677. *The Thermochemistry of Organo-boron Compounds. Part II.* Tri-*n*-butylboron, and the Di-*n*-butylboron Halides.*

By H. A. Skinner and T. F. S. Tees.

Values are reported for the heats of reaction of liquid tributylboron (*a*) with hydrogen bromide at 56·5° ($\Delta H = -22{\cdot}6 \pm 1$ kcal./mole) and (*b*) with hydrogen iodide at 25° ($\Delta H = -20{\cdot}2 \pm 0{\cdot}7$ kcal./mole). The heats of hydrolysis of the liquid dibutylboron halides in water at 25° were measured as follows: chloride, $\Delta H = -18{\cdot}54 \pm 0{\cdot}2$; bromide, $\Delta H = -21{\cdot}96 \pm 0{\cdot}5$; iodide, $\Delta H = -24{\cdot}94 \pm 0{\cdot}5$ kcal./mole. The latent heats of vaporisation of tributylboron, dibutylboron chloride, and dibutylboron bromide were obtained from vapour-pressure measurements of these substances over a range of temperature.

The assumption that the dissociation energy $D(\mathrm{Bu_2B{-}Cl})$ is the same as the mean bond-dissociation energy in boron trichloride, leads to the following values (kcal./mole): $D(\mathrm{Bu_2B{-}OH}) = 118{\cdot}3$, $D(\mathrm{Bu_2B{-}Cl}) = 93{\cdot}9$, $D(\mathrm{Bu_2B{-}Br}) = 74{\cdot}7$, $D(\mathrm{Bu_2B{-}I}) = 56{\cdot}2$. The differences between these D values are established, although the absolute magnitude of the D values depends on the initial assumption.

Thermochemical information on the alkylborons is limited to the single item of the heat of combustion of trimethylboron (Long and Norrish, *Phil. Trans.*, 1949, **241**, *A*, 587). By combining the heat of combustion with the value for the heat of formation of boric oxide (Prosen, Johnson, and Pergiel, Nat. Bur. Stand. Report No. 1552, March, 1952), one may derive the heat of formation of trimethylboron, *viz.*, ΔHf° (BMe_3, liq.) = $-33{\cdot}5$ kcal./mole, and ΔHf° (BMe_3, gas) = $-27{\cdot}8$ kcal./mole. Long and Norrish estimate the limits of error in the combustion heat measurements at 0·4%, or ±3 kcal./mole; Prosen *et al.* assign a maximum error of ±0·75 kcal./mole to their value for ΔHf° (B_2O_3, cryst.), so that the overall error associated with ΔHf° (BMe_3) may be *ca.* ±4 kcal./mole. These data lead to a derived value for the *mean* B–CH_3 bond-dissociation energy in trimethylboron of $74{\cdot}3 \pm 3$ kcal./mole (cf. Part I, *loc. cit.*).

In this paper, we report some thermochemical studies on tri-*n*-butylboron and on the di-*n*-butylboron halides: this work is part of a series of studies on boron compounds now being made. The chemistry of tri-*n*-butylboron has been examined in detail by Johnson, Snyder, and van Campen (*J. Amer. Chem. Soc.*, 1938, **60**, 115), who describe a number of the simpler reactions, some of which are stated to take place quantitatively. Such reactions should prove amenable to thermal study, and one of them (tributylboron and hydrogen bromide) is examined here. The reaction

$$\mathrm{BBu_3 + HBr \longrightarrow BBu_2Br} + n\text{-}\mathrm{C_4H_{10}} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

takes place with moderate speed at 60°, and gives an almost quantitative yield (>99%) of dibutylboron bromide. This reaction (and the similar reaction with hydrogen iodide) was studied thermally in the adiabatic calorimeter described below.

Di-*n*-butylboron chloride may be prepared by the analogous reaction to (1) with hydrogen chloride and we have found that the reaction of tributylboron and hydrogen iodide takes place easily at room temperature to give dibutylboron iodide, a compound not previously described. Each of the dibutylboron halides is hydrolysed readily, and the heats of hydrolysis are now reported.

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* Part I, Charnley, Skinner, and Smith, *J.*, 1952, 2288.

EXPERIMENTAL

(a) *Preparation of Compounds.*—Tri-*n*-butylboron was prepared by interaction of the complex of boron trifluoride and ethyl ether with *n*-butylmagnesium bromide, according to Johnson, Snyder, and van Campen (*loc. cit.*). The crude product was purified by fractional distillation in a pure nitrogen atmosphere at low pressure (5—8 mm.).

Di-*n*-butylboron chloride was prepared, as described by Booth and Kraus (*J. Amer. Chem. Soc.*, 1952, **74**, 1415), by interaction of hydrogen chloride with tributylboron at 110°. The bromide was prepared by the analogous reaction at 60°, and the iodide by passing hydrogen iodide through tributylboron at room temperature. The halide derivatives were purified by fractional distillation at low pressures; the chloride and bromide (both of which are more volatile than tributylboron) were thus obtained pure without difficulty; but the iodide, which is of very similar volatility to tributylboron, could not be completely separated from the trialkylboron, and the best samples prepared were not more than 90—95% pure.

Tributylboron and the dibutylboron halides are rapidly oxidised in air, and all manipulation of these compounds was done *in vacuo* or in an atmosphere of pure nitrogen.

(b) *Calorimeters.*—The adiabatic calorimeter was designed and built for us by Dr. T. Charnley. The reactions were carried out in the glass reaction vessel (see figure), the body of which was completely immersed in transformer oil contained in a Dewar vessel of *ca.* 1 l. capacity. The Dewar vessel itself was encased by a metal can, fitted with a flanged metal lid. The whole assembly of the Dewar vessel was immersed in the outer oil-bath. A set of differential thermocouples, working between the contents of the Dewar flask and the outer oil-bath, operated heaters in the latter to maintain a small constant temperature difference between the two; the adiabatic condition was held automatically by a galvanometer–photocell control, similar to that described by Carson, Hartley, and Skinner (*Proc. Roy. Soc.*, 1949, **195**, *A*, 500). The glass reaction vessel was divided by a flat plate into an upper reaction compartment, of *ca.* 190 c.c. capacity, and a lower mercury-filled compartment which gave ballast to the vessel. A capillary inlet, entering the reaction vessel centrally, terminated at the upper end in a cone-tap seal. The reaction vessel was floated on a pool of mercury lying in the bottom of the Dewar vessel, and was held in a central position within the Dewar flask by a bearing in the flange lid. The reaction vessel could be rotated at constant speed (150 r.p.m.) by a drive from an induction motor to the capillary inlet. The motor was supported vertically above the oil tank. The temperature of the calorimetric fluid (light transformer oil) was measured in terms of the resistance of a shielded thermistor element. This was held in a fixed position in the Dewar vessel from a chimney in the flange lid. Two similar chimneys allowed the entrance of the Dewar thermocouples (ten copper–constantan units in series) and of an encased wire-wound heating-coil. This latter was used in the electrical calibration of the calorimeter, and it also served to supply heat to the contents of the Dewar vessel to bring them to the desired starting temperature.

The hydrolysis reactions were carried out in the calorimeter previously described in Part I (*loc. cit.*). The hydrolyses were studied at 25°.

(c) *Units.*—The unit of heat in which all the results are given is the thermochemical calorie (4·1840 abs. joules).

(d) *Vapour Pressures.*—The vapour pressures of pure samples of tributyboron, dibutylboron chloride, and dibutylboron bromide were measured over a range of temperature (20—90°) in an apparatus similar to that described by Burg and Schlesinger (*J. Amer. Chem. Soc.*, 1937, **59**, 780). The results are presented in the vapour-pressure equations given below, from which the latent heats of vaporisation were derived by application of the Clapeyron–Clausius equation :

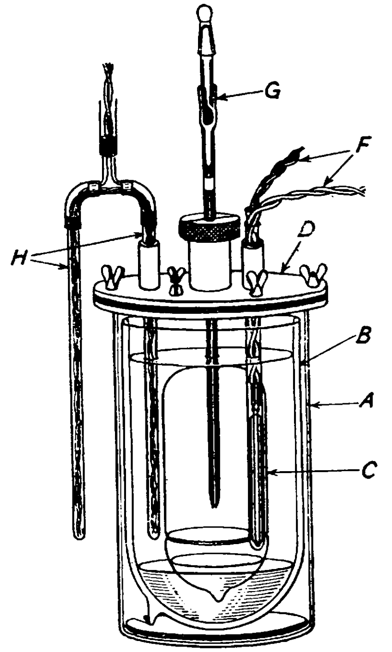
Tributylboron : $\log p = 8{\cdot}797 - 2857/T$; $\lambda_{\text{vap.}} = 13{\cdot}07\ (\pm 0{\cdot}25)$ kcal./mole.
Dibutylboron bromide : $\log p = 8{\cdot}682 - 2643/T$; $\lambda_{\text{vap.}} = 12{\cdot}09\ (\pm 0{\cdot}20)$ kcal./mole.
Dibutylboron chloride : $\log p = 8{\cdot}592 - 2518/T$; $\lambda_{\text{vap.}} = 11{\cdot}52\ (\pm 0{\cdot}20)$ kcal./mole.

Results.—(a) *Reaction of hydrogen bromide with tributylboron.* This reaction was studied at 56·5°, at which temperature complete reaction times of 1—2 hr. were required, and adiabatic calorimetry was adopted to deal with this comparatively slow reaction. The reaction occurs cleanly, yielding butane and dibutylboron bromide. The extent of the reaction was analysed by measuring the volume of butane produced, and by titration of the bromide ion obtained on hydrolysis of the dibutylboron bromide formed.

The experimental procedure was as follows : a sample of tributylboron was distilled from stock *in vacuo*, and condensed in the reaction vessel, which was then fitted in position in the

Dewar vessel, the flanged lid bolted on, and the assembly lowered into the outer oil-bath. The temperature of both bath and Dewar flask contents was raised to *ca.* 56°, and the automatic adiabatic control mechanism then set in action. The reaction vessel was connected to the stirring motor, and the system allowed to reach thermal equilibrium.

The thermistor resistance was measured at regular intervals during an hour or more, before the reaction was started. The stirring motor was then temporarily disconnected,* whilst hydrogen bromide (preheated to the bath-temperature) was allowed to enter and fill the reaction vessel *via* the cone-tap seal of the capillary inlet. (The tributylboron was present, initially, under vacuum; on the cone-tap's being turned, the hydrogen bromide entered to fill the vacuous space.) The reaction vessel then reconnected to the stirring motor, and the measurements of the thermistor resistance were recorded for a further period of *ca.* 120 min.



A, Metal can; B, Dewar vessel; C, glass reaction vessel; D, flanged lid; F, thermistor and heater leads; G, cone-tap seal; H, thermocouples.

The reaction vessel was removed from the calorimeter, and attached to the gas-analysis apparatus. The volume of butane was measured at 20° (corrections to ideal gas and standard conditions were made from the data of Sagi, Webster, and Lacey, *Ind. Eng. Chem.*, 1937, **29**, 118). The dibutylboron bromide (retained in the reaction vessel) was hydrolysed with distilled water, and the hydrobromic acid determined by titration (Volhard's method). In general, agreement within 2% was attained between the analyses based on butane and those based on bromide ion.

The observed heats ($\Delta H_{\text{obs.}}$) of the reaction (at 56·5°) :

$$\text{BBu}_3 \text{ (liq.)} + \text{HBr (g.)} \longrightarrow \text{BBu}_2\text{Br (liq.)} + \text{BuH (g.)} \quad . \quad . \quad . \quad (2)$$

are listed in Table 1. Here, the moles of borine are mean values as determined by butane and bromide-ion analyses. The final column of Table 1 gives the values of $(x - a)$, where $x = \Delta Hf^\circ$ (BBu_3, liq.), and $a = \Delta Hf^\circ$ (BBu_2Br, liq.), derived from the thermal equation † :

$$(x - a) = \Delta Hf^\circ \text{ (BuH, g.)} - \Delta Hf^\circ \text{ (HBr, g.)} - \Delta H_{\text{obs.}} \quad . \quad . \quad . \quad (3)$$

The values ΔHf° (BuH, g.) $= -29{\cdot}81$ kcal./mole and ΔHf° (HBr, g.) $= -8{\cdot}66$ kcal./mole recommended in N.B.S. tables (Circular 500), were used in calculating $(x - a)$. The overall limits of error in $\Delta H_{\text{obs.}}$ we would estimate at *ca.* ± 1 kcal./mole, arising partly from the possible

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* Correction for the stirring-heat loss during this period was made by applying a similar stirring interruption in the electrical calibration experiments.

† In this equation, we have assumed that the observed heat of reaction at 56·5° may be carried over unchanged to the standard temperature of 25°, and that the heats of mixing of liquid dibutylboron bromide with the excess of tributylboron, and of solution of the gaseous butane in the small volume of liquid product in the reaction vessel, are negligible.

error of *ca.* ±2% in the estimation of the moles of borine which reacted, and from an error of similar magnitude in the operation of the calorimeter.

TABLE 1. *Reaction of tributylboron and hydrogen bromide.*

Expt.	BBu_3 (10^{-2} mole)	$-\Delta H_{obs.}$ (kcal.)	$(x - a)$ (kcal.)	Expt.	BBu_3 (10^{-2} mole)	$-\Delta H_{obs.}$ (kcal.)	$(x - a)$ (kcal.)
1	0·7585	22·33	1·18	4	0·7474	23·42	2·27
2	0·7606	22·87	1·72	5	0·7678	22·09	0·94
3	0·7716	22·11	0·96		Mean values	22·56	1·41

(b) *Reaction of hydrogen iodide with tributylboron.* This reaction occurs at moderate speed at room temperature, so we were able to investigate it at the standard temperature (25°). Otherwise, the procedure was similar to that used in the analogous reaction with hydrogen bromide. The extent of reaction was measured by the volume of butane produced, and by titration of hydrolysable iodine in the product, dibutylboron iodide. Good agreement (generally within 1%) was obtained between these two measures.

A selection from the results is presented in Table 2. Observed reaction heats are listed under $\Delta H_{obs.}$, and the final column gives values of $(x - b)$, where $x = \Delta Hf^\circ$ (BBu_3, liq.), $b = \Delta Hf^\circ$ (BBu_2I, liq.), derived from the thermal equation

$$(x - b) = \Delta Hf^\circ\ (\text{BuH, g.}) - \Delta Hf^\circ\ (\text{HI, g.}) - \Delta H_{obs.} \quad . \quad . \quad . \quad . \quad (4)$$

The values recommended in the N.B.S. tables (Circular 500) were accepted, *viz.*, ΔHf° (BuH, g.) = −29·81, ΔHf° (HI, g.) = 6·20 kcal./mole.

TABLE 2. *Reaction of tributylboron and hydrogen iodide.*

Expt.	BBu_3 (10^{-2} mole)	$-\Delta H_{obs.}$ (kcal.)	$(x - b)$ (kcal.)	Expt.	BBu_3 (10^{-2} mole)	$-\Delta H_{obs.}$ (kcal.)	$(x - b)$ (kcal.)
1	0·8542	20·24	−15·77	4	0·8129	20·04	−15·97
2	0·8620	20·00	−16·01	5	0·7915	20·35	−15·66
3	0·7900	20·15	−15·86		Mean values	20·16	−15·85

TABLE 3. *Heats of hydrolysis of dibutylboron halides.*

Halide (10^{-2} mole)	n	$-\Delta H_{obs.}$ (kcal.)	$y - \Delta Hf^\circ$ (Bu_2BX) (kcal.)	Halide (10^{-2} mole)	n	$-\Delta H_{obs.}$ (kcal.)	$y - \Delta Hf^\circ$ (Bu_2BX) (kcal.)
			Dibutylboron chloride.				
0·6547	6400	18·45	−46·79	0·5620	7400	18·64	−46·98
0·8680	4800	18·56	−46·91	1·635	2500	18·48	−46·85
0·8350	5000	18·57	−46·92	Mean values :		18·54	−46·89 (± 0·2)
			Dibutylboron bromide.				
0·4563	9100	22·00	−61·46	0·5415	7700	21·41	−60·85
0·5502	7570	22·00	−61·46	0·6950	6050	21·94	−61·40
0·5931	7050	22·47	−61·93	Mean values :		21·96	−61·42 (±0·5)
			Dibutylboron iodide.				
0·6097	6850	24·81	−79·79	0·8805	4730	24·99	−79·98
0·5693	7300	25·54	−80·52	0·5183	8000	24·58	−79·56
0·7508	5550	24·73	−79·72	Mean values :		24·94	−79·93 (±0·5)
0·5970	7000	25·01	−79·99				

The overall error in $\Delta H_{obs.}$ is estimated at *ca.* ±¾ kcal./mole.

(c) *Hydrolysis of the dibutylboron halides.* The dibutylboron halides are hydrolysed rapidly at room temperature, to form the corresponding halogen hydracids and dibutylboronic acid, $Bu_2B{\cdot}OH$, which is a sparingly soluble oily liquid absorbing oxygen from the air with evolution of heat. To avoid the spurious thermal effects that might ensue from this oxidation process, all the hydrolysis experiments were conducted under an atmosphere of pure nitrogen.

The measured heats of hydrolysis ($\Delta H_{obs.}$) given in Table 3 refer to the general equation :

$$Bu_2BX(\text{liq.}) + (n + 1)H_2O(\text{liq.}) \longrightarrow Bu_2B{\cdot}OH(\text{liq.}) + HX{,}nH_2O(\text{soln.}) \quad . \quad . \quad (5)$$

This equation leads to the thermochemical relation

$$\Delta Hf^\circ\ (Bu_2B{\cdot}OH,\ \text{liq.}) - \Delta Hf^\circ\ (Bu_2BX,\ \text{liq.}) = \Delta H_{obs.} + \Delta Hf^\circ\ (H_2O,\ \text{liq.}) - \Delta Hf^\circ\ (HX{,}nH_2O) \quad . \quad (6)$$

The value of ΔHf° ($Bu_2B{\cdot}OH$, liq.) is represented in Table 3 by the symbol y, and is not known independently at present. The values of ΔHf° (H_2O, liq.) and ΔHf° ($HX{,}nH_2O$) were taken from the N.B.S. tables (Circular 500).

The experiments were conducted by breaking thin glass ampoules containing known weights of dibutylboron halide under the surface of 750 g. of distilled water, contained in the Dewar-vessel calorimeter. The temperature changes were followed in terms of the resistance change of a shielded thermistor element immersed in the reaction vessel. At the end of each experiment, aliquot samples of the solution in the Dewar vessel were analysed for their halogen content (Volhard's method), as a check on purity of the dibutylboron halide used. The samples of dibutylboron chloride and bromide were found to be not less than 99% pure, but the iodide was only 90—95% pure (see p. 3379). The thermal results given on dibutylboron iodide in Table 3 are based on the purity as determined by halogen content.

DISCUSSION

The results of the previous section may be summarised in the five equations (all in terms of kcal./mole), *viz.*, (i) $x - a = 1{\cdot}41 \pm 1$, (ii) $x - b = -15{\cdot}85 \pm 0{\cdot}75$, (iii) $y - a = -61{\cdot}42 \pm 0{\cdot}5$, (iv) $y - b = -79{\cdot}93 \pm 0{\cdot}5$, and (v) $y - c = -46{\cdot}89 \pm 0{\cdot}2$, where $c = \Delta Hf^\circ$ (BBu_2Cl, liq.), and x, y, a, and b have already been defined. By combining equations (i) and (ii), one obtains $(a - b) = -17{\cdot}26 \pm 1{\cdot}75$, compared with $(a - b) = -18{\cdot}51 \pm 1{\cdot}0$ from equations (iii) and (iv). The equations are thus not entirely consistent with each other, although the inconsistencies appear to lie well within the combined error limits attached to the individual measurements.

It is convenient to express the quantities y, a, b, and c in terms of the single unknown, x. The following mean values are obtained:

$$y = \Delta Hf^\circ\ (BBu_2{\cdot}OH,\ \text{liq.}) = x - 63{\cdot}45\ (\pm 1{\cdot}4)\ \text{kcal./mole} \quad . \quad . \quad . \quad (7)$$

$$c = \Delta Hf^\circ\ (BBu_2Cl,\ \text{liq.}) = x - 16{\cdot}56\ (\pm 1{\cdot}6)\ \text{kcal./mole} \quad . \quad . \quad . \quad (8)$$

$$a = \Delta Hf^\circ\ (BBu_2Br,\ \text{liq.}) = x - 1{\cdot}72\ (\pm 1{\cdot}5)\ \text{kcal./mole} \quad . \quad . \quad . \quad (9)$$

$$b = \Delta Hf^\circ\ (BBu_2I,\ \text{liq.}) = x + 16{\cdot}16\ (\pm 1{\cdot}4)\ \text{kcal./mole} \quad . \quad . \quad (10)$$

In these equations, x is the heat of formation of *liquid* tributylboron; for the further discussion we shall require the set of equations (11)—(14), in which the ΔHf° terms relate to the *gaseous* states of the molecules concerned, *viz.*:

$$y' = \Delta Hf^\circ\ (BBu_2{\cdot}OH,\ \text{g.}) = x' - 61{\cdot}5\ (\pm 3)\ \text{kcal./mole} \quad . \quad . \quad . \quad (11)$$

$$c' = \Delta Hf^\circ\ (BBu_2Cl,\ \text{g.}) = x' - 18{\cdot}11\ (\pm 2)\ \text{kcal./mole} \quad . \quad . \quad . \quad (12)$$

$$a' = \Delta Hf^\circ\ (BBu_2Br,\ \text{g.}) = x' - 2{\cdot}70\ (\pm 2)\ \text{kcal./mole} \quad . \quad . \quad . \quad (13)$$

$$b' = \Delta Hf^\circ\ (BBu_2I,\ \text{g.}) = x' + 16{\cdot}1\ (\pm 2{\cdot}2)\ \text{kcal./mole} \quad . \quad . \quad . \quad (14)$$

Eqns. (11)—(14) make use of the heats of vaporisation given on p. 3379, and of two *assumed* values,* $\lambda_{\text{vap.}}$ (BBu_2I) $= 13 \pm 0{\cdot}5$, and $\lambda_{\text{vap.}}$ ($BBu_2{\cdot}OH$) $= 15 \pm 2$ kcal./mole.

Although the value x' has not yet been determined, it is nevertheless possible to examine a number of bond-energy inter-relations in these molecules, starting from the equations (11)—(14). Consider the (gaseous) dissociation process $Bu_2BX \longrightarrow Bu_2B + X$, and let the heat of disruption (the bond-dissociation energy) be represented by $D(Bu_2B\text{–}X)$; correspondingly, for the process $Bu_2BY \longrightarrow Bu_2B + Y$, the bond-dissociation energy is represented by $D(Bu_2B\text{–}Y)$. Then we may write, quite generally, the thermal equation:

$$\Delta D\begin{bmatrix} X \\ Y \end{bmatrix} = D(Bu_2B\text{–}X) - D(Bu_2B\text{–}Y) = \Delta Hf^\circ\ (X) - \Delta Hf^\circ\ (Y) + \Delta Hf^\circ\ (BBu_2Y) - \Delta Hf^\circ\ (BBu_2X) \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Accepting the values (recommended in the N.B.S. tables) ΔHf° (OH, g.) $= 10{\cdot}0$, ΔHf° (Cl, g.) $= 29{\cdot}0$, ΔHf° (Br, g.) $= 26{\cdot}7$, and ΔHf° (I, g.) $= 25{\cdot}5$ kcal./mole, together with the eqns. (11)—(14), and applying eqn. (15), we obtain:

$$\Delta D\begin{bmatrix} OH \\ Cl \end{bmatrix} = 24{\cdot}4\ (\pm 5)\ \text{kcal./mole},\ \Delta D\begin{bmatrix} Cl \\ Br \end{bmatrix} = 17{\cdot}7\ (\pm 4),\ \text{and}\ \Delta D\begin{bmatrix} Br \\ I \end{bmatrix} = 20{\cdot}0\ (\pm 4).$$

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* The similarity in volatility of BBu_2I and BBu_3 suggests that the values of $\lambda_{\text{vap.}}$ of these compounds are of the same magnitude. The $\lambda_{\text{vap.}}$ of alcohols, relative to alkyl iodides, are generally larger by 2—3 kcal./mole, and a similar difference is assumed between the $\lambda_{\text{vap.}}$ of $BBu_2{\cdot}OH$ and BBu_2I.

These ΔD relations represent the limiting point to which we can go in a strict manner at present. To proceed further requires the measure of at least one of the D values involved, or alternatively, we need to introduce at least one assumption.

The assumption commonly made in problems of this type is also the simplest—*i.e.*, the assumption of constant bond-energy terms, transferable from one molecule to another. In the present case, *e.g.*, we might assume that $D(\mathrm{Bu_2B{-}Cl})$ is the same as the mean bond-dissociation energy, $\bar{D}(\mathrm{B{-}Cl})$, in boron trichloride. The heat of formation of boron trichloride has been determined recently by Skinner and Smith (*Trans. Faraday Soc.*, 1953, **49**, 601) and by Johnson, Miller, and Prosen (N.B.S. Report No. 2257, Jan., 1953), from which the value $\bar{D}(\mathrm{B{-}Cl}) = 93{\cdot}9$ kcal./mole may be derived [ΔHf° (BCl_3, g.) $= -97{\cdot}5$; ΔHf° (B, g.) $= 97{\cdot}2$ kcal./mole]. The identification of $D(\mathrm{B{-}Cl})$ with $D(\mathrm{Bu_2B{-}Cl})$ then leads to the additional values: $D(\mathrm{Bu_2B{-}OH}) = 118{\cdot}3$ $D(\mathrm{Bu_2B{-}Br}) = 76{\cdot}2$, and $D(\mathrm{Bu_2B{-}I}) = 56{\cdot}2$ kcal./mole. It is encouraging to note that the value obtained for $D(\mathrm{Bu_2B{-}Br})$ is close to the value, $\bar{D}(\mathrm{B{-}Br}) = 74{\cdot}7$ kcal./mole, determined from the heat of formation of boron tribromide (Part I, *loc. cit.*)—so that we may accordingly predict the unknown $D(\mathrm{B{-}I})$ in boron tri-iodide at 56 ± 5 kcal./mole with some measure of confidence. The value obtained for $D(\mathrm{Bu_2B{-}OH})$ is appreciably larger than the run of values $\bar{D}(\mathrm{B{-}OR})$ in the alkyl borates, $B(OR)_3$ (Charnley, Mortimer, and Skinner, *J.*, 1953, 1181), but this is a not uncommon feature that emerges from a comparison of dissociation energies of the type M–OH and M–OR—*e.g.*, $D(\mathrm{H{-}OH}) = 119$ kcal./mole, whereas $D(\mathrm{H{-}OMe}) = 99$ kcal./mole.

The assumption of constant transferable bond-energy terms may be alternatively expressed in the statement that redistribution reactions involve no overall change in enthalpy.* Applied to the present case, this assumption would allow us to write: $2BBu_3(g.) + BCl_3(g.) \longrightarrow 3BBu_2Cl(g.)$, $\Delta H = 0$, from which it would follow that $x' = \Delta Hf^\circ$ (BBu_3, g.) $= -43{\cdot}2$ (± 7) kcal./mole. This estimate leads to the value $\bar{D}(\mathrm{B{-}Bu}) = 66{\cdot}3$ (± 3) kcal./mole [ΔHf° (Bu, g.) $= 19{\cdot}5$ (± 1) kcal./mole, from Mortimer, Pritchard, and Skinner, *Trans. Faraday Soc.*, 1952, **48**, 220, and Stevenson, *Discuss. Faraday Soc.*, 1951, **10**, 113].

However, several redistribution reactions are known which do not comply with the thermoneutrality condition as required by the simple postulate of constant bond-energy terms. The reactions, for example, of the type $HgR_2 + HgX_2 \longrightarrow 2HgRX$ (Hartley, Pritchard, and Skinner, *Trans. Faraday Soc.*, 1950, **46**, 1019; and later papers in this series) are usually exothermic, and we suspect that the reaction discussed above may be similar in this respect. We reserve further comment pending an independent determination of the heat of formation of tributylboron.

Added in Proof.—Our attention has recently been drawn to a new determination of the heat of sublimation of boron by Searcy and Myers, who obtained ΔHf° (B,g.) $= 140{\cdot}9 \pm 2{\cdot}0$ kcal./mole. This value differs appreciably from the figure recommended in the N.B.S. tables (97·2 kcal./mole) which is used in this paper. If the new value is accepted, *all D* and $\bar{D}$ values of boron bonds given in the text are *increased* in magnitude by 14·6 kcal./mole.

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* A redistribution reaction is one in which bonds may change in relative position, but not in total number or formal character.