

to the third and fourth coordination positions is from 10^5 (for chloride) to 10^{14} (for cyanide) weaker than to the first two. It should be noted also that the ratio of the association constant of methylmercury to that of hydrogen for EDTA is much less

than this ratio for other metals, except the alkali metals and alkaline earths. Therefore EDTA is useful as a complexing agent to remove interfering metals in studies of mercury-sulfhydryl association.

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A Cryoscopic Study of the Diammoniate of Diborane in Liquid Ammonia¹

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Molecular weight studies on the diammoniate of diborane, $[\text{H}_2\text{B}(\text{NH}_3)_2][\text{BH}_4]$, in liquid ammonia, using a freezing point depression technique to a precision of $\pm 0.005^\circ$ indicate that the system is well behaved. Observed concentration dependence is characteristic of a salt. Anomalous concentration dependence observed in previous investigations, using vapor pressure depression methods was not observed. No evidence was found for the existence of a higher molecular weight substance such as $[\text{HB}(\text{NH}_3)_3][\text{BH}_4]$, which has been previously postulated to form in solutions allowed to age at -45° or higher for extended periods of time. Comparison of the results of this investigation with that of Rathjens and Pitzer indicates that the initial reaction of diborane with ammonia may lead to non-dissociated two boron atom species.

Introduction

Although the structural formula of the diammoniate of diborane seems to be well established as $[\text{H}_2\text{B}(\text{NH}_3)_2][\text{BH}_4]$ through both physical and chemical studies,² there exist some unsolved problems with respect to its nature in liquid ammonia. From reactions with sodium in liquid ammonia and molecular weight studies in liquid ammonia, determined through vapor pressure depression techniques, it would seem as though another species of higher apparent molecular weight is formed upon prolonged standing of the solution at temperatures of -45° or higher. One of the structures proposed for the "high temperature form" is $[\text{BH}(\text{NH}_3)_3][\text{BH}_4]$. This structure previously has been referred to as "diammoniate II."^{3,4} However, later studies by Parry and Kodama⁵ and Parry and Shore⁶ raise some serious questions with respect to the existence of the "diammoniate II." Furthermore, careful examination of the existing molecular weight data presents some problems in rationalization. First, the molecular weight seems to rise with increasing dilution, even at concentrations where solvation effects would not seriously affect the observed apparent molecular weight. Secondly, the data seem to distinguish between high and low molecular weight species, yet the data were obtained over extended periods of time, at temperatures presumed to be conducive to the formation of the higher molecular weight material. There was no evidence that a specific sample of specific concentration, which had a low apparent molecular weight initially, was converted under the conditions of the study to the higher molecular weight form.

Because of the uncertainty in molecular weight studies, it seemed desirable to examine again the apparent molecular weight of the diammoniate of diborane in liquid ammonia. A freezing point technique was used in which freezing point depressions could be determined to a precision of about $\pm 0.005^\circ$. Measurements were made more rapidly and at lower temperatures than in the vapor pressure depression method. It was possible to determine the apparent molecular weight of a sample of "authentic" diammoniate of a given concentration which had not been above -78° and then observe whether storing the solution at -45° for an extended period of time had an effect on the apparent molecular weight. Also, through the use of X-ray powder diffraction techniques, it was possible to determine, at room temperature, whether solids isolated from solutions stored at -45° or higher differed in crystalline nature from solids isolated from solutions stored at -78° .

Experimental

A. Materials.—1. Diborane was prepared and purified according to well known methods.⁷ 2. Ammonia was dried over sodium and then distilled into a weighing bulb containing anhydrous lithium nitrate which had previously been heated to 160° and pumped on for a period of one week. The saturated solution of lithium nitrate in ammonia had a vapor pressure of less than one atmosphere at room temperature. Thus, a desired amount of ammonia, of the order of several grams, could be distilled from the bulb which had been weighed at room temperature. 3. Diammoniate of diborane was prepared according to a set of carefully prescribed conditions.⁸

B. Apparatus.—1. Standard high vacuum techniques were used for handling materials. 2. A freezing point cell⁷ was used in conjunction with a Mueller Type G-2 Temperature Bridge and a calibrated four lead, capsule platinum resistance thermometer. The resistance could be read directly to 0.0001 ohm. On the particular thermometer used, this corresponded to about 0.001° .

C. Experimental Procedure.—About 10 g. of ammonia, weight known to ± 0.5 mg., was condensed into the freezing point cell. The ammonia was warmed to a temperature

(1) Presented before the Inorganic Division at the 139th Meeting of the American Chemical Society, St. Louis, Missouri, March, 1961.

(2) R. W. Parry, P. R. Girardot, D. R. Schultz and S. G. Shore, *J. Am. Chem. Soc.*, **80**, 1 (1958); R. C. Taylor, D. R. Schultz and A. R. Emery, *ibid.*, **80**, 27 (1958); T. P. Onak and I. Shapiro, *J. Chem. Phys.*, **32**, 952 (1960).

(3) R. W. Parry and S. G. Shore, *J. Am. Chem. Soc.*, **80**, 15 (1958).

(4) R. W. Parry, G. Kodama and D. R. Schultz, *ibid.*, **80**, 24 (1958).

(5) R. W. Parry, G. Kodama and S. G. Shore, WADC Technical Report 59-207.

(6) I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik and G. B. L. Smith, *J. Am. Chem. Soc.*, **74**, 901 (1952).

(7) Details of the construction of this cell can be obtained from S. G. Shore, Department of Chemistry, The Ohio State University, Columbus 10, Ohio.

TABLE I
RESULTS OF FREEZING POINT DEPRESSION MEASUREMENTS ON $[\text{BH}_2(\text{NH}_2)_2][\text{BH}_4]$ IN NH_3

Concentration (molal)	Treatment of solution		Temp. ($^{\circ}\text{C}.$)	ΔT^a ($^{\circ}\text{C}.$)	Apparent K_f (deg./mole/kg.)		Apparent molecular weight, M	
	Time at given temp. (hr.)	Total time (hr.)						
0.0503	22.0	65.5	-78	0.067	1.3		44	
	28.0		-45	.068	1.4	1.4 av.	43	42 av.
	15.5		-78	.077	1.5		39	
.0933	6.0	91.5	-78	.112	1.20		49.2	
	34.0		-45	.108	1.15	1.19 av.	51.3	49.5 av.
	51.5		-78	.115	1.23		48.0	
.1740	0.0	212	-78	.207	1.19		49.6	
	43.0		-78	.200	1.15		51.3	
	30.0		-45	.205	1.18	1.17 av.	50.0	50.4 av.
	49.5		-45	.202	1.16		50.8	
	89.5		-78	.203	1.17		50.5	
.3011	6.0	108	-78	.353	1.17		50.5	
	67.0		-45	.363	1.21	1.20 av.	48.8	49.2 av.
	35.0		-78	.368	1.22		48.4	
.5061	2.5	113	-78	.592	1.17		50.5	
	41.5		-45	.582	1.15	1.16 av.	51.3	50.8 av.
	69.0		-78	.593	1.17		50.5	

^a Value obtained from at least three cooling curves per treatment.

several degrees above its freezing point, and cooling was initiated by placing around the cell, a close fitting, partially evacuated Dewar flask which was immersed in a cryostat containing a methylene chloride slush (-97°). A cooling curve of resistance *versus* time was plotted at approximately one minute intervals. A minimum of three separate cooling curves was used to establish an average freezing point. In general, a freezing point from an individual curve could be estimated with a precision of $\pm 0.002^{\circ}$. The maximum deviation from the average of the separate cooling curves, of either pure ammonia or solution, was of the order of $\pm 0.003^{\circ}$. The freezing point depression was determined to a precision of about $\pm 0.005^{\circ}$.

After the freezing point of a given sample of ammonia had been determined, it was distilled from the cell. A known quantity of diammoniate was then prepared in the cell and was isolated as the dry solid through sublimation of excess ammonia at -78° . In general, a dry sample was not permitted to warm up more than a few degrees above -78° before the molecular weight study was initiated. The sample of ammonia whose weight and freezing point had previously been determined was condensed into the cell and the effect upon the freezing point of storing the solution of diammoniate at -78 and -45° for extended periods of time was studied.

Checks for the appearance of noncondensable gas at various stages of the study, especially after allowing a solution to stand at -45° , indicated at most a minute extent of decomposition.

Results

The principal results of this investigation are given in Table I. Observations were made on solutions of five separate samples of what might be termed "authentic" diammoniate, considering the nature of synthesis.³ The time listed opposite each concentration represents the period for which the solution was aged at a specified temperature before an average freezing point depression was determined.

For the purpose of discussion, it is convenient to represent the results in terms of an apparent cryoscopic or molecular depression constant, K_f (apparent), and an apparent molecular weight, M . These quantities were calculated from the equations

$$K_f \text{ (apparent)} = \Delta T/m$$

$$M = K_f \text{ (theory)} 1000 W_2/\Delta T W_1$$

where

ΔT = the freezing point depression from pure ammonia
 m = the molality (number of formula weights of $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3/1000 \text{ g. NH}_3$)

K_f (theory) = theoretical cryoscopic constant for non-dissociated species, based upon the heat of fusion and freezing point of ammonia⁸

W_1 = grams of solvent
 W_2 = grams of solute

Discussion

A. Behavior of the Diammoniate.—From the data in Table I, it is seen that storing solutions of carefully prepared diammoniate in ammonia at -45° for extended periods of time has relatively little effect upon its apparent molecular weight. The solutions seemed to be well behaved, not only with respect to constancy of molecular weight for a given concentration, but also with respect to the concentration dependence of the molecular weight.

Figure 1 depicts the change in molecular weight as a function of concentration. From this investigation it is seen that the molecular weight decreases markedly at high dilutions. Such behavior is normal for an electrolyte. It indicates an increase in apparent ionization or dissociation, with increasing dilution. The salts NH_4NO_3 , NaNO_3 and KI display a similar concentration dependence and similar magnitudes of apparent ionization in liquid ammonia, using the freezing point depression method.⁹

No simple explanation can be provided for the observations of Stock and Pohland¹⁰ and Parry, Kodama and Schultz⁴ who used the vapor pressure depression method. Nevertheless, an increase in apparent molecular weight of a salt at high dilutions

(8) R. Overstreet and W. F. Giauque, *J. Am. Chem. Soc.*, **59**, 254 (1937).

(9) L. D. Elliott, *J. Phys. Chem.*, **28**, 611 (1924).

(10) A. Stock and E. Pohland, *Ber.*, **58**, 657 (1925).

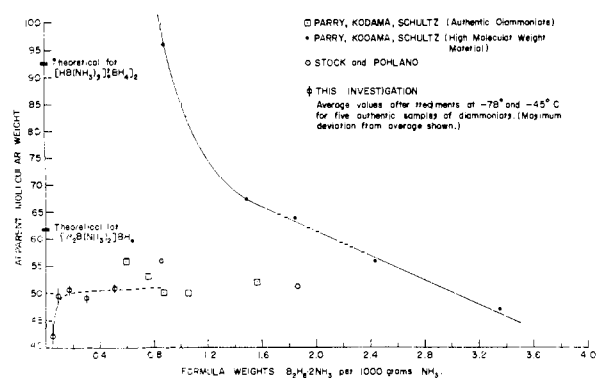


Fig. 1.—Comparison of apparent molecular weights.

has been observed by other investigators¹¹ who studied the boiling point elevation of ammonia solutions of NaNO_3 and KI . It is of interest to note, therefore, that some salts can show anomalous colligative character when studied by a vapor pressure depression method but appear to be normal when studied by a freezing point depression technique. It would seem then, that in liquid ammonia cryoscopic methods offer a distinct advantage over vapor pressure depression methods for the characterization of substances.

B. Lack of Evidence for High Molecular Weight Species.—The evidence of Parry, Kodama and Schultz⁴ that the diammoniate can be converted to a material of higher apparent molecular weight is given in Fig. 1. Their sample which produced this curve was prepared in the usual fashion³ but was isolated as a dry solid by sublimation of excess ammonia at -45° , rather than the usual -78° . From this solid, ammonia solutions were prepared for the investigation. When samples used in this study were treated in the same manner, abnormally high molecular weights were *not* observed. For given concentrations, values consistent with those given in Table I were obtained. The apparent molecular weights of these specially treated samples did not exceed 49.5.

It was noted, however, that solid samples could be protolyzed by ammonia to give off hydrogen at temperatures above -45° . Solutions of the protolyzed solids were made up and found to have significantly higher molecular weights than the samples had originally. Undoubtedly these solutions contained some polymeric H_2NBH_2 . No detailed effort was made to correlate the increase in molecular weight with extent of protolysis, but perhaps Parry, Kodama and Schultz's observations can in part be attributed to protolysis of their solid samples by excess ammonia.

In this investigation, the observed constancy of the molecular weight for a given concentration indicates that the diammoniate is not converted to another material under the conditions of treatment. However, for the sake of argument, it could be pointed out that conversion might occur at -45° to produce a material which coincidentally yields the same number of solute particles at a given concentration. In fact, it might even be argued that the postulated structure $[\text{HB}(\text{NH}_3)_3][\text{BH}_4]_2$ ^{3,4}

(11) E. C. Franklin and C. A. Kraus, *Am. Chem. J.*, **20**, 836 (1898).

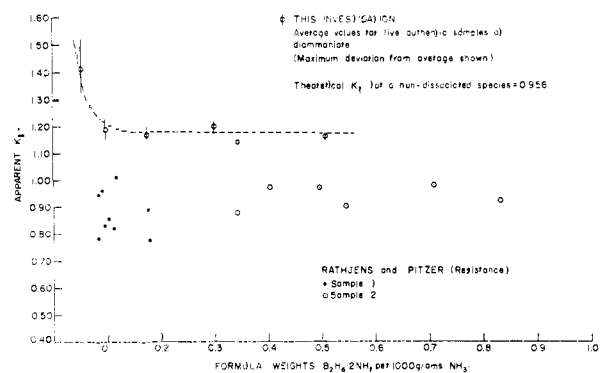


Fig. 2.—Comparison of apparent cryoscopic constants.

is formed and through partial apparent ionization yields a similar apparent molecular weight. If such a new material were formed and were crystalline, it could be detected through X-ray powder diffraction patterns.

The X-ray powder diffraction pattern produced at room temperature by freshly prepared diammoniate, from which ammonia had been sublimed at -78° , was compared with room temperature patterns of samples which had been handled under the various conditions of this investigation, including removal of ammonia at -45° and -78° . The patterns were essentially identical. No new crystalline material was found. The "*d*" values obtained were substantially identical and in good agreement with data reported by Parry and Shore.⁵

On the basis of the molecular weight and X-ray studies of this investigation, it is concluded that the diammoniate of diborane in liquid ammonia is a stable material in the temperature range -45° to -78° . There is no evidence for the existence of $[\text{HB}(\text{NH}_3)_3][\text{BH}_4]_2$.

C. Comparison of Apparent Cryoscopic Constants with the Data of Rathjens and Pitzer.—Using a calorimetric technique, Rathjens and Pitzer¹² measured freezing point depressions in the diborane-ammonia system. Apparent cryoscopic constants were calculated from their data and are compared in Fig. 2 with the results of this investigation. The precision with which their measurements were made was not as favorable as in this work. The interesting point, however, is that their values are consistently lower than those obtained in this study. The higher values of this study are comparable to those obtained from univalent salts in liquid ammonia⁹ and are, therefore, consistent with the formula $[\text{H}_2\text{B}(\text{NH}_3)_2][\text{BH}_4]$. On the other hand, Rathjens and Pitzer's¹² values are indicative of non-dissociated species in liquid ammonia. Elliott⁹ reports an average cryoscopic constant of $0.97^\circ/\text{mole kg}$. The theoretical value is $0.956^\circ/\text{mole kg}$. Applying these considerations, it is concluded that the measurements of Rathjens and Pitzer were not made on a system containing appreciable quantities of the diammoniate but rather on a system containing molecular species.

(12) G. W. Rathjens, Jr., and K. S. Pitzer, *J. Am. Chem. Soc.*, **71**, 2783 (1949).

The method used by Rathjens and Pitzer did not involve the isolation of diammoniate at any stage. Diborane was distilled into a calorimeter containing solid ammonia. Successive portions of ammonia were melted by supplying electrical energy. The process of melting the ammonia was a slow, controlled one, requiring a good many hours.¹³ Under such conditions, it is conceivable that diborane was not converted to the diammoniate but that an intermediate species was formed.

The technique used in this investigation does not provide the control of melting that was available to Rathjens and Pitzer in their calorimeter; it required a relatively harsh treatment of the solutions involving warming to several degrees above their melting points and the use of vigorous stirring. As a result, intermediate molecular species could not be detected in freshly prepared solutions. The apparent cryoscopic constants obtained for such solutions were never below 1.17, indicating essentially complete conversion of diborane to the diammoniate. Nevertheless, it has been recognized that under sufficiently mild conditions of addition of diborane to ammonia, complete conversion to the diammoniate does not necessarily

(13) K. S. Pitzer, private communication.

take place.^{3,14,15} Comparison of the results of this investigation with those of Rathjens and Pitzer provides additional support to this interpretation of the chemical observations.

The nature of the intermediate material in solution is unknown, except that it would be a non-dissociated two boron atom molecule. It might be molecular diborane in ammonia or perhaps a single hydrogen bridge structure $H_2B-H-BH_3$



as suggested by Parry and Shore.³ This structure seems to be particularly attractive since Brown and co-workers¹⁶ have been able to provide evidence for the existence of $H_2B-H-BH_3$ and other analogous materials.



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(14) G. W. Schaeffer, M. D. Adams and F. J. Koenig, *J. Am. Chem. Soc.*, **78**, 725 (1956).

(15) A. B. Burg and G. W. Campbell, Jr., *ibid.*, **74**, 3744 (1952).

(16) H. C. Brown, P. F. Stehle and P. A. Tierney, *ibid.*, **79**, 2020 (1957).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MANCHESTER, MANCHESTER, U. K.]

The γ -Radiolysis of Methanol and Methanol Solutions

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Product yields from γ -irradiated neutral methanol agree with those obtained by Meshitsuka and Burton. It is suggested that trace impurities which scavenge a reactive precursor to hydrogen are responsible for the lower yields which have been reported. The variation of yields with temperature, acid and various solutes has been investigated. The presence of two precursors to hydrogen is indicated by the results and a reasonable interpretation is obtained by assuming that one is the H atom and the other an electron.

The major products from the γ -radiolysis of liquid methanol are hydrogen, formaldehyde, ethylene glycol and small amounts of methane and carbon monoxide. There is still a considerable lack of agreement among the various investigators¹⁻⁴ on the 100 e.v. yields (G) of these products. Values of $G(H_2)$ have been reported from 4.0 to 5.4, $G(CH_2O)$ from 1.3 to 2.2, $G(\text{glycol})$ from 2.9 to 3.6 and $G(CH_4)$ from 0.2 to 1.2. It seems probable that, as in the radiation chemistry of water, trace amounts of impurities can affect the yields by acting as radical and atom scavengers.

In extending earlier work³ we have observed a slight increase in $G(H_2)$ with increasing time of irradiation, which continued on prolonged irradiation but ultimately reached a constant value. Since none of the products affect $G(H_2)$, we were led to suspect the presence of impurities which were consumed during irradiation. We have therefore investigated the purification procedure and in the

(1) G. Meshitsuka and M. Burton, *Radiation Research*, **8**, 285 (1958).

(2) W. R. McDonnell and S. Gordon, *J. Chem. Phys.*, **23**, 208 (1955).

(3) G. E. Adams and J. H. Baxendale, *J. Am. Chem. Soc.*, **80**, 4125 (1958).

(4) N. N. Lichtin, *J. Phys. Chem.*, **63**, 1449 (1959).

light of this repeated and extended the earlier work.

Experimental

Materials.—The purification of methanol is described subsequently. Ferric chloride hexahydrate, 2,4-dinitrophenylhydrazine, hydrochloric, periodic and sulfuric acids, benzene, naphthalene and anthracene were of analytical reagent grade and were used without further purification. Benzoquinone was subjected to two sublimations from room temperature to liquid nitrogen. Biphenyl was recrystallized from methanol. Chromotropic acid was a specially purified grade for formaldehyde determination. A 30% solution of methyl borate was obtained by refluxing boric anhydride with methanol and collecting the middle cut of the azeotropic mixture.

Irradiations.—These were done on 50 or 25 cc. samples contained in 4 cm. diameter tubes fitted with a stopcock attached by a cone and socket. Deaeration was accomplished by short periods of pumping at room temperature after equilibrating gas and liquid with a vibro-shaker. Two Co^{60} sources were used, giving maximum dose rates in the vessels of 2×10^{15} and 3×10^{16} e.v. cc.⁻¹ min.⁻¹. Doses were calculated from calibrations using the ferrous sulfate dosimeter assuming the energies absorbed proportional to the liquid densities and $G(Fe^{3+}) = 15.6$.

Analyses.—Hydrogen and carbon monoxide were measured by first equilibrating the irradiated liquid with the gas phase and then expanding the gas from the vessel cooled in Dry Ice through a liquid nitrogen trap into the sample bulb of a mass spectrometer, thus eliminating the collection procedure used previously.³ This technique gave lower meth-