

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 $\text{PBr}_5(\text{c})$, $\text{BPCl}_8(\text{c})$, and $\text{BPBr}_8(\text{c})$ have been determined as -60.5 ± 0.6 , $-223.9_5 \pm 0.6$, and -135.5 ± 0.7 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, $[\text{X}_4\text{P}][\text{BX}_4]$ (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 data⁶ 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 Tarible⁸ (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 cm³, 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

† Throughout this paper, 1 cal = 4.184 J; 1 Torr = (101.325/760) kPa, and 1 Å = 10⁻¹⁰ m.

¹ A. Finch, P. J. Gardner, and I. H. Wood, *J. Chem. Soc.*, 1965, 40.

² K. K. SenGupta, Ph.D. Thesis, London University, 1967.

³ P. J. Gardner, *Inorg. Chem.*, 1969, **8**, 1187.

⁴ V. P. Petro and S. G. Shore, *J. Chem. Soc.*, 1964, 336.

⁵ A. Finch, P. N. Gates, and F. J. Ryan, *J.C.S. Dalton*, 1973, 1863.

⁶ W. Gabe and K. Olie, *Acta Cryst.*, 1970, **B26**, 443.

⁷ R. R. Holmes, *Inorg. Synth.*, 1963, **7**, 79.

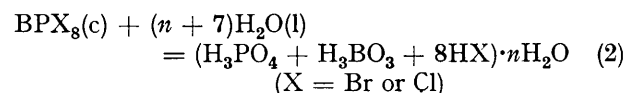
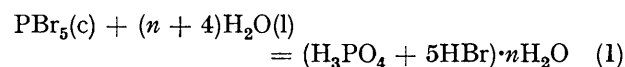
⁸ M. Tarible, *Compt. rend.*, 1893, **116**, 1521.

⁹ E. J. Prosen and M. W. Kilday, *J. Res. Nat. Bur. Stand.*, 1973, **A77**, 581.

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) = -7.104 ± 0.006 kcal mol⁻¹. Prosen and Kilday⁹ obtained ΔH (298.15 K, N = 1 345) = -7.115 ± 0.007 kcal mol⁻¹ for the same reaction; N is the mole ratio of H₂O 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)



and (2) are collected in the Table. Ignoring the heats of mixing of the products and with the following ancillary data, ΔH_f° (H_3PO_4 , 40H₂O) = -309.34 ± 0.38 ,¹¹ ΔH (dilin. H_3PO_4 , 40H₂O \rightarrow nH₂O) = -1.165 ,¹² ΔH_f° (HCl, 4 700 H₂O) = -39.902 ± 0.020 ,¹² ΔH_f° (HBr, 4 000 H₂O) [in equation (1)] = -29.001 ± 0.020 ,¹² ΔH_f° (HBr, 15 000 H₂O) [in (2), X = Br] = -29.024 ± 0.020 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), ΔH_f° (H_3BO_3 , c) = -261.59 ± 0.31 (mean of two^{13,14} recent data), ΔH (soln. H_3BO_3) = -5.25 ,⁹ and ΔH_f° (H_2O , l) = -68.315 ± 0.010 kcal mol⁻¹, we¹⁵ obtain ΔH_f° (BPCl_8 , c) = $-223.9_5 \pm 0.6$, ΔH_f° (PBr_5 , c) = -60.5 ± 0.6 , and ΔH_f° (BPBr_8 , c) = -135.5 ± 0.7 kcal mol⁻¹. The value for PBr_5 lies between the

¹⁰ G. I. Birley and H. A. Skinner, *Trans. Faraday Soc.*, 1968, **64**, 3232.

¹¹ A. J. Head and G. B. Lewis, *J. Chem. Thermodynamics*, 1970, **2**, 701.

¹² D. D. Wagman, W. H. Evans, V. B. Parker, J. Halow, S. M. Bailey, and R. H. Schumm, Nat. Bur. Stand. Tech. Note 270-3, U.S. Govt. Printing Office, Washington, D.C., 1968.

¹³ W. D. Good and M. Mansson, *J. Phys. Chem.*, 1966, **70**, 97.

¹⁴ G. K. Johnson and W. N. Hubbard, *J. Chem. Thermodynamics*, 1969, **1**, 459.

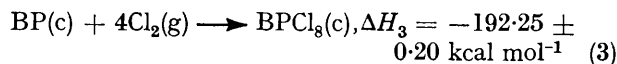
¹⁵ Report of the ISCU-CODATA Task group on Key Values in Thermodynamics, November 1971, *J. Chem. Thermodynamics*, 1972, **4**, 331.

result from previous measurements¹ (-54.6 ± 1.2 kcal mol⁻¹) and the N.B.S. recommended value¹² (-64.5 kcal mol⁻¹). This latter figure derives from a weighted mean of results from hydrolysis,¹⁶ PBr₃-bromination,¹⁶ red P-bromination,¹⁷ and PBr₅-decomposition^{18,19} experiments. We are unable to account for the difference in the results from the present and previous¹ hydrolysis experiments.

The heat of hydrolysis for BPCl₈ 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

hydrated phosphate ion. Since the hydrolysis of metal tetrachloroborates is known²⁰ to be fast, presumably a similar explanation can be invoked for [Cl₄P][BCl₄], and possibly [Br₄P][BBr₄]. However, the rapid hydrolysis of PBr₅ does not lend support to this argument.

Gal'chenko²¹ has reported the enthalpy of chlorination of boron phosphide [equation (3)] and combining



this with ΔH_f° (BP, c) = -27.6 ± 1.1 kcal mol⁻¹ (ref. 22) we derive ΔH_f° (BPCl₈, c) = -219.9 ± 1.2 kcal

Reactant masses and enthalpy changes for equations (1) * and (2) * at 298.15 K

<i>m</i> †/g	$-\Delta H_1/$ kcal mol ⁻¹	<i>m</i> †/g	$-\Delta H_2(\text{X} = \text{Cl})/$ kcal mol ⁻¹	<i>m</i> †/g	$-\Delta H_2(\text{X} = \text{Br})/$ 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 ($\pm 2\sigma$)	121.7 \pm 0.4	Mean ($\pm 2\sigma$)	183.9 \pm 0.3	0.07322	185.6
				0.07719	185.9
				0.10452	184.4
				0.11791	185.2
				Mean ($\pm 2\sigma$)	185.3 \pm 0.5

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

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 BPCl₈) formation of the stoichiometric 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

mol⁻¹, which differs significantly from the present result ($-223.9_5 \pm 0.60$ kcal mol⁻¹), possibly due, as suggested earlier,²² to interaction between Cl₂ and BPCl₈.

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²¹ G. L. Gal'chenko, B. I. Timofeev, D. A. Godakyan, Y. K. Grinberg, and Z. S. Medvideva, *Izvest. Akad. Nauk S.S.S.R., Neorg. Materialy*, 1966, 2, 1410 (*Chem. Abs.*, 1966, 65, 19367a).

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¹⁶ J. Ogier, *Compt. rend.*, 1881, 92, 83.

¹⁷ R. B. Jacobs, *J. Chem. Phys.*, 1937, 5, 945.

¹⁸ G. S. Harris and D. Payne, *J. Chem. Soc.*, 1958, 3732.

¹⁹ M. van Driel and H. Gerding, *Rec. Trav. chim.*, 1941, 60, 869.