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The Preparation and Properties of Hexamminecobalt(III) Borohydride, Hexamminechromium(III) Borohydride and Ammonium Borohydride[1]

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Methods for the preparation of hexamminecobalt(III) borohydride, hexamminechromium(III) borohydride and ammonium borohydride are described. Hexamminechromium(III) borohydride is a stable compound up to 60°, the cobalt compound decomposes at 25° under high vacuum and ammonium borohydride is unstable above −20°. The thermal decomposition of these compounds, as well as their decomposition in aqueous solution, has been studied.

The synthesis of penetration-type metal ammine borohydrides may be achieved by metathesis reactions in liquid ammonia of the general type

$$MF_x + xNaBH_4 \xrightarrow[-45^\circ]{\text{liq. } NH_3} xNaF + M(BH_4)_x$$

This reaction has been effected for those cases in which M is the hexamminechromium(III) ion, the hexamminecobalt(III) ion and the ammonium ion. The resulting new compounds, hexamminechromium(III) borohydride[1] and hexamminecobalt(III) borohydride, are described herein. Although ammonium borohydride was mentioned briefly by Armstrong[2] in a previously classified industrial report, little information on its properties was available. In a study of the "diammoniate of diborane" the properties of this compound and of the metal ammine salts became important, and a more thorough investigation was warranted. From the academic standpoint ammonium borohydride is interesting since it represents borohydridic acid in liquid ammonia.

Experimental

A. **Materials.**—1. The best grade of commercially available reagent was dried and used except as noted below. Commercial $NaBH_4$ was recrystallized twice from liquid ammonia before use.

2. **Hexamminecobalt(III) Fluoride.**—Freshly precipitated Ag_2O was ground with hexamminecobalt(III) chloride for 1 hr. in a cold mortar (0°). The solids were filtered off and the filtrate and washings were neutralized with HF (*p*H 7) using a polyethylene beaker. The neutral solution was placed in a vacuum desiccator over concentrated H_2SO_4. After drying one week, the crystals which formed were filtered on a sintered glass frit, washed with a very small amount of cold distilled water and finally with absolute alcohol. The product was dried overnight at 105°.

The absorption spectrum of the product indicated the presence of the $[Co(NH_3)_6]^{+++}$ ion and an analysis gave: Co, 26.9%; NH_3, 46.6%; F^-, 26.4%; free HF, 0.13%. Calculated values for $[Co(NH_3)_6]F_3$ are: Co, 27.02%; NH_3, 46.84%; F^-, 26.13%.

Since $[Co(NH_3)_6]F_3$ is hygroscopic and very soluble in water, while the acid salt $[Co(NH_3)_6](HF_2)_3$ is insoluble in acid solution, *p*H must be controlled carefully during precipitation to prevent bifluoride contamination.

3. **Hexamminechromium(III) Fluoride.**—This compound has not been reported previously. The synthetic process used is represented by the equation

$$[Cr(NH_3)_6]Cl_3 + 3AgF \xrightarrow[25^\circ]{H_2O} [Cr(NH_3)_6]F_3 + 3AgCl$$

An AgF solution, prepared from Ag_2O and 6 *N* HF, was added carefully to a solution containing 0.034 mole of hexamminechromium(III) chloride. After filtering off solids, the clear solution (*p*H 6.3) was placed in a vacuum desiccator over concentrated sulfuric acid. The crystals which formed in a week were filtered on a sintered glass frit with exclusion of moist air and dried over NaOH. *Anal.* Calcd. for $[Cr(NH_3)_6]F_3$: F, 27.0; Cr, 24.63; NH_3, 48.38; F^-, 26.99; H^+, 0.00. Found: Cr, 24.1; NH_3, 47.0; free H^+, 1.0. The analysis suggests slight contamination with the bifluoride salt.

B. **General Procedure for the Metathesis Reaction.**—The metathesis reaction could be carried out at any desired low temperature by means of the apparatus shown in Fig. 1.[3] Stoichiometric amounts of the appropriate dry fluo-

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[1] The systematic name for the BH_4^- ion is tetrahydridoborate (III); however, because of the widespread usage of the trivial designation, borohydride, this term is used herein.

[2] Aerojet Engineering Corp., Biennial Report No. 420, January 26, 1950; RTM-66 May 26, 1950.

[3] The actual apparatus used to prepare NH_4BH_4 differed somewhat from that described here, but the essential principles of operation were the same.

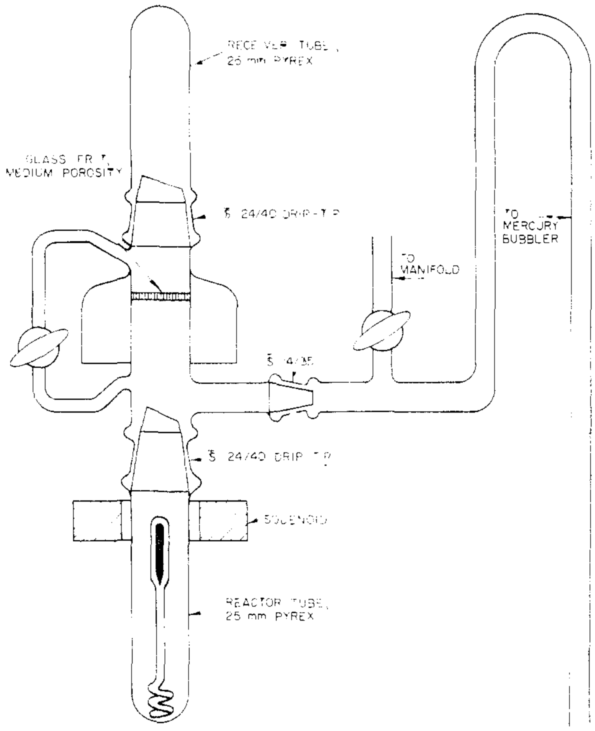

Fig. 1.—Apparatus for conducting metathesis reactions and filtrations at low temperatures.

rides and sodium borohydride were weighed out in a controlled-atmosphere gloved box and placed in the reactor tube. The tube was attached to the vacuum system. Ammonia was condensed into the reactor and metathesis was carried out at −65 to −45°. The mixture was agitated by an electromagnetic plunger-type stirrer. After 3 to 5 hr., the contents of the tube were frozen with liquid nitrogen; the apparatus was inverted by turning through 180° about the ₮ 14/35 joint. At this point a metal can with a hole cut in the bottom was placed on the inverted reactor tube in place of the solenoid. The hole in the can was just large enough to permit a snug fit around the tube and was placed 1.5 inches from its end. Dry Ice and isopropyl alcohol were placed in this can and in the cup around the filter. The remainder of the reactor tube was wrapped with glass wool. If necessary, additional cooling could be effected by pouring a small amount of liquid N_2 over the glass wool.

The solid reaction mixture gradually melted, ran down the sides, and was held on the filter frit. As the pressure increased a Dry Ice–isopropyl alcohol bath was placed around the receiver tube and the solution filtered through the frit. Effective washing of the precipitate and the sides of the reactor could be accomplished by placing an empty Dewar flask around the receiver, opening the stopcock in the by-pass around the filter and adding more Dry Ice to the can around the reactor tube. The stopcock on the by-pass was closed and when the receiver was cooled, the solution would filter again. Usually five washings were required to extract all of the product. The solvent ammonia was carefully evaporated, leaving the complex borohydride. The apparatus was finally "filled" with dry nitrogen and taken off the line. The products were removed and handled in the dry box.

C. The Thermal Decomposition of Hexamminemetal-(III) Borohydrides of Cobalt and Chromium and of Ammonium Borohydride.—Decomposition was effected by gradually heating the complex in the evacuated reactor tube (Fig. 1). Exit gases were passed through a trap cooled with liquid nitrogen to remove condensable products. H_2 in gases was identified by molecular weight; ammonia by molecular weight and vapor pressure.

After essentially complete gas removal, liquid ammonia was condensed into the reactor and mixed with the solid black residue. The ammonia soluble portion was filtered and the residue was washed with liquid ammonia.

After removal of the ammonia the residues were removed in the dry box for analysis. The colorless ammonia soluble residue contained boron and nitrogen in a ratio of 1 to 1.08. H_2 was the only other element present. The solubility of the residue in liquid ammonia and its B/N ratio suggested the material $(BNH_6)_x$. The ammonia insoluble residue consisted of 4.40 matoms H, 0.879 matom Co, 2.42 matoms N, 3.29 matoms B. Such a mixture would correspond to 0.18 mmole of CoB and 0.22 mmole of $(BNH_x)_n$. For the chromium salt, the ammonia soluble portion was stained with a trace of undecomposed $[Cr(NH_3)_6](BH_4)_3$. After correcting for this contaminant about 0.35 mmole of BNH_6 was found. B/N ratio found was 1.02. The ammonia insoluble fraction contained 0.88 matom Cr, 2.42 matoms N and 3.29 matoms B. Such a mixture would correspond to 0.88 mmole of CrB and 2.41 mmoles of $(BNH_x)_n$ where x = 0 to 4.

Ammonium borohydride gave slow hydrogen evolution at temperatures above −40°. The rate of decomposition increased rapidly with temperature. A sample heated to 180° for 2.5 hr. gave H_2 and borazene in about 15% yield. The very small scale of the reaction (0.04 mm. $B_3N_3H_6$) undoubtedly contributed to the low yield [50% reported from $B_2H_6 \cdot 2NH_3$]. The borazene was identified by molecular weight (value = 77) and vapor pressure.

D. Molecular Weight Measurements on NH_4BH_4 and its Decomposition Products.—The method used involved vapor pressure depression of liquid ammonia solutions. Apparatus and general procedure are described elsewhere.[4] Special techniques were required for ammonium borohydride since it decomposes above −40°. The sample was prepared as described earlier, except that the receiver on the filtration apparatus (Fig. 1) was replaced by the sample bulb used for molecular-weight determinations. The product was washed carefully into the bulb and the solvent ammonia was removed slowly at −45° to prevent spattering. The decomposition at this point, as measured by H_2 evolution, was less than 2%. The vacuum apparatus was filled with dry nitrogen and the chilled sample vessel was transferred rapidly to the molecular-weight apparatus. After evacuating the cold tube (−196°), known amounts of solvent ammonia were condensed on the sample and the vapor-pressure depressions were measured. Temperature was always maintained below −40°.

After making measurements on the ammonium borohydride, the solvent ammonia was removed and the sample was warmed to room temperature. The hydrogen evolved was measured. The value (2.11 mm. H_2) permitted an estimate of the amount of ammonium borohydride present. Following H_2 evolution known amounts of ammonia were condensed on the resulting BNH_6 residue, and molecular-weight measurements were made.

After completion of the molecular-weight measurements, ammonia was removed under high vacuum at room temperatures, the apparatus was filled with nitrogen, transferred to a dry box, and the sample bulb was weighed (76.0 mg. solid). Hydrolysis of the sample and subsequent Kjeldahl analysis (29.6 mg. N) indicated the amount of BNH_6 present. The value (2.11 mm.) confirmed the earlier estimate of NH_4BH_4 based on H_2 evolution. The difference in total weight based on analysis and direct weighing (6.7 mg.) was attributed to $NaBH_4$. By use of this value and the previously determined curve for the molecular weight of $NaBH_4$ in liquid ammonia, the results were corrected for the small $NaBH_4$ contamination. Values of about 34 and 63, respectively, were estimated for NH_4BH_4 and the decomposition product, $[H_3NBH_3]_x$. More detailed data are available elsewhere.[5]

Discussion

Ammonium Borohydride.—Ammonium borohydride is a white crystalline solid which decomposes at room temperature to give hydrogen and a solid of composition $[BNH_6]_x$. At 25° one sample of NH_4BH_4 was 50% decomposed in 6 hr. Such an

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[4] R. W. Parry, G. Kodama and D. R. Schultz, This Journal, **80**, 24 (1958).

[5] D. R. Schultz, Doctoral Dissertation, Univ. of Mich., Ann Arbor, Mich., 1954.

observation suggests that NH_4^+ and BH_4^- are not compatible in the same structure at room temperature.

Anal. Calcd. for NH_4BH_4: NH_3, 51.79; B, 32.91; H, 12.20. Found: NH_3, 51.6; B, 31.4; H, 9.10. Low values for hydrogen were attributed to incomplete hydrolysis in the analytical process. Identification of the solid as a borohydride was established unequivocally from the Raman spectrum of its liquid ammonia solution. The spectrum compared favorably in every detail, including the shape of the envelope and intensity of the lines, with the comparable spectrum of $NaBH_4$. Detailed consideration of the spectra of borohydrides is given elsewhere.[6] The molecular weight in liquid ammonia was about 34 as compared to a theoretical value of 32.89. The measurement has some uncertainties for this solute.

The solid of composition $(BNH_6)_x$ which results from the thermal decomposition of NH_4BH_4 appears to be the "diammoniate of diborane," since the observed molecular weight of about 63 is not in agreement with the value for the recently discovered monomer, H_3NBH_3.[7] Isolation of borazene from the thermal decomposition of the solid likewise supports the belief that the solid is the "diammoniate." Finally the Raman spectrum of a liquid ammonia solution of this solid can be interpreted[6] as supporting this conclusion.

Hexamminecobalt(III) Borohydride and Hexamminechromium(III) Borohydride.—Both ammonia soluble complexes were isolated from liquid ammonia solution as long yellow needles. Analytical data indicate the formulas $[Cr(NH_3)_6](BH_4)_3 \cdot {}^1/_2NH_3$ and $[Co(NH_3)_6](BH_4)_3 \cdot 1.0NH_3$. Attempts to remove excess ammonia resulted in darkening and some decomposition of the cobalt compound. Analysis of the cobalt complex gave: Co, 26.6; NH_3, 53.8; B, 14.2; hydridic H, 5.0. Theoretical for $[Co(NH_3)_6](BH_4) \cdot 1.0NH_3$ is: Co, 26.4; NH_3, 53.5; B, 14.6; H, 5.4. Analysis of the chromium complex gave: Cr, 25.3; NH_3, 53.3; B, 15.6; hydridic H, 5.7. Theory for $[Cr(NH_3)_6](BH_4)_3 \cdot 0.5NH_3$ is: Cr, 25.1; NH_3, 53.3; B, 15.7; hydridic H, 5.8%.

Dry hexamminecobalt(III) borohydride loses ammonia and undergoes irreversible decomposition when the ammonia pressure is reduced below 50 mm. at 25°. In contrast, the dry hexamminechromium(III) borohydride is remarkably stable at 25° even under high vacuum; the decomposition under these conditions was less than 2% as measured by hydrogen evolution. When the chromium complex was heated *in vacuo* to 60°, its decomposition became comparable to that of the cobalt complex at 25°.

Data now available indicate that the instability of the cobalt complex is to be associated with the strong reducing properties of the borohydride group and with the fact that $[Co(NH_3)_6]^{+3}$ is reduced more easily than its chromium counterpart. The reduction potential for the aqueous couple: $e^- + M(NH_3)_6^{+3} \rightarrow M(NH_3)_6^{+2}$ is about 0.1 volt for Co and more negative than about −0.5 volt forCr. Although the thermal decomposition of the borohydride is complex, the unbalanced equation which best describes the main process is

$$[M(NH_3)_6](BH_4)_3 \longrightarrow \underbrace{M_aB_{a+b}N_bH_x}_{\substack{\text{solid black mixture apparently} \\ \text{of MB and } NBH_{x/b}}} + (BH_3NH_3)_n + NH_3 + H_2$$

The hydrogen and ammonia were identified positively as gaseous decomposition products. The compound $(H_3BNH_3)_n$ was extracted from the solid residue with liquid ammonia and the empirical formula was established by analysis. During the slow decomposition of $[Cr(NH_3)_6](BH_4)_3$ two relatively large clear crystals of solid formed in the cold trap through which gases were removed. Although these crystals were not identified at the time, more recent experience with the new crystalline compound H_3NBH_3 suggests that the crystals were probably this monomeric species. The bulk of the material of composition $(H_3NBH_3)_n$ remained in the reaction vessel, however, and was apparently the "diammoniate of diborane." The over-all composition of the ammonia insoluble, solid black residue suggested a mixture of metal boride and polymeric BNH_x, where x ranged from 0 to 4. Unequivocal identification of separate phases in this solid never was achieved.

The Reaction between Water and the Hexammine Metal(III) Borohydrides of Chromium and Cobalt.—The hexamminecobalt(III) borohydride dissolved in water to give a yellow solution which decomposed rapidly. A black ferromagnetic precipitate was obtained which gave cobalt(II) ion when acidified. The same black solid also was observed when sodium borohydride was added to a hexamminecobalt(III) chloride solution. Hydrogen always was liberated. Stewart and Schaeffer[8] reported a reaction of rather similar type when BH_4^- was added to $CoBr_2$ solution.

The chromium complex borohydride reacted very slowly with water to liberate a small amount of hydrogen, but no precipitate appeared during this period. In the absence of air, the blue chromous ion was produced upon acidification. It is consistent with the above observation to note that hexamminechromium(III) chloride and sodium borohydride gave no apparent reaction in water solution except for the very slow evolution of hydrogen. Reaction ensued, however, when acid was added. Data for the over-all hydrolysis reactions of both complex borohydrides in acid solution are consistent with the equation

$$[M(NH_3)_6](BH_4)_3 + 5H_3O^+ + H_2O \longrightarrow M^{+2} + 3BO_2^- + 6NH_4^+ + 11.5H_2$$

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ANN ARBOR, MICH.

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[6] R. C. Taylor, D. R. Schultz and A. R. Emery, THIS JOURNAL, **80**, 27 (1958).

[7] S. G. Shore and R. W. Parry, *ibid.*, **77**, 6084 (1955).

[8] A. C. Stewart and G. W. Schaeffer, *J. Inorg. Nuclear Chem.*, **3**, 194 (1956).