the free ends forming a V—overcomes most of the difficulties met with the single fibre, and was preferred in the present research.

The apparatus consisted of a high-vacuum pumping system, connecting to the quartz-fibre gauge and the sample tube containing the compound under investigation. A side-arm from the main vacuum line led to a Phillips-type ionization gauge, and a McLeod gauge. The quartz-fibre gauge was firmly clamped to an iron framework supported from a massive iron table which stood on a concrete block let through the floor of the room. The gauge was thus isolated from external vibrations. The V-shaped vibration element was mounted in a quartz tube which terminated in a standard (B.14) cone-joint by which it was connected to the main vacuum line. The fibre could be set into vibration by momentarily energizing a small electromagnet placed near a magnetic bead attached to the tip of the V.

The fibre was illuminated, and a small section of it observed through a low-power microscope. The microscope produced an image of the fibre in the focal plane of the eyepiece where there was a graticule 1 cm. long, graduated in 0·1 mm. When at rest, the fibre image appeared in the centre coinciding with division 5 on the graticule. The fibre was set vibrating, and the time required for the images of the edges, initially at divisions 4 and 6 on the graticule, to move to divisions 4·5 and 5·5, respectively, was measured with a stop-watch. This time is referred to as the " period " of the gauge.

The expression relating the pressure in the gauge to the time of damping between two given amplitudes was deduced by Haber and Kerschbaum (*Z. Electrochem.*, 1914, **20**, 296), who obtained the formula

$$t^{-1} = pA\sqrt{M/T} + B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where t is the " period " of the gauge, p the pressure, M the molecular weight of the gas, and T the temperature in °K.; A and B are constants of the instrument, and in principle it is only necessary to know the " period " and pressure at two points with a gas of known molecular weight in order to determine the values of these constants. In practice, a large number of measurements of t and p were made and a graph plotted of t^{-1} against p from which best values of A and B were obtained. Nitrogen was chosen for the calibration experiments, in which the pressures were measured by means of a McLeod gauge. The " period," t, was taken from the mean of about 10 readings, and the McLeod reading taken at the beginning and end of each set of " period " measurements. Sixty sets of " period " measurements were taken, covering a pressure range from 2·9 × 10⁻⁴ to 9·7 × 10⁻² mm. Hg, and on plotting the reciprocal of the " periods " against pressure, a straight-line graph fitting the equation

$$t^{-1} = (1·712p + 2·9 \times 10^{-4}) \text{ sec.}^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

was obtained (p in mm. Hg).* On comparison of this equation with equation (1), and substitution for the molecular weight of nitrogen, the calibration gives the formula for the gauge as

$$t^{-1} = (0·323M^{\frac{1}{2}}p + 2·9 \times 10^{-4}) \text{ sec.}^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

at the average room temperature of 17°.

The vapour pressures of the alkylmercuric halides were obtained over a temperature range of 20—30°, by use of equation (3) and the measured " periods " of the gauge when vibrating in the vapour of the substance under investigation. The sample tube was immersed in a large Dewar flask, containing water or brine, the temperature of which could be held constant (within 0·1°) by a simple device. The gauge and sample tube were very thoroughly pumped out before measurements of the " period " were made, in order to ensure the removal of volatile impurities (moisture, occluded gases) from the system. At each bath temperature, the mean of about 50 separate readings was taken as the " period " corresponding to that temperature. For pressure measurements with the bath temperature above that of the room, the gauge and connecting lines were heated with a nichrome winding. In the case of the ethyl mercury halides, it seemed that the pressure of an isolated sample of vapour increases slowly with time, possibly owing to slight decomposition in the light.

TABLE I.

Vapour pressures of HgRX compounds.

1. Methylmercury chloride. / 2. Methylmercury bromide.

Temp.	t, sec.	p × 10⁴, mm. Hg.	Temp.	t, sec.	p × 10⁴, mm. Hg.	Temp.	t, sec.	p × 10⁴, mm. Hg.	Temp.	t, sec.	p × 10⁴, mm. Hg.
−6·0°	275	6·55	4·0°	104	18·2	−6·0°	290	5·68	10·0°	54·4	32·6
−3·0	211	8·68	10·0	57·6	33·4	0·0	146	11·8	14·0	37·2	47·9
0·0	152	12·3	12·0	47·6	40·5	5·0	91·0	18·3			

3. Methylmercury iodide. / 4. Ethylmercury chloride.

Temp.	t, sec.	p × 10⁴, mm. Hg.	Temp.	t, sec.	p × 10⁴, mm. Hg.	Temp.	t, sec.	p × 10⁴, mm. Hg.	Temp.	t, sec.	p × 10⁴, mm. Hg.
−10·0	369	4·05	11·0	45·5	36·3	10·0	576	2·75	22·0	177	10·2
0·0	136	11·8	14·0	33·8	48·9	12·0	510	3·18	25·0	135	14·1
5·0	79·9	20·4	17·0	26·2	63·4	15·0	375	4·52	28·0	100	18·2
						18·0	279	6·27	30·0	86·2	21·5
						20·0	219	8·14			

5. Ethylmercury bromide. / 6. Ethylmercury iodide.

Temp.	t, sec.	p × 10⁴, mm. Hg.	Temp.	t, sec.	p × 10⁴, mm. Hg.	Temp.	t, sec.	p × 10⁴, mm. Hg.	Temp.	t, sec.	p × 10⁴, mm. Hg.
12·5	508	2·96	24·5	157	10·7	13·0	541	4·06	27·0	129	19·4
15·0	398	3·91	30·0	90·9	18·8	16·0	413	5·55	30·0	97·1	26·0
17·5	329	4·84				20·0	267	9·01			

* This expression ceased to hold for pressures >*ca.* 5 × 10⁻² mm. Hg.

TABLE II.

Heats of sublimation of HgRX.

Compound.	A.	B.	$\lambda_{sub.}$ (kcals. mole^{-1}).	Compound.	A.	B.	$\lambda_{sub.}$ (kcals. mole^{-1}).
HgMeCl	9·48	3385	15·5	HgEtCl	10·50	3987	18·2
HgMeBr	10·03	3546	16·2	HgEtBr	10·47	4000	18·3
HgMeI	9·53	3404	15·6	HgEtI	11·14	4162	19·0

Results.—The results are summarised in Tables I and II. The plots of the logarithms of the vapour pressures against the reciprocals of the corresponding absolute temperatures gave in each case good straight lines obeying an equation of the form

$$\log_{10} p = A - B/T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The " best " straight line was fitted to the points by the method of least squares, and the latent heat of sublimation, $\lambda_{sub.}$, was calculated from the expression :

$$\lambda_{sub.} = -2\cdot303 \times 1\cdot986 \, d(\log p)/d(T^{-1})$$
$$= 2\cdot303 \times 1\cdot986B \text{ cals. mole}^{-1} . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The internal diameter of the sample tubes at the surface of the constant-temperature bath was *ca.* 8 mm., which corresponds in order of magnitude to the molecular mean free path of the HgRX compounds—so that it may be that corrections should be made to allow for the effect of thermal transpiration (see Coolidge, *J. Amer. Chem. Soc.*, 1924, **46**, 680). On the other hand, Tompkins and Wheeler (*Trans. Faraday Soc.*, 1933, **29**, 1248) have shown that the full effect of thermal transpiration does not enter until the mean free path is at least ten times the tube diameter. Under the conditions of our experiments, full allowance for the thermal transpiration effect would increase the values of $\lambda_{sub.}$ (given in Table II) by only 0·2 kcal. mole^{-1}, so the correction is small, even if—as seems doubtful—it is necessary to make it.

The estimated overall error in the quoted values of $\lambda_{sub.}$ amounts to $\pm0\cdot4$ kcal. mole^{-1} in the case of the methyl, and $\pm0\cdot7$ kcal. mole^{-1} in that of the ethyl compounds.

DISCUSSION.

Bond Dissociation Energies, D(R–HgX).—As stated on p. 1921, the bond dissociation energies, D(R–HgX), can be derived from the Q_f(HgRX, gas) values, themselves obtainable from the heats of formation reported by Hartley, Pritchard, and Skinner (*loc. cit.*), and the $\lambda_{sub.}$ values given here. The dissociation energies are calculated from the equation

$$D(\text{R–HgX}) = Q_f(\text{HgRX, g.}) - Q_f(\text{HgX, g.}) - Q_f(\text{R, g.}) \quad . \quad . \quad . \quad . \quad (6)$$

and are listed in Table III. These values differ slightly from those provisionally quoted by Hartley *et al.* (*loc. cit.*), and should be accepted as superseding the earlier values.

From the data given in Table III, we may note that the differences, $\Delta D = D(\text{Me–HgX}) - D(\text{Et–HgX})$, are all of similar magnitudes, *viz.* (in kcals. mole^{-1}) :

$$\Delta D \begin{cases} \text{Me–HgCl} \\ \text{Et–HgCl} \end{cases} = 5\cdot4 \qquad \Delta D \begin{cases} \text{Me–HgBr} \\ \text{Et–HgBr} \end{cases} = 5\cdot7 \qquad \Delta D \begin{cases} \text{Me–HgI} \\ \text{Et–HgI} \end{cases} = 6\cdot7$$

and moreover compare with the difference of 5 kcals. mole^{-1} between the values we have accepted as correct for D(Me–H) and D(Et–H). An explanation of the fall in D(R–H) in passing from R = Me to R = Et has been put forward by Baughan, Evans, and Polanyi (*Trans. Faraday Soc.*, 1941, **37**, 377), and one might well presume that the fall in D(Et–HgX) compared with D(Me–HgX) is explicable in similar manner, particularly as the mercury atom does not, in general, behave as a strongly electropositive metal.

It is of interest to compare the values in Table III with some results obtained by Warhurst and Gowenlock (Gowenlock, Thesis, Manchester Univ., 1949) on the energies of rupture of the

TABLE III.

Bond dissociation energies, D(R–HgX).

Compound.	Q_i(HgRX, g.), kcals.	$\lambda_{sub.}$, kcals.	Q_f(HgRX, g.), kcals.	Q_f(R, g.), kcals.	Q_f(HgX, g.), kcals.	D(R–HgX),* kcals.
HgMeCl	27·68 ± 1·5 [a]	15·5 ± 0·4	12·2 ± 1·9	−32·6 ± 1 [a]	−19·0 [b]	63·8 ± 2·9
HgMeBr	20·46 ± 1·4 [a]	16·2 ± 0·4	4·3 ± 1·8	,,	−24·4 [b]	61·3 ± 2·8
HgMeI	10·20 ± 1·2 [a]	15·6 ± 0·4	−5·4 ± 1·6	,,	−31·3 ± 0·5 [b]	58·5 ± 3·1
HgEtCl	32·3 ± 1·5 [a]	18·2 ± 0·7	14·1 ± 2·2	−25·3 ± 2 [a]	−19·0	58·4 ± 4·2
HgEtBr	24·2 ± 1·5 [a]	18·3 ± 0·7	5·9 ± 2·2	,,	−24·4	55·6 ± 4·2
HgEtI	14·2 ± 1·6 [a]	19·0 ± 0·7	−4·8 ± 2·3	,,	−31·3 ± 0·5	51·8 ± 4·8

[a] Hartley, Pritchard, and Skinner (*loc. cit.*). [b] These are derived from the energies, $\Delta E_0°$, of the processes HgX ⟶ Hg($'S_0$) + X, for which Wieland and his co-workers (*Helv. Physica Acta*, 1941, **14**, 420 ; *Helv. Chim. Acta*, 1943, **26**, 1025 ; 1949, **32**, 889) have obtained 24·0 kcals. mole^{-1} (X = Cl), 16·4 kcals. mole^{-1} (X = Br), and 8·3 ± 0·5 kcals. mole^{-1} (X = 1).

* The D(R–HgX) are the $-\Delta H°$ of the processes HgRX (g.) ⟶ R (g.) + HgX (g.) occurring at room temperature, *i.e.*, 20°.

first CH_3–Hg bond in $HgMe_2$, and the first C_2H_5–Hg bond in $HgEt_2$. These investigators found that D(Me–HgMe) $\sim$ 50—51 kcals. mole⁻¹, and D(Et–HgEt) $\sim$ 40 kcals. mole⁻¹, so the Hg–C bond dissociation energies in R–HgX seem to be significantly greater (by 10 kcals. mole⁻¹, or more) than in R–HgR. In this connection, the recent determination by Sheridan and Gordy (Sheridan, private communication) of the Hg–C bond-lengths in some methylmercury halides is of considerable interest, as these investigators find that the Hg–C bond is appreciably shorter in CH_3·HgCl than has been reported in $HgMe_2$.

The apparent decrease in D(R–HgX) as X changes from Cl through Br to I, correlates with the electronegativity trend in the halogens. This point has been discussed by Hartley (Ph.D. Thesis, Manchester Univ., 1950), who found that the strength of R–HgX bonds is related to the electronegativities of the R and X in HgRX, in that the greater the difference in electronegativity between R and X, the greater the strengthening of the R–HgX bond. The "electronegativity of the radical R" is here used in Kharasch's sense (*J. Amer. Chem. Soc.*, 1932, **54**, 674).

THE UNIVERSITY, MANCHESTER.