233. *Heat of Formation of Crystalline Complexes of Boron Trichloride and Tribromide with Pyridine and Piperidine.*

By N. N. GREENWOOD and P. G. PERKINS.

The heats of formation of crystalline boron tribromide–pyridine and –piperidine from boron tribromide and the appropriate ligand are greater than those of the corresponding boron trichloride adducts. Those of piperidine complexes are greater than those of the pyridine analogues.

BROWN and HOLMES showed[1] that the molar heats of reaction of the boron trihalides with pyridine in nitrobenzene solution and the molar heats of solution of the trihalides in nitrobenzene increase in the order $BF_3 < BCl_3 < BBr_3$. Because nitrobenzene is not an inert solvent for these systems and the structure and degree of solvation of the complexes are unknown, the present work was undertaken to determine the heats of formation of the crystalline complexes themselves. The values obtained for the bromide and chloride differ from those in solution by only about 1 kcal. mole^{-1} and confirm the view that more energy is evolved when pyridine is added to boron tribromide than when it reacts with boron trichloride. The measurements were extended to piperidine and the same sequence was observed for this ligand.

EXPERIMENTAL AND RESULTS

Materials.—Boron trichloride, m. p. −107°, b. p. 12·5°, was purified by repeated vacuum-distillation between −50° and −78° and was measured into the fragile bulbs by observing its pressure and temperature in a calibrated flask of volume 190 ml. Boron tribromide (kindly supplied by Borax Consolidated Ltd.) was freed from bromine by shaking it with mercury and then fractionated in a vacuum until a reproducible m. p. of −46° was obtained. Pyridine, m. p. −41°, b. p. 115·3°, was dried over potassium hydroxide and fractionated. Piperidine, m. p. −4°, b. p. 106·3°, was dried over barium oxide before fractionation. The complexes were prepared as outlined in the preceding paper [2] and were handled in a vacuum or in a glove-box under dry nitrogen. The m. p.s of the boron trichloride complexes have been recorded.[2] Boron tribromide–pyridine was prepared as white crystals by mixing benzene solutions of the components in stoicheiometric amounts and recrystallizing the product from benzene (Found: C, 18·1; H, 2·0; N, 4·8; Br, 72·1. $C_5H_5NBBr_3$ requires C, 18·0; H, 1·5; N, 4·2; Br, 72·0%). The compound melted with decomposition at 127—129° [lit.,[1] 128° (decomp.)]. Boron tribromide–piperidine was prepared by direct reaction of the components in a vacuum.

Calorimetry.—The ligands, which also served as the calorimetric liquid, were distilled into the calorimeter through a weighing flask.[3] Results are expressed in terms of the thermochemical calorie (4·1840 abs. joule). Precision of the measurements was 0·5—1%. The heats of solution of the acceptor ($-\Delta H_1$) and of the complex ($-\Delta H_2$) in excess of the ligand (L) were

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[1] Brown and Holmes, *J. Amer. Chem. Soc.*, 1956, **78**, 2173.

[2] Greenwood and Wade, preceding paper.

[3] Greenwood and Perkins, *J. Inorg. Nuclear Chem.*, 1957, **4**, 291.

measured at 25°, the difference between the two being the heat of formation of the crystalline complex ($-\Delta H_f$):

$$BX_3(l) + (n + 1)L(l) = BX_3,L \text{ (dissolved in } n \text{ moles of L); } -\Delta H_1$$
$$BX_3,L(c) + nL(l) = BX_3,L \text{ (dissolved in } n \text{ moles of L); } -\Delta H_2$$

therefore $$BX_3(l) + L(l) = BX_3,L(c);\ -\Delta H_f = -\Delta H_1 + \Delta H_2$$

The data for the heat of solution of boron trichloride in excess of pyridine are in Table 1. The weight of ligand and acceptor and their approximate molar ratio are given in the first three columns. The temperature rise ΔT is expressed in microvolts and this is related to the number of calories evolved by means of the electrical calibration which was carried out during each experiment. The molar heat of solution is given in the final column.

TABLE 1. $BCl_3(l)$ + *excess of* $C_5H_5N(l)$ = BCl_3,C_5H_5N (*in excess of* C_5H_5N).

C_5H_5N (g.)	BCl_3 (g.)	Molar ratio	ΔT (μv)	Calibrn. (cal. per μv)	$-\Delta H_1$ (kcal. mole^{-1})
120	0·2337	760 : 1	656·0	0·1170	$38{\cdot}5_0$
120	0·1172	1520 : 1	342·0	0·1135	$38{\cdot}8_1$
					Mean $38{\cdot}6_6$

TABLE 2. $BCl_3,C_5H_5N(c)$ + *excess of* $C_5H_5N(l)$ = BCl_3,C_5H_5N (*in excess of* C_5H_5N).

C_5H_5N (g.)	BCl_3,C_5H_5N (g.)	Molar ratio	ΔT (μv)	Calibrn. (cal. per μv)	$-\Delta H_2$ (kcal. mole^{-1})
114	0·0956	2950 : 1	−8·5	0·1096	$-1{\cdot}9_1$
69	0·0611	2800 : 1	−9·0	0·0735	$-2{\cdot}1_2$
					Mean $-2{\cdot}0_1$

Similar data for the heat of solution of the complex boron trichloride–pyridine in excess of pyridine are in Table 2. The negative value shows that there is no thermochemical evidence for the suspected incongruent 1 : 2 complex [2] in these solutions.

By difference:

$$BCl_3(l) + C_5H_5N(l) = BCl_3,C_5H_5N(c);\ -\Delta H_f = 40{\cdot}6_7 \pm 0{\cdot}25 \text{ kcal. mole}^{-1}$$

Tables 3 and 4 contain the data for boron trichloride–piperidine and lead to a heat of formation which is considerably larger than that of the pyridine complex:

$$BCl_3(l) + C_5H_{10}NH(l) = BCl_3,C_5H_{10}NH(c);\ -\Delta H_f = 84{\cdot}4 \pm 1{\cdot}4 \text{ kcal. mole}^{-1}$$

TABLE 3. $BCl_3(l)$ + *excess of* $C_5H_{10}NH(l)$ = $BCl_3,C_5H_{10}NH$ (*in excess of* $C_5H_{10}NH$).

$C_5H_{10}NH$ (g.)	BCl_3 (g.)	Molar ratio	ΔT (μv)	Calibrn. (cal. per μv)	$-\Delta H_1$ (kcal. mole^{-1})
119	0·2449	665 : 1	1857	0·1378	122·5
105	0·2498	580 : 1	2240	0·1162	122·1
106	0·1368	1060 : 1	1230	0·1173	123·6
					Mean 122·7

TABLE 4. $BCl_3,C_5H_{10}NH(c)$ + *excess of* $C_5H_{10}NH(l)$ = $BCl_3,C_5H_{10}NH$ (*in excess of* $C_5H_{10}NH$).

$C_5H_{10}NH$ (g.)	$BCl_3,C_5H_{10}NH$ (g.)	Molar ratio	ΔT (μv)	Calibrn. (cal. per μv)	$-\Delta H_2$ (kcal. mole^{-1})
103	0·0808	3040 : 1	142·5	0·1086	38·8
105	0·0831	3000 : 1	136·0	0·1148	38·0
105	0·0865	2860 : 1	143·0	0·1140	38·1
					Mean 38·3

Analogous thermochemical data for the addition of boron tribromide to pyridine and piperidine are in Tables 5—8. Values for the piperidine system are less accurate than those for

TABLE 5. $BBr_3(l)$ + *excess of* $C_5H_5N(l)$ = BBr_3,C_5H_5N (*in excess of* C_5H_5N).

C_5H_5N (g.)	BBr_3 (g.)	Molar ratio	ΔT (μv)	Calibrn. (cal. per μv)	$-\Delta H_1$ (kcal. mole^{-1})
133	0·5017	855 : 1	695·0	0·1183	$41{\cdot}0_6$
122	0·3479	1150 : 1	505·0	0·1129	$41{\cdot}0_7$
					Mean $41{\cdot}0_7$

pyridine because of the formation of a small amount of white precipitate. In principle this should not influence the accuracy of the determinations since the same final state is attained in each reaction. The lack of precision arises from the slowness with which the heat of reaction is evolved, particularly in those experiments (Table 8) where the complex is being dissolved in the excess of piperidine. The precipitate, always small in amount, was not identified. It is clear from the results that piperidine is again a stronger ligand than pyridine and that more heat is evolved when boron tribromide reacts with these donors than is evolved in the corresponding reactions of boron trichloride:

TABLE 6. $BBr_3,C_5H_5N(c)$ + *excess of* $C_5H_5N(l) = BBr_3,C_5H_5N$ (*in excess of* C_5H_5N).

C_5H_5N (g.)	BBr_3,C_5H_5N (g.)	Molar ratio	ΔT (μv)	Calibrn. (cal. per μv)	$-\Delta H_2$ (kcal. mole^{-1})
90	0·0404	9420 : 1	−6·0	0·1010	−4·9
90	0·0845	4460 : 1	−10·5	0·1004	−4·1
					Mean −4·5

TABLE 7. $BBr_3(l)$ + *excess of* $C_5H_{10}NH(l) = BBr_3,C_5H_{10}NH$ (*in excess of* $C_5H_{10}NH$).

$C_5H_{10}NH$ (g.)	BBr_3 (g.)	Molar ratio	ΔT (μv)	Calibrn. (cal. per μv)	$-\Delta H_1$ (kcal. mole^{-1})
112	0·4390	750 : 1	1965	0·1460	163·7
103	0·2715	1120 : 1	1327	0·1326	162·4
					Mean 163·1

TABLE 8. $BBr_3,C_5H_{10}NH(c)$ + *excess of* $C_5H_{10}NH(l) = BBr_3,C_5H_{10}NH$ (*in excess of* $C_5H_{10}NH$).

$C_5H_{10}NH$ (g.)	$BBr_3,C_5H_{10}NH$ (g.)	Molar ratio	ΔT (μv)	Calibrn. (cal. per μv)	$-\Delta H_2$ (kcal. mole^{-1})
103	0·2182	1800 : 1	300	0·1074	49·6
103	0·3291	1210 : 1	450	0·1037	47·6
					Mean 48·6

$$BBr_3(l) + C_5H_5N(l) = BBr_3,C_5H_5N(c);\ -\Delta H_f = 45{\cdot}5 \pm 0{\cdot}6 \text{ kcal. mole}^{-1}$$

$$BBr_3(l) + C_5H_{10}NH(l) = BBr_3,C_5H_{10}NH(c);\ -\Delta H_f = 114{\cdot}5 \pm 1{\cdot}6 \text{ kcal. mole}^{-1}$$

DISCUSSION

It is in keeping with the general chemistry of piperidine, and in particular with its lower ionization potential and greater basicity (proton affinity), that the heats of formation of the piperidine complexes are greater than those of pyridine. Quantitatively, the present results can be compared with the heats of formation, in the gas phase, of the adducts of trimethylboron with pyridine [4] and piperidine,[5] where piperidine is the stronger ligand, and trimethylboron is a weaker acceptor than the boron trihalides:

$$Me_3B(g) + C_5H_5N(g) = Me_3B,C_5H_5N(g);\ -\Delta H_f = 17{\cdot}0 \pm 0{\cdot}2 \text{ kcal. mole}^{-1}$$

$$Me_3B(g) + C_5H_{10}NH(g) = Me_3B,C_5H_{10}NH(g);\ -\Delta H_f = 19{\cdot}7 \pm 0{\cdot}1 \text{ kcal. mole}^{-1}$$

It is striking that boron tribromide is a stronger acceptor than boron trichloride for pyridine and piperidine. This confirms and extends recent work on the heat of reaction of pyridine with the boron trihalides in nitrobenzene solution:[1]

$$BCl_3(l) + C_5H_5N(\text{soln.}) = BCl_3,C_5H_5N(\text{soln.});\ -\Delta H_f = 39{\cdot}5 \pm 0{\cdot}4 \text{ kcal. mole}^{-1}$$

$$BBr_3(l) + C_5H_5N(\text{soln.}) = BBr_3,C_5H_5N(\text{soln.});\ -\Delta H_f = 44{\cdot}5 \pm 0{\cdot}4 \text{ kcal. mole}^{-1}$$

These values differ by only about 1 kcal. mole^{-1} from the present figures for the heats of formation of the crystalline complexes; so the heat of solution of pyridine in nitrobenzene must be similar to the heat of solution of the complexes in the same solvent (about

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[4] Brown and Barbaris, *J. Amer. Chem. Soc.*, 1947, **69**, 1137.

[5] Brown and Gerstein, *J. Amer. Chem. Soc.*, 1950, **72**, 2926.

—3 kcal. mole^{-1}). It is therefore unlikely that the observed order Br $>$ Cl is due fortuitously to crystal lattice energy stabilization in our experiments and to heats of solvation in the solution calorimetry. The effect persists in the gas phase, as can be seen by incorporating the heats of vaporization of the reactants and the heats of sublimation of the complexes. Values of ΔH_{va} (kcal. mole^{-1}) are: BCl_3 5·5,[6] BBr_3 8·2,[7] C_5H_5N 9·7,[8] $C_5H_{10}NH$ 8·9.[9] The heat of sublimation of $BCl_3,C_5H_{10}NH$ is 18·2 kcal. mole^{-1}.[2] The value for BCl_3,C_5H_5N is not known but, as the heats of sublimation of pyridine and piperidine complexes of gallium trichloride are similar,[10] it is unlikely that serious error will be introduced by assuming a value of 18 kcal. mole^{-1} for boron trichloride–pyridine. Likewise, the values for the boron tribromide complexes could not be determined but, since the heats of sublimation of bromine-containing compounds are usually somewhat greater than those of the corresponding chlorides, a value of ~20 kcal. mole^{-1} will be assumed for these complexes. Incorporation of these figures into the thermochemical data leads to the following heats for the gas-phase reactions:

$$BCl_3(g) + C_5H_5N(g) = BCl_3,C_5H_5N(g);\ -\Delta H_f \sim 37{\cdot}9\ \text{kcal. mole}^{-1}$$
$$BCl_3(g) + C_5H_{10}NH(g) = BCl_3,C_5H_{10}NH(g);\ -\Delta H_f = 80{\cdot}6\ \text{kcal. mole}^{-1}$$
$$BBr_3(g) + C_5H_5N(g) = BBr_3,C_5H_5N(g);\ -\Delta H_f \sim 43{\cdot}5\ \text{kcal. mole}^{-1}$$
$$BBr_3(g) + C_5H_{10}NH(g) = BBr_3,C_5H_{10}NH(g);\ -\Delta H_f \sim 111{\cdot}6\ \text{kcal. mole}^{-1}$$

It can be seen that, even if the heat of sublimation of boron tribromide–pyridine were 7·5 kcal. mole^{-1} greater than that of the boron trichloride complex, the heat of formation of the bromide complex would still be the greater in the gas phase, and that the order would be reversed for the piperidine complexes only if boron tribromide–piperidine had a most improbably high heat of sublimation ($>$51 kcal. mole^{-1}).

A survey of the data in the literature indicates that bromides are frequently better electron-acceptors than chlorides and fluorides though this occasioned little comment until the work on the boron halides mentioned above.[1] Examples involving halides of other elements will be reviewed in a forthcoming paper, but the same effect was observed for the heat of formation of the crystalline adducts of methyl cyanide with boron trifluoride and trichloride.[11] The greater heat of formation of boron trichloride–methyl cyanide was interpreted on the hypothesis that the energy required to distort the planar BF_3 molecule into a tetrahedral configuration was greater than the corresponding energy of distortion for boron trichloride. It was pointed out at the same time [11] that the dipole moment of BCl_3,MeCN was greater than that of BF_3,MeCN,[12] indicating a greater polarity of the B–N bond in the former compound. More extensive investigation of the dipole moment of pyridine adducts again indicated that the order of increasing acceptor power was $BF_3 < BH_3 \ll BCl_3 < BBr_3$.[13] The same trend is reflected in the general chemistry of these acceptors; for example, boron tribromide and trichloride form complexes with arsine [14] whereas boron trifluoride does not,[15] and only boron tribromide of these three acceptors combines with phosphorus trichloride.[1] Similarly, boron trichloride forms a complex with diphenyl ether, but boron trifluoride does not.[16] The order of increasing acceptor power can be interpreted in terms of (*a*) a decreasing tendency to form π-bonds by back-donation from the halogen atom into the vacant boron orbital, and (*b*) a decrease in the

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[6] Nat. Bur. Standards Circular 500, Washington, 1952.
[7] Stock and Kuss, *Ber.*, 1914, **47**, 3113; Kelly, *U.S. Bur. Mines Bull.*, 1935, No. 383.
[8] Herington and Martin, *Trans. Faraday Soc.*, 1953, **49**, 154.
[9] Riley and Bailey, *Proc. Roy. Irish Acad.*, 1929, **38**, *B*, 450.
[10] Greenwood and Wade, *J.*, 1958, 1663, 1671.
[11] Laubengayer and Sears, *J. Amer. Chem. Soc.*, 1945, **67**, 164.
[12] Ulich and Nespital, *Z. anorg. Chem.*, 1931, **44**, 752.
[13] Bax, Katritzky, and Sutton, *J.*, 1958, 1258.
[14] Stock, *Ber.*, 1901, **34**, 949; Stieber, *Compt. rend.*, 1932, **195**, 610.
[15] Martin and Dial, *J. Amer. Chem. Soc.*, 1950, **72**, 852.
[16] Healy and Palko, *J. Chem. Phys.*, 1958, **28**, 1956.

electrostatic repulsion between the B–X bond electrons and the lone-pair electrons on the ligand.[1,13] A simple molecular-orbital calculation of the π-bond energies confirms the view that the energy of reorganization from planar to tetrahedral configuration decreases in the sequence $BF_3 > BCl_3 > BBr_3$.[17]

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THE UNIVERSITY, NOTTINGHAM.

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[17] Cotton and Leto, *J. Chem. Phys.*, 1959, **30**, 993.