The Thermochemistry of Triphenoxyborane and the Lewis Acidity of the Boron Atom

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The heat of formation of gaseous triphenoxyborane has been derived ΔH_f° B(OPh)$_3$ (g) = $-591 \cdot 9 \pm 1 \cdot 9$ kJ mol^{-1}, and used to calculate the boron–oxygen mean bond dissociation energy $\bar{D}$(B–OPh) = $437 \cdot 0 \pm 14 \cdot 0$ kJ mol^{-1}. This value is compared with values for other boron–oxygen systems.

THE relative acidity of the boron atom in BL_3 compounds (L = H, halogen, alkyl, OR, and NR_2) has been a subject of controversy for some time. The arguments centre on the ability of L to compete with a reference Lewis base in donating electron density into the empty p orbital of the boron atom. The internal base L donates via a $p\pi-p\pi$ mechanism and the external Lewis base via a conventional co-ordinate sigma bond. If the internal base is strong, in the Lewis sense, then it becomes difficult to reorganise the planar molecule and consequently only weak adduct formation takes place, if at all. Such studies are hampered by the obvious fact that a change of L completely alters the system and true comparisons are difficult.

When L = OR however, it is possible to observe a fair range of acidity without drastic alterations to the important atoms involved. This is achieved by altering the basicity of the oxygen atoms and hence the degree of backbonding, by varying the electronic properties of R. When R = H or alkyl the boron atom is a very weak Lewis acid.[1] When R = aryl [2] or a fully halogenated alkyl group [3] the acidity is considerably enhanced. In the latter case the oxygen basicity is reduced by a direct inductive mechanism whilst in the phenoxides there is the additional possibility of a resonance interaction between the oxygen and the aromatic ring.

It is of interest therefore to obtain quantitative data on such effects. One way of doing this is to observe changes in the boron–oxygen mean bond dissociation energies of the different systems. Accordingly the gas-phase heat of formation of triphenoxyborane has been derived from the enthalpy change for reaction (1) and ancilliary data.

$$B(OPh)_3(s) + 3H_2O(l) \xrightarrow{\Delta H_1} H_3BO_3(s) + 3PhOH(s) \quad (1)$$
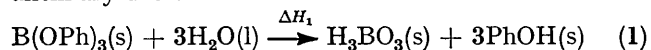
RESULTS AND DISCUSSION

The enthalpy change for reaction (1) can be computed from the enthalpy changes for the reactions of an excess of 1M-sodium hydroxide solution with $B(OPh)_3(s)$, $H_3BO_3(s)$, and PhOH(s), (ΔH_2, ΔH_3, and ΔH_4 respectively) at 298 K in an Isoperibol calorimeter. Then $\Delta H_1 = \Delta H_2 - (\Delta H_3 + 3\Delta H_4) = -62 \cdot 56 \pm 0 \cdot 14$ kJ mol^{-1}. This scheme assumes negligible heat of mixing between the products of the reaction of triphenoxyborane and an excess of sodium hydroxide solution. Experiments similar to those performed previously for another system [4] showed that this assumption is correct.

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[2] T. Colclough, T. W. Gerrard, and M. F. Lappert, *J. Chem. Soc.*, 1955, 907.

[3] E. W. Abel, D. J. Walker, J. N. Wingfield, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 139; E. W. Abel, N. Giles, D. J. Walker, and J. N. Wingfield, *J. Chem. Soc. (A)*, 1971, 1991; D. E. Young, L. R. Anderson, and W. B. Fox, *Chem. Comm.*, 1971, 736.

[4] J. W. Wilson, *J. Chem. Soc. (A)*, 1971, 981.

The experimental results are given in Table 1. Using the following values for $\Delta H_f°H_3BO_3(s) = -1095\cdot0 \pm 1\cdot3$ kJ mol^{-1},[5] $\Delta H_f°H_2O(l) = -285\cdot83 \pm 0\cdot04$ kJ mol^{-1},[6] $\Delta H_f°PhOH(s) = -165\cdot10 \pm 0\cdot33$ kJ mol^{-1},[7] the standard heat of formation of crystalline triphenoxyborane $\Delta H_f°B(OPh)_3(s) = -670\cdot25 \pm 1\cdot64$ kJ mol^{-1}.

TABLE 1

Heat of reaction of an excess of sodium hydroxide solution

Compd.	No. of measurements	Heat of reaction (kJ mol^{-1})	
B(OPh)$_3$(s)	7	$-143\cdot45 \pm 0\cdot05$	ΔH_2
H$_3$BO$_3$(s)	13	$-22\cdot63 \pm 0\cdot04$	ΔH_3
PhOH(s)	8	$-19\cdot42 \pm 0\cdot04$	ΔH_4

The heat of fusion of the compound, $+17\cdot0$ kJ mol^{-1}, was measured by differential scanning calorimetry at the University of Lancaster. The vapour pressure of the compound measured manometrically over the temperature range 470—512 K gave reproducible results represented by the equation $\log p$ mm $= 7\cdot58 - (3206/T)$. The heat of vaporisation is therefore $+61\cdot4$ kJ mol^{-1}, giving a value for the heat of sublimation of $+78\cdot4$ kJ mol^{-1} with an estimated accuracy of $\pm1\cdot0$ kJ mol^{-1}. The standard heat of formation of gaseous triphenoxyborane is then $\Delta H_f°B(OPh)_3(g) = -591\cdot9 \pm 1\cdot9$ kJ mol^{-1}. The mean bond dissociation energy of the boron–oxygen bond is given by $\bar{D}(B-OPh) = \frac{1}{3}[\Delta H_f°B(g) + 3\Delta H_f°\dot{O}Ph(g) - \Delta H_f°B(OPh)_3(g)] = 437\cdot0 \pm 14\cdot0$ kJ mol^{-1} where $\Delta H_f°B(g) = 555\cdot6 \pm 16\cdot8$ kJ mol^{-1},[8] and $\Delta H_f°\dot{O}Ph(g) = 54\cdot4 \pm 12\cdot5$ kJ mol^{-1}.[9]

The $\bar{D}(B-OR)$ values for other boron–oxygen systems are given in Table 2. Comparison shows a marked decrease in the boron–oxygen bond strength in triphenoxyborane which is consistent with its Lewis acid properties.

TABLE 2

Mean bond dissociation energies for boron–oxygen systems [8]

R	$\bar{D}(B-OR)$ kJ mol^{-1} *
H	$555\cdot6 \pm 7\cdot0$
Me	$493\cdot7 \pm 10\cdot0$
Et	$492\cdot5 \pm 10\cdot0$
Pr	$497\cdot9 \pm 10\cdot0$
Bu	$497\cdot5 \pm 10\cdot0$
Ph	$437\cdot0 \pm 14\cdot0$

* Differences between $\bar{D}$ values will exclude the high error in $\Delta H_f°$ B(g) and the error in such values will decrease accordingly.

EXPERIMENTAL

Calorimetry.—The calorimeter was a modified version of that designed by Sunner and Wadso.[10] It consisted of a glass reaction vessel with a capacity of *ca.* 120 cm^3. This was connected to the lid of a silver-plated brass can by means of a screw and flange device and the joint was made gas tight by the use of an O ring. Two specially thinned pockets set into the top of the calorimeter contained a thermistor (I.T.T. type G53B) and a small Manganin heating coil. Both were immersed in silicone oil and the pockets sealed.

The stirrer-ampoule holder was machined from solid nylon rod. This screwed into a piece of machined Tufnol which fitted almost exactly into the central chimney of the can and acted as a very efficient bearing. The whole stirrer was driven by a constant speed motor from which it could be disengaged and depressed by a simple clutch mechanism. This facilitated the breaking of frangible, sealed, mould-blown, ampoules on a sapphire-tipped rod in the base of the calorimeter. The calorimeter can was sealed by use of small screw clamps and a suitable O ring. It could be evacuated if necessary. The assembly was suspended in a constant temperature bath held at $298\cdot00 \pm 0\cdot01$ K. The whole apparatus was assembled in a room thermostatted at $296\cdot0$ K.

The electrical calibration circuit was of standard design [11] and incorporated a variable resistance, a calibrated 1 Ω standard resistance in series with the heater, and a 12 V accumulator. Switching from the dummy to the calorimeter heater activated a Venner Electronics Digital timer type TSA 6614. The potential drop across the standard resistance during a heating run was measured as previously described.[4]

Temperature changes in the calorimeter were monitored by making the thermistor one arm of a d.c. Wheatstone bridge network. The out of balance signal from the bridge during an experiment was fed into a Perkin-Elmer Potentiometric Recorder type 165. The temperature-time plots obtained were analysed by the Dickenson method.[12] The change in thermistor resistance was taken to be directly proportional to the temperature change. This has been shown to result in negligible error over the temperature changes of about $0\cdot3$ K studied in this work.[13]

The heat of reaction of tris(hydroxymethyl)aminomethane in $0\cdot1$M-HCl was used to check the accuracy of the apparatus. The value obtained for 11 determinations was $-29\cdot799 \pm 0\cdot018$ kJ mol^{-1} (lit.,[14] $-29\cdot744 \pm 0\cdot003$ kJ mol^{-1}).

All uncertainties are expressed as single standard deviations of the mean and refer to true mass. The heat of vaporisation was conveniently measured using a very similar apparatus and techniques to those described by Hesset and Perkins.[15] Results were reproducible for different samples with no residual pressure.

Materials and Techniques.—Triphenoxyborane. Triethoxyborane (19·8 g) and phenol (38·3 g) were refluxed for 4 h in dry AnalaR toluene (250 ml). The displaced ethanol was then removed as the ethanol–toluene azeotrope. Excess of toluene was removed under reduced pressure leaving the colourless crystalline solid, m.p.

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[6] National Bureau of Standards, Technical Note 270-3, Washington, D.C., 1968.

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[9] D. H. Fine and J. B. Westmore, *Canad. J. Chem.*, 1970, **48**, 395.

[10] S. Sunner and I. Wadso, *Acta Chem. Scand.*, 1959, **13**, 97.

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[13] S. R. Gunn, *J. Chem. Thermodynamics*, 1971, **3**, 19.

[14] J. O. Hill, G. Ojelund, and I. Wadso, *J. Chem. Thermodynamics*, 1969, **1**, 111.

[15] B. Hessett and P. G. Perkins, *J. Chem. Soc. (A)*, 1970, 3229.

365·1—367·1 K (lit.,[2] 365·1—366·1 K) (Found: B, 3·7. $C_{18}H_{15}O_3B$ requires B, 3·7%).

The compound was stored *in vacuo* in sealed tubes and manipulated in a dry-box or on a vacuum line.

Phenol. AnalaR phenol was distilled prior to use.

Boric Acid. AnalaR boric acid was dried by pumping under high vacuum for two days.

Ampoules were loaded with sufficient reactant to produce the required temperature change and sealed *in vacuo*.