The Standard Enthalpy of Formation of Diphenylborinic Acid

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THE value of the standard enthalpy of formation, ΔH_f^0, of diphenylborinic acid, Ph_2BOH, is of peculiar importance, since the acid results from the simple hydrolysis of many diphenylboron compounds:

$$Ph_2B{\cdot}R \xrightarrow[\text{step 1}]{\text{hydrolysis}} Ph_2BOH \xrightarrow[\text{step 2}]{\text{aq. oxidation}} PhOH + B(OH)_3$$

R = halogen, ester, thioester, *etc.*

Hence if ΔH_f^0 of Ph_2BOH is known, a knowledge of the enthalpy of reaction of step 1 permits evaluation of the standard enthalpy of formation of any appropriate parent boron compound; thermochemically, therefore, diphenylborinic acid is a "key" compound in arylboron chemistry.

Previous work[1] on diphenylboron compounds, and relevant (*e.g.*, bond-energy) calculations, relied on an *estimate* of ΔH_f^0 for Ph_2BOH. This Communication summarises the experimental determination of this quantity using solution–reaction-calorimetric techniques described elsewhere.[2]

Two reactions were studied thermochemically at 75°: (i) hydrolysis of diphenylboron chloride in a saturated aqueous solution of diphenylborinic acid (step 1), and (ii) oxidative hydrolysis of diphenylboron chloride in a solution 0·1M with respect both to hydrogen peroxide and to sodium hydroxide (steps 1 and 2). Using standard ancillary data,[3] the following results were derived:

$$\Delta H_f^0[\mathrm{Ph_2BOH}]_{(l)} = \pm 77{\cdot}4 \pm 1{\cdot}8 \text{ kcal.mole}^{-1}$$
$$\Delta H_f^0[\mathrm{Ph_2BCl}]_{(l)} = -31{\cdot}9 \pm 1{\cdot}8 \text{ kcal.mole}^{-1}$$

At 25°, diphenylborinic acid is an intractable oil;[4] this is the standard state.

From previously reported experiments[1] on the heat of reaction of diphenylboron bromide with water we also derive:

$$\Delta H_f^0[\mathrm{PhBBr}]_{(l)} = -16{\cdot}1 \pm 1{\cdot}9 \text{ kcal.mole}^{-1}$$

It is interesting to note that the value of $\Delta H_f^0[\mathrm{Ph_2BOH}_{(l)}]$ reported here is in good agreement with a previous estimate (-78 kcal.mole^{-1}). The latent heats of vaporization of both diphenylborinic chloride and diphenylborinic bromide are known,[1] and hence, assuming the B–X bond-energies found in the trihalides, the bond energies of the boron–carbon bond in the diphenylboron halides are also calculable:

$$E(\text{B–C}) \text{ in } \mathrm{Ph_2BBr} = 109{\cdot}1 \pm 2{\cdot}4 \text{ kcal.mole}^{-1}$$
$$E(\text{B–C}) \text{ in } \mathrm{Ph_2BCl} = 111{\cdot}3 \pm 2{\cdot}4 \text{ kcal.mole}^{-1}$$

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[1] A. Finch, P. J. Gardner, and G. B. Watts, *Trans. Faraday Soc.*, 1967, **63**, 1880.
[2] A. Finch and P. J. Gardner, *J. Chem. Soc.*, 1964, 2985.
[3] See *e.g.*, A. Finch and P. J. Gardner, *Trans. Faraday Soc.*, 1966, **62**, 3314.
[4] G. N. Chremos, H. Weidmann, and H. K. Zimmerman, *J. Org. Chem.*, 1961, **26**, 1683.