ammonolysis products are not observed even when these solutions are heated from −68 to 110° and held at the latter temperature for 72 hr. It seems highly improbable that there exists at −68° a solvolytic equilibrium that provides any detectable concentration of ammonium ion and that is temperature independent.

The properties of the ammoniates of aluminum (III) iodide also argue against the occurrence of ammonolysis. The experiments described above demonstrate the conversions

$$AlI_3\cdot 20NH_3 \rightleftharpoons AlI_3\cdot 6NH_3 \rightleftharpoons AlI_3\cdot 5NH_3$$

The 6-ammoniate is stable in ammonia solution up to at least 110° and is formed reversibly from the 20-ammoniate; the 5-ammoniate is stable in gaseous ammonia up to 220° and reverts to the 20-ammoniate when dissolved in liquid ammonia.

In the light of the results described above, the turbidity commonly observed when aluminum(III) iodide is dissolved in ammonia[7,19,20] is most probably attributable to the presence of hydrated aluminum(III) oxide (or possibly its precursors, *i.e.*, *aquo*-basic iodides) resulting from the unusual susceptibility of the iodide to hydrolysis. The earlier conclusion[6] that these solids consist of *ammono*-basic iodides is not convincing in the absence of analytical data for nitrogen. Although not extensive, the data given above indicate that in the normal laboratory atmosphere or in air saturated with water vapor, aluminum(III) iodide 6-ammoniate hydrolyzes to form mixtures of hydrates of NH_4I and AlO(OH).

The assumption of the presence of significant concentrations of ammonium ion[5,6] in liquid ammonia solutions of aluminum(III) iodide is not necessary to account for the evolution of variable quantities of hydrogen[2,3,5,6] when potassium is added to such solutions at or below the boiling point of the solvent. If, for example, Al^+ is formed even transitorily, hydrogen could result from the reduction of ammonia

$$Al^+ + 2NH_3 \longrightarrow Al^{3+} + H_2 + 2NH_2^-$$

at a rate that precludes detection of reducing properties attributable to lower oxidation states of aluminum. This interpretation is entirely analogous to that given by Raijola and Davidson[21] for their inability to detect Al^+ formed in aqueous solutions. Their work together with that described above serves to render even more plausible the assumption of the transitory existence of lower oxidation states of aluminum in liquid ammonia solutions.[2]

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(19) H. S. Booth and M. Merlub-Sobel, *ibid.*, **35**, 3303 (1931).

(20) W. L. Taylor, J. Kleinberg and E. Griswold, private communication, 1954.

(21) E. Raijola and A. W. Davidson, THIS JOURNAL, **78**, 556 (1956).

AUSTIN, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Molybdenum(V) and Molybdenum(VI) Complexes with Ethylenediaminetetraacetic Acid[1]

BY ROBERT L. PECSOK AND DONALD T. SAWYER

An investigation of polarographic methods for the determination of molybdenum has led to a study of the complexes of molybdenum(V) and (VI) with ethylenediaminetetraacetic acid (EDTA) and its salts. Continuous variations studies of the spectrum of the complexed molybdenum(V) indicated two molybdenums per EDTA in the complex. Solid chelates were synthesized and analyzed for the elements. All data support the proposal that these chelates contain a molar ratio of metal to EDTA of 2.0. The formulas are $Na_2Mo_2O_{12}H_{12}C_{10}N_2\cdot H_2O$ and $Na_4Mo_2O_{14}H_{12}C_{10}N_2\cdot 8H_2O$ for the (V) and (VI) oxidation states, respectively.

Many chelating agents are known to improve the nature of the polarographic wave for molybdenum(VI).[2] Since ethylenediaminetetraacetic acid and its salts (hereafter referred to as EDTA and designated H_4Y, H_3Y^-, H_2Y^{--}, HY^{-3} and Y^{-4}) are now commonly used as supporting electrolytes, it was of interest to investigate the nature of the molybdenum species present in these solutions. The results of a systematic study of the chelates formed between molybdenum(V) and molybdenum(VI) and EDTA are presented below. The composition of the chelates has been established by several independent methods. Structures have been proposed, together with electrode reactions which are consistent with the data.

Although the polarography of molybdenum(VI) has been studied extensively, most of the data pertain to solutions more acidic than *p*H 2.[2-11] The waves obtained are frequently complex and irreversible and, except for an interpretation of the change in oxidation state, very little is known concerning the nature of the complexes. The polarographic behavior of molybdenum(VI) in EDTA was reported briefly by two groups of investigators.[12,13]

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(1) This research was supported by the Research Corporation and submitted by Donald T. Sawyer in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the faculty of the University of California, Los Angeles, June, 1956. Presented before the Analytical Division of the American Chemical Society in Dallas, Texas, April, 1956.

(2) R. L. Pecsok and R. M. Parkhurst, *Anal. Chem.*, **27**, 1920 (1955).

(3) P. Beran, J. Čihalik, J. Deležal, V. Sinron and J. Zýku, *Chem. Listy*, **47**, 1315 (1953).

(4) D. F. Boltz, T. De Vries and M. G. Mellon, *Anal. Chem.*, **21**, 563 (1949).

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(6) M. Codell, J. J. Mikula and G. Norwitz, *Anal. Chem.*, **25**, 1441 (1953).

(7) Y. P. Gokhshtein, *Trudy Komissi Anal. Khim., Otdel. Khim. Nauk, Akad. Nauk S. S. S. R.*, **2**, (5) 54 (1949).

(8) G. P. Haight, Jr., *Anal. Chem.*, **23**, 1505 (1951).

(9) M. G. Johnson and R. J. Robinson, *ibid.*, **24**, 366 (1952).

(10) L. Meites, *ibid.*, **25**, 1752 (1953).

(11) E. P. Parry and M. G. Yakubik, *ibid.*, **26**, 1294 (1954).

(12) R. D. Feltham and E. L. Martin, *ibid.*, **25**, 1935 (1953).

(13) R. Pribil and A. Blazek, *Collection Czechoslov. Chem. Communs.*, **16**, 561 (1951).

Experimental

Polarographic data were obtained with a calibrated Sargent Model XXI Recording Polarograph according to standard procedure. A modified cell was used to prevent attack by strongly basic solutions on the agar in the salt bridge.[14] All measurements were made at 25.0°. Solutions were deaerated with purified nitrogen. Diffusion currents were measured using the tops of the oscillations (maximum current) and were corrected for residual current. All potentials were measured and reported *versus* the saturated calomel electrode. Half-wave potentials were measured to an accuracy of ±3 millivolts. The rate of flow of mercury was 1.50 mg./sec., and the drop time was 5.63 sec. at −0.8 volt applied potential.

Spectrophotometric data were obtained with a Cary Model 11 PMS recording spectrophotometer. A Beckman Model G *p*H meter (with Type E electrode for high *p*H) was used for *p*H measurements.

Molybdenum(VI) solutions were prepared from Merck reagent grade molybdic anhydride (assay greater than 99.5% MoO_3) dried for 1 hr. at 110° or from sodium molybdate standardized by titration with permanganate.[15] Molybdenum(V) solutions were prepared by reduction of standard molybdenum(VI) solutions with mercury by vigorous shaking in the presence of 3 *F* hydrochloric acid.[5] The reduced solution was stored in the presence of mercury and standardized with ceric sulfate.[16] EDTA solutions were prepared determinately from the reagent grade disodium salt sold by Versenes, Incorporated. All other materials were reagent grade.

Results and Discussion

Polarography of Molybdenum(VI).—In the region from *p*H 2 to *p*H 7, the complexes give essentially reversible reduction waves. Reversibility was determined by subtracting the one-quarter wave potential from the three-quarter wave potential.[17] Waves were considered reversible if the difference was less than 80 millivolts, although 56 millivolts is the theoretical value. Typical polarograms are shown in Fig. 1. From *p*H 2.5 to *p*H 4.5, two waves occur, the relative heights of which change with *p*H. The first wave disappears above *p*H 4.5 and the second wave disappears above *p*H 7. The total heights of these waves decrease with increasing *p*H, which is also true for the single wave from *p*H 4.5 to *p*H 7 (Fig. 2).

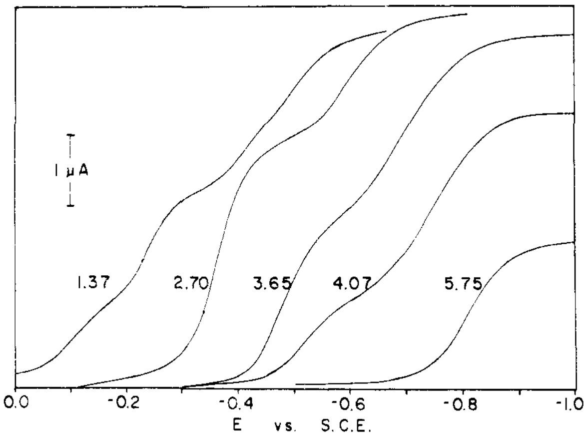

Fig. 1.—Polarograms of molybdenum(VI) in the presence of EDTA at various *p*H's, as noted on each curve. The solutions had the following composition: Mo(VI), 5.2×10^{-4} *F*; EDTA, 4.0×10^{-3} *F*; K_2SO_4 0.1 *F*.

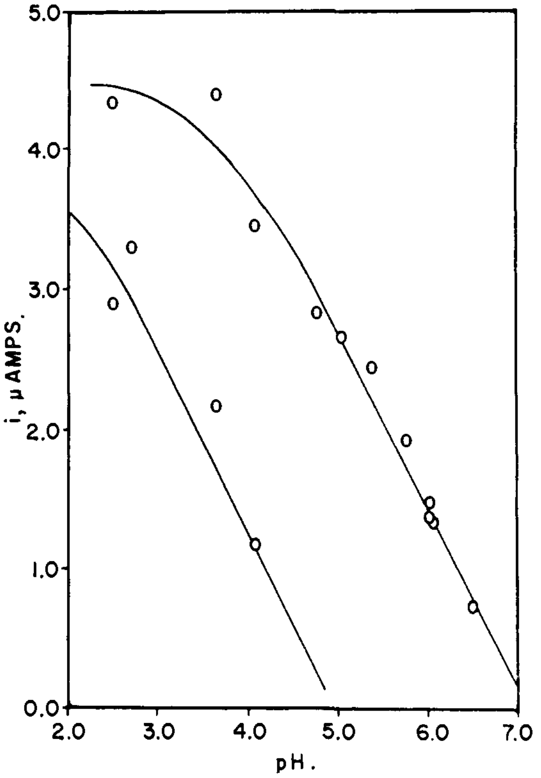

Fig. 2.—Effect of *p*H on the polarographic wave heights of molybdenum(VI) in the presence of EDTA. Curve A is the height of the first wave, in microamperes. Curve B gives the total wave height of the second wave. The solutions had the following composition: Mo(VI), 5.2×10^{-4} *F*; EDTA, 4.0×10^{-3} *F*; K_2SO_4 0.1 *F*.

Variations in the concentration of EDTA produce several effects on the cathodic wave. As shown in Fig. 3, the wave height increases with increasing concentration of EDTA. In addition, at *p*H's above 5, concentrations of EDTA above 0.01 *F* cause apparent maxima. These maxima are thought to be due to a desorption phenomenon similar to that noted by Parry and Yakubik.[11] Evidence was obtained by them that molybdenum(VI) in tartaric acid must be absorbed before reduction can occur. With increasing negative potential a slight desorption is believed to take place causing a decrease in the diffusion current. From this interpretation it was concluded that the tops of the maxima should be used for determining wave heights and half-wave potentials. The effects of inert salts, potassium sulfate and sodium chloride, are also indicated in Fig. 3. These variations of current with inert salts appear to be due to the change in ionic strength of the supporting electrolyte, with the doubly charged sulfate giving a more pronounced increase in wave height. The inert salts do not promote maxima.

The effect of *p*H on the half-wave potential is shown in Fig. 4. At *p*H 2.5 the double wave has half-wave potentials of −0.33 and −0.58 v. In the absence of EDTA at this *p*H, a triple wave oc-

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[14] R. L. Pecsok and R. S. Juvet, Jr., *Anal. Chem.*, **27**, 165 (1955).

[15] W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p. 308.

[16] N. H. Furman and W. M. Murray, Jr., THIS JOURNAL, **58**, 1689 (1936).

[17] I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952.

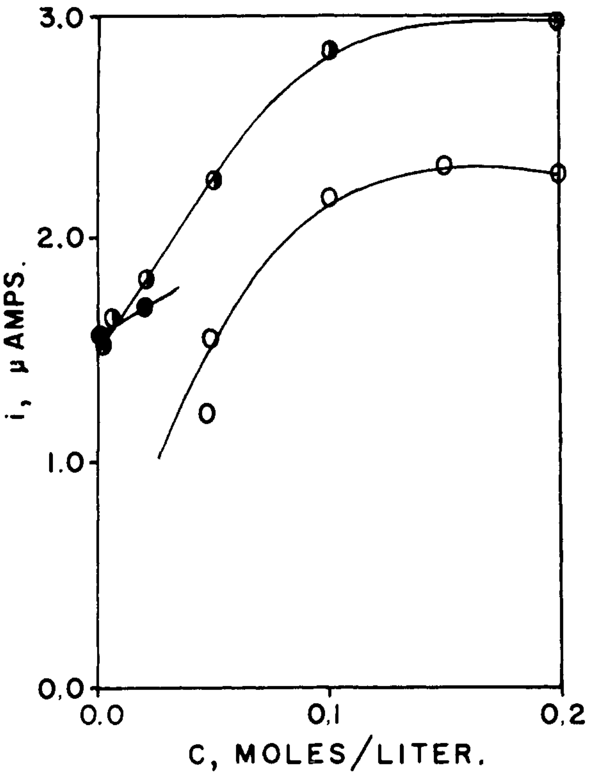

Fig. 3.—Effect of supporting electrolyte concentration on the polarographic wave heights of molybdenum(VI) in the presence of EDTA. All solutions were 5.2×10^{-4} *F* in Mo(VI) and had a *p*H of 5.8: ○, variation of EDTA concentration; ◑, variation of K_2SO_4 concentration, 0.05 *F* EDTA; ●, variation of NaCl concentration, 0.06 *F* EDTA.

curs, with half-wave potentials of −0.34, −0.52 and −0.71 v. The slopes of the lines in Fig. 4 indicate that two hydrogen ions per molybdenum are involved in the electrode reaction below *p*H 4.5 and that one-half hydrogen ion per molybdenum is involved above *p*H 4.5.

The half-wave potential is essentially independent of the concentration of EDTA at the *p*H's considered, which indicates that the ratio of EDTA to molybdenum is the same for both the (V) and (VI) oxidation states.

Satisfactory determinations of molybdenum with EDTA as a supporting electrolyte require carefully controlled conditions of *p*H, ligand concentration and ionic strength. If these conditions are met, the wave height is proportional to the molybdenum concentration over the region from 2×10^{-5} *F* to 1.3×10^{-3} *F* molybdenum. The method of standard addition is highly recommended in situations of this kind.[17] The diffusion current constant, I, is 1.71 in 0.050 *F* EDTA at *p*H 5.80 (maximum rather than average current).

Polarography of Molybdenum(V).—Anodic waves for molybdenum(V) in the *p*H range 2 to 7 were not satisfactory because of the oxidation wave of mercury in the presence of EDTA. In 0.005 *F* EDTA at *p*H 6, an anodic wave is observed. Higher concentrations of EDTA can be used at higher *p*H. The irreversible anodic wave in 0.2 *F* EDTA becomes reversible from *p*H 11.5 to *p*H 12.3, with one hydroxide ion per molybdenum involved in the electrode reaction. Again, the half-wave potential is independent of EDTA concentration. The half-wave potential at *p*H 12 in 0.2 *F* EDTA is −0.530 v. compared to −0.550 v. in the absence of EDTA.

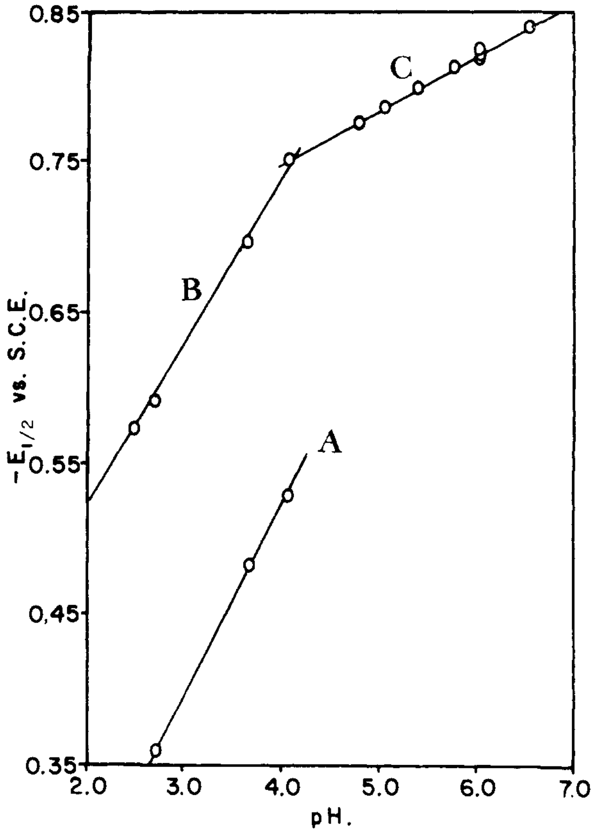

Fig. 4.—Effect of *p*H on the half-wave potential of molybdenum(VI), in the presence of EDTA. The solutions had the following composition: Mo(VI), 5.2×10^{-4} *F*; EDTA, 4.0×10^{-3} *F*; K_2SO_4, 0.1 *F*.

	Curve	Slope
First wave	A	−0.127
Second wave	B	−0.108
Wave above *p*H 4.5	C	−0.036

The waves for alkaline solutions have a maximum which disappears after allowing the solutions to stand for 20 minutes. The molybdenum(V) is subject to rapid air oxidation at high *p*H, and adequate precautions must be taken to exclude air. Consequently, analytical applications in this region are severely limited.

Spectrophotometry of Molybdenum(V).—The spectrum of the molybdenum(V)–EDTA chelate was studied in an attempt to establish its composition. In the presence of EDTA the spectrum is not noticeably different from that without EDTA. A broad absorption band occurs with a maximum at 298 mμ. However, in the absence of EDTA, this band disappears within a few minutes because of the oxidation of molybdenum(V). That oxidation actually took place was confirmed polarographically, EDTA stabilizes the molybdenum(V) solution below *p*H 7, and the spectrum remains essentially unchanged for weeks.

Solutions of varying composition were prepared, and the absorbance measured either immediately or after the solution had stood until all the uncomplexed molybdenum(V) had become oxidized. Job's method of continuous variations[18] was applied, with the results indicated in Fig. 5. The sharp maximum at 66.8 mole % molybdenum is evidence for a very stable complex at *p*H 6 having a molar ratio of 2 Mo/Y. The ratio is further confirmed in Fig. 6, which represents the absorbances of a series of solutions having a constant molybdenum concentration, and increasing EDTA concentrations. The intersection indicates a ratio of 2.2 Mo/Y. Similar results were obtained at *p*H 2.5 for the two methods.

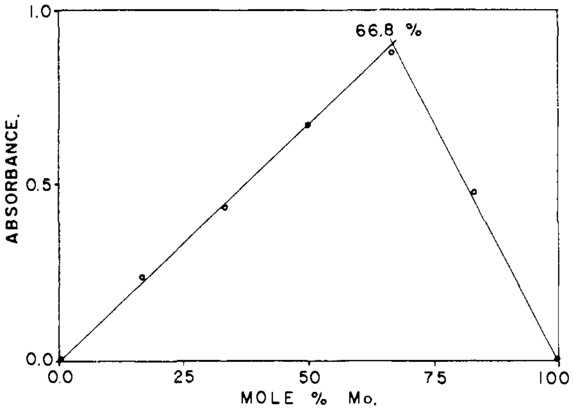

Fig. 5.—Job's method of continuous variations for molybdenum(V) in the presence of EDTA. The sum of the Mo(V) concentration and the EDTA concentration is equal to 3.0 × 10^{-4} *F*. Absorbance is plotted *versus* mole % Mo(V) at *p*H 6.0.

The occurrence of two molybdenum atoms per ligand is thought to be unique in the field of metal EDTA complexes. Previous work has always indicated one or more ligands per metal ion.[19] Rosenheim and Bertheim[20] did prepare dimolybdic-oxalic acid, but their proposed structure does not involve chelation. Pariselle and Chirvani[21] isolated a compound from a solution of potassium molybdate and saccharic acid which contains seven molybdenum atoms per three saccharate molecules. They did not propose a structure.

Molybdenum (VI) did not give an observable spectrum in the presence of EDTA.

Preparation of Solid Chelates.—A molybdenum (V)–EDTA compound was prepared by mixing 100 ml. of 0.1 *F* Mo(V) solution and 25 ml. of 0.2 *F* Na_2H_2Y with sufficient 18 *F* sodium hydroxide to adjust the *p*H to 6.0. The solution was evaporated to 50 ml. and 95% ethanol added until a turbidity appeared. Upon cooling in an ice-bath, bright reddish-orange crystals formed. The product was recrystallized three times from a water–ethanol mixture in order to free it from the large amount of sodium chloride present. It was finally washed and dried in a vacuum desiccator at room temperature for 48 hr.

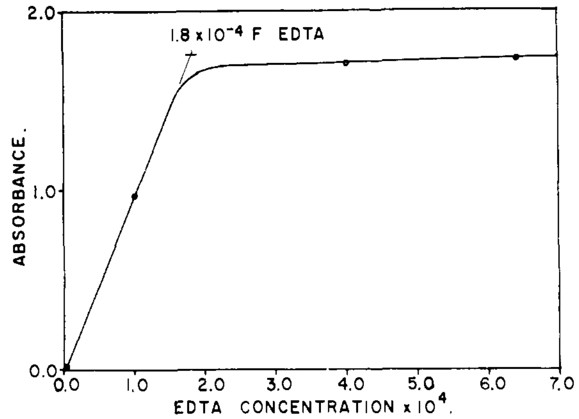

Fig. 6.—Effect of EDTA concentration on the absorbance of Mo(V). The absorbances for a series of solutions containing a Mo(V) concentration of 4.0 × 10^{-4} *F* are plotted *versus* EDTA concentration at *p*H 6.0.

A molybdenum(VI)–EDTA compound was prepared by a similar procedure, using sodium molybdate. The product was a white crystalline material.

Both products were analyzed by a number of methods. Carbon–hydrogen analyses were performed in two separate micro-analytical laboratories. The molybdenum was determined polarographically. Chloride tests with silver nitrate were negative even on prolonged standing. Finally, the compounds were ignited in a muffle furnace at 790° for 1 hr., and the residue was weighed and analyzed for molybdenum by permanganate titration[15] from which the percentage of sodium could be determined by difference. Nitrogen was estimated from the known ratio of N/C in EDTA and oxygen by difference. A summary of the analyses is given in Table I.

TABLE I

COMPOSITION OF MOLYBDENUM–EDTA COMPOUNDS

	A. Molybdenum(V): $Na_2Mo_2O_{13}H_{14}C_{10}N_2$		B. Molybdenum(VI): $Na_4Mo_2O_{22}H_{28}C_{10}N_2$	
	Exp., wt. %	Theor., wt. %	Exp., wt. %	Theor. wt. %
Mo	31.87	31.56	23.76	23.63
C	19.87	19.75	14.90	14.79
N	4.63	4.61	3.48	3.45
H	2.24	2.32	3.42	3.47
Na	7.64	7.56	11.39	11.33
O	33.75	34.20	43.05	43.34
	100.00	100.00	100.00	100.00

Structures of the Chelates.—From the analyses of the solid products, the following molecular formulas and structures are proposed.

***p*H Titration.**—Solutions were prepared from the solid chelates, 0.01 *F* in each case. The *p*H's of these solutions were 4.50 and 4.49 for the (V) and (VI) chelates, respectively. In addition, a solution was prepared by mixing 100 ml. of 0.1 *F* sodium molybdate, *p*H 6.90, and 25 ml. of 0.2 *F* disodium EDTA, *p*H 4.46, diluted until the Mo(VI) concentration was about 0.066 *F*, or 0.033*F* in terms of the complex. The resulting solution,

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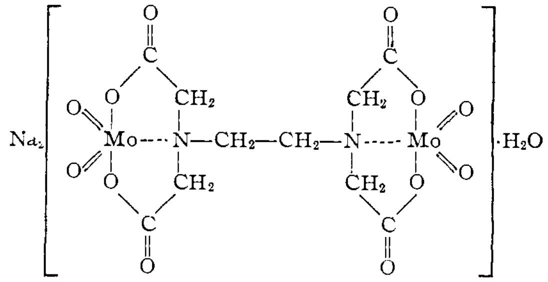
(18) P. Job, *Ann. chim.* [10] **9**, 113 (1928).

(19) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelates," Prentice-Hall, Inc., New York, N. Y., 1952.

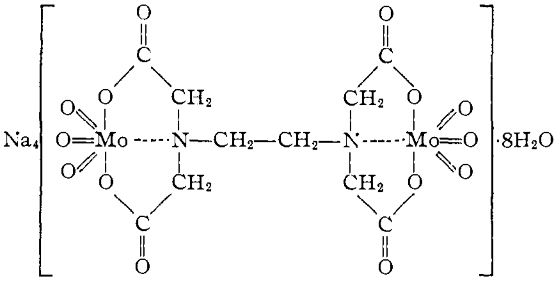
(20) A. Rosenheim and A. Bertheim, *Z. anorg. Chem.*, **34**, 427 (1903).

(21) H. Pariselle and F. Chirvani, *Compt. rend.*, **202**, 482 (1936).

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 *p*H 7.70, was titrated with standard sulfuric acid, giving an inflection at *p*H 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 *p*H 4.5.

Electrode Reactions.—The preceding sections provide strong evidence that the chelates at *p*H 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 *p*H greater than 4.5

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

At *p*H 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 *p*H less than 4.5 to one for *p*H 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 *p*H titration.

LOS ANGELES 24, CALIFORNIA

[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).