1308. *Thermochemistry of the Complexes of Boron Trifluoride with Dimethyl Sulphoxide and Ethyl Acetate, and the Thermal Decomposition of the Diphenyl Sulphoxide–Boron Trichloride Complex*

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The condensed-phase heats of formation of BF_3,Me_2SO, $BF_3,MeCO_2Et$, and BF_3,C_5H_5N from gaseous reactants are $-42{\cdot}3 \pm 0{\cdot}2$, $-32{\cdot}9 \pm 0{\cdot}2$, and 46 ± 2 kcal. mole^{-1}, respectively. This indicates that, with respect to BF_3, the donor strengths of the ligands decrease in the series $C_5H_5N > Me_2SO > MeCO_2Et$. Displacement reactions are consistent with this order.

The complex BCl_3,Ph_2SO afforded *p*-$Cl{\cdot}C_6H_4{\cdot}S{\cdot}C_6H_5$ when heated.

RECENTLY, we examined the reactions of dimethyl sulphoxide [1] and ethyl acetate [2] with some halides of Group III and IV elements. In general, the first step is the formation of molecular addition compounds. These have variable stability and some [*e.g.*, BCl_3,Ph_2SO (see below) or $BCl_3,MeCO_2Et$ [3]] readily decompose irreversibly. The boron trifluoride complexes, on the other hand, dissociate when heated. The sulphoxide–boron trichloride system is quite complicated. With dimethyl sulphoxide, we previously showed that the

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[1] M. F. Lappert and J. K. Smith, *J.*, 1961, 3224.

[2] M. F. Lappert, *J.*, 1961, 817; 1962, 542.

[3] W. Gerrard and M. A. Wheelans, *J.*, 1956, 4296.

products are hydrogen chloride, $BOCl,MeS{\cdot}CH_2Cl$, and $BCl_3,MeS{\cdot}CH_2Cl$ [which may have the structure $(MeS{\cdot}CH_2)^+(BCl_4)^-$].[1] By contrast, several other sulphoxides (Ph_2SO, Bu^t_2SO, and Pr^iBu^tSO) gave 1 : 1 adducts. We now find that the diphenyl sulphoxide complex decomposes on heating, as follows.

$$3Ph_2SO,BCl_3 \longrightarrow 3p\text{-}Cl{\cdot}C_6H_4{\cdot}S{\cdot}C_6H_5 + (BOCl)_3 + 3HCl$$

$$(BOCl)_3 \longrightarrow B_2O_3 + BCl_3$$

The same sulphide is formed from diphenyl sulphoxide and several other non-metal chlorides (see ref. 1).

In view of the dearth of data on the thermochemistry of dimethyl sulphoxide and ethyl acetate as ligands, we undertook to investigate the BF_3–Me_2SO and BF_3–$MeCO_2Et$ systems, and to compare the results with those available for BF_3–C_5H_5N. The enthalpy change ($-\Delta H$) for the reaction $SbCl_5$ ($C_2H_4Cl_2$ solution) + $MeCO_2Et$ ($C_2H_4Cl_2$ solution) = Complex ($C_2H_4Cl_2$ solution), has been determined as 17·08 kcal. mole^{-1}.[4] By differential calorimetry, and with respect to $SbCl_5$ as acceptor, it is qualitatively established that dimethyl sulphoxide is a stronger donor than ethyl acetate.[5] Moreover, there is considerable circumstantial evidence that amines are stronger donor than either of these ligands.[6]

EXPERIMENTAL AND RESULTS

General Procedures.—Ethyl acetate, b. p. 78°, and pyridine, b. p. 115°, were dried over calcium chloride and barium oxide, respectively, and were carefully fractionated before use. The complexes were prepared as described previously,[1, 2] or from BF_3,Et_2O (see below).

Calorimetry.—The calorimetric apparatus used was essentially that described by Greenwood and Perkins.[7] All results refer to 25°. Equations (1) and (2) are based on the thermochemical data given in the Table, where the weights of reactants together with their molar ratios are shown. The temperature rise accompanying the reaction is expressed in microvolts, and is related to the number of calories evolved by means of the electrical calibration which was carried out during each experiment.

Heats of solution of BF_3,L in excess pyridine

Eqn.	Pyridine (g.)	L in BF_3,L	BF_3,L (g.)	Molar ratio	ΔT (μv)	Calibration (cal. per μv)	Molar heat of soln. ($-\Delta H$ in kcal. mole^{-1})
(1)	120	Me_2SO	0·4586	483 : 1	72	0·1467	3·36
	120		0·4782	463 : 1	72	0·1552	3·41
(2)	120	$MeCO_2Et$	0·5830	406 : 1	210	0·1548	8·7
	120		0·3401	696 : 1	121	0·1569	8·7

The Pyrolysis of Boron Trichloride–Diphenyl Sulphoxide.—Boron trichloride–diphenyl sulphoxide[1] (8·8 g.) was heated at 150° for 1 hr. The residue (6·7 g.) was agitated with methylene dichloride (50 ml.). Boric oxide (1·0 g., 100%) (identified spectroscopically) was separated by filtration. Removal of solvent from the filtrate at 20°/10 mm. gave *p*-chlorophenyl phenyl sulphide (5·4 g., 89%). On distillation, this afforded the pure sulphide (4·0 g.), b. p. 154°/7 mm., n_D^{20} 1·6353 (also identified spectroscopically).

The Reaction of Dimethyl Sulphoxide with Boron Trifluoride–Diethyl Ether.—The sulphoxide (1 mol.) was added to the ether complex (1 mol.) at 20°. There was a vigorous reaction and a white solid was immediately formed. This was filtered off, washed with ether, and identified as the 1 : 1 complex of boron trifluoride and dimethyl sulphoxide (>95%) (authentic infrared spectrum[1]).

The Reaction of Ethyl Acetate with Boron Trifluoride–Diethyl Ether.—The addition of ethyl acetate (1 mol.) to the ether complex (1 mol.) was not noticeably exothermal. Evidence that some reaction had taken place was found by examining the infrared spectrum of the resultant solution. This showed that ethyl acetate and its boron trifluoride complex were present in equilibrium, with each in substantial amount. The ratio of the intensities of the bands at 1740 [ν(C=O) in $MeCO_2Et$] and 1625 cm.$^{-1}$ [ν(C=O) in $BF_3,MeCO_2Et$][2] was ~2 : 1, immediately

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[4] G. Olofsson, I. Lindqvist, and S. Sunner, *Acta Chem. Scand.*, 1963, **17**, 259.

[5] I. Lindqvist and M. Zackrisson, *Acta Chem. Scand.*, 1960, **14**, 453.

[6] I. Lindqvist, " Inorganic Adduct Molecules of Oxo-Compounds," Springer Verlag, Berlin, 1963.

[7] N. N. Greenwood and P. G. Perkins, *J. Inorg. Nuclear Chem.*, 1957, **4**, 291.

after mixing and also either after prolonged standing at 20°, or refluxing. Crystallisation of the ethyl acetate complex was finally achieved after ~14 days at 20°; the process was not appreciably hastened by attempts to remove volatile components under a vacuum.

The Me_2CO_2Et–BF_3,OEt_2–Me_2SO *System*.—To a mixture of ethyl acetate (1 mol.) and boron trifluoride–diethyl ether (1 mol.), dimethyl sulphoxide (1 mol.) was added. The mixture separated into two liquid layers. Infrared spectra revealed that both contained, in the main, mixtures of BF_3,Me_2SO [ν(S=O), 948 cm.$^{-1}$] [1] and ethyl acetate [ν(C=O) at 1740 cm.$^{-1}$]. The lower layer showed a larger proportion of the sulphoxide complex. There was no evidence for the presence of $BF_3,MeCO_2Et$ (transparent 1600—1700 cm.$^{-1}$).

The BF_3–Me_2SO–$MeCO_2Et$ *System*.—The complex BF_3,Me_2SO (1 mol.) was shaken with ethyl acetate (large excess) at 20°. About half of the solid went into solution. The solid was identified (infrared spectra) as the unchanged complex, whilst the solution contained BF_3,Me_2SO, and a trace of Me_2SO. None of the ethyl acetate was present as $BF_3,MeCO_2Et$. The sulphoxide complex could be recrystallised from ethyl acetate.

DISCUSSION

The heats of solution in excess of pyridine of the crystalline 1 : 1 complexes of boron trifluoride with dimethyl sulphoxide and ethyl acetate are given by equations (1) and (2).

$$\begin{aligned}&\mathrm{BF_3,Me_2SO\ (c) + excess\ C_5H_5N\ (l) = BF_3,C_5H_5N\ (in\ C_5H_5N\ solution)}\\&\quad\mathrm{+\ Me_2SO\ (in\ C_5H_5N\ solution);}\ -\Delta H = 3{\cdot}39\ \mathrm{kcal.\ mole^{-1}}\end{aligned}\qquad(1)$$

$$\begin{aligned}&\mathrm{BF_3,MeCO_2Et\ (c) + excess\ (C_5H_5N\ (l) = BF_3,C_5H_5N\ (in\ C_5H_5N}\\&\quad\mathrm{solution) + MeCO_2Et\ (in\ C_5H_5N\ solution);}\ -\Delta H = 8{\cdot}7\ \mathrm{kcal.\ mole^{-1}}\end{aligned}\qquad(2)$$

As dimethyl sulphoxide and ethyl acetate, severally, have negligible heats of solution in excess of pyridine, and as other thermochemical data are available (see below), it is possible to compute [equations (3)—(5)] the heats of formation of the crystalline 1 : 1 complexes from their gaseous components.

$$\mathrm{BF_3\ (g) + Me_2SO\ (g) = BF_3,Me_2SO\ (c);}\ -\Delta H = 42{\cdot}3 \pm 0{\cdot}2\ \mathrm{kcal\ mole^{-1}}\qquad(3)$$

$$\mathrm{BF_3\ (g) + MeCO_2Et\ (g) = BF_3,MeCO_2Et\ (c);}\ -\Delta H = 32{\cdot}9 \pm 0{\cdot}2\ \mathrm{kcal.\ mole^{-1}}\qquad(4)$$

$$\mathrm{BF_3\ (g) + C_5H_5N\ (g) = BF_3,C_5H_5N\ (c);}\ -\Delta H = 46 \pm 2\ \mathrm{kcal.\ mole^{-1}}\qquad(5)$$

Equations (3)—(5) are derived by Hess's law calculations from equations (1), (2), and (6)—(10), and the observation that Me_2SO (l) and $MeCO_2Et$ (l) have negligible heats of solution in pyridine.

$$\begin{aligned}&\mathrm{BF_3\ (g) + excess\ C_5H_5N\ (l) = BF_3,C_5H_5N\ (in\ C_5H_5N\ solution);}\\&\qquad -\Delta H = 32{\cdot}87 \pm 0{\cdot}16\ \mathrm{kcal.\ mole^{-1}}\end{aligned}\qquad(6)$$

$$\mathrm{Me_2SO\ (l) \longrightarrow Me_2SO\ (g);}\ \Delta H_v = 12{\cdot}8\ \mathrm{kcal.\ mole^{-1}}\qquad(7)\ ^{8}$$

$$\mathrm{MeCO_2Et\ (l) \longrightarrow MeCO_2Et\ (g);}\ \Delta H_v = 8{\cdot}7\ \mathrm{kcal.\ mole^{-1}}\qquad(8)\ ^{9}$$

$$\mathrm{C_5H_5N\ (l) \longrightarrow C_5H_5N\ (g);}\ \Delta H_v = 9{\cdot}7\ \mathrm{kcal.\ mole^{-1}}\qquad(9)\ ^{10}$$

$$\begin{aligned}&\mathrm{BF_3,C_5H_5N\ (c) + excess\ C_5H_5N\ (l) = BF_3,C_5H_5N\ (in\ C_5H_5N\ solution);}\\&\qquad \Delta H = 1{\cdot}4\text{—}5{\cdot}4\ \mathrm{kcal.\ mole^{-1}}\end{aligned}\qquad(10)$$

Equation (6) is computed from the known [11] heat of formation of BF_3,C_5H_5N (in $C_6H_5{\cdot}NO_2$ solution), and the heats of solution in nitrobenzene of BF_3 (g) and C_5H_5N (l). Equation (10) is an estimate based on the knowledge [12] that the heats for the corresponding changes involving BCl_3 and BBr_3 complexes are 2·0 and 4·5 kcal. mole^{-1}, respectively.

In order definitively to compare the donor strengths of the three ligands, with respect to BF_3 as reference acid, equations (3)—(5) are not strictly satisfactory. The ideal ones

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[8] H. Mackle and P. A. G. O'Hare, *Trans. Faraday Soc.*, 1961, **57**, 2119.

[9] Calculated from the data of J. Wade and R. W. Merriman, *J.*, 1912, **101**, 2438.

[10] E. F. G. Herrington and J. F. Martin, *Trans. Faraday Soc.*, 1953, **49**, 154.

[11] H. C. Brown and D. Gintis, *J. Amer. Chem. Soc.*, 1956, **78**, 5378.

[12] N. N. Greenwood and P. G. Perkins, *J.*, 1960, 1141.

for this purpose would relate to the gas-phase enthalpy changes. Unfortunately, the dimethyl sulphoxide and ethyl acetate complexes are not sufficiently stable in the gas phase to make the study of either the gas-phase equilibria, or the latent heats of sublimation (ΔH_s), of the complexes possible. It is probable, however, that ΔH_s for each of the three complexes (as they are related compounds) is of a similar order of magnitude and is 18 ± 5 kcal. mole^{-1}. All the heats of sublimation of MX_3,L complexes (where MX_3 is a Group III halide and L is a unidentate ligand) which have been measured to date fall within this range. On the basis of our results, it seems safe, therefore, to conclude that the order $C_5H_5N > Me_2SO \gg MeCO_2Et$ is established for BF_3 as acceptor.

We also show that pyridine will displace both dimethyl sulphoxide and ethyl acetate from their respective BF_3 complexes, and likewise that the sulphoxide will displace the acetate from BF_3,$MeCO_2Et$. In general, such displacement reactions qualitatively reflect free-energy changes for reactions, allowing that solubility factors affect each complex similarly (they are all insoluble in hydrocarbons). There is no theoretical reason why values of ΔG and ΔH should run parallel, except that the entropy changes in these related reactions are likely to be similar (for relevant information, see ref. 13); moreover, wherever displacement results and gas-phase enthalpy data are available, the two give qualitatively similar results.[13]

Our conclusions relating to relative donor strengths of Me_2SO and $MeCO_2Et$ are further strengthened by the observation that the BF_3 complex of the former is virtually undissociated in solution, unlike that of the latter. From the displacement reactions with BF_3,Et_2O it further appears that even ethyl acetate has greater basicity than diethyl ether.

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[13] F. G. A. Stone, *Chem. Rev.*, 1958, **58**, 101; T. D. Coyle and F. G. A. Stone, " Progress in Boron Chemistry," ed. H. Steinberg and A. L. McCloskey, Pergamon, Oxford, vol. 1 ch. 2.