[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

STUDIES RELATING TO BORON. I. REACTION OF BORON TRIFLUORIDE WITH AMMONIA AND ALKYLAMINES

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I. Introduction

The chemistry of boron is of particular interest in the light of the modern atomic theory. Seemingly, boron has a marked tendency to form compounds corresponding to a valence greater than might be expected from its position in the periodic system. This is best seen in the simplest hydride whose composition corresponds to the formula BH_3 but whose molecular weight corresponds to the formula B_2H_6.[1] The tendency of boron to function with a higher valence than 3 also appears in other compounds. Thus Krause,[2] in reducing triphenylboron with the alkali metals in ether, obtained a salt corresponding to the formula $NaB(C_6H_5)_3$. The electron due to sodium is evidently associated with the triphenylboron group, but it is not held very firmly since it is reduced by triphenylmethyl. Triphenylboron also forms remarkably stable compounds with one molecule of ammonia or an amine.[3] When these compounds are reduced by means of the alkali metals in suitable solvents,[4] they add an atom of metal to form compounds of the type $NaB(C_6H_5)_3 \cdot NH_3$. Trimethylboron also combines with various hydroxides[5] and triphenylboron combines with the amides[6] of the alkali metals. These compounds are now under investigation and will be reported later.

The boron trihalides appear to have a marked tendency to combine with ammonia or amines. In particular, boron trifluoride combines with ammonia with the evolution of a great deal of heat to form a seemingly stable solid compound. Unfortunately, it is not easy to distinguish between an addition compound and a mixture of compounds due to ammonolysis. It is the purpose of the present investigation to determine definitely whether or not boron trifluoride is capable of adding ammonia or an amine directly without ammonolysis. As the results will show, this is the case, although, at the same time, there is clear evidence that, when boron trifluoride is dissolved in ammonia or an amine, it is ammonolyzed to an appreciable extent.

The reaction between boron trifluoride and ammonia was first observed

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[1] Stock and Friederici, *Ber.*, **46**, 1959 (1913).

[2] Krause and Polack, *ibid.*, **59**, 777 (1926).

[3] Stock and Zeidler, *ibid.*, **54**, 531 (1921); Krause, *ibid.*, **57**, 813 (1924).

[4] Unpublished observations by Wade B. Robinson in this Laboratory.

[5] Frankland, *Ann. Chem.*, **124**, 129 (1862).

[6] Unpublished observations by W. W. Hawes in this Laboratory.

by Gay-Lussac.[7] The reaction was further studied by J. Davy.[8] Neither of these investigators definitely established whether or not an addition compound is formed. Davy, in particular, showed that the initial solid compound is soluble in excess of ammonia.

According to Mellor,[9] the solid compound is probably monoammino-boron trifluoride, $BF_3 \cdot NH_3$, while the products containing greater quantities of ammonia are mixtures of ammonium fluoride and boron amides.

Mixter[10] prepared monoammino boron trifluoride by passing boron trifluoride into dry ammonia gas. He analyzed this product for ammonia and found values approximating that required for the formula $BF_3 \cdot NH_3$. He determined the molecular weight of the vapor of this material by the Victor Meyer method at temperatures above the melting point of zinc. The values found lay in the neighborhood of 46, or approximately one-half that of monoammino boron trifluoride, indicating practically complete dissociation of the compound into its constituents.

Joannis[11] studied the interaction between boron trichloride and liquid ammonia and concluded that the chloride is completely ammonolyzed. This might lead one to infer that a similar reaction occurs in the case of boron trifluoride. It should be noted, in this connection, that the weight of the final product gives no safe indication of whether or not ammonolysis has occurred. Thus, reaction might take place as follows

$$2\,BF_3 + 2\,NH_3 = NH_4BF_4 + BF_2NH_2$$

If boron trifluoride ammonolyzes with the formation of ammonium fluoride, the latter compound might well combine with boron trifluoride to form ammonium borofluoride. The resulting mixture would have the same composition as a compound of the formula $BF_3 \cdot NH_3$.

As indicating a marked tendency of boron trifluoride to form addition compounds, it might be mentioned that Gasselin[12] found that it combines readily with one molecule of ether to form a comparatively stable product boiling at 125°. An ether solution of boron trifluoride was found very useful in the present investigation in preparing pure compounds of boron trifluoride with ammonia and various amines.

II. Preparation and Properties of Monoammino Boron Trifluoride

Materials.—Boron trifluoride was prepared by heating a mixture of ammonium borofluoride with a slight excess of boric oxide in concentrated sulfuric acid.

Ammonium borofluoride was prepared by dissolving boric acid in a slight excess

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[7] Gay-Lussac, *Mémoires de la Société d'Arcueil*, **2**, 211 (1809).

[8] J. Davy, *Phil. Trans.*, **30**, 365 (1812).

[9] Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, **1924**, Vol. V, p. 122.

[10] W. G. Mixter, *Am. Chem. J.*, **2**, 153 (1881).

[11] Joannis, *Compt. rend.*, **135**, 1106 (1902).

[12] Gasselin, *Ann. Chim.*, **3**, 50 (1894).

of aqueous hydrogen fluoride and neutralizing with ammonium hydroxide. The solution was concentrated, filtered and allowed to cool, when fine colorless crystals separated.

Preparation of $BF_3 \cdot NH_3$.—A reliable method for the preparation of monoammino boron trifluoride was not found in the literature. Accordingly, four different methods were tried out, of which the last proved the most convenient. These methods were: (1) to pass a mixture of dry nitrogen and boron trifluoride through liquid ammonia, (2) to introduce alternately small quantities of boron trifluoride and ammonia into an evacuated bulb at room temperatures, (3) to bubble pure boron trifluoride into liquid ammonia from underneath a surface of mercury, (4) to saturate an ether solution of boron trifluoride with ammonia.

Methods 1 and 2 were quite unsatisfactory. Method 3 proved fairly convenient but the presence of mercury was disadvantageous. Method 4 proved satisfactory and may be described in some detail. The desired quantity of boron trifluoride, dissolved in ether, is saturated with ammonia at zero degrees by passing a stream of ammonia vapor over the surface of the solution under constant agitation. Monoammino boron trifluoride is precipitated as a fine, white solid. The supernatant liquid is decanted and adhering solvent removed by means of a pump.

Properties of $BF_3 \cdot NH_3$.—Monoammino boron trifluoride is soluble in liquid ammonia, ethylamine and diethylamine. It is practically insoluble in ether, benzene and petroleum ether. When heated in an evacuated tube, it sublimes at temperatures above 180°, leaving only a slight residue. Fusion sets in at 180°, an opaque pasty mass resulting. This seems to indicate that under these conditions the material is not homogeneous.

Monoammino boron trifluoride, dissolved in liquid ammonia, is appreciably ammonolyzed, since, when treated with metallic sodium, hydrogen is evolved. The reaction takes place in several stages, indicating that not all the fluorine atoms are hydrolyzed with equal ease. The fact that the corresponding ethylamine derivative can be completely ammonolyzed by means of lithium in ethylamine leaves no doubt that an analogous reaction occurs in liquid ammonia.

Analysis of Monoammino Boron Trifluoride.—The compound prepared by passing ammonia through an ethereal solution of boron trifluoride was analyzed for ammonia and boron. To determine the ammonia, an alkaline solution of the compound was distilled, the distillate being collected in an excess of 0.1 *N* hydrochloric acid which was titrated back with 0.1 *N* sodium hydroxide.

Anal. Subs., 0.3151, 0.4147: 36.33, 48.01 cc. of 0.1021 *N* HCl. Calcd. for $BF_3 \cdot NH_3$: N, 16.47. Found: N, 16.48, 16.54.

In analyzing for boron, weighed samples were dissolved in water containing a slight excess of sodium hydroxide. The resulting solutions were neutralized with 0.1 *N* hydrochloric acid, using methyl red as indicator. When the end-point was reached, about 1 g. of mannitol was added and the boric acid titrated with 0.1 *N* sodium hydroxide, using phenolphthalein as indicator.

Anal. Subs., 0.1829, 0.2949, 0.5671: 21.98, 31.66, 62.65 cc. of 0.10727 *N* NaOH. Calcd. for $BF_3 \cdot NH_3$: B, 12.95. Found: B, 14.25, 12.65, 13.00.

The nitrogen content of the compound is in good agreement with the formula $BF_3 \cdot NH_3$ but the boron analyses are less satisfactory. In fact, unless conditions can be carefully controlled, it is extremely difficult to get entirely satisfactory results for boron by any of the usual analytical methods.

As will be shown below, boron trifluoride combines with triethylamine to form the compound $BF_3 \cdot N(C_2H_5)_3$. When this compound is treated with ammonia, a product is formed which has the properties of monoammino boron trifluoride. Its solubility, melting point and other properties correspond closely with those of the compound directly precipitated by passing ammonia into an ethereal solution of boron trifluoride. The product formed by the treatment of the triethylamine derivative with ammonia was analyzed for nitrogen, as described above.

Anal. ($BF_3 \cdot NH_3$ precipitated from triethylamine). Subs., 0.0394, 0.0275: 4.54, 3.19 cc. of 0.1021 *N* HCl. Calcd. for $BF_3 \cdot NH_3$: N, 16.47. Found: N, 16.46, 16.52.

It was found that monoammino boron trifluoride is soluble in triethylamine in the presence of excess ammonia. When the excess ammonia is slowly removed, the ammonia derivative crystallizes from the solution. A quantity of this material was prepared and analyzed for nitrogen.

Anal. (Recrystallized $BF_3 \cdot NH_3$). Subs., 0.1192, 0.0947: 13.88, 11.01 cc. of 0.1021 *N* HCl. Calcd. for $BF_3 \cdot NH_3$: N, 16.47. Found: N, 16.63, 16.61.

The analyses show that the product formed on passing ammonia through an ethereal solution of boron trifluoride has a mean composition corresponding to the formula $BF_2 \cdot NH_3$. Either a compound corresponding to this formula exists or the product consists of a mixture of BF_2NH_2 and NH_4BF_4. Since the compound prepared by the action of ammonia on a triethylamine solution of boron trifluoride is identical with that obtained from an ethereal solution and since, moreover, the product formed in ethylamine is completely soluble in this solvent in the presence of excess ammonia and can be recrystallized from this solvent, and since, further, the crystallized product, on analysis, shows a composition corresponding to the formula $BF_3 \cdot NH_3$, it follows that the original product formed by the action of ammonia on the ethereal solution of boron trifluoride is, in fact, an addition compound $BF_3 \cdot NH_3$. Triethylamine is a very indifferent solvent for salt-like substances, being inferior even to ether in this respect. It is inconceivable that ammonium borofluoride would be soluble in such a mixture. Furthermore, in the process of recrystallization, there is no evidence of a second product. Accordingly, it may be concluded that boron trifluoride combines with one molecule of ammonia to form the compound $BF_3 \cdot NH_3$.

III. Triethylammino Boron Trifluoride

Preparation.—The interaction between boron trifluoride and triethylamine is of particular interest since ammonolysis cannot well take place in this solvent. The compound was first prepared by introducing a known quantity of triethylamine into a weighed reaction tube cooled to liquid ammonia temperatures, into which an excess of boron trifluoride was then introduced. When the reaction was completed, the excess fluoride was pumped off and the reaction tube was weighed. Thus the amount of boron trifluoride combined with the amine could be found.

The product formed was a solid melting at room temperatures and turning brown upon standing for a comparatively short time. In three experiments the following results were obtained: 3.125, 0.534, 1.565 g. of amine combined with 1.924, 0.392, 0.928 g. of BF_3. These data yield for the ratio $BF_3/(C_2H_5)_3N$ the values 0.951, 1.076, 0.877.

In other words, approximately 1 mole of boron trifluoride was found to combine with one mole of triethylamine. It was found that the product is soluble in the presence of excess ammonia and that it is reprecipitated in crystalline form as the ammonia is removed. The resulting crystalline material appeared to be identical with monoammino boron trifluoride.

In one experiment ammonia was added to the triethylamine derivative, after which the tube containing the material was pumped to constant weight at −33°. Under these conditions the excess ammonia, as well as the triethylamine formed in the reaction with ammonia, was removed. It was found that 2.4821 g. or 0.0246 mole of amine initially combined with 1.6805 or 0.0247 mole of BF_3 and, after treating with ammonia, the weight indicated the presence of 0.4389 g. or 0.0258 mole of NH_3. From these data it is seen that 1 mole of boron trifluoride combines with 1 mole of triethylamine which, in turn, may be substituted quantitatively by ammonia. The final product obtained in this reaction was analyzed for ammonia, the data being given on page 2693.

A second and more satisfactory method of preparing triethylammino boron trifluoride consists in treating an ethereal solution of the trifluoride with an excess of triethylamine at liquid ammonia temperatures. The amine (in excess) was condensed on the ethereal solution of BF_3 and when the two layers were mixed, a white precipitate was formed. This precipitate melted at room temperatures and rapidly acquired a brown tint, indicating some decomposition. After removing all excess materials, the product was finally distilled at a temperature of 80° under a pressure of 3 mm. The liquid which distilled over solidified in the colder portions of the apparatus. This compound proved to be triethylammino boron trifluoride $(C_2H_5)_3N{\cdot}BF_3$.

Analysis and Molecular Weight.—The nitrogen content of the redistilled material was determined by adding water and boiling off the amine in an evacuated two-legged tube. The distillate was titrated with standard hydrochloric acid.

Anal. Subs., 0.0783, 0.0688: 5.13, 4.41 cc. of 0.09077 *N* HCl. Calcd. for $(C_2H_5)_3N{\cdot}BF_3$: N, 8.27. Found: N, 8.32, 8.14.

The fluorine content of the compound was determined as lead chlorofluoride. The sample was dissolved in water and 16 drops of concentrated hydrochloric acid were added, after which the solution was made slightly acid with nitric acid and 10 drops of acetic acid were added. Lead chlorofluoride was precipitated on the addition of a 10% solution of lead acetate.

Anal. Subs., 0.0389, 0.0889: PbClF, 0.1751, 0.4068. Calcd. for $BF_3{\cdot}(C_2H_5)_3N$: F, 33.69. Found: F, 32.67, 34.38.

The analyses for fluorine are not entirely satisfactory but, as is well known, it is extremely difficult to obtain satisfactory analyses for this element, particularly with the small quantities of material available. There can be no doubt, however, that the compound involves a single molecule each of triethylamine and boron trifluoride. This was further borne out by its molecular weight in benzene as determined by the freezing-point method.

Molecular weight of $BF_3{\cdot}(C_2H_5)_3N$ in benzene: solute, 0.1262, 0.2312, 0.3574 g.; solvent, 22.69, 22.69 g.; Δt, 0.170°, 0.300°, 0.437°; mol. wt. found, 163.5, 169.8, 180.1; mol. wt. calcd. for $(C_2H_5)_3N{\cdot}BF_3$, 169.2.

As may be seen from the data given, the molecular weight of the compound in benzene solution corresponds closely to that required.

Properties.—Triethylammino boron trifluoride melts sharply at 29.5°. It decomposes slowly, especially at room temperatures, turning brown and giving off amine. It is very soluble in alcohol, benzene, ether and hot petroleum ether. It is difficultly soluble in water, but if first dissolved in a small quantity of ether the resulting solution is completely soluble in water. The compound, when dissolved in triethylamine, is not affected by freshly cut sodium or lithium.

IV. Diethylammino Boron Trifluoride

Preparation.—Monoammino boron trifluoride was dissolved in diethylamine, the excess amine removed with a pump, the product washed with ether and the last traces of solvent were removed with a pump. The product was a white solid which melted at 150–151°.

Anal. Subs., 0.0672, 0.0817: 5.31, 5.96 cc. of 0.09077 *N* HCl. Calcd. for $BF_3\cdot(C_2H_5)_2NH$: N, 9.91. Found: N, 10.41, 9.27.

In one experiment 0.9648 g. (0.0113 mole) of $BF_3\cdot NH_3$ was treated with diethylamine in a weighed reaction tube. After exhausting, the product weighed 1.6054 g. Assuming that the ammonia was replaced by diethylamine, the weight of amine present corresponded to 0.0118 mole, which agrees fairly well with 0.0113, the number of moles of boron trifluoride present.

In another preparation diethylamine was distilled into an ethereal solution of boron trifluoride at liquid ammonia temperatures. A white crystalline solid was formed, the supernatant liquid was decanted and the solid was washed several times with ether. It was then dried rapidly on a filter paper. It melted at 165° but not sharply.

Anal. Subs., 0.1360, 0.1113: 9.34, 9.69 cc. of 0.09077 *N* HCl. Calcd. for $BF_3\cdot(C_2H_5)_2NH$: N, 9.91. Found: N, 8.72, 8.79.

On analyzing this material for boron by the lead chlorofluoride method, there were obtained, respectively, 46.33 and 45.00% of fluorine against 40.36 required.

In another preparation an ethereal solution of boron trifluoride was added drop by drop to diethylamine cooled in ice water. The resulting product was dissolved in alcohol and ether was added to precipitate the compound. After washing, the product was dried on a pump and analyzed.

Anal. Subs., 0.0613, 0.0812: 3.73, 4.84 cc. of 0.1083 *N* HCl. Calcd.: N, 9.91. Found: N, 9.23, 9.04.

Several analyses for fluorine yielded 50% in place of 40.36% required for the compound $BF_3\cdot(C_2H_5)_2NH$. None of the analyses, either for fluorine or nitrogen, is entirely satisfactory. The first preparation gave, on the whole, the most satisfactory results. Seemingly the compound loses diethylamine fairly readily. This is further borne out by the fact that the melting points obtained were variable and in general not sharp.

Properties.—Diethylammino boron trifluoride is practically insoluble in ether, benzene and petroleum ether. It is very soluble in diethylamine, alcohol and water. It melts in the neighborhood of 160°. The high melting point is quite unexpected as the triethylamine derivative melts at 29.5° while the ethylamine derivative melts at 89°.

V. Ethylammino Boron Trifluoride

Preparation.—The ethylamine derivative was prepared by condensing a quantity of ethylamine on monoammino boron trifluoride in one leg of a two-legged tube. Any undissolved material was allowed to settle out, after which the supernatant liquid was decanted into the second leg of the tube. The excess of amine was then distilled and the last traces were removed by means of a pump.

The compound was also prepared by adding an excess of amine to an ethereal solution of boron trifluoride and distilling off the ether and excess amine.

Analyses.—Products prepared as described above were analyzed for nitrogen in the usual manner.

Subs., 0.0736, 0.0756, 0.2250, 0.2315: 6.40, 7.31, 19.51, 20.16 cc. of 0.1021 *N* HCl. Calcd. for $BF_3\cdot(C_2H_5)NH_2$: N, 12.38. Found: N, 12.43, 13.82, 12.39, 12.45.

The product was likewise analyzed for fluorine by the lead chlorofluoride method.

Subs., 0.0782, 0.0920: PbClF, 0.559, 0.6851. Calcd. for $BF_3\cdot(C_2H_5)NH_2$: F, 50.39. Found: F, 51.60, 51.94.

The molecular weight of the ethylamine derivative was determined in ether by a modification of the Cottrell method.

Subs., 0.3253, 0.1505, 0.0704; ether, 33.06, 29.23, 40.37; Δt, 0.141°, 0.1079°, 0.029°. Calcd. for $BF_3\cdot(C_2H_5)NH_2$: mol. wt., 113.1. Found: mol. wt., 147.0, 137.5, 133.3.

Properties.—Ethylammino boron trifluoride melts sharply at 89°. It decomposes rapidly when heated in air above its melting point. It is soluble in benzene and slightly soluble in ether, from which solvents it may be recrystallized. Its reaction with lithium in ethylamine solution will be described in a subsequent paper.

Taking into account the results of analysis and molecular weight determinations, as well as the fact that the compound may be recrystallized from various solvents, there can be little doubt that ethylamine forms an addition compound with boron trifluoride corresponding to the formula $BF_3\cdot(C_2H_5)NH_2$.

Summary

1. Several methods for the preparation of monoammino boron trifluoride, $BF_3\cdot NH_3$, are described. This compound has been characterized and some of its properties determined.

2. Boron trifluoride combines with triethylamine to form the compound $BF_3\cdot(C_2H_5)_3N$, which melts at 29.5°. The method of its preparation and its properties are described.

3. Boron trifluoride combines with diethylamine to form the compound $BF_3\cdot(C_2H_5)_2NH$, which melts in the neighborhood of 160°. This compound is relatively less stable than other ammino derivatives and has not been so well characterized.

4. Boron trifluoride combines with ethylamine to form the compound $BF_3\cdot C_2H_5NH_2$, which melts at 89°. The properties of this compound are described and methods of preparation are given.

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