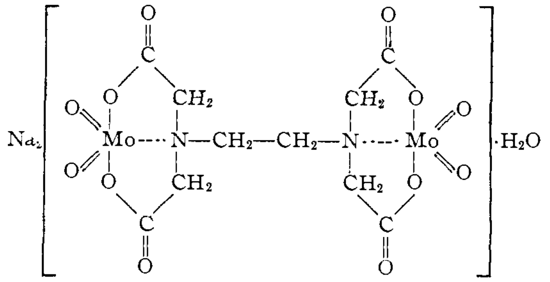
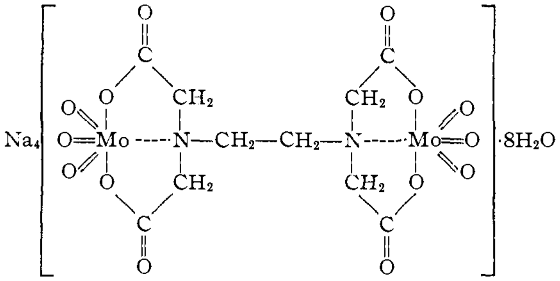
A. Molybdenum(V)-EDTA: $Na_2Mo_2O_{13}H_{14}C_{10}N_2$, mol. wt., 608.13



B. Molybdenum(VI)-EDTA: $Na_4Mo_2O_{22}H_{28}C_{10}N_2$, mol. wt., 812.23



initially pH 7.70, was titrated with standard sulfuric acid, giving an inflection at pH 4.35 after the addition of 2.0 hydrogen ions per chelate molecule. This behavior is consistent with the formula proposed for the chelate at pH 4.5.

Electrode Reactions.—The preceding sections provide strong evidence that the chelates at pH 4.5 have the form $Mo_2O_4Y^=$ and $Mo_2O_6Y^{-4}$ for the (V) and (VI) oxidation states, respectively. When these observations are combined with the polarographic data, one can propose the reduction reactions

At pH greater than 4.5

$$Mo_2O_6Y^{-4} + 3H^+ + 2e^- = Mo_2O_5YH^{-3} + H_2O \quad (1)$$

At pH less than 4.5, First wave

$$Mo_2O_6YH^{-3} + 4H^+ + 2e^- = Mo_2O_4YH^- + 2H_2O \quad (2a)$$

Second wave

$$Mo_2O_6Y^{-4} + 4H^+ + 2e^- = Mo_2O_4Y^= + 2H_2O \quad (2b)$$

There is essentially complete evidence for reactions 2a and 2b, but some conflict in the case of reaction 1, since the polarographic evidence indicates only one hydrogen in the reaction. The latter seems questionable since a change from four hydrogen ions at pH less than 4.5 to one for pH greater than 4.5 would not be expected, but rather from four to three. The latter expectation was used in writing reaction 1, which is also in accord with the pH titration.

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[CONTRIBUTION FROM E. I. DU PONT DE NEMOURS & CO.]

The Ammonolysis of BF_3NH_3

BY WILMER A. JENKINS

RECEIVED MAY 25, 1956

Solutions of BF_3NH_3 in liquid ammonia were studied over the temperature range −78° to 50°. It was found that the ammonolytic reaction $BF_3NH_3 + NH_3 \rightarrow NH_4F + BF_2NH_2$ reported by earlier workers does not take place under these conditions. X-Ray spacing and intensity values for BF_3NH_3 are reported.

Introduction

Interest in the compound BF_2NH_2 led us to try to prepare it by the partial ammonolysis of BF_3NH_3, reaction (1)

$$BF_3NH_3 + NH_3 \longrightarrow NH_4F + BF_2NH_2 \quad (1)$$

Kraus and Brown studied[1] the properties of liquid ammonia solutions of BF_3NH_3 by adding sodium to the solutions. They found that hydrogen was evolved when sodium was added and concluded that BF_3NH_3 is ammonolyzed to some extent in liquid ammonia. Since the first stage of ammonolysis should take place according to reaction 1, this seemed like a convenient way to prepare BF_2NH_2.

Behavior of BF_3NH_3 in Liquid Ammonia.—BF_3NH_3 was prepared as described below and dissolved in liquid ammonia. The solutions were held under dry nitrogen at various temperatures and for varying lengths of time. The ammonia was then boiled off at −33° and the solid residue was examined by X-ray and wet analytical methods to ascertain the nature and extent of any reaction which might have taken place. In no case was any evidence found for reaction 1. The solid recovered from ammonia solution was in all cases identical in composition and physical properties with the original BF_3NH_3. The data obtained in these experiments are shown in Table I.

TABLE I

		Anal. results on solid products recovered from soln. by evaporation of NH_3				
Temp., °C.	Time, hr.	B,[a] %	NH_3,[a] %	Mol. wt.[a]	M.p.,[a] °C.	X-Ray
−78	12	12.7	20.3	..	..	BF_3NH_3 only
−33	6	12.6	20.1	..	164	BF_3NH_3 only
25	2	12.8	20.0	83	168	BF_3NH_3 only
25	20	12.7	19.9	83	166	BF_3NH_3 only
50	22	12.7	20.1	84	167	BF_3NH_3 only

[a] The BF_3NH_3 used to make up the solutions had the following properties: B, 12.8%; NH_3, 19.9%; mol. wt., 83; m.p., 168°.

These data, which show that BF_3NH_3 does not react with liquid ammonia between −78° and 50°, can be reconciled with the results of Kraus and Brown by reference to the work of Keenan and McDowell.[2] They discovered that sodium in liquid ammonia reacts directly with BF_3NH_3 in

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(1) C. A. Kraus and E. Brown, THIS JOURNAL, **51**, 2690 (1929).

(2) C. W. Keenan and W. J. McDowell, *ibid.*, **75**, 6348 (1953).

solution to produce hydrogen and BF_2NH_2, in accordance with eq. 2

$$BF_3NH_3 + Na \xrightarrow{NH_3} BH_2NH_2 + {}^1/_2H_2 + NaF \quad (2)$$

The stability of BF_3NH_3 in liquid ammonia is in marked contrast to the ammonolytic instability of BCl_3NH_3. The latter compound is so unstable in the presence of ammonia that it has never been isolated; the action of ammonia on BCl_3 invariably produces boron nitrogen compounds with an N/B atomic ratio greater than one.

The X-Ray Pattern of BF_3NH_3.—Laubengayer and Condike[3] first reported spacing and intensity values for BF_3NH_3. Keenan and McDowell[2] reported values which do not agree with those of Laubengayer and Condike. Our spacing and intensity values agree very well with those of Keenan and McDowell. The three sets of data are given in Table II.

TABLE II

X-RAY DATA FOR BF_3NH_3

Laubengayer and Condike		Keenan and McDowell		This work	
d, Å.	Intensity	d, Å.	Intensity	d, Å.	Intensity
4.22	S	4.87	M	4.87	M
				4.62	M
3.88	S	4.01	S	4.04	S
3.60	M	3.65	S	3.69	S
3.00	M	3.37	S	3.37	S
2.55	M	2.87	M	2.84	M
2.19	W	2.72	S	2.73	M
		2.45	M	2.44	W
		2.34	M	2.35	W
		2.24	M	2.23	M
		1.97	W	1.97	W
		1.81	M	1.81	M
				1.76	W
		1.65	M	1.65	W

Experimental

Preparation and Analysis of BF_3NH_3.—BF_3NH_3 was prepared by the method used by Laubengayer and Condike.[3] Boron trifluoride and ammonia gases were mixed in a resin kettle cooled in an ice-bath. The reaction was allowed to proceed for several hours, after which time the solid salt was scraped out of the kettle and recrystallized from distilled water.

Anal. Calcd. for BF_3NH_3: B, 12.8; NH_3, 20.0; mol. wt., 84. Found: B, 12.8; NH_3, 19.9; mol. wt., 83.

BF_3NH_3 was analyzed for nitrogen by the standard Kjeldahl method. The boron analysis was carried out as follows. The sample was dissolved in water and the solution acidified and allowed to stand for at least one hour at room temperature. The *p*H of an aliquot was then adjusted to 6.3, mannitol was added, and the solution titrated with standard base back to a *p*H of 6.3. If the original solution was not allowed to stand for at least one hour, the results were invariably low. If the titration was taken to *p*H 9, the results invariably were high.

Melting Point, Molecular Weight and X-Ray Data.—The melting point of BF_3NH_3 samples was determined by dropping very small crystals of the sample on the hot stage of a Fisher melting point apparatus and noting the temperature at which they melted within one second after touching the stage. Although this method gives results which are somewhat high, it was found that the values were reproducible within a degree. Laubengayer and Condike obtained a melting point of 163° on a Dennis–Shelton melting point bar.

Molecular weights were determined cryoscopically in water.

The X-ray powder photographs were taken on a North American Philips diffraction unit using filtered Cu $K\alpha$ radiation.

Acknowledgments.—I am indebted to Mr. Willard M. Johnston for boron and nitrogen analyses, to Mr. Albert F. Biddle for X-ray analyses, to Dr. Russell B. Eaton for much helpful advice, and to the Pigments Department for permission to publish this work.

WILMINGTON, DELAWARE

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(3) A. W. Laubengayer and G. F. Condike, THIS JOURNAL, **70**, 2274 1948).

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Equilibria of the Metastable Crystalline Form of Beryllium Hydroxide. $Be(OH)_2$ in Hydrochloric Acid, Perchloric Acid and Sodium Hydroxide Solutions at 25°

BY R. A. GILBERT[1] AND A. B. GARRETT

RECEIVED APRIL 5, 1956

The solubility of beryllium hydroxide has been determined in dilute acid and base at 25 ± 0.02° and the hydrolysis of beryllium chloride has been measured. The principal equilibria present in these solutions are believed to be the following: $Be(OH)_2(s) + OH^- \rightleftarrows HBeO_2^- + H_2O$, $K_2 = 3.2 \times 10^{-3}$; $Be(OH)_2(s) + 2OH^- \rightleftarrows BeO_2^= + 2H_2O$, $K_3 = 2.0 \times 10^{-3}$ $Be(OH)_2(s) + 2H^+ \rightleftarrows Be^{++} + 2H_2O$, $K_5 = 7.3 \times 10^6$; $xBe(OH)_2(s) + Be^{++} \rightleftarrows Be(OBe)_x^{++} + xH_2O$, moles Be^{++}/moles Be_2O^{++} = 0.60; $2Be^{++} + H_2O \rightleftarrows Be_2O^{++} + 2H^+$, $K_8 = 1.6 \times 10^{-7}$; $Be(OH)_2(s) \rightleftarrows HBeO_2^- + H^+$, $K_9 = 3.2 \times 10^{-17}$; $Be(OH)_2(s) \rightleftarrows BeO_2^= + 2H^+$, $K_{11} = 2.0 \times 10^{-31}$; $Be(OH)_2(s) \rightleftarrows Be^{++} + 2OH^-$, $K_1 = 7.3 \times 10^{-22}$. The hydrolysis constant given is believed to represent an upper limit in view of the polynuclear ions that are reported to be present.

The purpose of this investigation was to obtain data on the equilibria of the metastable form of crystalline beryllium hydroxide in dilute solutions of sodium hydroxide, hydrochloric acid and perchloric acid. Such data make possible (1) the determination of the character of the ions existing in dilute acid and alkali and (2) the evaluation of the free energies of formation of such ions and the evaluation of the solubility product of the hydroxide.

Many early investigators attempted to determine the exact constitution of precipitated beryllium hydroxide. Haber and Van Oordt[2] showed that the freshly precipitated hydroxide is an amorphous jelly-like material which is transformed with time

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(1) Taken from the dissertation presented by Robert A. Gilbert to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the Ph.D. degree, 1953.

(2) F. Haber and B. Van Oordt, *Z. anorg. Chem.*, **38**, 377 (1940).