of $(CH_3)_3NSO_2$. It is also not difficult to understand the wide difference of stability, between $(CH_3)_3NSO_3$ and $(CH_3)_3NSO_2$, since greater electron density in the latter would tend to weaken the N→S link. Since both compounds are fairly soluble, it seems unlikely that the difference of lattice energy would be an important factor.

The high dative bonding power of trimethylamine oxide already was discernible in the considerable stability of the dihydrate,[12] and now is still more clearly evident. It is easily explained in terms of the singly-bonded oxygen atom in the

structure $R:\overset{R}{\underset{R}{N}}:O:^-$, an oxygen atom which

appears to be in essentially the same condition as that in the hydroxyl ion, an unusually strong electron-donor. It therefore would have been reasonable to expect an attachment to sulfur dioxide, so strong that only the destruction of the amine oxide structure would allow a release of the sulfur dioxide, and also strong enough to destroy the attraction of the amine oxide toward water.

The attachment of more sulfur dioxide to $(CH_3)_3NOSO_2$, to form a definite secondary addition compound, may be regarded as a residual effect of the high external bonding power of the amine oxide oxygen atom. It seems useless to attempt a decision of the question whether the

second sulfur dioxide molecule links to the oxygen of the amine oxide or to one of the SO_2 oxygen atoms, since the tensiometric evidence of dimerization in SO_2 solution leaves doubt concerning the structural plan of this compound. The dimerization might be only a dipole effect, or it might represent a structure quite different from that implied by the formula $(CH_3)_3NOSO_2$.

Summary

Trimethylamine reacts with sulfur dioxide, yielding the solid compound $(CH_3)_3NSO_2$. For the reverse reaction, $\Delta F^0 = 28.95 - 0.07404\ T$ (kcal.). No definite secondary addition compounds could be recognized, but extensive solvation seems to occur in liquid sulfur dioxide solutions. Neither ionization nor association was evident. The compound $(CH_3)_3NSO_3$ is less soluble and less evidently solvated.

Anhydrous trimethylamine oxide absorbs sulfur dioxide at $-80°$, forming the compound $(CH_3)_3NO(SO_2)_2$. This easily loses SO_2 to form the very stable $(CH_3)_3NOSO_2$, distinctly different from $(CH_3)_3NSO_3$. The amine oxide addition compound appears to be dimeric in solution in sulfur dioxide.

The relation of the results to the electron theory of chemical bonding is discussed.

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The Addition of Boron Fluoride to Hexamethylenetetramine

By Anton B. Burg and La Verne Lee Martin[1]

Hexamethylenetetramine, which contains four equivalent tertiary-amine nitrogen atoms,[2,3] appears to offer interesting possibilities for the study of the effect of complex bonding at one nitrogen atom upon the dative bonding power of nearby nitrogen atoms. Such an effect should be most clearly recognizable if one employs only singly-coördinating molecules, such as the boron halides, sulfur trioxide, or phosphorus pentafluoride, for forming the complex compounds with

the polynitrogen tertiary amine. Studies of this character, insofar as they may yield intelligible results, should aid the understanding of numerous metal-complexes of polyfunctional bases.

Each of the four nitrogen atoms of hexamethylenetetramine might be expected to employ its unshared pair of electrons for bonding a molecule of boron fluoride; hence one would expect the addition of four equivalents of boron fluoride as an upper limit. This limit actually can be reached, but only by a very special method.

Treatment of $(CH_2)_6N_4$ with BF_3.—When boron fluoride, generated from potassium fluoborate and purified by a B_2O_3–H_2SO_4 washing tube,[4] was passed into a chloroform

(1) Most of the results here described were taken from a thesis presented by La Verne Lee Martin to the Graduate School of the University of Southern California, in partial fulfillment of the requirements for the degree of Master of Arts, June, 1940. Much of the experimental work was performed in the laboratories at La Verne College, La Verne, California.

(2) Dickinson and Raymond, THIS JOURNAL, 45, 22 (1923).

(3) Hampson and Stosick, ibid., 60, 1814 (1938).

(4) Booth and Willson, ibid., 57, 2273 (1935); "Inorganic Syntheses," McGraw-Hill Book Co., Inc., New York. N. Y., 1939, Vol. I, p. 21.
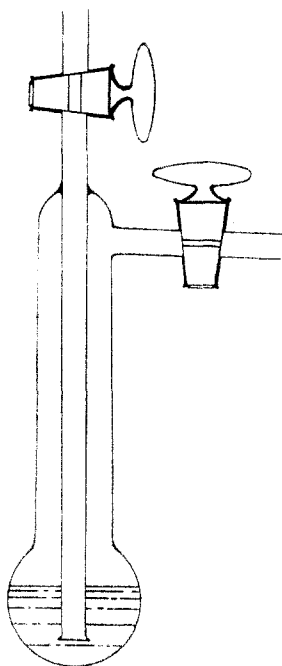
Fig. 1

solution of hexamethylene-tetramine, contained in a weighable bubbler-tube (Fig. 1), the amine was at once precipitated. The chloroform was pumped off at room temperature and the boron fluoride addition could be recognized by the gain in weight. Separate experiments gave combining ratios of 0.67, 0.85, 1.40, 1.50, 1.78, 1.91 and 2.14 moles of boron fluoride per mole of amine. The white solid products were stable toward damp air, and their melting points (with decomposition) ranged from 155 to 185°. The variation of composition appeared to be related to the concentration of the original solution (varying from 13 g. to 4 g. per 100 ml.). It seemed probable that the amine was precipitated before receiving its full quota of boron fluoride, and that further reaction was prevented by the burying of uncoördinated amine units in the solid mass. The reaction therefore could be completed only by use of a solvent capable of exercising a specific attraction for an amine-nitrogen atom, but having less bonding power than boron fluoride.

Such a solvent is sulfur dioxide, which has been shown to add rather weakly to trimethylamine, yielding a compound highly soluble in liquid sulfur dioxide.[5] As a test of its value for the present problem, an extraction experiment was tried: the incomplete-addition product was contained in a weighed alundum thimble, through which sulfur dioxide was refluxed for four hours by means of a "cold finger" at −80°. All but 0.1% of the sample thus was washed through the thimble. Hence it was argued that sulfur dioxide would sufficiently dissolve the products of incomplete addition of boron fluoride, to allow adequate access of boron fluoride.

Accordingly, 0.4304 g. of hexamethylenetetramine was placed in a weighable reaction tube (Fig. 1), dissolved in liquid sulfur dioxide, and treated with boron fluoride at −20°, first for eighty minutes, and then again for eighty minutes on the following day. The sulfur dioxide now was pumped off (finally at room temperature) by a pump having a limit of 6 mm., and the gain in weight was found to be 0.8588 g., representing a ratio of 4.028 moles of boron fluoride per mole of the amine. Evidence that the gain in weight was not partly due to sulfur dioxide, was found during the study of the thermal dissociation: the evolved gas was pumped through cold bromine water, which afterward showed no test for sulfate.

This experiment was repeated by means of the high-vacuum apparatus: in 2 cc. of liquid sulfur dioxide, at −20°, 119 mg. of (CH₂)₆N₄ (19.0 cc. at S. C.) absorbed

(5) Burg, THIS JOURNAL, 65, 1629 (1943).

75.0 cc. of boron fluoride from a 93.2-cc. sample; the remaining boron fluoride was isolated from the sulfur dioxide, identified, and measured back. In this case the ratio $BF_3/(CH_2)_6N_4$ was 3.95. The sulfur dioxide was quantitatively recovered.

The product, $(CH_2)_6N_4 \cdot 4BF_3$, is a white solid which fumes slightly in moist air and melts *in vacuo* at 155-160°. It undergoes irreversible decomposition with darkening at 180°, nearly 100° lower than the charring temperature of hexamethylenetetramine itself.
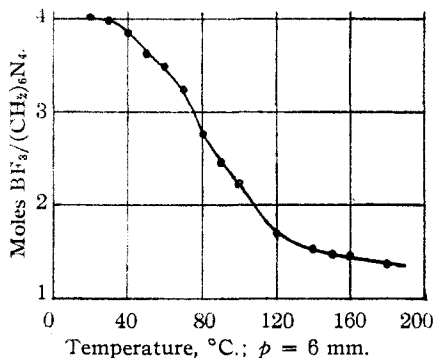

Fig. 2.

Thermal Dissociation of $(CH_2)_6N_4 \cdot 4BF_3$.—The loss of boron fluoride by $(CH_2)_6N_4 \cdot 4BF_3$ was studied by pumping the weighed reaction tube, containing the sample, to apparently constant weight at each of a series of ten-degree stages of rising temperature. Since the pressure always was 6 mm., the shape of the composition–temperature curve (Fig. 2) indicates fairly clearly the increasing difficulty of removal of boron fluoride as the nitrogen atoms are bared. The numerical data (presented in Table I) may not represent true equilibrium conditions, for the solid does not quickly respond to the removal of boron fluoride, and at the higher mole ratios it is nearly inert to added boron fluoride. However, when the compound $(CH_2)_6N_4 \cdot 4BF_3$ was prepared in the high vacuum apparatus, the subsequent attempts to obtain a pressure–composition isotherm at 100° gave results consistent with the curve. Thus at 3.06 boron fluoride, the pressure was 60 mm.; at 2.80, 55 mm.; and at 2.50, 49 mm., all at 100°. The compositions of the latter two points were approached from two directions, but they still may involve some small degree of metastability. It never was possible to obtain a constancy of pressure with slightly varying composition. The original $(CH_2)_6N_4 \cdot 4BF_3$ exhibited a decomposition pressure between 10 and 20 mm. at 23°, but this dropped off very sharply as boron fluoride was removed. It appears that the system involves solid solutions, and that

TABLE I

TEMPERATURE–COMPOSITION ISOBAR OF $(CH_2)_6N_4$–BF_3 AT 6 MM.

Temp., °C.	20	30	40	50	60
Mole ratio $BF_3/(CH_2)_6N_4$	4.03	3.99	3.86	3.63	3.51
Temp., °C.	70	80	90	100	120
Mole ratio $BF_3/(CH_2)_6N_4$	3.25	2.76	2.45	2.25	1.70
Temp., °C.	140	150	160	180	
Mole ratio $BF_3/(CH_2)_6N_4$	1.52	1.47	1.46	1.37	

definite stages of addition of boron fluoride cannot be demonstrated.

Discussion.—From the composition–temperature curve (Fig. 2) it appears that one molecule of boron fluoride is held so firmly that it cannot be liberated at any temperature below the charring point (180°). Apparently the other three molecules of boron fluoride are held much less firmly, as would be expected from a consideration of the electronic induction effects of the first complex-bonded nitrogen atom upon the other three. However, no very precise relation to electron theory can be established here, partly because the character of the secondary addition is not perfectly clear, and also because the changes of lattice energy are not known.

The use of liquid sulfur dioxide as a specific aid in the formation of $(CH_2)_6N_4 \cdot 4BF_3$, represents a technique applicable to numerous similar cases. Its use in studies involving trimeric phosphorus chloronitride, sulfur nitride, and phosphorous anhydride will be reported later.

Summary

The compound $(CH_2)_6N_4 \cdot 4BF_3$ has been prepared by adding boron fluoride to hexamethylene-tetramine, in an assisting solvent, liquid sulfur dioxide. The removal of boron fluoride from this compound, at constant pressure, progresses without discontinuities as the temperature is increased, and tends toward a limit roughly corresponding to $(CH_2)_6N_4 \cdot BF_3$.

The Behavior of Phosphoryl Chloride, Thionyl Chloride and Sulfuryl Chloride toward Boron Halides

BY ANTON B. BURG AND MELVYN K. ROSS[1]

An investigation of the behavior of phosphoryl chloride, thionyl chloride, and sulfuryl chloride toward boron trifluoride and boron trichloride resulted in only one addition compound—the already known $POCl_3 \cdot BCl_3$.[2] When boron fluoride was bubbled into liquid thionyl chloride at −80°, there was no observable reaction, and the liquid showed no gain in weight after warming to room temperature. Sulfuryl chloride was similarly treated at −45.7°, and again the result was negative. A saturated solution of phosphoryl chloride in light petroleum ether was treated with boron fluoride at −80°, also without forming any solid. Experiments at higher temperatures also were negative. Sulfuryl chloride and thionyl chloride, each placed with equivalent quantities of boron trichloride in a closed glass tube, were exposed to varying temperatures down to −80°, without any evidence of combination. In view of the usual experience that addition compounds of boron fluoride form rapidly even at very low temperatures, it seems reasonable to conclude that the expected addition compounds do not exist under the conditions indicated.

The failure of thionyl chloride and sulfuryl chloride to form addition compounds with either of these boron halides, even at temperatures as low as −80°, indicates that the electron-dative external bonding power of oxygen in these compounds is extremely slight. A parallel indication is found in the fact that these sulfur oxychlorides form very stable addition compounds with tertiary amines such as trimethylamine.[3] The sulfur atom in these oxychlorides thus appears to be strongly electron-receptive, and it seems reasonable to attribute this tendency to the availability of 3d orbitals in this atom. A similar weakness may be expected in other oxygen-acid halides, especially of heavier elements not far less electronegative than sulfur.

In the case of phosphoryl chloride, one would expect the central atom, phosphorus, to be less strongly electron-receptive, and the electrons of the oxygen thus conceivably could be employed for bonding a boron halide. However, the ability of phosphoryl chloride to bond boron chloride,

(2) Gustafson, *Z. Chem.*, **7**, 417 (1871); *Ber.*, **4**, 975 (1871).

(3) John C. Mosher and Walter A. Bardrick, unpublished results obtained in this Laboratory.