820. *The Thermochemistry of Organo-boron Compounds. Part III.* Trisdimethylaminoborine,* $B(NMe_2)_3$. *The Strength of the Boron–Nitrogen Link.*

By H. A. Skinner and N. B. Smith.

The heat of hydrolysis of trisdimethylaminoborine in N-hydrochloric acid has been measured at 25°: $\Delta H_{obs.} = -68{\cdot}8 \pm 0{\cdot}3$ kcal./mole. From this, the heat of formation of liquid trisdimethylaminoborine is derived: $\Delta Hf^\circ[B(NMe_2)_3, liq.] = -77{\cdot}1 \pm 1{\cdot}0$ kcal./mole.

The mean bond dissociation energy of the $B-NMe_2$ bond in $B(NMe_2)_3$ is obtained relative to the N–H dissociation energy in dimethylamine: $\bar{D}(B-NMe_2) = D(H-NMe_2) - 4{\cdot}3$ kcal./mole. An estimate of $D(H-NMe_2) \sim 94$ kcal./mole is made, leading to $\bar{D}(B-NMe_2) = 89{\cdot}7$ kcal./mol.

Mean bond energy term values, $\bar{E}(B-N)$, in trichloroborazole and in trisdimethylaminoborine are obtained in good agreement with one another. The differences between the bond dissociation energies of some B–O and B–N linkages in the covalent and the co-ordinate forms are examined and discussed.

TRISDIMETHYLAMINOBORINE is a colourless oil that floats on water, and is but slowly hydrolysed at room temperature. In acid solution, however, hydrolysis is much faster, and hydrolysis in N-hydrochloric acid proved to be a suitable reaction for thermal study. The products of hydrolysis—boric acid and dimethylamine hydrochloride—are both of known heat content, so that the heat of hydrolysis enables the heat of formation (ΔHf°) of the borine derivative to be determined. Thence an estimate of the strength of the B–N bond can be made.

EXPERIMENTAL

Preparation of Compounds.—Wiberg and Schüster (*Z. anorg. Chem.*, 1933, **213**, 94) have described the preparation of trisdimethylaminoborine by interaction of dimethylamine and boron trichloride. We used Coates's modification of this method (*J.*, 1950, 3481). Boron trichloride, dissolved in dry pentane, was added slowly with stirring to a solution of dimethylamine in pentane, cooled in ice–salt. Six equivs. of dimethylamine were used for each equiv. of boron trichloride. The solid products formed (mainly dimethylamine hydrochloride) were separated by filtration, and the excess of pentane was distilled away *via* a filter pump. The remaining liquid was distilled through a 6″ steel-gauze-packed column under reduced pressure. The fraction of b. p. 43°/12 mm. was retained. After further distillation *in vacuo*, the pure product was collected and sealed in thin weighed glass ampoules.

Calorimeter.—The calorimeter has been described previously (Skinner and Smith, *Trans. Faraday Soc.*, 1953, **49**, 601). The ampoules were broken under 500 c.c. of N-hydrochloric acid in the Dewar vessel, and the temperature changes followed in terms of the resistance changes of a shielded thermistor element immersed in the solution. Hydrolysis was normally complete within 5 min. The calorimeter was calibrated electrically by the substitution method.

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* Part II, Skinner and Tees, *J.*, 1953, 3378.

Units.—All heat quantities are given in thermochemical calories, defined by 1 calorie = 4·1840 abs. joule.

Results.—The observed heats, $\Delta H_{\text{obs.}}$, refer to the reaction system

$$\text{B(NMe}_2)_3\text{(liq.)} + 3\text{H}_2\text{O(liq.)} + (n+3)\text{HCl(54H}_2\text{O)} \longrightarrow [\text{H}_3\text{BO}_3 + 3\text{NH}_2\text{Me}_2\text{Cl,54H}_2\text{O}],n\text{HCl(54H}_2\text{O)} \quad . \quad . \quad (1)$$

where the excess of hydrochloric acid is denoted by n. The values of $\Delta Hf°[\text{B(NMe}_2)_3\text{,liq.}]$ were derived from the thermochemical equation appropriate * to eqn. (1), *viz.*

$$\Delta Hf°\text{B(NMe}_2)_3\text{,liq.} = \Delta Hf°[\text{H}_3\text{BO}_3\text{,54}n\text{H}_2\text{O}] + 3\Delta Hf°[\text{NH}_2\text{Me}_2\text{Cl,18}n\text{H}_2\text{O}] - 3\Delta Hf°[\text{H}_2\text{O,liq.}] - 3\Delta Hf°[\text{HCl,54H}_2\text{O}] - \Delta H_{\text{obs.}} \quad . \quad (2)$$

The following thermal data were assumed when using eqn. (2) : $\Delta Hf°[\text{H}_3\text{BO}_3\text{,5000H}_2\text{O}] = -257·33$ ($\pm$0·4) kcal./mole (Prosen, Johnson, and Pergiel, Nat. Bur. Stand. Report, No. 1552, 1953); $\Delta Hf°[\text{NH}_2\text{Me}_2\text{Cl,2000H}_2\text{O}] = -70·775$ kcal./mole (from the "Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Stand., Washington, Circular No. 500); $\Delta Hf°[\text{H}_2\text{O,liq.}] = -68·317$ kcal./mole (N.B.S. tables); $\Delta Hf°[\text{HCl,54H}_2\text{O}] = -39·595$ kcal./mole (N.B.S. tables).

A selection from the results obtained is given in Table 1.

TABLE 1. *Heat of hydrolysis of* $\text{B(NMe}_2)_3$ *in* N-HCl.

Expt.	$\text{B(NMe}_3)_2$ (g.)	n	$-\Delta H_{\text{obs.}}$ (kcal.)	$\Delta Hf°[\text{B(NMe}_2)_3\text{,liq.}]$ (kcal./mole)	
1	0·6774	106	68·63	−77·29	Mean values : $-\Delta H_{\text{obs.}}$ 68·80 kcal.
2	0·6660	108	68·92	−77·00	
3	0·6694	107	68·66	−77·26	
4	0·6666	108	68·79	−77·13	$\Delta Hf°$ −77·12 kcal./mole.
5	0·6594	109	69·01	−76·91	

The overall error limits in $\Delta H_{\text{obs.}}$ are estimated at $\pm$0·3 kcal./mole, and in $\Delta Hf°$ at $\pm$1·0 kcal./mole.

DISCUSSION

Burg and Randolph (*J. Amer. Chem. Soc.*, 1951, **73**, 953) have measured the vapour pressure over a range of temperature for trisdimethylaminoborine, and from their data the heat of vaporisation, $\Delta H^{25}_{\text{vap.}} = 11·2 \pm 0·2$ kcal./mole, may be derived. By combining this with our value for $\Delta Hf°[\text{B(NMe}_2)_3\text{,liq.}]$, the heat of formation of gaseous trisdimethylaminoborine is obtained as $\Delta Hf°[\text{B(NMe}_2)_3\text{,g.}] = -65·9 \pm 1·2$ kcal./mole.

We define the mean bond dissociation energy of the B–N bond in $\text{B(NMe}_2)_3$ as equal to one-third of the heat of the disruption process

$$\text{B(NMe}_2)_3\text{(g.)} \longrightarrow \text{B(g.)} + 3\text{NMe}_2\text{(g.)} : \Delta H = 3\bar{D}(\text{B–NMe}_2) \quad . \quad . \quad (3)$$

The thermal equation appropriate to eqn. (3),

$$\Delta H = \Delta Hf°(\text{B,g.}) + 3\Delta Hf°(\text{NMe}_2\text{,g.}) - \Delta Hf°[\text{B(NMe}_2)_3\text{,g.}] \quad . \quad . \quad (4)$$

and the values $\Delta Hf°[\text{B(NMe}_2)_3\text{,g.}] = -65·9 \pm 1·2$ kcal./mole, and $\Delta Hf°(\text{B,g.}) = 97·2$ kcal./mole (N.B.S. tables), enable us to write

$$\bar{D}(\text{B–NMe}_2) = \Delta H/3 = 54·5\ (\pm 0·4) + \Delta Hf°(\text{NMe}_2\text{,g.}) \quad . \quad . \quad . \quad (5)$$

Eqn. (5) may be presented in an alternative form, replacing the unknown $\Delta Hf°(\text{NMe}_2\text{,g.})$ in terms of the bond dissociation energy, $D(\text{H–NMe}_2)$, in dimethylamine. We have

$$D(\text{H–NMe}_2) = \Delta Hf°(\text{NMe}_2\text{,g.}) + \Delta Hf°(\text{H,g.}) - \Delta Hf°(\text{NMe}_2\text{H,g.}) \quad . \quad . \quad (6)$$

which, with the values $\Delta Hf°(\text{H,g.}) = 52·1$ kcal./mole, and $\Delta Hf°(\text{NHMe}_2\text{,g.}) = -6·6$ kcal./mole (N.B.S. tables), simplifies to

$$\Delta Hf°(\text{NMe}_2\text{,g.}) = D(\text{H–NMe}_2) - 58·7 \text{ kcal./mole} \quad . \quad . \quad . \quad . \quad (7)$$

Substituting eqn. (7) into eqn. (5) gives,

$$\bar{D}(\text{B–NMe}_2) = D(\text{H–NMe}_2) - 4·3 \text{ kcal./mole} \quad . \quad . \quad . \quad . \quad (8)$$

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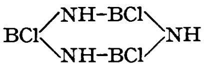
* Eqn. (2) neglects the heat of mixing of boric and hydrochloric acids, which is presumed to be small at the dilutions employed.

Szwarc (*Proc. Royal Soc.*, 1949, *A*, **198**, 267, 285) obtained the value $D(\text{H–NH}_2) = 104 \pm 2$ kcal./mole from kinetic studies on the pyrolysis of hydrazine, and a less reliable figure, $D \sim 100$ kcal./mole, from studies with benzylamine. An experimental determination of $D(\text{H–NMe}_2)$ has not yet been made, but it seems probable to us that $D(\text{H–NH}_2) > D(\text{H–NMe}_2)$. It is established that the C–H bond dissociation energies in paraffin hydrocarbons decrease along the series $D(\text{H–CH}_3) > D(\text{H–CH}_2\text{Me}) > D(\text{H–CHMe}_2)$; the difference $\Delta D\left[\begin{matrix}\text{H–CH}_3\\ \text{H–CHMe}_2\end{matrix}\right]$ being *ca.* $8\frac{1}{2}$ kcal./mole (cf. Pritchard, Mortimer, and Skinner, *Trans. Faraday Soc.*, 1952, **48**, 220). An analogous trend, and for similar reasons (Roberts and Skinner, *ibid.*, 1949, **45**, 339), might be expected in the series $D(\text{H–NH}_2)$, $D(\text{H–NHMe})$, $\text{D}(\text{H–NMe}_2)$. Here the falling trend may be sharper than in the hydrocarbon series—an analogy is the large difference (*ca.* 20 kcal./mole) between $D(\text{H–OH})$ and $D(\text{H–OMe})$. These considerations, together with the value $D(\text{H–NH}_2) = 104$ kcal./mole, lead us to an estimated $D(\text{H–NMe}_2)$ of $\sim$94 kcal./mole, and thence, from eqn. (8), to $\bar{D}(\text{B–NMe}_2) = 89{\cdot}7$ kcal./mole.



(I)

Van Artsdalen and Dworkin recently (*J. Amer. Chem. Soc.*, 1952, **74**, 3401) measured the heat of hydrolysis of trichloroborazole (I), from which they derived $\Delta Hf^{\circ}(\text{B}_3\text{N}_3\text{H}_3\text{Cl}_3,\text{cryst.}) = -252{\cdot}2$ kcal./mole. This should now be amended [making use of Prosen's value (*loc. cit.*) for the heat of formation of boric acid] to $\Delta Hf^{\circ} = -258{\cdot}5$ kcal./mole. An estimate of the mean bond energy term value, $\bar{E}(\text{B–N})$, in trichloroborazole may be made as follows: (i) $\Delta Hf^{\circ}(\text{B}_3\text{N}_3\text{H}_3\text{Cl}_3,\text{g.}) = -241{\cdot}4$ kcal./mole; (ii) heat of atomisation of $\text{B}_3\text{N}_3\text{H}_3\text{Cl}_3 = (776{\cdot}3 + 3D/2)$ kcal., where D = dissociation energy of N_2; (iii) $\bar{D}(\text{B–Cl})$ in $\text{BCl}_3 = 93{\cdot}9$ kcal./mole (Skinner and Smith, *loc. cit.*); (iv) $\bar{D}(\text{N–H})$ in $\text{NH}_3 = 55{\cdot}8 + D/6$ kcal./mole; (v) assume that $\bar{D}(\text{B–Cl})$ in BCl_3, and $\bar{D}(\text{N–H})$ in NH_3 may be carried over unchanged to the trichloroborazole molecule; then $\bar{E}(\text{B–N}) = (54{\cdot}5 + D/6)$ kcal./mole. The heat of dissociation of nitrogen is not yet finally established, and the choice rests between two values, $D(\text{N}{\equiv}\text{N}) = 171{\cdot}2$ and $225{\cdot}8$ kcal./mole (cf. Springall, *Trans. Faraday Soc.*, 1947, **43**, 177). The " low " value of D gives $\bar{E}(\text{B–N}) = 83{\cdot}0$ kcal./mole, and the " high " value, $\bar{E}(\text{B–N}) = 92{\cdot}1$ kcal./mole.

The good agreement between our value for $\bar{D}(\text{B–NMe}_2)$ and the higher alternative of the $\bar{E}(\text{B–N})$ values cannot be regarded as evidence for the " high " dissociation energy of N_2. The $\bar{D}$, $\bar{E}$, symbolism here used is purposeful (cf. Springall and Skinner, *Nature*, 1948, **162**, 343), the former referring to an experimentally observable fact, whereas the latter is derived from assumptions not in themselves observable by experiment [in this particular case, the assumptions (v) of the previous paragraph]. The presumption of an identity between a $\bar{D}$ and an $\bar{E}$ value involves deeper assumptions, that usually cannot be verified, and is a risky, if not a questionable, procedure.

If comparison between the B–N energies in $\text{B}_3\text{N}_3\text{H}_3\text{Cl}_3$ and $\text{BN}_3\text{C}_6\text{H}_{18}$ were sought at all, it were best in terms of $\bar{E}$ values in both cases. For example, we might carry over $\bar{D}(\text{N–H})$ from NH_3 to the NHMe_2 molecule, giving $\bar{E}(\text{N–Me}) = (D/6) + 34{\cdot}0$, and then carry this over to $\text{BN}_3\text{C}_6\text{H}_{18}$, to obtain $\bar{E}(\text{B–N}) = (D/6) + 51{\cdot}5$ kcal./mole. The comparison with $\bar{E}(\text{B–N})$ in $\text{B}_3\text{N}_3\text{H}_3\text{Cl}_3$ is close, and one might, with some empirical justification (cf. Skinner, *Trans. Faraday Soc.*, 1945, **41**, 645; Evans, *Proc. Roy. Soc.*, 1951, *A*, **207**, 1), deduce from this that the nature of the B–N bonding—as reflected in, *e.g.*, the bond length—is similar in both molecules.

Van Artsdalen and Dworkin (*loc. cit.*) drew attention to the large differences in energy and length of the B–N linkage in its covalent and its co-ordinate form, and similar differences are shown by the covalent and the co-ordinate form of the B–O linkage. Bauer and Beach (*J. Amer. Chem. Soc.*, 1941, **63**, 1394) from an electron-diffraction study found $r(\text{B–O})$ in methyl borate $= 1{\cdot}38 \pm 0{\cdot}02$ Å, whereas in the boron trifluoride–dimethyl ether complex Bauer, Finlay, and Laubengayer (*ibid.*, 1943, **65**, 889; 1945, **67**, 339) obtained $r(\text{B}{\leftarrow}\text{O}) = 1{\cdot}50 \pm 0{\cdot}06$ Å. The structure of trisdimethylaminoborine has not been determined, but (see above) we may expect the B–N bond to be of similar length to that in trichloroborazole, where $r(\mathrm{B{-}N}) = 1{\cdot}41 \pm 0{\cdot}01$ Å (Coursen and Hoard, *ibid.*, 1952, **74**, 1742), compared with the value $r(\mathrm{B\leftarrow N}) = 1{\cdot}58$ Å found by Geller and Hoard (*Acta Cryst.*, 1950, **3**, 121) in the boron trifluoride–methylamine complex, and $r(\mathrm{B\leftarrow N}) = 1{\cdot}585$ Å in the boron trifluoride–trimethylamine complex (*ibid.*, 1951, **4**, 399). The differences in bond energy between the covalent and the co-ordinate links are even more pronounced than are the differences in bond length. Table 2 summarises some of the relevant experimental data available.

TABLE 2. *Dissociation energies of co-ordinate and covalent links.**

Bond	Energy (kcal.)	ΔD	Bond.	Energy (kcal.)	ΔD
$\bar{D}(\mathrm{B{-}OMe})$ in $\mathrm{B(OMe)_3}$	103·0 [a]	89·1	$\bar{D}(\mathrm{B{-}NHMe})$	(94) [c]	76·4
$D(\mathrm{F_3B\leftarrow OMe_2})$	13·9 [b]		$D(\mathrm{Me_3B\leftarrow NH_2Me})$	17·6 [d]	
$\bar{D}(\mathrm{B{-}OEt})$ in $\mathrm{B(OEt)_3}$	104·7 [a]	92·2	$\bar{D}(\mathrm{B{-}NMe_2})$ in $\mathrm{B(NMe_2)_3}$	89·7	70·4 61·7
$D(\mathrm{F_3B\leftarrow OEt_2})$	12·5 [b]		$D(\mathrm{Me_3B\leftarrow NHMe_2})$	19·3 [d]	
$\bar{D}(\mathrm{B{-}NH_2})$	(99·7) [c]	85·9 82·7 ± 10	$D(\mathrm{F_3B\leftarrow NMe_3})$	(28) [f]	
$D(\mathrm{Me_3B\leftarrow NH_3})$	13·8 [d]				
$D(\mathrm{F_3B\leftarrow NH_3})$	(17 ± 10) [e]				

[a] Charnley, Mortimer, and Skinner, *J.*, 1953, 1181; cf. *J.*, 1952, 2288. [b] Laubengayer and Finlay, *J. Amer. Chem. Soc.*, 1943, **65**, 884. [c] Estimated; the values $\bar{D}(\mathrm{B{-}NR_2})$, where R = H or Me, are assumed to vary in the same way as $D(\mathrm{H{-}NR_2})$. [d] Brown, Bartholomay, and Taylor, *J. Amer. Chem. Soc.*, 1944, **66**, 435. [e] An estimate based on the heat of formation of crystalline $\mathrm{BF_3,NH_3}$ (Laubengayer and Condike, *ibid.*, 1948, **70**, 2274) and an estimated heat of crystallisation of 25 ± 10 kcal./mole. Such a high sublimation energy seems probable, in view of the evidence of appreciable hydrogen-bonding in the crystal (Hoard, Geller, and Owen, *Acta Cryst.*, 1951, **4**, 405). The value of $D(\mathrm{F_3B\leftarrow NH_3}) = 9$ kcal./mole, quoted by Skinner ("Cationic Polymerization," ed. P. H. Plesch, Heffer & Co. Ltd., Cambridge, 1953) is an error. [f] Phillips, Hunter, and Sutton, *J.*, 1945, 146; cf. Burg and Green, *J. Amer. Chem. Soc.*, 1943, **65**, 1839.

* See note added in proof, *J.*, 1953, 3383.

The column headed ΔD gives differences between covalent- and co-ordinate-bond dissociation energies in examples which are strictly comparable. Some of the values given are less certain than might be desired, but the ΔD values are in all cases large enough to leave no doubt of the weakness of the co-ordinate linkage relative to its covalent counterpart.

The variations shown in the ΔD values are of interest, particularly in view of the recent discussions by Mulliken (*J. Amer. Chem. Soc.*, 1952, **64**, 811) on the stability of co-ordination complexes. It is noticeable that the ΔD values in the B–N series fall as the donor changes progressively from $\mathrm{NH_3}$ to $\mathrm{NMe_3}$, and this trend may be correlated with the fall in ionisation potential of the donor molecules [Sugden, Walsh, and Price, *Nature*, 1941, **148**, 372, give $I(\mathrm{NH_3}) = 10{\cdot}8$ ev, $I(\mathrm{NH_2Me}) = 9{\cdot}8$ ev, $I(\mathrm{NHMe_2}) = 9{\cdot}6$ ev, and $I(\mathrm{NMe_3}) = 9{\cdot}4$ ev; Morrison and Nicholson (*J. Chem. Phys.*, 1952, **20**, 1021) give $I(\mathrm{NH_3}) = 10{\cdot}52$ ev and $I(\mathrm{NH_2Me}) = 9{\cdot}41$ ev]. The point has been discussed elsewhere by Skinner ("Cationic Polymerization," *op. cit.*) in terms of a description of the co-ordinate link similar to, but less complete than, that of Mulliken (*loc. cit.*). The trend of ΔD in the B–O series, on the other hand, is apparently the reverse of that in the B–N series [Sugden, Walsh, and Price (*loc. cit.*) give $I(\mathrm{Me_2O}) = 10{\cdot}5$ ev and $I(\mathrm{Et_2O}) = 10{\cdot}2$ ev], but the variations here are barely large enough to merit serious consideration.

Hoard, Geller, and Owen (*loc. cit.*) have commented on the instability of the complex of methyl cyanide and boron trifluoride, which exists in the crystalline form only, and is completely dissociated in the vapour phase. The inference is that $D(\mathrm{F_3B\leftarrow NCMe})$ is small, if not zero. It is relevant that the ionisation potential of methyl cyanide is appreciably larger than that of ammonia [Morrison and Nicholson (*loc. cit.*) give $I(\mathrm{MeCN}) = 12{\cdot}39$ ev], and that this would lead us to expect a much weaker bond than is found in the ammonia–boron trifluoride complex.

UNIVERSITY OF MANCHESTER.

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