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 hexamethylenetetramine, 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 $(CH_2)_6N_4 \cdot BF_3$.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE UNIVERSITY OF SOUTHERN CALIFORNIA]

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,

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[1] The experimental results here reported were abstracted from a thesis presented by Melvyn K. Ross to the Graduate School of the University of Southern California in partial fulfillment of the requirements for the degree of Master of Science, February, 1942. The major part of the experimental work was performed at the San Diego State College, the use of whose facilities is gratefully acknowledged.

[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.

but not boron fluoride, is a contrast not readily explained by electron-theoretical arguments. The difference may be a question of crystal geometry.

In order to obtain quantitative information on the strength of the complex link in the compound $POCl_3 \cdot BCl_3$, its dissociation pressures were measured at temperatures between 10 and 35°. This work was done by means of an apparatus patterned after the Jackson gage chamber described by Phipps, Spealman and Cooke.[4] The special all-glass pressure gage, which was necessary because the vapors are reactive toward mercury, was used as a null-manometer.

The compound was prepared by the reaction of highly purified phosphoryl chloride and boron chloride (present in excess), in a small tube attached to the bottom of the chamber surrounding the gage. After an hour at room temperature, the excess boron chloride was pumped off and the compound was sublimed into the evacuated gage-chamber (surrounded by solid carbon dioxide). The reaction tube then was sealed off and the chamber was surrounded by a bath which could be maintained at various fixed temperatures. The temperatures were measured by means of a Bureau of Standards calibrated thermometer. The reliability of this technique was tested by measurement of the vapor tensions of water. The preparative technique here used was essentially the same as that employed by Ingram, whose analysis of the product showed 77.9 and 78.5% chlorine (calcd., 78.6%).[5]

The resulting dissociation pressures, which determine the equation $\log_{10} P_{\text{mm.}} = 11.0836 - (2857/T)$, are presented in Table I. Check measurements, made after pumping away a part of the sample, also agreed with this equation. Equilibrium always was reached very quickly. The material remained solid at all points.

TABLE I

DISSOCIATION PRESSURES OF $POCl_3 \cdot BCl_3$

t, °C.	10.2	12.5	14.0	15.8	19.2	22.5	25.2	27.8	30.2	35.0
$P_{\text{mm.}}$ (obsd.)	10.2	12.1	13.7	15.9	20.6	26.3	32.4	38.9	46.5	65.3
$P_{\text{mm.}}$ (calcd.)	10.06	12.12	13.67	15.77	20.55	25.81	32.30	39.09	46.46	65.10

The density of the vapor evolved from the compound $POCl_3 \cdot BCl_3$ was measured by a modified Dumas method: known samples were vaporized in a completely immersed bulb connecting with an oil null-manometer. From the results, it was calculated that the vapor was 89.5 to 91.2% dissociated at temperatures slightly above the condensation point. The apparent deviation from complete dissociation may properly be attributed to van der Waals forces.

On the assumption that the vaporization is essentially represented by the equation $POCl_3 \cdot BCl_3\ (s) \rightleftarrows POCl_3\ (g) + BCl_3\ (g)$, the pressure-temperature equation may be converted to $\log_{10} K_{\text{atm.}} = 15.803 - (5714/T)$, from which was obtained the expression $\Delta F^0 = 0.0723T - 26.13$ (kcal.). The standard free energy of dissociation thus is calculated as $\Delta F^0_{298} = -4.6$ kcal., subject to the non-ideal behavior indicated by the vapor density results.

Summary

Thionyl chloride and sulfuryl chloride were found to be unreactive toward boron trifluoride and boron trichloride. Phosphoryl chloride fails to react with boron trifluoride, but does form the compound $POCl_3 \cdot BCl_3$, a rhombic-crystalline solid whose stability is represented by an approximate value of the free energy of dissociation: $\Delta F^0_{298} = -4.6$ kcal.

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(4) Phipps, Spealman and Cooke, *J. Chem. Ed.*, **12**, 318-323 (1935).

(5) Ingram, Master's Dissertation, The University of Chicago Libraries, 1939, p. 13.