427. *Thermochemistry of Organo-boron Compounds. Part I. Esters of Boric Acid.*

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From measurements of the heats of hydrolysis of four alkyl borates, the following values of the heats of formation (ΔHf°) at 25° are derived : methyl borate $-224{\cdot}0 \pm 0{\cdot}8$; ethyl borate $-251{\cdot}3 \pm 1{\cdot}0$; *n*-propyl borate $-272{\cdot}7 \pm 1{\cdot}4$; *n*-butyl borate $-291{\cdot}9 \pm 1{\cdot}5$ kcal./mole (all values refer to liquid state). The data are used to derive the *mean* bond dissociation energies of the B–O links in the alkyl borates : it is found that $\bar{D}$(B–O) in $R_3BO_3 = D$(RO–H) + x kcal./mole, where $x = 4{\cdot}1$ (R = Me), 4·3 (R = Et), $5{\cdot}0_5$ (R = Pr^n), and 5·5 (R = Bu^n). The probable value of $\bar{D}$(B–O) in alkyl borates lies in the range 110 ± 5 kcal./mole.

The thermochemistry of the organo-boron compounds has received scant attention. From the thermal standpoint this may have been partly due to the lack (until recently) of a reliable value for the heat of formation (ΔHf°) of boric oxide. Values reported for the heat of combustion of crystalline boron have ranged from 349 (Roth and Boerger, *Ber.*, 1937, **70**, 48, 971) to 281 kcal./mole (Eggergluess, Monroe, and Parker, *Trans. Faraday Soc.*, 1949, **45**, 661) : the diversity reflects the difficulty in preparing boron in a completely pure state. The new measurement of $\Delta Hf^\circ(B_2O_3$, cryst.) by Prosen and his co-workers at the National Bureau of Standards in Washington makes an ingenious indirect approach to the problem through the heats of hydrolysis and of thermal dissociation of diborane (Prosen, Johnson, and Yenchius, Nat. Bur. Stand. Techn. Rept., 1948; and personal communication from E. J. Prosen). Their value, $\Delta Hf^\circ(B_2O_3$, cryst.) $= -306{\cdot}04 \pm 0{\cdot}85$ kcal./mole, has been checked by Stegemann and Nathan by re-investigation of the heat of combustion of elementary boron (Davis, Mason, and Stegemann, *J. Amer. Chem. Soc.*, 1949, **71**, 2775).

The heat of formation of boric oxide is a prerequisite to the interpretation of the heats of combustion of organo-boron compounds, of which only one (trimethylboron) has so far been reported (Long and Norrish, *Phil. Trans.*, 1948, *A*, **241**, 598). It is also required for interpretation of the results recorded in this paper, which deals with the heats of hydrolysis of methyl, ethyl, *n*-propyl, and *n*-butyl borate. These esters are readily hydrolysed to the alkyl alcohol and boric acid. The heats of formation of the alcohols are known from their heats of combustion (Rossini, *J. Res. Nat. Bur. Stand.*, 1934, **13**, 195), and the heat of formation of boric acid (in aqueous solution) from $\Delta Hf^\circ(B_2O_3$, cryst.), the heat of solution of B_2O_3 in water (Southard, *J. Amer. Chem. Soc.*, 1941, **63**, 3147), and the heats of solution of boric acid (Smisko and Mason, *ibid.*, 1950, **72**, 3679).

Experimental

Methyl and ethyl borate were prepared according to Webster and Dennis (*J. Amer. Chem. Soc.*, 1933, **55**, 3233), and *n*-propyl and *n*-butyl borate by Bannister's method (U.S.P. 1,668,797; cf. Johnson and Tompkins, *Org. Synth.*, 1933, **13**, 16). The crude products were carefully fractionated through a gauze-packed column designed by Imperial Chemical Industries Limited, Billingham. The purified samples had b. p.s within a range of 0·1° as follows : Me_3BO_3, 67·8°/742 mm.; Et_3BO_3, 44·5°/45 mm.; Pr_3BO_3, 64·0°/9 mm.; Bu_3BO_3, 105·2°/9 mm. These samples were further distilled *in vacuo*, and collected and sealed in weighed glass phials.

The calorimeter was similar to that described by Pritchard and Skinner (*J.*, 1950, 272). For each experiment, the Dewar vessel was charged with 750 g. of distilled water, and the reactions were carried out by breaking glass phials containing known weights of the alkyl borate under the water surface. A stainless-steel plate, supported inside the Dewar vessel, served as a platform on which the phials could be shattered. The temperature changes were followed in terms of the change in resistance of a thermistor element. The apparatus was calibrated electrically, by passing a measured amount of electrical energy through the calibration heater so as to obtain a similar change in the thermistor resistance to that observed in a typical hydrolysis experiment. The Dewar vessel was immersed in an oil-bath, at 24·50°, in a constanttemperature room (23·5°). Hydrolyses occurred almost instantaneously in case of methyl and ethyl borates, rapidly with propyl borate, and rather less so with butyl borate.

RESULTS

The experimental results are summarised in the tables below. All heat quantities are quoted in units of the thermochemical calorie, defined by 1 thermochemical calorie = 4·1840 abs. joule. The observed heats of reaction, $\Delta H_{\text{obs.}}$, refer to the heats of the overall reaction,

$$R_3BO_3 \text{ (liq.)} + (n + 3)\ H_2O \text{ (liq.)} \longrightarrow (3ROH + H_3BO_3) \text{ dissolved in } n \text{ moles of } H_2O \ . \quad (1)$$

$\Delta H_{\text{obs.}}$ may be broken down into two parts, *viz.* :

$$\Delta H_{\text{obs.}} = \Delta H_{\text{hyd.}} + \Delta H_{\text{soln.}} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

where $\Delta H_{\text{hyd.}}$ measures the heat of the standard hydrolysis reaction,

$$R_3BO_3 \text{ (liq.)} + 3H_2O \text{ (liq.)} \longrightarrow 3ROH \text{ (liq.)} + H_3BO_3 \text{ (cryst.)} \quad . \ . \ . \quad (3)$$

and $\Delta H_{\text{soln.}}$ measures the net heat of solution of the products of reaction in n moles of water. Values of $\Delta H_{\text{soln.}}$ were calculated from the heats of solution of boric acid given by Smisko and Mason (*loc. cit.*) and the heats of solution of alcohols given by Bose (*Z. physikal. Chem.*, 1907, **58**, 585); for butyl borate, separate measurements of the heat of solution of butyl alcohol were made to supplement Bose's data. The following *individual* heats of solution were used (*i.e.*, ΔH at 24·5°) : MeOH = − 1·62, EtOH = − 2·35, Pr^{n}OH = − 2·40, Bu^{n}OH = − 2·27, and H_3BO_3 = + 5·17 kcal./mole; corresponding values of the net heat of solution terms ($\Delta H_{\text{soln.}}$ in eqn. 2) were : 0·31, −1·88, −2·03, and −1·54 kcal./mole in the hydrolyses of methyl, ethyl, propyl, and butyl borates respectively.

TABLE 1.

R_3BO_3 (g.)	n (moles)	$-\Delta H_{\text{obs.}}$ (kcal.)	$-\Delta H_{\text{hyd.}}$ (kcal.)	Mean $\Delta H_{\text{hyd.}}$	R_3BO_3 (g.)	n (moles)	$-\Delta H_{\text{obs.}}$ (kcal.)	$-\Delta H_{\text{hyd.}}$ (kcal.)	Mean $\Delta H_{\text{hyd.}}$
		Methyl borate					n-*Propyl borate*		
3·6876	1171	4·30	4·61		5·5070	1420	6·68	4·65	
3·7477	1152	4·28	4·59		5·3355	1465	6·59	4·56	
3·0818	1402	4·31	4·62	−4·615	6·8904	1134	6·66	4·63	−4·60
2·7186	1590	4·35	4·66	±0·05	4·9479	1581	6·73	4·70	±0·06
4·1752	1034	4·29	4·60		4·7676	1641	6·59	4·56	
3·5605	1213	4·30	4·61		7·6518	1021	6·55	4·52	
		Ethyl borate					n-*Butyl borate*		
3·2338	1876	7·23	5·35		2·0302	4715	6·19	4·65	
2·2339	2717	7·25	5·37		5·1928	1842	6·16	4·62	
2·6510	2289	7·22	5·34	−5·38	5·2796	1811	6·14	4·60	−4·66
2·3716	2559	7·24	5·36	±0·06	4·8524	1971	6·22	4·68	±0·06
2·6294	2308	7·31	5·43		4·4949	2128	6·29	4·75	
1·6160	3757	7·33	5·45						

TABLE 2. *Heats of formation of alkyl borates.*

Alkyl borate	$\Delta Hf°$ (liq.) (kcal./mole)	$\Delta Hf°$ (gas) (kcal./mole)
Me_3BO_3	−224·0 ± 0·8	−215·7 [a] (± 1·0)
Et_3BO_3	−251·3 ± 1·0	−240·8 [a] (± 1·2)
n-Pr_3BO_3	−272·7 ± 1·4	−260·9 [b] (± 2·4)
n-Bu_3BO_3	−291·9 ± 1·5	−279·4 [b] (± 2·5)

[a] Using the values λ_e^{25} (Me_3BO_3) = 8·3 kcal. and λ_e^{25} (Et_3BO_3) = 10·5 kcal., based on the vapour-pressure data of Wiberg and Sütterlin (*Z. anorg. Chem.*, 1931, **202**, 1). The estimated error in these figures is ±0·2 kcal. [b] Estimated values : λ_e (Pr_3BO_3) = 11·8 kcal.; λ_e (Bu_3BO_3) = 12·5 kcal. The errors in these estimates may be as high as ±1 kcal. The overall probable errors quoted are computed by *addition* of the uncertainties in each of the component data.

The heats of formation given in Table 2 are derived from the thermochemical equation describing the standard hydrolysis reaction (3), *i.e.*,

$$\Delta H_{\text{hyd.}} = 3\Delta Hf°(\text{ROH, liq.}) + \Delta Hf°(H_3BO_3\text{, cryst.}) - 3\Delta Hf°(H_2O\text{, liq.}) - \Delta Hf°(R_3BO_3\text{, liq.}) \quad . \ . \quad (4)$$

by using the following standard heats of formation (kcal./mole) :

MeOH (liq.) = − 57·04 ± 0·05; EtOH (liq.) = − 66·39 ± 0·10;
Pr^nOH (liq.) = − 73·27 ± 0·25; Bu^nOH (liq.) = − 79·69 ± 0·30;
H_2O (liq.) = − 68·317 ± 0·10; H_3BO_3 (cryst.) = − 262·45 ± 0·6.

DISCUSSION

The ΔHf° values of the esters of boric acid are useful for the determination of the strength of the B–O bond. We shall define the quantity $\bar{D}$(B–O), the *mean* bond-dissociation energy, by the equation :

$$\bar{D}(\text{B–O}) = (D_1 + D_2 + D_3)/3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where D_1, D_2, and D_3 are the individual bond dissociation energies corresponding to the processes

$$\begin{aligned}&\text{(i) } \mathrm{B(OR)_3} \longrightarrow \mathrm{B(OR)_2} + \mathrm{OR}: \ \Delta H_1 = D_1\\ &\text{(ii) } \mathrm{B(OR)_2} \longrightarrow \mathrm{B(OR)} + \mathrm{OR}: \ \Delta H_2 = D_2\\ &\text{(iii) } \mathrm{B(OR)} \longrightarrow \mathrm{B(gas)} + \mathrm{OR}: \ \Delta H_3 = D_3\end{aligned}$$

The sum of the three terms, D_1, D_2, and D_3, is given by the thermochemical equation

$$(D_1 + D_2 + D_3) = \Delta Hf^\circ(\text{B, g.}) + 3\Delta Hf^\circ(\text{OR, g.}) - \Delta Hf^\circ(\mathrm{R_3BO_3}, \text{g.}) \quad . \quad (6)$$

Of the terms in eqn. (6), the last is given in Table 2, and a value ΔHf°(B, g.) = 97·2 kcal./mole is recommended in the Tables of Selected Values of Chemical Thermodynamic Properties, published by the National Bureau of Standards (Table 58—1, 1949) : the term ΔHf°(OR, g.) offers some difficulty and can only be estimated approximately at the present time. We can, however, express ΔHf°(OR, g.) in an alternative manner, in terms of the O–H bond dissociation energies in the alcohols, *viz.* :

$$\Delta Hf^\circ(\text{OR, g.}) = D(\text{RO–H}) + \Delta Hf^\circ(\text{ROH, g.}) - \Delta Hf^\circ(\text{H, g.}) \quad . \quad . \quad (7)$$

Combining eqns. (6) and (7), and using the well-established ΔHf°(H, g.) = 52·09 kcal./mole, one obtains

$$(D_1 + D_2 + D_3) = 3D(\text{RO–H}) + 3\Delta Hf^\circ(\text{ROH, g.}) - \Delta Hf^\circ(\mathrm{R_3BO_3}, \text{g.}) - 59{\cdot}07. \quad (8)$$

From eqn. (8), and the ΔHf°(ROH, g.) values given by Rossini (*loc. cit.*), the following $\bar{D}$ values in the boric esters are derived :

$\bar{D}$ in Me_3BO_3 = D(MeO–H) + 4·1 kcal./mole
$\bar{D}$ in Et_3BO_3 = D(EtO–H) + 4·3 kcal./mole
$\bar{D}$ in Pr_3BO_3 = D(PrO–H) + 5·05 kcal./mole
$\bar{D}$ in Bu_3BO_3 = D(BuO–H) + 5·5 kcal./mole

Values of the O–H bond dissociation energies in the straight-chain alkyl alcohols have not yet been measured experimentally, but in one case (*tert.*-butyl alcohol) Murawski, Roberts, and Szwarc (*J. Chem. Phys.*, 1951, **19**, 698) have derived the value $D(Bu^tO\text{–}H)$ = 106 kcal./mole. This figure might reasonably be accepted as a rough guide to the order of magnitude of D(RO–H) in general : it is not incompatible with an indirect evaluation that can be made, following a suggestion by Gray (*Discuss. Faraday Soc.*, 1951, **10**, 310). Gray pointed out that the initial step in the thermal decomposition of alkyl nitrates and nitrites occurs at the O–N bond, giving the radical RO– and the corresponding oxide of nitrogen—NO in nitrites, NO_2 in nitrates—so that it is perhaps permissible to identify the activation energy of the unimolecular thermal decomposition with the heat of fission of the O–N bond. In this event, the heats of formation of the radicals MeO– and EtO– may be derived from the following experimental data :

(i) EtO·NO (g.) $\longrightarrow$ EtO + NO; ΔH = 37·7 kcal./mole[a];
ΔHf°(EtO·NO, g.) = – 24·8 kcal./mole[b]; ΔHf°(NO, g.) = 21·6 kcal./mole[b];
whence ΔHf°(EtO) = – 8·7 kcal./mole.
(ii) EtO·NO_2 (g.) $\longrightarrow$ EtO + NO; ΔH = 39·5 kcal./mole[c];
ΔHf°(EtO·NO_2, g.) = – 36·2 kcal./mole[b]; ΔHf°(NO_2, g.) = 8·1 kcal./mole[b];
whence ΔHf°(EtO) = – 4·8 kcal./mole.
(iii) MeO·NO (g.) $\longrightarrow$ MeO + NO; ΔH = 36·4 kcal./mole[a];
ΔHf°(MeO·NO, g.) = – 16·7 kcal./mole[c];
whence ΔHf°(MeO) = – 1·9 kcal./mole.
(iv) MeO·NO_2 (g.) $\longrightarrow$ MeO + NO_2; ΔH = 39·5 kcal./mole[c];
ΔHf°(MeO·NO_2, g.) = 29·4 kcal./mole[c];
whence ΔHf°(MeO) = 2·0 kcal./mole.

[a] Steacie and Shaw, *J. Chem. Phys.*, 1934, **2**, 345. [b] Selected Values of Chemical Thermodynamic Properties. [c] Data quoted by Gray (*loc. cit.*).

The mean values, ΔHf°(EtO) = – 6·8 kcal./mole and ΔHf°(MeO) = 0·0 kcal./mole, correspond to the values D(EtO–H) = 101·5 kcal./mole and D(MeO–H) = 100·1 kcal./mole. These figures should be accepted with reserve, as both the kinetic and the thermochemical data used in their derivation require confirmation. On the basis of the admittedly inadequate evidence referred to above, we have chosen a value D(RO–H) = 105 ± 5 kcal./mole, leading to values of the mean B–O bond dissociation energies in the alkyl borates in the range 110 ± 5 kcal./mole.

The B–O bond is thus one of the strongest bonds formed by the boron atom, as may be seen from Table 3 in which are listed $\bar{D}$ values of a number of bonds to boron.

TABLE 3. *Mean bond dissociation energies of boron bonds.*

Molecule	ΔHf° (gas)	Bond	$\bar{D}$ (kcal./mole)
BF_3	–267·5	B–F	140·5
R_3BO_3	Table 2	B–O	110 ± 5
BCl_3	–96·6	B–Cl	93·6
BBr_3	–46·7	B–Br	74·7
BMe_3	–27·4	B–C	73·9

According to Sidgwick ("Chemical Elements and their Compounds," Oxford Univ. Press, Vol. I, 1950) the most stable links of boron are in the order B–F > B–N > B–O > B–Cl, but thermochemical evidence is not given to substantiate the statement. The present work justifies Sidgwick's placing B–O between B–F and B–Cl. The position of B–N in the series seems to us anomalous, and thermochemical studies leading to the B–N bond-energy are planned.

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