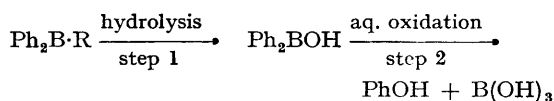


The Standard Enthalpy of Formation of Diphenylborinic Acid

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



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

Hence if ΔH_f° 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 work¹ on diphenylboron compounds, and relevant (*e.g.*, bond-energy) calculations, relied on an *estimate* of ΔH_f° 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:

$$\Delta H_f^0[\text{Ph}_2\text{BOH}]_{(l)} = \pm 77.4 \pm 1.8 \text{ kcal.mole}^{-1}$$

$$\Delta H_f^0[\text{Ph}_2\text{BCl}]_{(l)} = -31.9 \pm 1.8 \text{ kcal.mole}^{-1}$$

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

From previously reported experiments¹ on the heat of reaction of diphenylboron bromide with water we also derive:

$$\Delta H_f^0[\text{PhBBr}]_{(l)} = -16.1 \pm 1.9 \text{ kcal.mole}^{-1}$$

It is interesting to note that the value of

$\Delta H_f^0[\text{Ph}_2\text{BOH}]_{(l)}$ reported here is in good agreement with a previous estimate ($-78 \text{ kcal.mole}^{-1}$). 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:

$$E(\text{B-C}) \text{ in Ph}_2\text{BBr} = 109.1 \pm 2.4 \text{ kcal.mole}^{-1}$$

$$E(\text{B-C}) \text{ in Ph}_2\text{BCl} = 111.3 \pm 2.4 \text{ kcal.mole}^{-1}$$

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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.