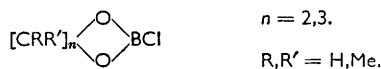**574.** *Cyclic Boron Compounds. Thermochemistry of some Borolans and Borinans.*

By ARTHUR FINCH and P. J. GARDNER.

Values for the standard heats of formation and hydrolysis of several boron heterocycles are reported. Ring strain is defined and its relevance to association in dioxaborolans is discussed.

THE synthesis and properties of compounds of the type

$$[CRR']_n \diamondsuit{\begin{smallmatrix}O\\O\end{smallmatrix}}BCl \qquad \begin{matrix} n = 2,3. \\ R,R' = H,Me. \end{matrix}$$

are established.[1-4] The considerable physical and chemical differences between the five-membered (-olan) and six-membered (-inan) compounds is usually attributed to ring strain, appreciable in the former and absent in the latter. This strain is relieved by intermolecular

[1] Blau, Gerrard, and Lappert, *J.*, 1957, 4116.
[2] Brotherton and McCloskey, *J. Org. Chem.*, 1961, **26**, 1668.
[3] Finch, Lockhart, and Pearn, *J. Org. Chem.*, 1961, **26**, 3250.
[4] Finch and Gardner, *J. Inorg. Nuclear Chem.*, 1963, **25**, 927.

association of which the precise nature is uncertain.[4] Information on the energetics of such association processes is limited to measurements of the heat of complexing of the *n-butyl ethers* of the above cyclic systems (BuO for Cl) with pyrrolidine and with benzylamine in octane solution.[5] In this work we consider the enthalpy change on hydrolysis of associated and non-associated *B*-chloro-derivatives. Results from these derivatives should be internally consistent as the hydrolyses proceed to completion and no steric hindrance is to be expected from the degrading nucleophile.

<div align="center">EXPERIMENTAL</div>

Preparation of Compounds.—All compounds were synthesised by condensing one mole of boron trichloride with one mole of the appropriate diol in methylene chloride. The evolved hydrogen chloride was trapped and estimated to confirm the stoicheiometry. The compounds were then vacuum-distilled and subsequently handled in a dry-box.
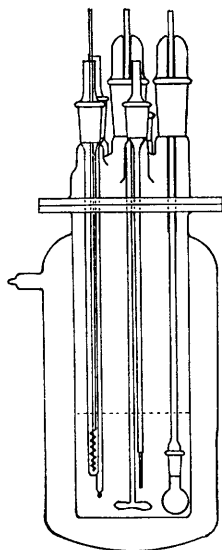

FIG. 1.

Calorimeter.—The calorimeter was of the constant-temperature environment type (" iso-thermal ") consisting of a flanged glass Dewar vessel immersed completely in a thermostat maintained at $25 \pm 0.01°$. The stirrer and ampoule breaker were mounted in the flanged top *via* ground-glass joints and precision-bore tubing (see Fig. 1). The hydrolyses and heats of solution were studied by breaking thin-glass ampoules under the surface of distilled water (100 g.). Precautions were taken to ensure that the calorimeter and contents were equilibrated before measurements were taken. The temperature change throughout the determination was followed by using a calibrated thermistor (F53, Standard Telephone and Cable Ltd.) in one arm of a Wheatstone bridge. Temperature differences obtained in this manner were accurate to $\pm 0.0015°$. In addition, the entire calorimetric run was monitored with a miniature platinum resistance thermometer (sheathed in thin glass) accurate to $\pm 0.01°c$ and coupled to a six-inch potentiometric recorder (Elliot). From this recorder trace thermal leakages were estimated by the " first Geophysical Laboratory method " outlined by Sturtevant.[6,7] The calorimeter was electrically calibrated by measuring the potential-drop across a sub-standard resistance (1 ohm) and across the heater resistance [Nichrome wire (8·23 ohms) in oil encased in thin glass]. Potential readings were measured on a Tinsley type 3387B potentiometer accurate to ± 0.00005 v. The time of heating was measured electrically to ± 0.05 sec. with an electric timer (Precision Scientific Co.) coupled to the heater circuit. Enthalpies were calculated from an expression of the form:

$$\Delta H_{T,N} = \frac{IVtM}{10^3 \, Jw} \cdot \frac{\Delta T'}{(\Delta T \pm \varepsilon)} \text{ kcal./mole,}$$

where $\Delta H_{T,N}$ is enthalpy change at $T°$ and mole ratio N; I the heater current (in A); V the potential-drop across heater (in v); M the molecular weight of the reactant; w the weight of reactant (g.); ΔT^1 the temperature rise during reaction period (°c); ΔT the temperature rise during calibration period (°c); and ε the thermal leakage correction (°c).

The expression used for temperature rise was:

$$\Delta T = \frac{B \ln (R_2/R_1)}{\ln (R_1/A) \ln (R_2/A)},$$

where A and B are thermistor constants ($9.084 \times 10^{-2} \Omega$, 3.214×10^3 °A); R_1 the resistance at T_1; and R_2 that at T_2; and ($\Delta T = T_1 - T_2$).

The accuracy of the calorimeter was checked by measuring the integral heat of solution of

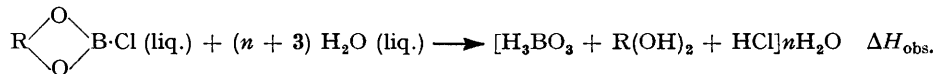[5] Hubert, Hargitay, and Dale, *J.*, 1962, 931.
[6] Weissberger, Ed., " Physical Methods of Organic Chemistry," Interscience, Vol. I, 1946, p. 335.
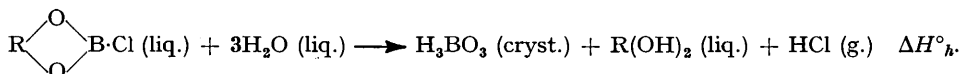[7] Dilke, Eley, and Sheppard, *Trans. Faraday Soc.*, 1950, **46**, 261.

potassium chloride in water (ΔH_S = 4·24, 4·22, 4·19 $\pm$ 0·02 kcal./mole at 25°, and N = 200, lit.,[8,9] 4·2065 $\pm$ 0·0003 kcal./mole at 25° and N = 200). The precision and accuracy of the subsequent measurements is hence limited by the purity and thermal stability of the compounds studied and not by the apparatus.

Units.—Heat quantities are quoted in thermochemical calories, 1 cal. = 4·1840 abs. joules.

Results.—All hydrolyses occurred rapidly (*i.e.*, within 10 sec.) but without undue violence. The observed heat of hydrolysis, $\Delta H_{obs.}$ refers to the reaction:

$$R\overset{O}{\underset{O}{\diamond}}B\cdot Cl \text{ (liq.)} + (n + 3) H_2O \text{ (liq.)} \longrightarrow [H_3BO_3 + R(OH)_2 + HCl]nH_2O \quad \Delta H_{obs.}$$

The quantity of reactant used was determined by direct weighing where possible and where not possible by post-hydrolysis boron and chlorine analysis. The standard heat of hydrolysis, ΔH°_h, refers to the reaction

$$R\overset{O}{\underset{O}{\diamond}}B\cdot Cl \text{ (liq.)} + 3H_2O \text{ (liq.)} \longrightarrow H_3BO_3 \text{ (cryst.)} + R(OH)_2 \text{ (liq.)} + HCl \text{ (g.)} \quad \Delta H^{\circ}_h.$$

These two functions are connected *via* the expression: $\Delta H_{obs.} = \Delta H^{\circ}_h + \Sigma \Delta H_S$ (reaction products), where ΔH_S = heat of solution at 25° and mole ratio N. Standard heats of formation, ΔH°_f, of the heterocycles were obtained using the expression:

$$\Delta H^{\circ}_f [RO_2BCl, \text{ liq.}] = \Delta H^{\circ}_f [R(OH)_2, \text{ liq.}] + \Delta H^{\circ}_f [H_3BO_3, \text{ cryst.}]$$
$$+ \Delta H^{\circ}_f [HCl, \text{ g.}] - 3\Delta H^{\circ}_f [H_2O, \text{ liq.}] - \Delta H^{\circ}_h.$$

The following data were taken from the National Bureau of Standards Circular 500: the standard heats of formation, solution, and dilution of hydrochloric acid, the standard heat of formation and solution of ethane-1,2-diol.

Heats of solution of all other diols were measured in the calorimeter described above at mole ratios spanning the reaction mole ratio to show that dilution effects were small. The standard heats of formation of the diols, with the exception of ethane-1,2-diol and propane-1,3-diol were taken from Moureau and Dode's [10] data. These data, reported in 1937, were corrected [11] for currently accepted values of the standard enthalpies of formation of water and carbon dioxide. Also, as the determinations were performed at 17°, the small uncertainty in combining these results with other data obtained at 25°c was expressed by the arbitrary assignment of ± 1 kcal./mole to all corrected data of Moureau and Dode. A value for the standard heat of formation of propane-1,3-diol was estimated from the above data and assigned an error of ± 2 kcal./mole. Standard heats of solution and dilution of boric acid were taken from van Artsdalen's [12] data. The standard heat of formation of boric acid (crystal) was a value of $-261\cdot47 \pm 0\cdot20$ kcal./mole reported by Good, Månsson, and McCullogh at the " Symposium on Thermodynamics and Thermochemistry," Lund, 1963.

TABLE 1.

Heats of solution and formation of diols.

Diol	T (°c)	ΔH_S (exp.)	N	ΔH_S (accepted)	ΔH°_f (liq.)
Propane-1,3-diol............	25	$-2\cdot05$	105	$\left.\right\}-2\cdot04 \pm 0\cdot02$	-112 ± 2
	25	$-2\cdot03$	206		
Propane-1,2-diol............	25·6	$-2\cdot62$	145	$\left.\right\}-2\cdot63 \pm 0\cdot01$	$-118\cdot9 \pm 1$
	25·6	$-2\cdot63$	235		
Butane-2,3-diol *	26·2	$-3\cdot57$	174	$\left.\right\}-3\cdot58 \pm 0\cdot03$	$-128\cdot7 \pm 1$
	30·5	$-3\cdot54$	263		
	30·5	$-3\cdot62$	215		
Ethane-1,2-diol	25	†	>200	$-1\cdot5 \pm 0\cdot05$	$-108\cdot74 \pm 0\cdot1$ [12]

* This diol appears to solidify over the range 22—26°c; to avoid including ΔH (fusion) terms the solution was performed at ~30° as well as at 25°. † N.B.S. Circ. 500.

[8] Gunn, *Rev. Sci. Instr.*, 1958, **29**, 377.
[9] Somsen, Coops, and Tolk, *Rec. Trav. chim.*, 1963, **82**, 231.
[10] Moureau and Dode, *Bull. Soc. chim. France*, 1937, **4**, 637.
[11] Green, *Quart. Rev.*, 1961, **15**, 130.
[12] van Artsdalen and Anderson, *J. Amer. Chem. Soc.*, 1951, **73**, 579.

The extent to which possible complexing of diols with boric acid [13] might lead to anomalous $\Delta H°_h$ values was checked by measuring the heat of solution of butane-2,3-diol in saturated boric acid solution ($\sim 6\%$ by wt.). The value obtained (-3.40 kcal./mole) indicates that the effect is negligible.

TABLE 2.

Heats of hydrolysis and formation of boron heterocycles.

Compound	T (°c) *	N	$\Delta H_{obs.}$	$\Delta H_{obs.}$ (accepted)	$\Delta H°_h$ †	$\Delta H°_f$ †
O·CH₂·CH₂·CH₂·O·BCl (I)	27·5	336	$-22·2$	$-22·15 \pm 0·4$	$-7·51$ $\pm 0·5$	$-183·1$ ± 3
	25·2	329	$-22·1$			
O·CH₂·CH₂·O·BCl (II)	25·5	1410	$-21·2$	$-21·1 \pm 0·5$	$-6·91$ $\pm 0·6$	$-180·4$ ± 1
	26	870	$-21·7$			
	25·6	2230	$-20·9$			
	26	1074	$-21·2$			
	26	1098	$-20·4$			
O·CHMeCH₂·O·BCl (III)	26·2	838	$-22·6$	$-22·55 \pm 0·2$	$-7·23$ $\pm 0·3$	$-190·3$ ± 1
	25·2	1497	$-22·5$			
O·CHMe·CHMe·O·BCl (IV)	26·5	845	$-24·1$	$-24·5 \pm 0·4$	$-8·28$ $\pm 0·5$	$-199·0$ $\pm 1·7$
	26·5	812	$-24·8$			

* The temperature recorded here is the mean value of the reaction period. † Errors were computed by summing the constituent errors.

In addition to the above hydrolyses the heat of hydrolysis of a concentrated solution of 2-chloro-1,3,2-dioxaborolan (Table 2, cpd. II) in benzene ($\sim 40\%$ by wt.) was measured. High-speed stirring and a large water : benzene ratio (approx. 50 : 1) ensures abstraction of the

TABLE 3.

Heat of hydrolysis of a benzene solution of 2-chloro-1,3,2 dioxaborolan.

Experiment	N	T	$\Delta H_{obs.}$	$\Delta H_{obs.}$ (accepted)	$\Delta H°_h$
1	356	26·6	$-22·2$	$-21·7$ $\pm 0·5$	$-7·57$ $\pm 0·6$
2	308	27·0	$-21·3$		
3	616	26·6	$-21·6$		
4	443	26·7	$-21·7$		

hydrolysis products into the aqueous medium. The heat of solution of benzene in water (aqueous solubility 0·08 g./100 g. of water) was undetectable as indicated by a control experiment.

DISCUSSION

It is generally recognised that the stereochemical requirements of the 1,3,2-dioxa-borolan structure are such that the molecule exhibits ring strain,[4] somewhat analogous to the *I*-strain postulated by Brown.[14] Such strain may be described in two ways: in terms of the energy necessary for either (*a*) conversion into a cyclic structure of zero or reduced strain (ΔH_a) or (*b*) ring-opening (ΔH_b).

Strain may be relieved with retention of the cyclic structure by formation of a tetra-hedral configuration round the boron atom either through association or through Lewis-base addition. Experimental determinations of ΔH_a, which measures this, will therefore yield a quantity which is the sum of the energies of (i) the $sp^2 \longrightarrow sp^3$ reorganisation process and (ii) the formation of the appropriate associative or donor-acceptor bonds. In this work we are concerned with molecules where neither the detailed structure of the associated forms nor the intermolecular bonding is established.[4] It is therefore premature to discuss strain solely in terms of ΔH_a and we propose a function of the type ΔH_b.

[13] Boeseken, *Adv. Carbohydrate Chem.*, 1949, **4**, 189.
[14] Brown and Gerstein, *J. Amer. Chem. Soc.*, 1950, **72**, 2926; also Brown, Fletcher, and Johannesen, *ibid.*, 1951, **73**, 212.

Standard enthalpies of formation are not suitable unless the additivity of bond-energy terms for the ring substituents is assumed. We require a function which expresses the energy of ring-opening relative to that of a compound of similar structure but which itself is unstrained. The choice of reference compound is clearly arbitrary but a suitable molecule is diethyl chloroboronate, the acyclic analogue of (IV). Accurate thermodynamic data on the hydrolysis of this compound are available from work by Skinner,[15] from whose results we derive:

$$\Delta H^{\circ}_h = 6\cdot06 \pm 0\cdot8 \text{ kcal./mole.}$$

We therefore define ΔH_b specifically by the relationship

$$\Delta H_b = \Delta H^{\circ}_h[\text{RO}_2\text{BCl, liq.}] - \Delta H^{\circ}_h[(\text{EtO})_2\text{BCl, liq.}]$$

or, in terms of standard enthalpies of formation:

$$\Delta H_b = \{\Delta H^{\circ}_f[\text{RO}_2\text{BCl, liq.}] - \Delta H^{\circ}_f[\text{R(OH)}_2, \text{liq.}]\} -$$
$$\{\Delta H^{\circ}_f[(\text{EtO})_2\text{BCl, liq.}] - 2\Delta H^{\circ}_f[\text{EtOH, liq.}]\}.$$

Values of this function, together with relevant degrees of association of the pure phases, estimated from previous work,[4] are collected in Table 4.

TABLE 4.

ΔH_b and degree of association (α).

|		ΔH_b	α
O·CH$_2$·CH$_2$·CH$_2$·O·BCl	(I)	1·4	1·1
O·CH$_2$·CH$_2$·C·BCl	(II)	0·9	~5
O·CHMe·CH$_2$·O·BCl	(III)	1·2	~3
O·CHMe·CHMe·O·BCl	(IV)	2·2	1·1

The values quoted for α depend on the extrapolation of results obtained from colligative-property measurements made on benzene solutions of concentrations up to one molar. They are therefore approximate, though unlikely to be seriously in error. This is consistent with the observations (see Tables 2 and 3) that the difference between the standard heats of hydrolysis of the borolan (II) in the pure phase and in benzene solution (4·2M) is of the order of the experimental error. Hence, it is reasonable to assume that the degree of association is the same in the pure phase as in a solution of that molarity, in accord with previous work,[4] where a plot of α against molarity appeared to become asymptotic at concentrations greater than one molar.

The amount of strain is expected to be inversely proportional to the degree of association. This relationship is observed for the dioxaborolans (II, III, and IV) [see Table 4]. The unsubstituted ring (II), which from stereochemical arguments is expected to show considerably greater strain than the analogous dioxaborinan (I) is apparently less strained in the pure phase, as expected from its highly associated state. The 4,5-dimethyl compound (IV), however, which is little associated, presumably because of steric hindrance of the two methyl groups to " stacking " structures involving O⟶B bonding, such as that in Fig. 2, shows greatest strain. This may be taken as further evidence that self-association does not involve chlorine bridging,[4] since this would be unaffected by ring substitution.

The value of ΔH_b for compound (IV) may be taken, as a first approximation, as the strain in a dioxaborolan ring. It is interesting to note that the difference between this and the corresponding value ($\Delta H'_b$) for the analogous six-membered molecule (I) is surprisingly small, of the order of 1 kcal./mole. However, it is of the same order of magnitude of the strength of (dipole-dipole) association of tris-isopropanolamine borate

[15] Skinner and Smith, *J.*, 1954, 3930.

in benzene solution.[16] Relative magnitudes of ring strain in the five and six-membered systems are illustrated in the enthalpy diagram (Fig. 3).

FIG. 2.

FIG. 3.
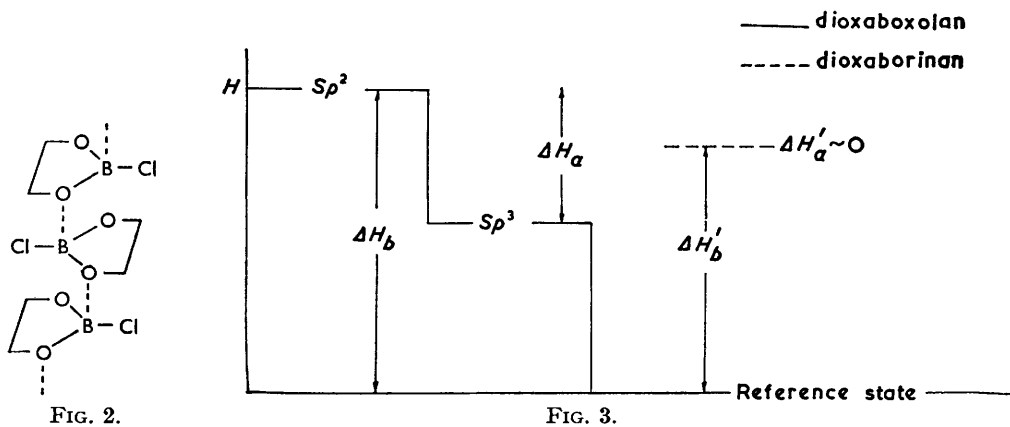
The reorganisation energy $\Delta H'_a$ in the dioxaborinan (I) is presumably less than the activation energy required for conversion into the sp^3 structure. This structure is moreover not expected, on stereochemical grounds, to be of lower energy than the trigonal configuration. Thus $\Delta H'_a \sim 0$, and formation of associated forms (or Lewis-base addition compounds) does not therefore readily occur. In view of the marked physical and chemical differences between dioxaborolans and dioxaborinans, the comparatively small enthalpy difference $(\Delta H_b - \Delta H'_b)$ of the entropy change may be the deciding factor. Dale's measurements [5] on the heat of complexing (ΔH_c) of benzylamine and pyrrolidine with the n-butoxy-series (II, III, and IV; BuO for Cl) are of interest and the results obtained with pyrrolidine are listed.

TABLE 5.

Heat of complexing of pyrrolidine with the n-butoxy-series (II, III, and IV; BuO for Cl).

	ΔH_c (kcal./mole)		ΔH_c (kcal./mole)
O·CH$_2$·CH$_2$·O·B·OBu^n	$-8\cdot3$	O·CHMe·CHMe·O·B·OBu^n ...	$-8\cdot3$
O·CHMe·CH$_2$·O·B·OBu^n	$-10\cdot5$	(Bu^{n}O)$_3$B *	$-0\cdot5$

* An unstrained molecule: comparable with the reference compound, (EtO)$_2$BCl.

These results are measures of ΔH_a and hence reflect energy terms associated with B ◄— N and not B ◄— O bonding. Neither these data nor those in Table 4 give a direct measure of $E(\text{B} ◄— \text{X})$, as bond energies are derivable from gas-phase reactions and the relevant heats of vaporisation for the compounds studied here are not available. The energies involved in amine complexing are larger, by an order of magnitude, than those observed in self-associating molecules. It is worthy of note that, in Dale's work,[5] since amine-complex formation is an equilibrium process and no complex was isolated (and only a few were precipitated in the case of benzylamine addition) the addition reactions probably did not proceed to completion. Thus, there is no certainty that the reactions were stoicheiometric, and hence the quantitative significance of the results is doubtful.

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[16] Pugh and Stokes, *Austral. J. Chem.*, 1963, **16**, 211.