Solution Thermochemistry of Phosphorus(v) Bromide, and Tetrachlorophosphonium Tetrachloroborate and Tetrabromoborate

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Using a solution calorimetric method the standard enthalpies of formation at 298·15 K of PBr_5(c), $BPCl_8$(c), and $BPBr_8$(c) have been determined as $-60{\cdot}5 \pm 0{\cdot}6$, $-223{\cdot}9_5 \pm 0{\cdot}6$, and $-135{\cdot}5 \pm 0{\cdot}7$ kcal mol^{-1}, respectively, the first two results differing significantly from literature sources.

THE solution thermochemistry and the derived heats of formation of PBr_5 and $BPCl_8$ have been reported previously.[1-3] Subsequent experiments in this laboratory have shown that hydrolysis of compounds containing the tetrachlorophosphonium ion is relatively slow (see Results and Discussion section). The earlier thermochemical studies [2,3] on $BPCl_8$ were suspect since only the initial rapid phase of the hydrolysis was considered in processing the results. Accordingly, further studies using a superior calorimeter not previously available have been undertaken. Similar measurements on PBr_5 and $BPBr_8$ are also reported. Both $BPCl_8$ [4] and $BPBr_8$ [5] have ionic structures in the solid phase, $[X_4P][BX_4]$ (X = Br or Cl).

EXPERIMENTAL

Materials.—Phosphorus(v) bromide (B.D.H.) was crystallised from freshly distilled, sodium-dried diethyl ether in a nitrogen-filled dry-box. Excess of ether was removed by pumping at 0·01 Torr at room temperature for 1 h.† Analysis for bromine was by a conventional Volhard titration on the hydrolysate (Found: Br, 92·6. Calc. for PBr_5: Br, 92·8%). The density of PBr_5 was calculated from crystallographic data [6] as 3·62 g cm^{-3}.

The compound $BPCl_8$ was prepared according to Holmes.[7] Analyses for chlorine and boron were by conventional titrimetric procedures (Found: B, 3·30; Cl, 87·2. Calc. for $BPCl_8$: B, 3·32; Cl, 87·16%). The compound $BPBr_8$ was prepared by mixing methylene chloride solutions of PBr_5 and BBr_3, a modification of the method of Tarible [8] (Found: Br, 93·2. Calc. for $BPBr_8$: Br, 93·9%). The densities of $BPCl_8$ and $BPBr_8$ were determined pycnometrically at 25 °C as 2·79 and 3·35 g cm^{-3} respectively.

Calorimeter.—An LKB 8700—1 precision calorimetry system was used with the out-of-balance signal displayed on a chart recorder. The calorimeter was filled with deionised water (100 cm^3, pH 6·0) and the ampoules were loaded in a nitrogen-filled dry-box. For both PBr_5 and $BPCl_8$, analysis of a post-calorimetry hydrolysate revealed no deterioration of the compounds on storage. The calorimeter was tested by measuring the enthalpy of neutralisation of tris[(hydroxymethyl)amino]methane (tham) in excess of 0·1 mol dm^{-3} HCl for which ΔH (298·15 K, $1\,280 < N < 1\,464$) = $-7{\cdot}104 \pm 0{\cdot}006$ kcal mol^{-1}. Prosen and Kilday [9] obtained ΔH (298·15 K, $N = 1\,345$) = $-7{\cdot}115 \pm 0{\cdot}007$ kcal mol^{-1} for the same reaction; N is the mole ratio of H_2O to tham. Uncertainties are expressed throughout as $\pm 2\sigma$, σ being the standard deviation of the mean.

RESULTS AND DISCUSSION

The hydrolysis of $BPCl_8$ was initially rapid but tailed off after 2—3 min and was complete only after *ca*. 30 min. This behaviour is similar to PCl_5.[10] The hydrolyses of PBr_5 and $BPBr_8$ were complete within *ca*. 3 and *ca*. 15 min respectively. Enthalpy changes for reactions (1)

$$PBr_5(c) + (n+4)H_2O(l) = (H_3PO_4 + 5HBr)\cdot nH_2O \quad (1)$$

$$BPX_8(c) + (n+7)H_2O(l) = (H_3PO_4 + H_3BO_3 + 8HX)\cdot nH_2O \quad (2)$$
(X = Br or Cl)

and (2) are collected in the Table. Ignoring the heats of mixing of the products and with the following ancillary data, $\Delta H_f^{\ominus}$ (H_3PO_4, $40H_2O$) = $-309{\cdot}34 \pm 0{\cdot}38$,[11] ΔH (diln. $H_3PO_4, 40H_2O \longrightarrow nH_2O$) = $-1{\cdot}165$,[12] $\Delta H_f^{\ominus}$ (HCl, 4 700 H_2O) = $-39{\cdot}902 \pm 0{\cdot}020$,[12] $\Delta H_f^{\ominus}$ (HBr, 4 000 H_2O) [in equation (1)] = $-29{\cdot}001 \pm 0{\cdot}020$,[12] $\Delta H_f^{\ominus}$ (HBr, 15 000 H_2O) [in (2), X = Br] = $-29{\cdot}024 \pm 0{\cdot}020$ [12] (the maximum errors caused by ignoring the extent of dilution of HX in the PBr_5, $BPCl_8$, and $BPBr_8$ experiments were 0·04, 0·07, and 0·13 kcal mol^{-1} respectively), $\Delta H_f^{\ominus}$ (H_3BO_3, c) = $-261{\cdot}59 \pm 0{\cdot}31$ (mean of two [13,14] recent data), ΔH (soln. H_3BO_3) = $-5{\cdot}25$,[9] and $\Delta H_f^{\ominus}$ (H_2O, l) = $-68{\cdot}315 \pm 0{\cdot}010$ kcal mol^{-1}, we [15] obtain $\Delta H_f^{\ominus}$ ($BPCl_8$, c) = $-223{\cdot}9_5 \pm 0{\cdot}6$, $\Delta H_f^{\ominus}$ (PBr_5, c) = $-60{\cdot}5 \pm 0{\cdot}6$, and $\Delta H_f^{\ominus}$ ($BPBr_8$, c) = $-135{\cdot}5 \pm 0{\cdot}7$ kcal mol^{-1}. The value for PBr_5 lies between the

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† Throughout this paper, 1 cal = 4·184 J; 1 Torr = (101·325/760) kPa, and 1 Å = 10^{-10} m.

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result from previous measurements[1] (−54·6 ± 1·2 kcal mol^{-1}) and the N.B.S. recommended value[12] (−64·5 kcal mol^{-1}). This latter figure derives from a weighted mean of results from hydrolysis,[16] PBr_3-bromination,[16] red P-bromination,[17] and PBr_5-decomposition[18,19] experiments. We are unable to account for the difference in the results from the present and previous[1] hydrolysis experiments.

The heat of hydrolysis for $BPCl_8$ reported here (−183·9 ± 0·3 kcal mol^{-1}) is considerably more exothermic than that (−155·0 ± 0·6 kcal mol^{-1}) obtained from the previous measurements[2,3] and this arises from the recognition of the long 'tailing' of the reaction period which follows the initial, very rapid, stage. The cause of this two-stage reaction is apparently not documented. Preliminary experiments in this laboratory using a selective chloride-ion electrode indicate that in the hydrolysis of phosphorus(V) chloride (which contains the same cation as $BPCl_8$) formation of the stoicheiometric quantity of chloride ions is very fast although the hydrolysis is known to exhibit a slow second phase.[10] Hence the rate-limiting step concerns the conversion of an oxophosphorus(V) species to its final state of hydrated phosphate ion. Since the hydrolysis of metal tetrachloroborates is known[20] to be fast, presumably a similar explanation can be invoked for $[Cl_4P][BCl_4]$, and possibly $[Br_4P][BBr_4]$. However, the rapid hydrolysis of PBr_5 does not lend support to this argument.

Reactant masses and enthalpy changes for equations (1) * and (2) * at 298·15 K

m† /g	$-\Delta H_1$/ kcal mol^{-1}	m† /g	$-\Delta H_2(X = Cl)$/ kcal mol^{-1}	m† /g	$-\Delta H_2(X = Br)$/ kcal mol^{-1}
0·09902	121·6	0·04081	184·2	0·02619	186·6
0·10176	121·4	0·04341	184·1	0·04856	185·1
0·10370	122·4	0·04841	183·6	0·05986	186·1
0·10814	121·1	0·05111	183·4	0·06357	184·2
0·12642	121·9	0·05151	183·5	0·06542	185·4
$0·14336_5$	121·9	0·05662	184·4	0·06655	184·4
Mean (±2σ)	121·7 ± 0·4	Mean (±2σ)	183·9 ± 0·3	0·07322	185·6
				0·07719	185·9
				0·10452	184·4
				0·11791	185·2
				Mean (±2σ)	185·3 ± 0·5

* In these equations n is given $32\,000 < n_1 < 44\,000$, $17\,000 < n_2\ (X = Cl) < 24\,000$, and $64\,000 < n_2\ (X = Br) < 289\,000$.
† Sample mass *in vacuo*.

Gal'chenko[21] has reported the enthalpy of chlorination of boron phosphide [equation (3)] and combining

$$BP(c) + 4Cl_2(g) \longrightarrow BPCl_8(c), \Delta H_3 = -192\cdot25 \pm 0\cdot20 \text{ kcal mol}^{-1} \quad (3)$$

this with $\Delta H_f^\ominus$ (BP, c) = −27·6 ± 1·1 kcal mol^{-1} (ref. 22) we derive $\Delta H_f^\ominus$ ($BPCl_8$, c) = −219·9 ± 1·2 kcal mol^{-1}, which differs significantly from the present result ($-223\cdot9_5 \pm 0\cdot60$ kcal mol^{-1}), possibly due, as suggested earlier,[22] to interaction between Cl_2 and $BPCl_8$.

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