

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY AT HARVARD UNIVERSITY]

Boron-Nitrogen Systems. III. Boron Trifluoride-Diamine Addition Compounds¹BY CHARLES A. BROWN, EARL L. MUETTERTIES² AND EUGENE G. ROCHOW

RECEIVED MARCH 19, 1953

Ethylenediamine·2BF₃ and hexamethylenediamine·2BF₃ have been prepared and some of their physical and chemical properties determined. Hydrolysis and alcoholysis of these compounds indicate that the ethylenediamine compound is significantly more reactive than hexamethylenediamine·2BF₃. This behavior is attributed to a pronounced group interaction in the former compound. Ethylenediamine·BF₃ has also been prepared and some properties of this compound are given.

Despite the fact that many studies have been published concerning the addition of amines to boron trifluoride, only the compound of hexamethylenetetramine with boron trifluoride,³ (CH₂)₆N₄·4BF₃, appears in the literature as a definite example of the behavior of boron trifluoride toward polyamines. One patent⁴ pertains to boron trifluoride-ethylenediamine but no definite compounds were reported and no physical or chemical properties described.

We have found that the addition of boron trifluoride (as diethyl etherate) to an ethereal solution of ethylenediamine precipitates a solid product of approximately the composition H₂NCH₂CH₂NH₂·BF₃. Purification of this substance was found to be difficult and further reaction of the compound with excess boron trifluoride etherate was very slow. However, the addition of boron trifluoride-tetrahydrofuran complex to solutions of the amine in tetrahydrofuran gave excellent yields of BF₃·NH₂CH₂CH₂NH₂·BF₃. Similarly, hexamethylenediamine reacted with boron trifluoride-tetrahydrofuran complex and formed BF₃·NH₂(CH₂)₆NH₂·BF₃.

A comparison of the rates of hydrolysis of ethylenediamine·2BF₃ and hexamethylenediamine·2BF₃ indicates that the latter is considerably more stable; the ratio of rates is approximately 48:1. Evidently the weakening effect of one semi-polar B-N bond upon the other (either through the chain or by a space effect, or both) is most significant when the connecting carbon chain is shortest.

Experimental

I. Boron Trifluoride and Ethylenediamine. Materials.—Boron trifluoride was subjected to bulb-to-bulb distillation in a vacuum system until spectroscopically free of silicon tetrafluoride. Eastman Practical ethylenediamine was dried by the method outlined in "Inorganic Syntheses,"⁵ and then further dried over sodium and distilled. The fraction boiling at 116–117° at atmospheric pressure was stored under an atmosphere of nitrogen.

Procedure.—A weighed sample of pure boron trifluoride (7.856×10^{-3} mole) was condensed into a 395-ml. reaction bulb attached to a vacuum chain. The pressure of the gas at 23° was measured by means of an attached mercury manometer. As ethylenediamine was added to the bulb in successive weighed portions (by liquid-nitrogen condensation), the pressures of the mixtures at 23° decreased toward zero at a composition C₂H₄(NH₂)₂·1.97BF₃. In the reverse proc-

ess (addition of BF₃ to ethylenediamine), the pressure-composition isotherm decreased linearly only in the range 0.4 to 0.9 mole BF₃/mole C₂H₄(NH₂)₂. At ratios of 0.9 to 1.9 the pressure was constant at 0.2 mm. pressure, and above a ratio of 1.9 it rose slowly. Thus both a 1:1 and a 2:1 compound are indicated, although the 1:1 compound requires further evidence.

II. Ethylenediamine·2BF₃ and Hexamethylenediamine·2BF₃. Preparation.—A sample of du Pont hexamethylenediamine, which was stated to be 99+ % purity, was used without further treatment. Stabilized du Pont tetrahydrofuran was refluxed over sodium hydroxide for 24 hours and distilled. The distillate was refluxed with lithium aluminum hydride for seven hours and distilled. The fraction boiling at 65–66° was saturated at 0° with boron trifluoride, and the crude etherate was distilled. The fraction boiling at 58° at 1.2 mm. pressure was collected. About 0.3 mole of this fraction and 25 g. of tetrahydrofuran was cooled in an ice-salt mixture and a solution of diamine (either ethylenediamine or hexamethylenediamine) in tetrahydrofuran (0.14 mole of diamine and 50 ml. of tetrahydrofuran), was added slowly through a dropping funnel. On completion of the addition, the solvent was removed from the reaction mixture by distillation at reduced pressure. The crude solid product was washed with small amounts of tetrahydrofuran and dried *in vacuo*. Quantitative yields were obtained.

The crude hexamethylenediamine·2BF₃ could be recrystallized from ethanol or water; the latter yielded a purer and more crystalline product. Water was the only medium found suitable for the recrystallization of ethylenediamine·2BF₃. All samples used further in this investigation were recrystallized twice from water. Slow hydrolysis of the complexes does occur (see below) but the hydrolysis products are quite soluble in water and hence are removed by fractional crystallization.

Anal. Calcd. for C₂H₄(NH₂)₂·2BF₃: C, 12.28; H, 4.10; N, 14.32; F, 58.26; mol. wt., 194.74. Found: C, 12.67; H, 4.40; N, 15.12; F, 58.46, 57.50, 57.70; mol. wt., 194 at 0.655 molal and 180 at 0.0100 molal.

Anal. Calcd. for (CH₂)₆(NH₂)₂·2BF₃: C, 28.61; H, 6.41; N, 11.11; F, 45.27; mol. wt., 251.84. Found: C, 29.24; H, 6.58; N, 11.22; F, 44.65, 44.67, 45.07; mol. wt., 263 at 0.127 molal and 255 at 0.100 molal.

Physical Properties.—Ethylenediamine·2BF₃ crystallizes as colorless equidimensional plates belonging to the monoclinic system. The mean refractive index is 1.390^m_D, and the density is 1.503 g./cc. at 25°. Hexamethylenediamine·2BF₃ crystallizes as colorless plates which have a mean refractive index at 1.397^m_D and a density of 1.234 g./cc. at 25°. Densities were determined pycnometrically using toluene as the immersion liquid.

The molar refractions were found to be 30.85 and 49.32 cc., respectively, for the ethylenediamine and hexamethylenediamine compounds. The difference is 18.47 cc., which is identical with the theoretical value calculated using $R_D = 4.618$ cc. for each CH₂ group.

Ethylenediamine·2BF₃ and hexamethylenediamine·2BF₃ melt at 169–170° and 179–180.5°, respectively. Both melting points are dependent on the rate of heating, as the complexes undergo slow thermal decomposition well below their melting points. Both substances are insoluble in diethyl ether, benzene, toluene and chloroform. They are soluble in tetrahydrofuran, alcohols and water but react slowly with the last two solvents. The ethylenediamine compound is soluble in water to the extent of 4 g./100 cc. at 0° while the hexamethylenediamine analog is much less soluble, 0.4 g./100 cc. Infrared spectra of samples of the complexes dispersed in Nujol are shown in Fig. 1.

(1) In part taken from a Ph.D. thesis submitted by Earl L. Muetterties to the Graduate School of Arts and Sciences, Harvard University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Procter and Gamble Fellow in Chemistry, Harvard University, 1951–1952.

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

(4) M. A. Miller (to the Aluminum Co. of America), U. S. Patent 2,238,069 (April 15, 1941).

(5) "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, pp. 197–198.

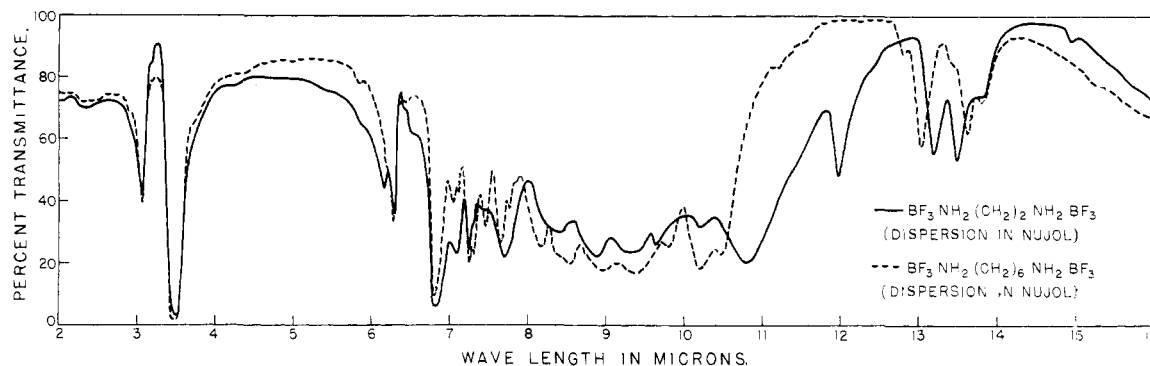


Fig. 1.—Infrared spectra of $\text{BF}_3 \cdot \text{NH}_2(\text{CH}_2)_2 \text{NH}_2 \cdot \text{BF}_3$ and $\text{BF}_3 \cdot \text{NH}_2(\text{CH}_2)_6 \text{NH}_2 \cdot \text{BF}_3$.

Hydrolysis of Complexes.—Estimates of the reactivity of ethylenediamine- 2BF_3 and hexamethylenediamine- 2BF_3 , toward water were obtained by determining the change of conductance of 0.01 M solutions with time. A "dip" cell with platinum electrodes was employed in conjunction with a conductance bridge. Solutions of the complexes (0.02 M) were placed in covered platinum crucibles and heated on a steam-bath for ten hours. These solutions were diluted to 0.01 M and the conductances determined. The measurements were assumed to give the conductances of solutions of completely hydrolyzed complexes. Representative data are presented in Table I. The rates of change of conductance are nearly constant over a period of the first two hours, and comparison of the average rate of change of conductance in this region for either complex indicates that ethylenediamine- 2BF_3 hydrolyzes 48 times as fast as hexamethylenediamine- 2BF_3 .

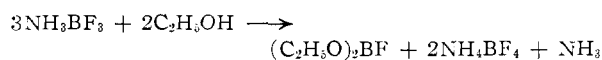
TABLE I
RATES OF HYDROLYSIS OF DIAMINE-BORON TRIFLUORIDE COMPLEXES

Ethylenediamine- 2BF_3 (0.01 M)		Hexamethylenediamine- 2BF_3 (0.01 M)	
Time elapsed, hr.	Specific conductance, mhos	Time elapsed, hr.	Specific conductance, mhos
0.1	34.6×10^{-6}	0.25	4.13×10^{-6}
.2	47.1×10^{-6}	.43	4.49×10^{-6}
.47	75.4×10^{-6}	.85	5.29×10^{-6}
.87	110×10^{-6}	1.18	5.77×10^{-6}
1.51	150×10^{-6}	1.67	6.57×10^{-6}
1.95	180×10^{-6}	2.42	7.55×10^{-6}
2.5	210×10^{-6}	2.8	8.08×10^{-6}
5.8	334×10^{-6}	11.3	14.7×10^{-6}
11.7	504×10^{-6}	16.3	19.9×10^{-6}
24.6	759×10^{-6}	22.9	23.8×10^{-6}

Complete hydrolysis 2350

Complete hydrolysis 2080

Reactions with Alcohols.—The reactions of ammonia- BF_3 , ethylenediamine- 2BF_3 and hexamethylenediamine- 2BF_3 with ethanol were briefly investigated. The compound NH_2BF_3 was prepared first and purified by the method of Laubengayer⁶; on refluxing with ethanol it reacted with the evolution of ammonia and (after five hours) a precipitated ammonium fluoborate. The vapors which passed through the reflux condenser burned with a bright green flame. On refluxing with ethanol in this way, a 0.95-g. sample of NH_2BF_3 yielded 0.70 g. of ammonium fluoborate. The theoretical yield of 0.78 g. is indicated by the equation



Ethylenediamine- 2BF_3 on refluxing with alcohol yields no free amine, but the presence of a volatile ester again was confirmed. After 1.5 hr. of reflux, a flocculent precipitate appeared. Fractional crystallization of this product from

alcohol yielded two substances which appear to be $\text{BF}_4\text{NH}_3 \cdot (\text{CH}_2)_2 \cdot \text{NH}_3\text{BF}_4$ and $\text{BF}_4\text{NH}_3(\text{CH}_2)_6 \cdot \text{NH}_3\text{BF}_4$. These were analyzed by the nitron acetate method for fluoborate.⁷

Anal. Calcd. for $\text{BF}_4\text{NH}_3(\text{CH}_2)_2 \cdot \text{NH}_3\text{BF}_4$: HBF_4 , 74.75. Found: HBF_4 , 73.91. Calcd. for $\text{BF}_4\text{NH}_3(\text{CH}_2)_6 \cdot \text{NH}_3\text{BF}_4$: HBF_4 , 52.30. Found: HBF_4 , 53.09.

A 2.1-g. sample of hexamethylenediamine- 2BF_3 was added to 80 ml. of ethanol and refluxed for five days. After about 16 hours of reflux a small amount of white solid precipitated, and at the end of the reflux period 0.01 g. of this material was collected. Analysis showed that the solid contained carbon, hydrogen and fluorine, but no boron. The fluorine content was 42.10%. The unidentified material does not melt but begins to sublime at about 270°.

The filtrate from the alcoholysis of hexamethylenediamine- 2BF_3 was evaporated and one of the products was obtained in a pure state by fractional crystallization. Analysis showed this substance to be hexamethylenediamine dihydrofluoborate, $\text{BF}_4\text{NH}_3(\text{CH}_2)_6 \cdot \text{NH}_3\text{BF}_4$. *Anal.* Calcd. HBF_4 , 60.20; found, 59.95. The compound melted at 254–256°. Even the prolonged refluxing with ethanol gave incomplete reaction and again illustrates the difference in activity of the ethylenediamine and hexamethylenediamine complexes.

The reactions of ethylenediamine- 2BF_3 and hexamethylenediamine- 2BF_3 with alcohol also were followed conductometrically. The initial rates of change of conductivity with time were found to be almost identical to the corresponding rates in water.

Thermal Properties.—Ethylenediamine- 2BF_3 and hexamethylenediamine- 2BF_3 were sublimed at 170° *in vacuo*. The sublimate is gummy, non-crystalline materials which had analyses corresponding closely to those of the pure addition compound. Positive tests for the presence of small amounts of fluoborate were obtained in each case.

Thermal stability was determined by heating 0.1-g. samples *in vacuo* for two hours at various temperatures. The lowest temperature that gave rise to a positive test for fluoborate was taken as the decomposition temperature. Ethylenediamine- 2BF_3 began to decompose at 115° and hexamethylenediamine- 2BF_3 at 123°. Products of the thermal decomposition were not isolated.

III. Ethylenediamine- BF_3 . Preparation.—Ethylenediamine (0.167 mole) in 500 ml. of ether was added to 0.167 mole of boron trifluoride diethyl etherate in 50 ml. of ether at 0°. When the addition was completed, the resulting slurry was filtered and the solid reaction product washed with ether and dried *in vacuo*. The yield of 1:1 compound were nearly quantitative. The fluorine content of samples from a number of preparations varied from 44 to 48%. (Calcd. for $\text{C}_2\text{H}_4(\text{NH}_2)_2 \cdot \text{BF}_3$, 44.56%). No method for the purification of the crude product was found.

Properties.—The crude ethylenediamine- BF_3 melted at 70–74°. The melting point was dependent upon the rate of heating; decomposition began at 66° with partial loss of ethylenediamine. The compound was unstable in air and rapidly turned to a yellow oil. Water, formamide, alcohols, amines and dioxane dissolved the complex but in all cases solution was accompanied by decomposition. Both boron trichloride and boron trifluoride gases reacted exothermally

(6) A. W. Laubengayer and G. E. Condit, *This Journal*, **70**, 2274 (1948).

(7) W. Lange, *Ber.*, **59**, 2407, 2432 (1926).

with the complex. The amount of boron trichloride adsorbed never exceeded 0.2 mole BCl_3 per mole of complex, whereas boron trifluoride was absorbed to the extent of about 0.85 mole of BF_3 per mole of complex.

Thermal decomposition of ethylenediamine- BF_3 at 260° in a sealed tube produced ammonium fluoborate. *Anal.* Calcd. for NH_4BF_4 : HBF_4 , 84.30; N, 13.60; H, 3.81. Found: HBF_4 , 83.70; N, 13.35; H, 3.84. In addition small amounts of ammonia and ethylenimine were found in

the decomposition products and were identified by their infrared spectra.

Acknowledgment.—The authors are indebted to Dr. Benjamin W. Howk of the Chemical Department, E. I. du Pont de Nemours & Co., for a sample of pure hexamethylenediamine.

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[CONTRIBUTION FROM THE REFINING TECHNICAL AND RESEARCH DIVISIONS, HUMBLE OIL AND REFINING COMPANY]

Diffusion Currents at Cylindrical Electrodes. A Study of Organic Sulfides

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RECEIVED NOVEMBER 23, 1953

A theory of diffusion currents at stationary cylindrical electrodes with linear variation of applied potential is presented. Ferro- and ferricyanide ions approach closely the behavior predicted for a reversible electrochemical system. In general, these results justify the conclusion that convection effects can be reduced to minor importance in conventional polarographic operation without elaborate precautions and that the current-voltage curves obtained in the manner described are amenable to theoretical interpretation. Evidence of irreversibility is found in anodic polarograms of a series of organic sulfides. The reaction is shown to be a 2-electron process, corresponding to formation of the sulfoxide. Diaryl sulfides are more difficult to oxidize electrolytically than other types.

The theory of diffusion currents at plane electrodes with linear variation of applied potential has been developed in papers on oscillographic polarography.¹⁻³ The same equations are valid approximately for stationary spherical and cylindrical electrodes if the time of electrolysis is sufficiently short. Specifically, the error in calculated maximum current at a cylindrical electrode does not exceed 5% when $D/ta^2 \leq 3 \times 10^{-3}$, where D is the diffusion coefficient of the current-controlling species, t the time of electrolysis, and a the radius of the cylinder.³ Ordinary polarographic conditions correspond to values of this term about one thousand times greater, and in such cases it becomes necessary to consider the curvature of the surface in an accurate theoretical treatment.

In the present investigation, current-voltage curves of good reproducibility, resembling qualitatively those obtained by the oscillographic technique, were observed at wire electrodes with an automatic voltage change of a few millivolts per second. It is known, however, that the steady state currents measured manually at constant voltage on stationary wires depend upon convection effects due to density gradients produced by the electrode reaction and, therefore, are greater than those which would result from diffusion in an unstirred solution.^{4,5} Some workers with stationary electrodes have approached this steady state by slow automatic change of voltage⁶; others have employed usual rates of polarographic recording⁷ but have not made an exact theoretical study of the results.

The following discussion of cylindrical electrodes

(1) J. E. B. Randles, *Trans. Faraday Soc.*, **44**, 327 (1948).

(2) A. Sevcik, *Collection Czechoslov. Chem. Commun.*, **13**, 349 (1948).

(3) T. Berzins and P. Delahay, *THIS JOURNAL*, **75**, 555 (1953).

(4) H. A. Laitinen and I. M. Kolthoff, *ibid.*, **61**, 3344 (1939).

(5) H. A. Laitinen and I. M. Kolthoff, *J. Phys. Chem.*, **45**, 1061 (1941).

(6) D. B. Julian and W. R. Ruby, *THIS JOURNAL*, **72**, 4719 (1950).

(7) L. B. Rogers, H. H. Miller, R. B. Goodrich and A. F. Stehney, *Anal. Chem.*, **21**, 777 (1949).

extends the theory to take into account the curvature of the electrode surface.

Theory of Diffusion Currents at Cylindrical Electrodes

The fundamental differential equation for cylindrical diffusion is

$$\frac{\partial C}{\partial t} = D \left[\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \left(\frac{\partial C}{\partial r} \right) \right] \quad (1)$$

in which C is concentration and r is distance from the axis of the cylinder.

Boundary Conditions.—A numerical solution of equation 1 is sought for boundary conditions corresponding to a reversible reaction at a cylindrical electrode of radius a , with reactants and products soluble in the supporting electrolyte medium. It is assumed that none of the principal electrolysis product is present before the reaction, but that the current-controlling species has an initial concentration c^0 .

The fact that the flux of material diffusing to the electrode surface must be equal and opposite to that leaving it leads to the expression

$$(c_{\text{ox}})_a + (c_{\text{red}})_a = c^0 \quad (2)$$

for surface concentrations if the ratio of diffusion coefficients $D_{\text{ox}}/D_{\text{red}}$ is taken equal to unity.¹

The electrode potential E is given by

$$E = E_i \pm \alpha t \quad (3)$$

in which E_i is the initial potential and α is the magnitude of the rate of change of E with time. According to polarographic convention, the *plus* sign applies to an anodic reaction, the *minus* to a cathodic one. It is convenient to represent the conventional expression $nF(E - E^0)/2.3RT$ by the symbol τ . Equation 2 and the Nernst equation yield

$$\tau = \pm \log [(c^0 - c)/c] \quad (4)$$

where c is concentration of the current-controlling species and the signs are designated as for equation