

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

Donor-Acceptor Bonding. IV. Ammonia-Boron Trifluoride¹BY A. W. LAUBENGAYER AND G. F. CONDIKE²

Monoammonia-boron trifluoride, $H_3N:BF_3$, is the classical example of a molecular addition compound involving donor-acceptor bonding. Its formation was first observed by Gay-Lussac³ and the system was further investigated by Davy,⁴ who reported obtaining not only the mono-ammonate, but also di- and tri-ammonates, the last two described as colorless liquids. The properties of monoammonia-boron trifluoride were studied by Mixer⁵ and by Kraus and Brown,⁶ and Balz and Zinser⁷ reported vapor pressure data for the complex. The information in the literature is often contradictory and very incomplete.

Accordingly, the present investigation has been undertaken as a comprehensive study of the ammonia-boron trifluoride system. The properties of monoammonia-boron trifluoride, the only addition compound found to exist between ammonia and boron trifluoride, have been studied in detail and the consequences of donor-acceptor bonding in this system are discussed.

Experimental

Determination of Mole Combining Ratio.—Known amounts of ammonia and boron trifluoride were brought together in an evacuated glass apparatus in mole ratios varying from 0.4:1 to 3:1 and allowed to come to equilibrium at 25°. The combining ratio of the two gases was calculated from the residual pressure of the system by assuming that the uncombined gas, present in excess, obeys the ideal gas laws. Table I lists the results, which clearly show that only the compound monoammonia-boron trifluoride, $H_3N:BF_3$, was formed. It accumulated as a white solid when the gases were mixed and at no time was any transparent liquid produced.

TABLE I

Moles NH_3 added per mole BF_3	Residual pressure, mm.	Moles NH_3 combining per mole BF_3
0.399	71.6	0.994
1.000	1.4	0.996
1.440	49.6	1.020
1.990	112.2	1.004
2.530	174.6	1.030
2.950	225.6	1.015

Average 1.009

Preparation and Analysis.—Ammonia-boron trifluoride was prepared in quantity by mixing anhydrous ammonia and boron trifluoride in a one-liter three-necked flask. An outlet tube was provided for excess gases, and the flask was cooled with ice water. The vessel was first swept out with ammonia and then a slow flow of this gas

was maintained. Boron trifluoride was admitted at such a rate that approximately equimolar quantities of the reactants were provided. Since any uncombined boron trifluoride fumed immediately in contact with moist air, it served as its own indicator at the outlet tube. The addition compound accumulated in the reaction flask as a white powder.

To establish the composition of the product, ammonia was liberated by boiling the compound with an excess of a concentrated solution of sodium hydroxide, and was then absorbed and titrated in the usual manner. Boron was determined as boric acid by dissolving a weighed sample of the product in a slight excess of dilute sodium hydroxide and titrating the solution by the mannitol method, in which paranitrophenol was used as the first and phenolphthalein as the second indicator.

Anal. Calcd. for $H_3N:BF_3$: NH_3 , 20.05; B, 12.75. Found: NH_3 , 20.05, 19.90, 19.85; B, 12.80, 12.72, 12.65.

Melting Point and Density.—The melting point of ammonia-boron trifluoride was found to be $163 \pm 1^\circ$, the determination being made rapidly on a Dennis-Shelton melting point bar⁸ in order to avoid serious thermal decomposition. The density was determined pycnometrically to be 1.864²⁸, using benzene as the immersion reference liquid.

Solubility, Polarity and Molecular Weight in Solution.—The solubilities of the compound in several solvents other than water were tested microscopically by observing the progress of evaporation of the solvent from a well-stirred mixture of a drop of the solvent and a small amount of the solid compound. In solvents of low dipole moment (0.00 to 1.12 debye units), such as benzene, carbon disulfide, carbon tetrachloride and diethyl ether, the compound appeared to be insoluble; slight solubility in cyclohexanol (1:5) and somewhat greater solubility in methanol (1.68) and in ethyl alcohol (1.70) were observed. These results indicate that the compound itself probably has a considerable dipole moment.

In water the solubility, quantitatively determined, proved to be 36.0 g. per 100 g. of solvent at 25°. The aqueous solution is remarkably stable at this temperature. Thus the powder X-ray diffraction pattern was unchanged by recrystallizing a sample of the compound from water. Furthermore, the molecular weights, determined cryoscopically in three aqueous solutions containing, respectively, 15.77, 8.15 and 6.04 g. of the compound per 1000 g. of water were 81.0, 83.9 and 82.4. Since the molecular weight calculated for the compound $H_3N:BF_3$ is 84.8, the latter is evidently not appreciably hydrolyzed, dissociated nor associated in aqueous solution at about 0°.

Crystallographic and X-Ray Examination.—A microscopic examination of ammonia-boron trifluoride recrystallized from water was made. The compound crystallizes in rhomb-shaped plates which exhibit symmetrical extinction. The crystals are in the orthorhombic system, a combination of prism faces (110) and basal pinacoids (001) being common. The prism-prism interfacial angles are $57^\circ 30' \pm 15'$ and $121^\circ 30' \pm 15'$. $2V = 90^\circ \pm 3^\circ$; $2E = 146^\circ \pm 2^\circ$; OA Plane = 100. The direction of vibration of α is parallel to the b crystallographic axis, β to the a axis, and γ to the c axis. Refractive indices (white light): $\alpha = 1.335$, $\beta = 1.34-1.35$, $\gamma = 1.36$. It was dif-

(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Atlantic City meeting, April, 1947.

(2) Present address: Fitchburg State Teachers' College, Fitchburg, Mass.

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

(4) Davy, *Phil. Trans.*, **30**, 365 (1812).

(5) Mixer, *Am. Chem. J.*, **2**, 153 (1881).

(6) Kraus and Brown, *THIS JOURNAL*, **51**, 2690 (1929).

(7) Balz and Zinser, *Z. anorg. allgem. Chem.*, **221**, 236 (1935).

(8) Dennis and Shelton, *THIS JOURNAL*, **52**, 3128 (1930).

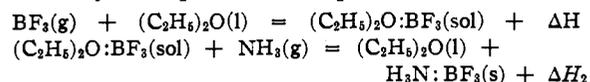
difficult to decide on the optic sign, since $2V$ is so close to 90° .

The prominent lines of the powder X-ray diffraction pattern obtained for the crystals are listed in Table II.

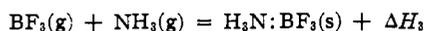
TABLE II

POWDER X-RAY DIFFRACTION PATTERN FOR $H_3N:BF_3$	d	Intensity
	4.22	Strong
	3.88	Strong
	3.60	Medium
	3.00	Medium
	2.55	Medium
	2.19	Weak

Calorimetric Determination of Heat of Formation.—A Bunsen ice calorimeter was used⁹ to measure the total heat effect produced at 0° by dissolving 100 cc. of gaseous boron trifluoride in diethyl ether and then introducing 100 cc. of ammonia gas into the solution. The reactions indicated by the equations took place



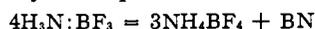
The sum of these reactions is



The value 41.3 kcal. per mole was obtained for ΔH_3 , the heat of formation of solid ammonia-boron trifluoride from the gases at 0° .

Thermal Decomposition.—Rapid heating of ammonia-boron trifluoride results in an initial fusion of the solid; then decomposition occurs and the melt resolidifies and partially sublimes. One of the products of the thermal decomposition was shown to be ammonium fluoborate by a study of the optical properties and the powder X-ray diffraction patterns of the crystals obtained by recrystallizing the soluble part of the product from water. The other product, insoluble in water, was identified as boron nitride, BN, by X-ray diffraction and by the fact that it yielded boric acid and ammonia upon hydrolysis by boiling water.

Quantitative measurements demonstrated that the thermal decomposition, which becomes appreciable at 125° and proceeds rapidly at 150° , is represented by the equation



These results suggest that the values reported by Balz and Zinser⁷ as equilibrium vapor pressures of the ammonia complex, actually are those of ammonium fluoborate. This interpretation was confirmed by making equilibrium vapor pressure measurements on the two systems. The straight line obtained by plotting the values of $\log p$ against $1/T$ for ammonium fluoborate was found to be identical with the curves obtained by us and those obtained by Balz and Zinser by heating ammonia-boron trifluoride. It is to be noted that boron nitride has a vapor pressure of only

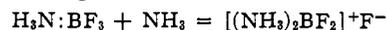
(9) Laubengayer and Finlay, *THIS JOURNAL*, **65**, 884 (1943).

9.4 mm. at 1240° ,¹⁰ and that its contribution to the total pressure of the system in the temperature range studied is negligible.

Saturation Vapor Pressure and Heat of Sublimation of NH_4BF_4 .—From the vapor pressure-temperature data obtained, the characteristic equation for NH_4BF_4 was calculated to be $\log_{10} p$ (mm.) = $-2469/T + 6.82$. The heat of sublimation of NH_4BF_4 is 11.3 kcal.

Discussion

The experimental results obtained in this investigation are in line with the general theory dealing with donor-acceptor bonding previously outlined.^{9,11,12} The nitrogen atom in ammonia can donate its unshared pair of electrons to establish a shared electron pair bond to the boron atom in boron trifluoride and a one:one molecular addition complex is formed. It is conceivable that $H_3N:BF_3$, under conditions other than those we have used, might combine with more ammonia.



However, such an ionic di-ammonate presumably would not be a liquid, as reported by Davy.⁴

The remarkable resistance to hydrolysis observed for $H_3N:BF_3$ would seem to be a result of the fact that, in forming the addition compound, both nitrogen and boron go from a coordination number of 3 to 4. This increase in the numbers of neighboring atoms strongly bonded to the central atoms appears to protect them from hydrolysis.

The configuration of $H_3N:BF_3$ may be expected to involve essentially tetrahedral bonding for both the nitrogen and boron atoms to give an ethane-like molecule. Professor Hoard of this Laboratory is now undertaking the X-ray determination of the crystal structure of the complex. It seems likely that hydrogen bonding will be pronounced in the solid.

The high polarity of $H_3N:BF_3$ and the resultant low solubility in non-polar solvents and high solubility in polar solvents is to be expected from its structure. The formation of a donor-acceptor bond between the nitrogen and boron atoms involves a considerable displacement of charge. In addition, when the complex is formed the fluorine atoms probably move from positions coplanar with boron to tetrahedral positions. The three B-F bond dipoles no longer counterbalance each other but make a considerable contribution to the polarity of the complex.

Summary

1. Only one compound, ammonia-boron trifluoride, $H_3N:BF_3$, has been found to exist between ammonia and boron trifluoride at 25° . It has been prepared in quantity and its properties have been studied.

2. Cryoscopic measurements indicate that in

(10) Slade and Higson, *J. Chem. Soc.*, **115**, 215 (1929).

(11) Bauer, Finlay and Laubengayer, *THIS JOURNAL*, **65**, 889 (1943).

(12) Laubengayer and Sears, *ibid.*, **67**, 164 (1945).

water solution $\text{H}_3\text{N}:\text{BF}_3$ exists as a monomeric molecular species, and that it is not appreciably dissociated.

3. Optical studies have been made on crystals of ammonia-boron trifluoride, and its powder X-ray diffraction pattern has been established.

4. The heat of formation of solid ammonia-boron trifluoride from the gases at 0° has been determined calorimetrically as 41.3 kcal.

5. It has been shown that the compound undergoes irreversible thermal decomposition at

temperatures above 125° according to the equation: $4\text{H}_3\text{N}:\text{BF}_3 \xrightarrow{125^\circ} 3\text{NH}_4\text{BF}_4 + \text{BN}$.

6. Vapor pressure measurements obtained when ammonia-boron trifluoride is heated give values shown to be those of ammonium fluoborate, the only decomposition product volatile in the temperature range studied. The P.T. equation for NH_4BF_4 is $\log_{10} p(\text{mm.}) = -2469/T + 6.82$. The molar heat of sublimation of NH_4BF_4 is 11.3 kcal.

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Thermodynamics of Sodium Chloride in 50 Mole Per Cent. Aqueous Methanol from E. m. f. Measurements on Cells with Transference

By J. P. BUTLER AND A. R. GORDON

While concentration cells with transference have been used extensively in the study of electrolytes in aqueous solution^{1,2} and have yielded some of the most precise thermodynamic data now available for such solutions, lack of transference numbers has so far prevented their use with solvents other than water. One interesting exception is provided by the work of Harned and Dreby³ who employed cells with and without transference to yield indirectly transference numbers for hydrochloric acid in dioxane-water mixtures. Recent measurements in this laboratory⁴ have now made possible the use of this method for sodium chloride in 50 mole per cent. methanol-water solution. Apart from testing the precision of the measurements with a solvent other than water, the primary purpose of this research was to determine whether the thermodynamic mean ionic diameter was significant when comparing ionic transport processes in two different solvents.

The cells, the preparation of the electrodes, and the general experimental technique have been previously described.² In all cases, the observed e. m. f. has been corrected for bias potential as described by Hornibrook, Janz and Gordon. One rather surprising result was that the bias potentials for stable pairs of electrodes were of the same order as those found in aqueous solution, *viz.*, 0.03 mv. or less. Even more surprising was the fact that the bias potential for a given pair was not only independent (within a microvolt or so) of the salt concentration in the mixed solvent, but had also the same value within similar limits after the electrodes had stood for half an hour in a solution with pure methanol or pure water as solvent. This suggests that lightly plated, electrolytically

anodized Ag/AgCl electrodes are considerably sturdier than is generally assumed, provided a galvanometer of high current sensitivity is used.

The solutions were prepared as described by Schiff and Gordon.⁵ In computing the volume concentration C from the mass concentration, the density measurements of Shemilt, Davies and Gordon⁴ were employed; these give for the range of interest here

$$C/m = 0.88123(1 - 0.0134m) \quad (1)$$

where m is the molality.

The results are summarized in Table I under the heading E_{obs} . Only average values for round concentrations are given in the table; the method by which these were obtained from the results of individual runs, carried out at concentrations differing slightly from those recorded, will be described below.

TABLE I

$m_1 = 0.05$ MOLAL; 25°

m_2	$E_{\text{obs.}}$ mv.	$E_{\text{calo.}}$ mv.	m_2	$E_{\text{obs.}}$ mv.	$E_{\text{calo.}}$ mv.
0.003	+58.075	+58.075	0.04	+4.386	+4.391
.005	+47.145	+47.145	.06	-3.575	-3.564
.01	+32.565	+32.560	.07	-6.556	-6.560
.02	+18.293	+18.300	.08	-9.149	-9.147
.03	+10.114	+10.112			

The e. m. f. of a cell of the type Ag, AgCl/NaCl(m_1)/NaCl(m_2)/AgCl, Ag is of course given by the familiar expression

$$E = k\ell_+^0 \Delta \log \gamma m + \Delta F(t_+) \quad (2)$$

Here, $k = 118.28$ mv., ℓ_+^0 is the limiting transference number for the cation (0.4437), Δ stands for function (m_1) - function (m_2), and $F(t_+)$ is given by

$$F(t_+) = k \int_0^m (t_+ - \ell_+^0) d \log \gamma m \quad (3)$$

Eq. 2 can be solved by the usual method of suc-

(5) Schiff and Gordon, *ibid.*, **16**, 336 (1948).

(1) Brown and MacInnes, *THIS JOURNAL*, **57**, 1356 (1935); Shedlovsky and MacInnes, *ibid.*, **58**, 1970 (1936); **59**, 503 (1937).

(2) Hornibrook, Janz and Gordon, *ibid.*, **64**, 513 (1942); Janz and Gordon, *ibid.*, **65**, 218 (1943); MacWilliam and Gordon, *ibid.*, **65**, 484 (1943); McLeod and Gordon, *ibid.*, **68**, 58 (1946).

(3) Harned and Dreby, *ibid.*, **61**, 3113 (1939).

(4) Shemilt, Davies and Gordon, *J. Chem. Phys.*, **16**, 340 (1948).