Accurate comparison of the solvation entropies of the amide ion and symmetrical ions of like charge is difficult because of the ambiguity of the amide ionic radius which falls between 2.06 and 1.6 Å. depending on the criterion employed. Assuming the upper limit and freely rotating ions, we note that the solvation entropies of the borohydride and amide ions are in good agreement as should be the case in view of the similarity of charge and radius. Since it is likely, however, that the actual radius displayed by the amide ion is somewhat less than 2.06 Å., which value is based on the NH_2–H_2N distance of neighboring ions with opposed hydrogens, comparison should probably be made with a smaller ion such as the chloride ion for which the solvation entropy is more negative by 5 e.u. In view of present experimental uncertainties, this discrepancy is probably without significance. It is, of course, to be expected that the entropy of solvation of a monatomic ion should not be more negative relative to a polyatomic ion of similar charge and radius since loss of rotational motion of the latter would result in a more negative solvation entropy for the polyatomic ion.

Ionization Constant of Liquid Ammonia.—With the aid of the heat of ionization of liquid ammonia and the entropy of the amide ion determined in this research, the free energy of ionization of ammonia and the equilibrium constant of the reaction: $NH_3(l) = H^+{}_{(am)} + NH_2^-{}_{(am)}$, can be calculated. At 240°K., $\Delta H^0 = 26.1$[20] kcal.; $\Delta S^0 = \bar{S}^0[H^+] + \bar{S}^0[NH_2^-] - S^0[NH_3(l)] = 0.0$[29] $- 19.3$[12] $- 20.8$[30] $= -40.1$ cal. deg.$^{-1}$ mole^{-1}; $\Delta F^0 = 35.7$ kcal. and $K = 3.2 \times 10^{-33}$. Pleskov and Monoszon[31] calculated $K = 1.9 \times 10^{-33}$ from cell potential data at −50°. Correcting their value to 240°K. we obtain 1.3×10^{-31} which differs substantially from the K obtained in this research.

For the ionization of liquid ammonia at 298.15° K., $\Delta S^0 = \bar{S}^0[NH_2^-] + \bar{S}^0[H^+] - S^0[NH_3(l)] = -14.7$[12] $+ 0 - 24.7$[32] $= -39.1$ cal. deg.$^{-1}$ mole^{-1}; $\Delta F^0 = 37.76$ kcal. and $K = 2.2 \times 10^{-28}$. For comparison with this value we correct K (Pleskov and Monoszon) to 298°K. giving $K = 5.1 \times 10^{-27}$.

Although the difference between the constant obtained by Pleskov and Monoszon and the constant based on the thermodynamic properties of amides previously estimated by Jolly[32] has been narrowed substantially with the use of experimental entropy data for sodium amide, a considerable difference still remains. This difference may be explained, however, by the presence of unknown liquid junction potentials in the cells employed by Pleskov and Monoszon, by an incorrect degree of dissociation of potassium amide assumed for the calculation of their K or by the uncertainty in the free energy of solution of sodium amide employed in this research.

[29] By convention $\bar{S}^0[H^+{}_{(am)}] = 0.0$.

[30] R. Overstreet and W. F. Giauque, THIS JOURNAL, **59**, 254 (1937).

[31] V. A. Pleskov and A. M. Monoszon, *J. Phys. Chem.* (*U.S.S.R.*), **6**, 513 (1935).

[32] W. L. Jolly, *Chem. Revs.*, **50**, 351 (1952); U. S. Atomic Energy Commission, UCRL Report No. 2201, May, 1953; ref. 19b.

BOSTON, MASS.

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

Molecular Addition Compounds of Boron. II. Thiophane–Borane and Related Adducts[1,2]

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The addition compounds $(CH_2)_4S·BH_3$, $(CH_2)_4S·BF_3$, $Et_2S·BH_3$ and $Et_3S·BF_3$ have been prepared, and their liquid saturation pressures and dissociations in the gas phase examined. Gas-phase dissociation of the adduct $Me_2S·BH_3$ has been reinvestigated. As might be expected, all the complexes are weak. Indeed, only the borane adducts are sufficiently associated in the gas phase to permit reliable determination of thermodynamic constants. Nevertheless, it was clearly demonstrated that borane forms much more stable adducts than does boron trifluoride with the thioethers, whereas the reverse is true with ordinary ethers. Moreover, adducts like $Et_2S·BH_3$ are much more stable than their oxygen analogs. Furthermore, the order of coördination of the thioethers toward borane is $Me_2S \simeq Et_2S > (CH_2)_4S$, in contrast to the order displayed by ethers, *viz.*, $(CH_2)_4O > Me_2O > Et_2O$. It is probable that the thioethers display a similar sequence of coördination toward boron trifluoride but in this case, because of the weakness of the boron trifluoride adducts, experimental evidence is only qualitative.

Introduction

During the period 1942–1951, the gas-phase dissociations of many molecular addition compounds were studied by Brown and his co-workers and by Coates.[5] These addition compounds involved a variety of combinations of different Lewis acids with different Lewis bases, *e.g.*, $(CH_2)_4O·BF_3$, $Me_2S·AlMe_3$, $Me_3N·BMe_3$, $Me_3As·GaMe_3$ and $Me_3P·BF_3$, etc. It was natural that the relative stabilities of these compounds, usually compared in terms of relative heats of gas-phase dissociation, should excite interest. This was especially so on the realization that if one compared all the adducts made by Brown, *et al.*, and by Coates, it was possible to make a generalization. This generalization has been expressed in several different ways by several authors, *e.g.*, (i) "The order of stability of complexes formed by alkyl derivatives of the

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[1] Previous paper, W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **3**, 164 (1956).

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[3] Natvar Corporation Fellow at Harvard University, 1958–1959.

[4] Public Health Predoctoral Research Fellow of the National Heart Institute.

[5] For a review of molecular addition compounds of the Group III elements see F. G. A. Stone, *Chem. Revs.*, **58**, 101 (1957).

elements of the fifth and sixth group acting as donors to atoms which can accept only with p-orbitals (such as B, Al or Ga) is in the order $R_2O > R_2S > R_2Se$ and $R_3N > R_3P > R_3As > R_3Sb$ (H. C. Brown, personal communication; Coates, *J. Chem. Soc.*, 2003 1951))."[6] (ii) "According to H. C. Brown, base strength, for BX_3, AlX_3 and the like as reference acids, decreases in each of the series $NR_3 > PR_3 > AsR_3 > SbR_3$; $OR_2 > SR_2 > SeR_2 > TeR_2$."[7] So far as the dimethyl derivatives of the Group VI elements are concerned, later work by Graham[1] showed that statements such as these do not apply when borane and trimethylborane are the acceptors. Furthermore, in Group V Graham showed that the displacement reaction

$$Me_3N\cdot BH_3 + Me_3P \longrightarrow Me_3P\cdot BH_3 + Me_3N$$

took place, suggesting an order of affinity $Me_3P > Me_3N$ toward borane. Another result of Graham's work was the demonstration that whereas boron trifluoride and borane were of comparable Lewis acidity towards the first-row donor trimethylamine, toward second-row donors, borane coördinated much more strongly, *viz.*

$$Me_2S\cdot BH_3 > Me_2S\cdot BF_3$$

$$Me_3P\cdot BH_3 > Me_3P\cdot BF_3$$

The unusual orders of coördination toward borane suggest that the classical description of donor–acceptor bonding in terms of a dative σ-bond may be inadequate when applied to some borane adducts. At present, the exact nature of the boron–ligand bond is unknown; however, the experimental results are consistent with an interpretation which attributes unusual bonding properties to the borane group. It has been suggested[1] that the three 1s atomic orbitals of the three hydrogen atoms of the borane group combine to form a *pseudo* p-orbital having π-symmetry. This *pseudo* pπ-orbital could then overlap a vacant orbital of a ligand, if the ligand possessed such an orbital. Usually only donor atoms from the second or later rows of the Periodic Classification possess vacant orbitals. Thus whereas the donor–acceptor bonds in $Me_3N\cdot BH_3$ and $Me_2O\cdot BH_3$ are adequately described as being of the classical σ-type, the ligand–boron bonds in $Me_2S\cdot BH_3$ and $Me_3P\cdot BH_3$ may have σ,π-character. This would account for their being unexpectedly strong. Graham had been concerned only with the methyl derivatives of the Group VI and Group V elements in establishing orders of coördination toward BH_3. It was just possible that these orders of coördination were influenced by the nature of the groups on the donor atoms. For this reason it was decided to compare stabilities of the adducts $Et_2O\cdot BX_3$, $Et_2S\cdot BX_3$, $(CH_2)_4O\cdot BX_3$ and $(CH_2)_4S\cdot BX_3$, where X = H or F, with each other and with those of the methyl derivatives. The task was somewhat simplified because a few of the compounds had already been adequately investigated by others, *e.g.*, $Et_2O\cdot BF_3$ and $(CH_2)_4O\cdot BF_3$.[8]

Experimental

1. **Starting Materials.**—**Diborane** used in the work described below was part of a shipment from the Callery Chemical Company. The gas was purified immediately before it was used to make borane complexes by passage through a trap at −150° in the vacuum system. Its vapor pressure was 224.7 mm. at −111.9° (lit.[9] 225.4 mm.). **Tetrahydrofuran** was redistilled from lithium aluminum hydride prior to use. **Dimethyl sulfide** was treated with sodium until a tensimetrically pure sample with 0° vapor pressure of 166.9 mm. was obtained (lit.[10] 167 mm.). **Thiophane** (vapor pressure 39.7 mm. at 40.3°; literature[11a]: 39.9 mm.) and **diethyl sulfide** (vapor pressure 15.0 mm. at 0°; literature[11b]: 15.0 mm.) were also purified by sodium treatment. Gas-phase chromatography[12] showed that the thiophane and the diethyl sulfide possessed a minimum purity of 99.9%.

2. **Apparatus for the Study of Molecular Addition Compounds.**—Saturation pressures of the addition compounds were measured in an immersible tensimeter of the kind first described by Burg and Schlesinger.[13] The volume of the saturation pressure tensimeter was 94 cc. In all saturation pressure measurements comparable amounts of complex were studied. This is necessary because the apparent vapor pressure of a weak complex depends upon the ratio of volume of container to size of sample. Thus whenever volatility comparisons are made, the quantity of complex used and the temperature range over which pressures are recorded should be essentially equivalent.

The gas-phase dissociations of the various molecular addition compounds were studied in the special type of tensimeter developed by Brown, Taylor and Gerstein.[14] Temperature measurements were made with N.B.S. calibrated thermometers graduated in 1/10ths of a degree and were controlled to ±0.1°. In work of this nature a 0.5 hr. period is allowed for thermal equilibration. This was done for the BF_3 adducts, and for the BH_3 adducts below 60°. Because of the irreversible decomposition of diborane at elevated temperatures, however, only 15 minutes were allowed for thermal equilibration of borane complexes above 60°.

For a detailed discussion of the actual operation and limits of accuracy of the dissociation tensimeter, the reader is referred to the literature.[14] In order to check our equipment and techniques, the gas-phase dissociation of the two compounds trimethylamine–trimethylborane and trimethylphosphine–trimethylborane was studied. For $Me_3N\cdot BMe_3$ we obtained $\Delta H = 17.78 \pm 0.2$ kcal. mole^{-1} (lit.[14] 17.62 kcal. mole^{-1}) and for $Me_3P\cdot BMe_3$, $\Delta H = 16.53 \pm 0.2$ kcal. mole^{-1} (lit.[15] 16.49 kcal. mole^{-1}).

3. **Preparation and Study of Complexes. Tetrahydrofuran–Borane.**—The existence of this compound has been clearly demonstrated by phase studies,[16] and the adduct has proven very useful in preparative borane chemistry.[17] The compound $Me_2O\cdot BH_3$ is known to be completely dissociated in the gas phase.[18] There has been no reported study of the degree of dissociation of $(CH_2)_4O\cdot BH_3$ as gas, so it was thought worthwhile to determine whether this compound is also completely dissociated.

In a dissociation tensimeter, a sample of diborane matched with exactly twice its volume of tetrahydrofuran exerted a pressure of 60.50 mm. at 30.1°. The pressure expected for 100% dissociation was 60.09 mm. The compound is thus fully dissociated as gas at room temperature.

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(6) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, 351 (1954).

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(10) N. Davidson and H. C. Brown, *ibid.*, **64**, 316 (1942).

(11) (a) W. N. Hubbard, H. L. Finke, D. W. Scott, J. P. McCullough, C. Katz, M. E. Gross, J. F. Messerly, R. E. Pennington and G. Waddington, *ibid.*, **74**, 6025 (1953); (b) D. W. Scott, H. L. Finke, W. N. Hubbard, J. P. McCullough, G. D. Oliver, M. E. Gross, C. Katz, K. D. Williamson, G. Waddington and H. M. Huffman, *ibid.*, **74**, 4656 (1952).

(12) The apparatus used was a Reco Distillograph, Model D 2000.

(13) A. B. Burg and H. I. Schlesinger, This Journal, **59**, 780 (1937).

(14) (a) H. C. Brown, M. D. Taylor and M. Gerstein, *ibid.*, **66**, 431 (1944); (b) H. C. Brown and M. Gerstein, *ibid.*, **72**, 2923 (1950).

(15) S. Sujishi, Ph.D. Thesis, Purdue University, 1949.

(16) B. Rice, J. A. Livasy and G. W. Schaeffer, This Journal, **77**, 2750 (1955).

(17) A. B. Burg and J. L. Boone, *ibid.*, **78**, 1521 (1956).

(18) (a) H. I. Schlesinger and A. B. Burg, *ibid.*, **60**, 290 (1938); (b) *Chem. Revs.*, **31**, 1 (1942).

In the saturation pressure tensimeter, 50.0 cc.[19] of tetrahydrofuran and 25.0 cc. of diborane were brought together at −78°, forming a solid (saturation pressure ~1.6 mm. at −78°). Saturation pressures of liquid $(CH_2)_4O{\cdot}BH_3$, given in Table I, determine the equation $\log P_{\text{mm.}} = 6.592 - 1244T^{-1}$, whence one calculates the "boiling point" as 62°, and the Trouton constant as 17.0 cal. deg.$^{-1}$ mole^{-1}.

TABLE I

SATURATION PRESSURES OF LIQUID $(CH_2)_4O{\cdot}BH_3$

t, °C.	0.0	10.3	20.4	30.4	40.5
P_{mm} (obsd.)	109.5	160	224	311	425
P_{mm} (calcd.)	109.2	160	226	312	423

Thiophane–Boron Trifluoride.—A 69.3-cc. sample of thiophane was distilled into the saturation pressure tensimeter and 69.6 cc. of boron trifluoride added. On gradual warming, reaction was observed, but it was not complete inasmuch as about 32 mm. residual pressure remained after 16 hr. at −78.5°. The system was then allowed to warm to about −23° and was maintained at this temperature for 30 minutes. On cooling to −78.5° the residual pressure was very small, and, after removal of 0.5 cc. of boron trifluoride, could not be detected with a cathetometer. The 1:1 adduct thus formed is a solid at −45° and a liquid at −23°. Saturation pressures recorded in Table II enabled the constants for $(CH_2)_4S{\cdot}BF_3$ in Table IX to be calculated.

TABLE II

SATURATION PRESSURES OF LIQUID $(CH_2)_4S{\cdot}BF_3$

t, °C.	5.3	9.9	14.9	24.9	27.2	29.8
P_{mm} (obsd.)	42.3	53.7	68.5	111.7	124.1	139.2
P_{mm} (calcd.)	42.2	53.6	69.0	111.4	123.9	139.3

In a dissociation tensimeter (360.0-cc. volume), a 5.923-cc. sample of boron trifluoride was treated with 5.915 cc. of thiophane. At 28.7° the pressure observed was 27.41 mm., corresponding to 98.4% dissociation.[20] At the lowest temperature at which no liquid was present in the tensimeter, the adduct $(CH_2)_4S{\cdot}BF_3$ was so highly dissociated that a meaningful study of the variation of K_p with temperature was impossible. It should be noted that saturation pressures of the complex, obtained with a 69-cc. sample in a 94-cc. tensimeter, cannot be used to predict whether or not a liquid phase will be present in the large dissociation tensimeter. For this reason great care has to be taken to ensure that an "α" being measured is a true α and that no liquid is present in the tensimeter.

Diethyl Sulfide–Boron Trifluoride.—Diethyl sulfide (64.8 cc.) treated with boron trifluoride (64.4 cc.) yielded a liquid complex having no detectable saturation pressure at −78°. Saturation pressure measurements are given in Table III. These measurements lead to the constants recorded for $Et_2S{\cdot}BF_3$ in Table IX.

TABLE III

SATURATION PRESSURES OF LIQUID $Et_2S{\cdot}BF_3$

t, °C.	0.2	1.2	2.0	3.0	5.1	9.7	14.4	19.4
P_{mm} (obsd.)	41.4	42.9	45.3	48.2	54.0	70.6	90.2	116.1
P_{mm} (calcd.)	41.0	43.4	45.5	48.2	54.3	70.0	90.0	116.6

In a dissociation tensimeter (360.0-cc. volume) a 7.691-cc. sample of $Et_2S{\cdot}BF_3$ exerted a pressure of 34.58 mm. at 30.7°. This corresponds to 97.9% dissociation.

Thiophane–Borane.—A 59.0-cc. sample of thiophane with 29.5 cc. of diborane combined to form a solid at −78° in the saturation pressure tensimeter. At −78°, saturation pressure of the solid was about 0.7 mm. The complex melted over the range −30° to −35°, with slight gas evolution. At its melting point (−45°)[16] tetrahydrofuran–borane evolves gas vigorously.

Saturation pressures of liquid $(CH_2)_4S{\cdot}BH_3$ are as tabulated (Table IV). These values lead to the thermodynamic constants in Table IX.

TABLE IV

SATURATION PRESSURES OF LIQUID $(CH_2)_4S{\cdot}BH_3$

t, °C.	19.5	30.2	40.6	49.3	59.5
P_{mm} (obsd.)	4.64	9.17	16.4	25.4	40.5
P_{mm} (calcd.)	4.69	8.94	16.0	25.4	42.2

To make certain that hydrogen had not formed during study of the gas phase dissociation of a sample of $(CH_2)_4S{\cdot}BH_3$, the pressure reading at 60.5° was repeatedly checked. All determinations were made in a dissociation tensimeter of volume 347.2 cc. The quantities of donor and diborane used in three typical experiments were

Determination	B_2H_6 (cc.)	Thiophane (cc.)
1	2.177	4.308
2	2.778	5.557
3	2.468	4.901

Only in determination 2 were the samples matched with sufficient exactness so that the equation

$$K_p(\text{atm.})^{1/2} = \frac{\alpha(P_{\text{obsd.}} - P_{\text{calcd.}})^{1/2}}{(1-\alpha)(760)^{1/2}}$$

could be used to calculate data. In experiments 1 and 3 K_p values were calculated from the relationship

$$K_p(\text{atm.})^{1/2} = \frac{(P_{\text{obsd.}} - P'_{\text{L}})^{1/2}(2P_{\text{obsd.}} - 2P'_{B_2H_6} - P'_{\text{L}})}{2(P'_{B_2H_6} + P'_{\text{L}} - P_{\text{obsd.}})(760)^{1/2}}$$

where P'_{L} and $P'_{B_2H_6}$ are the pressures which would be exerted at a given temperature by the base ($(CH_2)_4S$) and by B_2H_6 if present individually in the tensimeter.

Dissociation data are given in Table V.

The pressure reading taken at 97.6° was not used at all in determining the relationship between $\log K_p$ and T^{-1}. If all other pressure readings are used, including the one at 88.1°, then

$$\log K_p(\text{atm.}^{1/2}) = 3.41 - 1123T^{-1} \qquad \text{(I)}$$

for the dissociation

$$(CH_2)_4S{\cdot}BH_3(g) \rightleftarrows (CH_2)_4S(g) + {}^1/_2B_2H_6(g)$$

If the 88.1 and 97.6° pressure readings are omitted then

$$\log K_p(\text{atm.})^{1/2} = 2.66 - 872.8T^{-1} \qquad \text{(II)}$$

Equation II is undoubtedly the more reliable one, leading to $\Delta H^0 = 4$ kcal. mole^{-1}, while (I) *serves to place an upper limit of 5.1 kcal. mole*$^{-1}$ *on* $\Delta H°$.

Diethyl Sulfide–Borane.—A 30.8-cc. sample of diborane combined with 62.1 cc. of diethyl sulfide at −78.5°, implying the formation of the molecular addition compound $Et_2S{\cdot}BH_3$. The adduct is a liquid at −78.5° and has no detectable saturation pressure at this temperature. Saturation pressure measurements are recorded in Table VI; they permit calculation of the constants for $Et_2S{\cdot}BH_3$ given in Table IX.

The dissociation of $Et_2S{\cdot}BH_3$ in the gas phase was studied in a tensimeter of volume 360.0 cc. In a representative experiment, using 3.510 cc. of diborane and 7.002 cc. of diethyl sulfide, the results given in Table VII were obtained.

The variation of K_p with temperature is represented by the equation

$$\log K_p(\text{atm.}^{1/2}) = 4.031 - 1351T^{-1}$$

whence

$$\Delta F^0{}_{\text{T}} = 6181 - 18.44T \text{ cal. mole}^{-1}$$

Therefore, for the reaction

$$Et_2S{\cdot}BH_3(g) \rightleftarrows Et_2S(g) + {}^1/_2B_2H_5(g),$$

$\Delta H^0 = 6.2$ kcal. mole^{-1}, and $\Delta S° = 18.4$ e.u.

Dimethyl Sulfide–Borane.—The gas-phase dissociation of this compound was studied by Graham,[1] but the tensimeter used was too small for accurate work. For this reason it was decided to reinvestigate the dissociation of $Me_2S{\cdot}BH_3$. In a representative experiment, using 11.99 cc. of $Me_2S{\cdot}BH_3$ in a tensimeter of volume 371.4 cc., the results presented in Table VIII were obtained.

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[19] Throughout this paper the abbreviation cc. refers to gases at standard conditions.

[20] In early experiments, spuriously low values of degree of dissociation were observed, which proved to be due to the occurrence of slight decomposition. By careful pre-conditioning of the tensimeter and prolonged degassing of the mercury at elevated temperatures, decomposition was eliminated and reproducible values of α were obtained.

TABLE V

GAS-PHASE DISSOCIATION OF $(CH_2)_4S\cdot BH_3$

	t, °C.	$P_{obsd.}$ (mm.)	$P_{calcd.}$, mm. $P'_{B_2H_6}$	$P'_{(CH_2)_4S}$	α	K_p (atm.$^{1/2}$)	K_p calcd. (atm.$^{1/2}$) (II)	(1)
Run 1	64.4	17.14	5.889	11.652	0.931	1.153	1.19	1.21
Run 2	56.6	21.42	14.696		.915	1.016	1.02	1.01
Run 3	55.4	18.88	6.497	12.903	.919	1.001	1.00	1.00
	60.5	19.21	6.598	13.130	.925	1.109	1.11	1.11
	65.5	19.53	6.697	13.300	.930	1.216	1.21	1.24
	60.5[a]	19.23						
	88.1	21.02	7.144	14.187	.956	2.047	1.75	2.00
	60.5[b]	19.17						
	97.6	21.64	7.332	14.560	.966	2.738	2.02	2.40
	60.5[c]	19.30						

[a] Check point. [b] Second check point, system probably beginning to show alteration. [c] Third check point, definite increase. Indicates that the 97.6° point is not usable.

TABLE VI

SATURATION PRESSURES OF LIQUID $Et_2S\cdot BH_3$

t, °C.	20.0	25.0	30.3	35.2	40.4	45.0	60.0	69.6
P_{mm} (obsd.)	6.5	8.9	12.3	16.4	22.1	28.4	61.6	99.6
P_{mm} (calcd.)	6.5	8.9	12.3	16.4	22.1	28.5	62.2	99.1

TABLE VII

GAS-PHASE DISSOCIATION OF $Et_2S\cdot BH_3$[a]

t, °C.	$P_{obsd.}$ (mm.)	$P_{calcd.}$, mm. $P'_{B_2H_6}$	P'_{Et_2S}	α	K_p (atm.$^{1/2}$)
48.1	24.99	8.717	17:387	0.872	0.682
52.0	25.37	8.822	17.598	.880	.743
56.5	25.83	8.945	17.842	.893	.857
60.2	26.19	9.045	18.042	.901	.939
64.4	26.62	9.159	18.269	.912	1.082
67.9	26.96	9.254	18.459	.918	1.183
60.2[b]	26.18	...	....	...	...

[a] In this and the succeeding table, dissociation data are given over a 20° temperature range of maximum reliability. Additional data were taken outside the 20° range, and the results were in good agreement with the equation determined by the shorter range. [b] Check point on cooling.

TABLE VIII

GAS-PHASE DISSOCIATION OF $Me_2S\cdot BH_3$

t, °C.	$P_{obsd.}$, (mm.)	$P_{calcd.}$, (mm.)	α	K_p (atm.$^{1/2}$)
42.9	39.94	28.384	0.814	0.540
46.2	40.54	28.680	.827	.598
48.9	41.02	28.922	.837	.645
52.0	41.58	29.201	.848	.712
55.0	42.08	29.470	.856	.764
58.0	42.60	29.740	.865	.832
60.9	43.12	30.000	.875	.918
55.0[a]	42.08			

[a] Check point on cooling.

For the reaction

$$Me_2S\cdot BH_3(g) \rightleftharpoons Me_2S(g) + {}^1/_2B_2H_6(g)$$

variation of K_p with temperature is represented by the equation

$$\log K_p\ (\text{atm.}^{1/2}) = 3.930 - 1327T^{-1}$$

whence $\Delta F^0{}_T = 6072\text{-}17.98T$ cal. mole^{-1}, $\Delta H^0 = 6.1$ kcal. mole^{-1}, and $\Delta S^0 = 18.0$ e.u. Graham[1] reported $\Delta H^0 = 5.2$ kcal. mole^{-1}. The new value for ΔH^0 does not of course change any of the relative orders of coördination previously established.[1]

Because $Me_2S\cdot BH_3$ is much less dissociated than $(CH_2)_4S\cdot BH_3$, it is probable that the enthalpy of dissociation (6.1 kcal.) is within ±0.5 kcal. This applies also to $Et_2S\cdot BH_3$.

Discussion

Results presented in the Experimental section show that the adducts $Et_2S\cdot BF_3$ and $(CH_2)_4S\cdot BF_3$ are nearly completely dissociated in the gas phase. The donor–acceptor bonds in these sulfide adducts are much weaker than those in $Et_2O\cdot BF_3$ and $(CH_2)_4O\cdot BF_3$ studied by Brown and Adams.[8] For the etherate $Et_2O\cdot BF_3$ the enthalpy change for dissociation is reported to be 10.9 kcal. mole^{-1}, while for $(CH_2)_4O\cdot BF_3$ it is reported to be 13.4 kcal. mole^{-1}. The adduct $Me_2S\ BF_3$ studied by Graham[1] is also much less stable than $Me_2O\cdot BF_3$.[8] Hence, toward boron trifluoride all the thioethers are weaker bases than their oxygen analogs. Results summarized in Table IX demonstrate the relatively low stabilities of boron trifluoride–thioether complexes. For $(CH_2)_4S\cdot BF_3$ and $Et_2S\cdot BF_3$ the difference in boiling point between the complex and the donor moiety (Δ(b.p.)) is a negative quantity. A similar situation occurs for $(CH_2)_4O\cdot BH_3$ ("b.p." complex 62°, b.p. tetrahydrofuran 66°). It appears to be a general rule that whenever Δ(b.p.) is negative, the complex proves to be so highly dissociated in the gas phase that meaningful studies of variation of K_p with temperature are very difficult.

With boron trifluoride as the reference acid, Brown and Adams[8] showed that the order of basicity of the ethers was $(CH_2)_4O > Me_2O > Et_2O$. It is of interest to establish an order of coördination for the thioethers toward boron trifluoride. Unfortunately, it is not possible to do this quantitatively by tensimetry because of the high degree of dissociation of the various adducts in the gas phase. However, it is possible to arrive at a probable order of donor power for the thioethers based on volatility considerations. For complexes of low stability it has long been customary to deduce relative stabilities from relative volatilities.[5] If two addition compounds have similar structures and molecular weight, the less stable has the higher saturation pressure. If two addition compounds differ in molecular weight and the heavier is the more volatile, this is taken to indicate that it is also more highly dissociated. This rule is somewhat limited in its application since it is often desired to compare stabilities of two addition compounds where the heavier is the least volatile. For example, in the work described in this paper it is of interest to determine the relative stabilities of $Me_2S{\cdot}BF_3$ and $(CH_2)_4S{\cdot}BF_3$. The former compound is the more volatile but since the latter has a higher molecular weight, it is not possible to infer that it is the most stable. For a situation of this kind we suggest that relative stability may often be determined from a consideration of Trouton constant values, and the difference in boiling point between that of the adduct and that of the donor molecule.[21]

The concept may be illustrated by first considering briefly trends in Trouton constant values for molecular addition compounds of the Group III elements. A summary of such Trouton constants has been given elsewhere.[5] For complexes which are highly stable (*e.g.*, $Me_3N{\cdot}BH_3$, $Me_3N{\cdot}BF_3$, $Me_3P{\cdot}AlMe_3$, $Me_3N{\cdot}GaMe_3$), Trouton constants are greater than 21 but usually less than 30, and variations in the values undoubtedly depend on the extent of dipole associations in a condensed phase in equilibrium with a vapor. For complexes of moderate or weak stability, those with high degrees of dissociation in the gas phase and low or immeasurable enthalpies of dissociation, Trouton constants vary from values as low as 17 to as high as 40. In such complexes other effects occur as well as dipole interactions. When high Trouton constants are observed, vaporization of the addition compound is being accompanied by an increase in dissociation. When low Trouton constants are observed, the addition compounds being highly dissociated in the gas phase, the adducts are undoubtedly well dissociated even as liquids. Therefore, in a series of *weak addition compounds*, having the same reference base or same reference acid, there appears to be a decrease in Trouton constant with decreasing stability. There are many examples of this behavior in the literature, *e.g.*, $Me_2HP{\cdot}BMe_3$ (T_c = 39 e.u., ΔH, 11.5 kcal.) and $MeH_2P{\cdot}BMe_3$ (T_c = 34 e.u., ΔH, too small to be measured)[22]; $Me_2S{\cdot}AlMe_3$ (T_c = 27 e.u., ΔH, 8.5 kcal.), $Me_2Se{\cdot}AlMe_3$ (T_c = 25.3, ΔH, 6 kcal.) and $Me_2Te{\cdot}AlMe_3$ (T_c = 22 e.u., ΔH, too small to be measured).[23] When vaporization of an addition compound is accompanied by dissociation, it is well known that extrapolation of the vapor pressure equation cannot give a true boiling point. The difference between the apparent boiling point of the complex and the boiling point of the ligand is significant, however, and merits consideration. From a study of data for weak complexes in the literature, it appears that for two adducts involving the pairing of two bases B or B′ with a reference Lewis acid A, the base strength of B is greater than that of B′ if

$$(\text{“b.p.”}_{B:A} - \text{b.p.}_{B}) > (\text{“b.p.”}_{B':A} - \text{b.p.}_{B'})$$
$$[\Delta_{(\text{b.p.})} > \Delta'_{(\text{b.p.})}]$$

Many pairs of weak complexes illustrate this rule, *e.g.*, $Me_2HP{\cdot}BF_3$ (ΔH = 14.7 kcal., Δ (b.p.) = 86°) and $MeH_2P{\cdot}BF_3$ (ΔH too small to be measured Δ(b.p.) = 33°).[24]

TABLE IX

SULFIDE ADDUCTS OF BORANE AND BORON TRIFLUORIDE

Compound	log p (mm.) = $B - AT^{-1}$ B	A	B.p.[a] (°C.)	B.p. of base (°C.)	Trouton constant of complex[a] (e.u.)	Δ[b] (b.p.) (°C.)
$Me_2S{\cdot}BH_3$[c]	9.220	2346	97	36	29.0	+61
$Et_2S{\cdot}BH_3$	8.991	2398	119.3	92	28.0	+27.3
$(CH_2)_4S{\cdot}BH_3$	8.602	2321	132.5	121	26.2	+11.5
$Me_2S{\cdot}BF_3$[d]	9.806	2227	48.4	36	31.6	+12.4
$Et_2S{\cdot}BF_3$	8.535	1893	61.6	92	25.9	−30.4
$(CH_2)_4S{\cdot}BF_3$	8.045	1788	73.0	121	23.6	−48.0

[a] By extrapolation of the vapor pressure equation. [b] Δ(b.p.) = boiling point of complex (extrapolated) minus boiling point of donor molecule. [c] From Graham, Ph.D. Thesis, Harvard University, 1956. [d] From reference 1.

Application of these ideas concerning Trouton constants and Δ(b.p.) values to the boron trifluoride adducts of the thioethers (Table IX) suggests a probable order of coördination, $Me_2S > Et_2S > (CH_2)_4S$ toward BF_3. We hope to test this idea by calorimetric studies.

The borane complexes of the thioethers are all clearly more stable than the borane complexes of dimethyl ether,[18] diethyl ether[25] and tetrahydrofuran.[16] Indeed, the thioether complexes of borane, in contrast to the thioether adducts of boron trifluoride, are sufficiently undissociated in the gas phase to permit evaluation of fairly reliable thermodynamic constants for reactions of the type

$$>S{\cdot}BH_3(g) \rightleftarrows >S(g) + {}^1/_2B_2H_6(g)$$

The results are summarized in Table X. Because of the high degree of dissociation of the adducts in the gas phase, the enthalpies of dissociation are not so reliable as those for relatively strong adducts like $Me_3N{\cdot}BMe_3$[14] and $Me_3P{\cdot}BMe_3$.[15] It is possible that for $(CH_2)_4S{\cdot}BH_3$ the uncertainty in $\Delta H°$ is as much as ± 1 kcal., but for the less easily dissociated $Me_2S{\cdot}BH_3$ the uncertainty in $\Delta H°$ is less, probably not more than ± 0.5 kcal. Hence, within the limits of error the adducts $Me_2S.BH_3$ and $Et_2S{\cdot}BH_3$ are of equal stability measured in terms of enthalpies of dissociation. Thiophane–borane is clearly less stable than either $Et_2S{\cdot}BH_3$ or $Me_2S{\cdot}BH_3$· therefore, toward borane, $Me_2S \simeq Et_2S > (CH_2)_4S$ in base strength. This sequence of coördination based on quantitative data is essentially in agreement with the qualitative results summarized in Table IX. For $(CH_2)_4S{\cdot}BH_3$, the Trouton constant and Δ(b.p.) are less than those for either $Me_2S{\cdot}BH_3$ or $Et_2S{\cdot}BH_3$, suggesting that thiophane–borane is less stable than the other two borane adducts. Since the gas-phase heats of dissociation of $Me_2S{\cdot}BH_3$ and $Et_2S{\cdot}BH_3$ within the limits of experimental accuracy are equal, it might have been anticipated that their Trouton constants and Δ(b.p.) values (Table IX) would have been much closer than they are. The observed divergence in these values could be the result of different degrees of dipole interactions for the two liquids, or per-

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[21] For a fuller treatment of this suggestion see H. D. Kaesz, Ph.D. Thesis, Harvard University, 1958.

[22] See reference 15 and H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

[23] G. E. Coates, *ibid.*, 2003 (1951).

[24] E. A. Fletcher, Ph.D. Thesis, Purdue University, 1952. See also H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

[25] H. E. Wirth, F. E. Massoth and D. X. Gilbert, *J. Phys. Chem.*, **62**, 870 (1958).

haps more likely it is due to the heats of dissociation of the two addition compounds in solution being different from their heats of dissociation in the gas phase.

TABLE X

GAS-PHASE DISSOCIATION DATA[a] FOR $Me_2S\cdot BH_3$, $(CH_2)_4S\cdot BH_3$ AND $Et_2S\cdot BH_3$

Compound	Log K_p (atm.$^{1/2}$) = $-A/T + B$ A	B	ΔH^0,[b] kcal. mole^{-1}	ΔS^0,[b] e.u.	ΔF_t^0,[b] at 60°, kcal.	K_p[b] at 60°, (atm.$^{1/2}$)
$Me_2S\cdot BH_3$	1332	3.949	6.1	18.1	0.076	0.894
$(CH_2)_4S\cdot BH_3$	872.8	2.66	4.0	12.2	− .061	1.10
$Et_2S\cdot BH_3$	1312	3.899	6.0	17.8	.058	0.918

[a] The values reported are averages, except for $(CH_2)_4S$, where constants have been calculated as described in the Experimental part. [b] ΔH^0, ΔS^0, ΔF_T^0 and K_p values are for the dissociation

$$L\cdot BH_3(g) \longrightarrow L(g) + {}^1/_2B_2H_6(g)$$

Of interest in borane chemistry is the enthalpy change for the reaction

$$>S\cdot BH_3(g) \longrightarrow >S(g) + BH_3(g)$$

For the reaction

$$ {}^1/_2B_2H_6(g) \longrightarrow BH_3(g) \qquad \Delta H^0 = 14.0 \text{ kcal. mole}^{-1} \quad \Delta S^0 = 17.1 \text{ e.u.}^{26}$$

Therefore, for

$$Me_2S\cdot BH_3(g) \longrightarrow Me_2S(g) + BH_3(g) \qquad \Delta H^0 = 20.1 \text{ kcal. mole}^{-1} \quad \Delta S^0 = 35.2 \text{ e.u.}$$

For the dissociation

$$(CH_2)_4S\cdot BH_3(g) \longrightarrow (CH_2)_4S(g) + BH_3(g) \qquad \Delta H^0 = 18.0 \text{ kcal. mole}^{-1} \quad \Delta S^0 = 29.3 \text{ e.u.}$$

and for

$$Et_2S\cdot BH_3(g) \longrightarrow Et_2S(g) + BH_3(g) \qquad \Delta H^0 = 20.0 \text{ kcal. mole}^{-1} \quad \Delta S^0 = 34.9 \text{ e.u.}$$

When compared to the order observed with the ethers $(CH_2)_4O > Me_2O > Et_2O$,[8,16,27] the order of base strength $Me_2S \simeq Et_2S > (CH_2)_4S$ observed toward borane, and probably toward boron trifluoride, is in accord with the idea that steric effects are much diminished with second-row ligand atoms. In this respect it is interesting that Graham[1] was able to isolate $Me_2S\cdot BMe_3$, but $Me_2O\cdot BMe_3$ did not exist down to −78°. It is very probable, however, that orbital hybridization of the donor atom in a sequence such as $Me_2S \simeq Et_2S > (CH_2)_4S$ plays an important part in base strength.[1,28] It is unfortunate that little information is available on the bond angles in Et_2S and $(CH_2)_4S$.

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(26) (a) R. E. McCoy and S. H. Bauer, THIS JOURNAL, **78**, 2061 (1956); (b) S. H. Bauer, *ibid.*, **78**, 5775 (1956).

(27) B. Rice and H. S. Uchida, *J. Phys. Chem.*, **59**, 650 (1955).

(28) J. H. Gibbs, *J. Chem. Phys.*, **22**, 1460 (1954).