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The Behavior of Boron Fluoride toward Some Amino Sulfur Compounds

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The compound $[(CH_3)_2N]_2S$ (m.p. 20°, b.p. est. 127°) holds $2BF_3$ firmly *in vacuo* at 165°, while $[(CH_3)_2N]_2SO$ (m.p. 31°, b.p. est. 209°) forms a less stable $1.5BF_3$ adduct for which $\log_{10} p_{diss.}$ (mm.) = 4.143 − 1274/*T*, and $[(CH_3)_2N]_2SO_2$ (known m.p. 73°, b.p. est. 225°) holds only one BF_3, still more weakly. It is argued that the main reason for such a trend of decreasing BF_3-bonding power is the inductive effect of O in increasing the N→S π-bonding, rendering the otherwise unshared electrons of N less available for bonding BF_3; steric and crystal-energy effects are regarded as minor. The compound CH_3NSO (b.p. 57°) forms the solid adduct $CH_3NSO\cdot BF_3$ ($\Delta F^0_{diss.}$ = 31.41 − 0.09105)*T* kcal.), supporting the assumption that BF_3 attaches to N in amine sulfoxides.

The series of compounds $[(CH_3)_2N]_2S$, $[(CH_3)_2N]_2SO$ and $[(CH_3)_2N]_2SO_2$ may be regarded as analogous to a series of alkyl esters of sulfoxylic, sulfurous and sulfuric acids. On this ground alone one might expect them to bond to a Lewis acid, such as boron fluoride, with the same decreasing order of bond-strengths as the order of diminishing proton-affinities of oxyanions of increasing oxygen content. Or it can be argued that any attachment of boron fluoride to the amino sulfur compounds should be through bonding to nitrogen rather than to oxygen or sulfur; then the attachment of O to S in $[(CH_3)_2N]_2S$ would make S more electronegative, strengthening the two one-sided N→S dative π-bonds (formed from N-2sp^3 and S-3d4s hybrid orbitals) and so lowering the external bonding power of the corresponding N-electrons. A second O on S should further weaken the external bonding power of N; also attachment of one BF_3 to N should weaken a second N→BF_3 bond.

These expectations are fully confirmed by experimental results showing that $[(CH_3)_2N]_2S\cdot 2BF_3$ is very stable, that $[(CH_3)_2N]_2SO\cdot 1.5BF_3$ is far less stable, probably dissociating to a stable $[(CH_3)_2N]_2SO\cdot BF_3$, and that $[(CH_3)_2N]_2SO_2\cdot BF_3$ is very unstable. That the bonding preference is for N→B rather than O→B or S→B is indicated by the formation of a moderately stable $CH_3NSO\cdot BF_3$, in contrast to the absence of bonding between SO_2 and BF_3 under comparable conditions.[2]

Although the qualitative predictions are verified, the bond-induction effects are not necessarily the only cause of the observed trend. An attachment of O to S should provide a steric hindrance to the bonding of BF_3 to N, but studies of molecular models, even allowing for a widened N–S–N angle on account of the π-bonding, show that the steric effect should be small. Another effect arises from the solid-state energies. Since $[(CH_3)_2N]_2S$ and $[(CH_3)_2N]_2SO$ are liquids just above room temperature while their BF_3-adducts are solids, some crystal-energy stabilization must be considered; on the other hand $[(CH_3)_2N]_2SO_2$ is itself a solid and might well be more closely-knit than its adduct. But the molar heats of fusion of these solids would be only 3 to 5 kcal. at most, and the differences would be far smaller. Also, there is no reason to expect any important differences of solid-state energy among the adducts. Hence the electronic induction effects would appear to be the main cause of the observed trend of adduct stability.

Experimental Part

I. Preparation and Physical Properties of Reactants

Thionyl Methylamine.—Thionylaniline was obtained by the reaction of thionyl chloride with aniline hydrochloride in benzene under reflux,[3] and treated with methylamine[4] in toluene at −40°. The mixture was warmed to −5° during 12 hours and allowed to stand for 12 hours at −5° and 3 hours at 20°. The desired CH_3NSO then was distilled out and purified by redistillation—finally with fractional condensation at −73° in the high-vacuum system,[5] to give a water-white product.

The vapor tensions of pure CH_3NSO, shown in Table I, determine the equation $\log_{10} p_{mm.}$ = 7.886 − 1650/*T*, from which the normal boiling point is computed to be 56.5° (obsd. 57–58°). The Trouton constant is 22.9 cal./deg. mole.

TABLE I

VAPOR TENSIONS OF LIQUID CH_3NSO

t (°C.)	−21.0	−16.0	−13.0	−8.0	0.0	3.8
$p_{mm.}$ (obsd.)	22.0	29.5	35.0	46.0	71	85
$p_{mm.}$ (calcd.)	22.0	29.5	35.0	46.0	70	85

N,N'-Thio-bis-dimethylamine.—Sulfur dichloride in ether was added dropwise to a 4 mole proportion of dimethylamine in ether,[6] stirred at −78°. A few days later the mixture was warmed to room temperature and the $(CH_3)_2NH_2Cl$ was filtered off. The $[(CH_3)_2N]_2S$ was isolated by distillation (38–43° (20 mm.)) and purified by repeated fractional condensation under high vacuum at −20°.

The vapor tensions of pure $[(CH_3)_2N]_2S$, measured in the immersible tensimeter[7] and shown in Table II, determine the equation $\log_{10} p_{mm.}$ = 8.116 − 2095/*T*, according to which the normal boiling point is 127° and the Trouton constant 23.9 cal./deg. mole. Measurements of the vapor density gave the molecular weight as 119.7 or 120.5 (calcd., 120.2). The melting point is 20°.

TABLE II

VAPOR TENSIONS OF LIQUID $[(CH_3)_2N]_2S$

t (°C.)	28.0	33.0	38.0	43.0	48.0	53.0
$p_{mm.}$ (obsd.)	14.5	18.6	24.2	30.6	39.5	49.5
$p_{mm.}$ (calcd.)	14.5	18.7	24.2	30.9	39.2	49.3

N,N'-Thionyl-bis-dimethylamine.—The calculated proportion of thionyl chloride was added dropwise to dimethylamine (both in ether) at −78°.[8] The product was isolated

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(2) A. B. Burg and L. L. Martin, THIS JOURNAL, **65**, 1635 (1943).

(3) A. Michaelis, *Ber.*, **24**, 746 (1891).

(4) A. Michaelis, *Ann.*, **274**, 187 (1893).

(5) A. B. Burg, THIS JOURNAL, **56**, 499 (1934).

(6) E. S. Blake, *ibid.*, **65**, 1267 (1943).

(7) A. B. Burg and H. I. Schlesinger, *ibid.*, **59**, 785 (1937).

(8) Method adapted from that used by A. Michaelis, *Ber.*, **28**, 1016 (1895), for the corresponding ethyl compound.

by crystallization and purified by distillation (63–65° (4 mm.)).

The vapor tensions of pure $[(CH_3)_2N]_2SO$, measured in the immersible tensimeter[7] and shown in Table III, determine the equation $\log_{10} p_{mm.} = 7.380 - 2170/T$, according to which the boiling point is near 209° and the Trouton constant 20.6 cal./deg. mole.

TABLE III

VAPOR TENSIONS OF LIQUID $[(CH_3)_2N]_2SO$

t (°C.)	p, mm. (obsd.)	p, mm. (calcd.)	t (°C.)	p, mm. (obsd.)	p, mm. (calcd.)
47.0	3.9	4.0	62.6	8.3	8.3
49.0	4.5	4.4	68.0	10.2	10.4
52.0	5.1	5.1	73.0	12.8	12.9
57.3	6.4	6.5	78.0	16.0	15.9

Tetramethylsulfamide.—Sulfuryl chloride was dropped into dimethylamine (calcd. proportion, both in chloroform) at 0° and the resulting $[(CH_3)_2N]_2SO_2$ was purified by recrystallization from ethanol,[9] followed by sublimation.

The vapor tensions of the product above the melting point (73°)[9] are shown in Table IV. They determine the equation $\log_{10} p_{mm.} = 8.492 - 2796/T$. The boiling point thus is 225° and the Trouton constant 25.7 cal./deg. mole. The vapor density implied a molecular weight value of 155 (calcd. 152).

TABLE IV

VAPOR TENSIONS OF LIQUID $[(CH_3)_2N]_2SO_2$

t (0°C.)	85.4	90.0	116.4	126.0	136.0	150.0
$p_{mm.}$ (obsd.)	4.94	6.17	20.3	30.6	45.4	77.3
$p_{mm.}$ (calcd.)	4.90	6.21	20.6	30.7	45.5	76.7

II. The Boron Fluoride Adducts

Thionyl Methylamine.—A sample of CH_3SNO was condensed in the immersible tensimeter[7] with a little more than an equimolar proportion of BF_3 and the mixture formed a white solid upon warming. The excess BF_3 was removed at a low temperature, leaving exactly a 1:1 proportion of CH_3NSO and BF_3 in the solid. No evidence could be found for any fluoride-shift reaction, such as would have led to CH_3NBF_2SOF or even $CH_3NBF + SOF_2$.

A known sample of the adduct was vaporized in a known volume, and pressures ranging from 110 mm. at 50.1° to 129.2 mm. at 101° implied average molecular weights ranging from 75.3 to 73.4; the average for complete dissociation would be 72.46. Hence the pressures corresponding to the solid–vapor equilibria, shown in Table V, represent dissociation pressures which are disturbed only slightly by vapor-phase interactions. These values determine the equation $\log_{10} p_{mm.} = 12.83 - 3432/T$, implying that $\Delta F°_{diss.} = 31.41 - 0.0883T$ kcal., uncorrected for vapor-phase interactions.

TABLE V

DISSOCIATION PRESSURES OF SOLID $CH_3NSO \cdot BF_3$

t (°C.)	15.4	20.0	25.0	30.0	35.0	40.0
$p_{mm.}$ (obsd.)	7.7	13.1	21.0	32.3	50.3	74.3
$p_{mm.}$ (calcd.)	8.3	13.3	20.9	32.3	49.3	74.3

N,N'-Thio-bis-dimethylamine.—The combination of $[(CH_3)_2N]_2S$ with BF_3 readily yielded solid adducts, at first in odd ratios such as 1.45 BF_3 per mole of $[(CH_3)_2N]_2S$. Only by heating (conveniently at 100°) with excess BF_3 was it possible to arrive at ratios determined as 1.96 and 2.05 in two different experiments. In a third experiment, special efforts were made to attach more BF_3, but only $[(CH_3)_2N]_2S \cdot 2BF_3$ resulted.

The sample empirically designated as $[(CH_3)_2N]_2S \cdot 1.96BF_3$ was heated under high vacuum at 165°, yielding a trace of BF_3, at a sharply diminishing rate—probably a desorption rather than a true dissociation. Thus the 2:1 adduct seemed to be essentially stable under these conditions.

N,N'-Thionyl-bis-dimethylamine.—As in the preceding case, the addition of more than one BF_3 to one $[(CH_3)_2N]_2SO$ occurred slowly and incompletely at room temperature but could be improved by heating at 100° with excess BF_3. However, the addition of the second BF_3 was easily reversible, and the total absorption could not be pushed beyond $1.67BF_3$ per mole. Even at this composition it appeared that a part of the BF_3 was only adsorbed, so that properly reversible dissociation pressures could be measured only at $1.5BF_3$ or lower. A series of such pressures at various temperatures (Table VI) determined the equation $\log_{10} p_{mm.} = 4.143 - 1274/T$.

TABLE VI

DISSOCIATION PRESSURES OF $[(CH_3)_2N]_2SO \cdot 1.5BF_3$

t (°C.)	53.0	63.0	69.0	79.5	90.0	97.5	105.0
$p_{mm.}$ (obsd.)	1.73	2.27	2.57	3.37	4.32	4.97	5.98
$p_{mm.}$ (calcd.)	1.73	2.25	2.63	3.39	4.32	5.02	5.94

It is assumed that the pressure was due entirely to BF_3 from the reaction $2[(CH_3)_2N]_2SO \cdot 1.5BF_3 \rightarrow BF_3 + 2[(CH_3)_2N]_2SO \cdot BF_3$ (solid), since the presence of a liquid or slightly volatile dissociation product would have disturbed the linearity of the graph of $\log p$ *vs.* $1/T$. On this assumption, $\Delta F°_{diss.} = 5830 - 5.774T$ cal./mole of BF_3. However, the meaning of this result is complicated by the question whether there is a solid–solution effect which would lead to a slightly different ΔF equation for a different composition. The main conclusion is qualitative —that the thionyl compound definitely holds less BF_3 less firmly than does the thio-bis-amine.

Tetramethylsulfamide.—A pure sample (0.648 mmole) of $[(CH_3)_2N]_2SO_2$ was treated with BF_3 in excess (0.968 mmole) at room temperature. After constant pressure was attained, the excess BF_3 was measured (0.337 mmole), establishing the combining ratio as $0.974BF_3$ per mole. The most elaborate attempts to increase the ratio beyond 1.00 (including an experiment in liquid sulfur dioxide) were unsuccessful.

Some solid–vapor equilibrium pressures developed by the 1:1 adduct in a 120-ml. tensimeter are shown in Table VII.

TABLE VII

DISSOCIATION EQUILIBRIA OF $[(CH_3)_2N]_2SO_2 \cdot BF_3$

t (°C.)	53.0	63.0	65.0	68.0
$p_{mm.}$ (obsd.)	2.98	7.25	9.8	12.0

These pressures do not correspond either to pure BF_3 over a mixture of non-volatile solids or to a vapor phase composed equally of BF_3 and $[(CH_3)_2N]_2SO_2$, since the latter has observable vapor tensions at the designated temperatures but these are never high enough to account for half of the observed pressures. Hence the results cannot be used to derive meaningful equilibrium constants, but they do show that $[(CH_3)_2N]_2SO_2 \cdot BF_3$ is the least stable BF_3-adduct of the bis-dimethylamino-sulfur series.

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(9) R. Behrend, *Ann.*, **222**, 119 (1884).