sistency of the results, it is believed that the accuracy of the thermal conductivity technique was well within 3% D in the range 50–100% D.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

Molecular Weight Measurements in Liquid Ammonia. The Molecular Weights of the Methylamine–Boranes, the "Diammoniate of Diborane," Ammonia–Boron Trifluoride and other Substances

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Molecular-weight measurements in liquid ammonia by vapor-pressure depression show that H_3NBF_3, MeH_2NBH_3, Me_2HNBH_3 and Me_3NBH_3 are all monomeric in liquid ammonia under conditions comparable to those used for studying the "diammoniate of diborane" prepared at −78.5°, but a higher value above 80 is indicated for the diammoniate prepared at −45°. The conversion of H_3NBF_3 to NH_4BF_4 in water solution is noted.

The original problem associated with the formulation of the ammonia–diborane addition compound arose from the early observation of Stock and Pohland[1] showing that the product corresponded to the formula $B_2H_6{\cdot}2NH_3$ in liquid ammonia. Rathjens and Pitzer[2] reported that freezing-point depression measurements confirmed the conclusions of Stock and Pohland[1]; however, recent work[3] has shown that the technique which Rathjens and Pitzer used does not produce the so-called classical "diammoniate" in liquid ammonia.

Although the "diammoniate of diborane" has long been considered to be unique among the boron hydride addition compounds, no molecular-weight measurements on H_2MeNBH_3, HMe_2NBH_3, Me_3NBH_3 or H_3NBF_3 have been carried out under conditions comparable to those used in the study of the diammoniate, hence the generality of the "diammoniate" structure under low-temperature conditions remains undetermined.

A study of molecular weights in liquid ammonia was undertaken: 1, to check the validity of Stock's observations as to the molecular weight of an authentic sample of the "diammoniate"; 2, to check the molecular weights of other better-known ionic solids in liquid ammonia in order to provide a frame of reference for interpretation; and 3, to check the molecular weights in liquid ammonia of methylamine–borane, dimethylamine–borane, trimethylamine–borane and ammonia–boron trifluoride.

These compounds had not been measured under conditions comparable to those used in studying the "diammoniate," hence a real question existed as to their nature in relation to the "diammoniate."

Experimental

A. **Materials.**—Commercial amines (Eastman Kodak Co.) were distilled through a low-temperature fractionating column at 400 mm. pressure and dried over sodium metal before use.

Commercial $NaBH_4$ (Metal Hydrides) was placed on the sintered glass frit of a vacuum-line extraction apparatus and extracted directly into the molecular-weight apparatus with liquid ammonia.

NH_4Br, reagent grade, was dried at 80° for 3 hr. then stored over $Mg(ClO_4)_2$ before use.

Ammonia–boron trifluoride was prepared by the interaction of dry NH_3 and commercial tank BF_3 which had been passed through a B_2O_3–H_2SO_4 mixture. A one-liter, three-necked flask cooled in ice-water served as the reaction vessel. The solid product was placed on a sintered glass frit and leached into the molecular-weight vessel with liquid ammonia. Ammonia analysis of the product gave 20.01% as compared to 20.05% theoretical for H_3NBF_3. An X-ray powder pattern of the solid checked the pattern reported by Keenan and McDowell,[4] by Koenig[5] and by Jenkins,[6] but not the pattern reported by Laubengayer and Condike.[7] It was also found that H_3NBF_3 was converted to NH_4BF_4 under conditions of this experiment by slow crystallization from water at room temperature. Isolation of crystalline NH_4BF_4 from the solution and precipitation of $As(C_6H_5)_4BF_4$ from the water solution indicated the change.

An X-ray powder pattern of H_3NBF_3 taken before and after the molecular-weight measurement in liquid ammonia showed that the sample had not changed on standing in liquid ammonia at −40°. No lines for NH_4BF_4 were found in the product. The observation confirms a similar report by Jenkins.[6]

The "diammoniate of diborane" was prepared in accordance with standard procedures described elsewhere.[3] The trimethylamine–borane was prepared by Dr. T. C. Bissot from diborane and trimethylamine, using standard procedures. Its observed melting point of 93° (lit., 94°) and the analytical hydridic H/B ratio of 3.03/1.00 establish its identity.

Dimethylamine–borane was prepared by condensing diborane and excess dimethylamine in a reactor at −160°. The system was allowed to warm up very slowly. At 0° excess amine was removed. The ratio of amine used in reaction to diborane consumed was 1.95/1.

Monomethylamine–borane was prepared from pure methylamine and diborane according to standard procedures. Although no analyses were run to confirm the identity of this material, it was noticed that when a small sample was warmed from ice temperature to room temperature, it melted just above ice temperature evolving a gas. The reported melting point of the compound is 5–10°.[8]

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[1] A. Stock and E. Pohland, *Ber.*, **58**, 657 (1925).

[2] G. W. Rathjens, Jr., and K. S. Pitzer, THIS JOURNAL, **71**, 2783 (1949).

[3] R. W. Parry and S. G. Shore, *ibid.*, **80**, 15 (1958).

[4] C. W. Keenan and W. J. McDowell, *ibid.*, **75**, 6348 (1953).

[5] Rev. F. J. Koenig, S.J., Summary Report XVI, Mathieson Chemical Corp. Project, Subcontract M-3181-14, Dept. of Chem., St. Louis Univ., St. Louis, Mo.

[6] W. A. Jenkins, THIS JOURNAL, **78**, 5500 (1956).

[7] A. W. Laubengayer and G. F. Condike, *ibid.*, **70**, 2275 (1948).

[8] E. Wiberg, *Naturwissenschaften*, **35**, 182 (1948).

B. Apparatus and Experimental Procedure.—Details of apparatus design were extremely important since very small temperature differences throughout the system caused serious vapor-pressure differences. Two-10 mm. tubes about 12 inches long were sealed to inside 14/35 ₸ joints and fastened to a high vacuum system designed such that pressure differences in the two tubes could be read across a differential manometer. The tubes, one of which contained pure solvent and one of which contained solution, were immersed in a rapidly stirred ethyl alcohol bath. The ethyl alcohol bath was immersed in a slush bath of dichloroethylene, contained in a one gallon dewar flask. The tops of all baths were closed by covers and by at least 2 inches of Styrofoam insulation. The Styrofoam was covered inside and out with aluminum foil. Solution and solvent inside the sample tubes were stirred by pulsating stirrers which were actuated by a pulsating electromagnet above the system. A diagram of the apparatus is available.[9]

The system could be effectively tested for temperature differences by putting solvent in both tubes. No pressure differential could be detected on the manometer when the system was operating properly. The stirrer could be removed from one of the dried tubes, then the tube capped and weighed. It could then be attached directly to a vacuum-line extractor, and moisture or air-sensitive solutes could be extracted directly into the tube with liquid ammonia. After ammonia was removed, the tube was filled with dry nitrogen, capped and reweighed. The dry stirrer was then inserted and the tube was sealed to the molecular-weight apparatus, using Apiezon W wax on the 14/35 ₸ joint. Ammonia was added from a flask containing a solution of lithium nitrate in ammonia. By weighing the lithium nitrate flask before and after addition of ammonia, the weight of solvent added to the system could be accurately determined. Pressure differences were read using a precision cathetometer. Stopcocks were lubricated with silicone grease.

C. Calibration of Apparatus.—To check the reliability of the procedure on a well-behaved solute, the molecular weight of urea was determined. Values obtained by three different observers using various modifications of the apparatus are recorded in Table I.

TABLE I

MOLECULAR WEIGHTS OF UREA

Observer	Molal concn. of soln.	Obsd. mol. wt.
A	0.267	60.8 ± 0.3
B	.202	60.0 ± .3
	.382	60.2 ± .3
C	.20	60 ± 1[a]
	.30	60 ± 1
	.60	60 ± 1
	1.2	62 ± 1
	1.6	64 ± 1

[a] These values agree well with the values for urea recalculated from the early boiling point observations of E. C. Franklin and C. A. Kraus, *Am. Chem. J.*, **20**, 836 (1898). The results of observers A and B were obtained after considerable refinement of techniques.

Results and Discussion

a. The Molecular Weights of Well-known Ionic Solids in Liquid Ammonia.—Molecular-weight determinations on NH_4Br, NH_4BF_4 and $NaBH_4$ were made. Results are presented in Table II. In the concentration range studied NH_4Br and $NaBH_4$ exist in ammonia solution as almost non-dissociated ion pairs. The data indicate that NH_4BF_4 was undergoing some dissociation in the more dilute solutions. Data on potassium iodide were somewhat erratic and showed an increase in molecular weight with dilution. The results of a number of measurements could be extrapolated to give a value of about 166 at zero concentration, but the precision of measurements in the potassium iodide study was in general low. Further study is needed for this solute.

TABLE II

MOLECULAR WEIGHTS OF NH_4Br, NH_4BF_4 AND $NaBH_4$ IN LIQUID AMMONIA

Salt	Molal concn. of soln.	Obsd. mol. wt.	
$NaBH_4$, theor. mol. wt. = 37.8	1.90	28.6	
	1.04	33.9	
	0.71	35.2	
	.56	35.4	
	.45	33.0	
	.41	34.7	
NH_4Br, theor. mol. wt. = 97.9	1.52	97.5	
	0.75	98.0	
	.50	98.0	
	.30	98.5	
NH_4BF_4, theor. mol. wt. = 104.8	1.58	92.0	
	0.80	96.0	
	.52	93.0	
	.30	85.0	dissociation
	.20	75.0	

b. The Molecular Weight of Ammonia Boron Trifluoride in Liquid Ammonia.—The only previous molecular-weight measurements on NH_3BF_3 were made in water solution.[6] Since at least under some conditions H_3NBF_3 may undergo conversion to NH_4BF_4 in water solution, additional molecular-weight data seemed desirable. The possible existence of a species in liquid ammonia, $[F_2B(NH_3)_2]BF_4$, analogous to $B_2H_6 \cdot 2NH_3$, seemed to be worthy of investigation at low temperatures. Data for liquid ammonia solutions are summarized in Fig. 1.

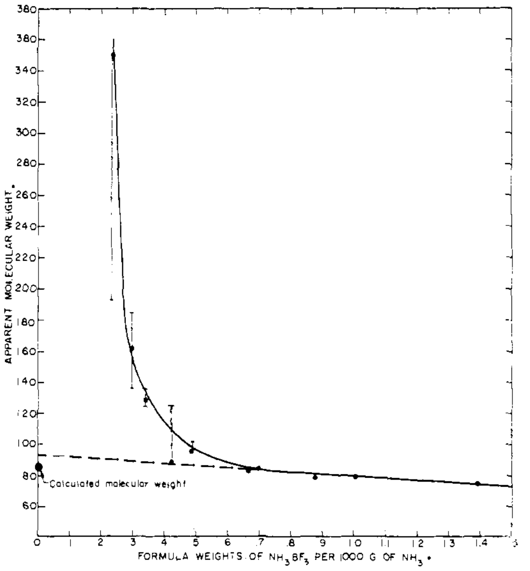

Fig. 1.—Determination of the molecular weight of NH_3BF_3 in liquid ammonia.

It was found that solutions with a molal concentration above 0.65 reached equilibrium in less than 0.5 hr. and held constant within ±2 molecular-weight units for at least 4 hr.; longer observations were not made. A linear extrapolation of these points to zero concentration gives a molecular weight of 93 as opposed to a theoretical value of 85 expected

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(9) R. W. Parry, *et al.*, "Chemistry of Boron Hydrides and Related Hydrides," WADC Tech. Report 56-318, 1956, p. 85.

for the monomer. These data indicate that H_3NBF_3 is indeed monomeric in liquid ammonia solution and a structure comparable to $B_2H_6 \cdot 2NH_3$ is eliminated. An unexplained characteristic of the measurement is clearly revealed, however, by the available data. For solutions in the concentration range 0.30 to 0.56, values were well above the extrapolated curve; the system was slow (2–9 hr.) in reaching equilibrium and an uncertainty of about ±5 molecular-weight units was observed. Both the uncertainty and time required to reach a steady state increased with dilution. In solutions more dilute than 0.3 molal, results were completely erratic; in the most dilute solutions no equilibrium value was apparent after more than 9 hr. The results were similar to those observed with KI in dilute solution. Although the exact cause of this behavior is unknown, it apparently is associated with the solute and not with the apparatus proper. Table I shows that a well-behaved solute such as urea gives consistent and reproducible values in the concentration range 0.2 to 0.4 molal; hence, systematic errors due to pressure measurement, etc., are not the primary cause of such behavior.

c. The Molecular Weights of the Methylamine–Boranes in Liquid Ammonia.—The variation of apparent molecular weight with concentration for the three methylamine–boranes is shown in Fig. 2.

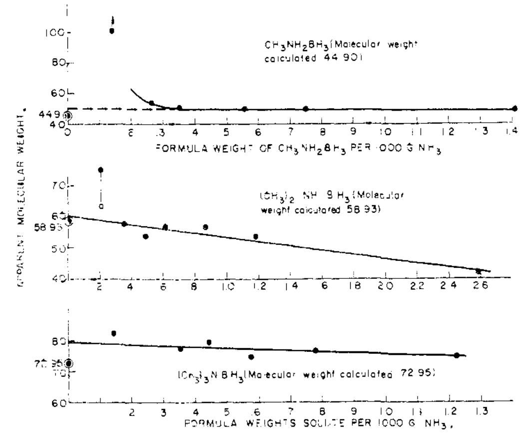
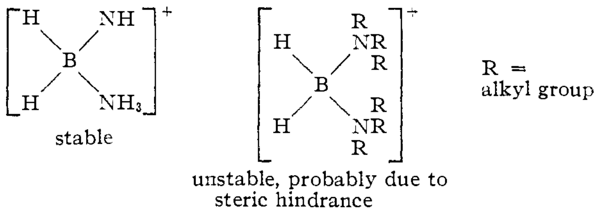


Fig. 2.—Molecular weights of the methylamine–boranes in liquid ammonia.

Again, if uncertainties of dilute solutions are neglected, an extrapolation of the data to zero concentration gives 51 for $CH_3NH_2BH_3$ as opposed to a value of 45 expected for the monomer, a value of about 61 for $(CH_3)_2NHBH_3$ as opposed to a value of 59 expected for the monomer and a value of 79 for $(CH_3)_3NBH_3$ as opposed to a value of 73 expected for the monomer. The data offer convincing proof that the methylamine adducts of diborane, prepared and measured under conditions comparable to those used in studying the "diammoniate of diborane," are not dimerized but are instead normal addition compounds of the borane group.[10]

Such observations have a precedent in the study of the metal coördination compounds. Dry cobalt(II) chloride will pick up ammonia to give the very stable compounds $CoCl_2 \cdot 2NH_3$, $CoCl_2 \cdot 4NH_3$ and $CoCl_2 \cdot 6NH_3$, yet Yoke and Parry[11] found that only one triethylamine will coördinate with dry $CoCl_2$. It would appear that the extra energy needed to expand the lattice of $CoCl_2$ in order to get more than one molecule of tertiary amine coördinated to the cobalt(II) is greater than the energy released in the coördination to the cation of the second molecule of the amine. In a similar manner it appears that the steric strains associated with the coördination of two methylamine molecules to the small boron(III) cation are greater than or comparable to the energy released in the coördination process for the second amine molecule. At the present time the data seem to be explained most easily by the concept of F-strain



d. The Molecular Weights of the "Diammoniate of Diborane" in Liquid Ammonia.—The extreme sensitivity to experimental conditions of the ammonia–diborane reaction already has been noted.[3] In Fig. 3 data are presented for molecular weights

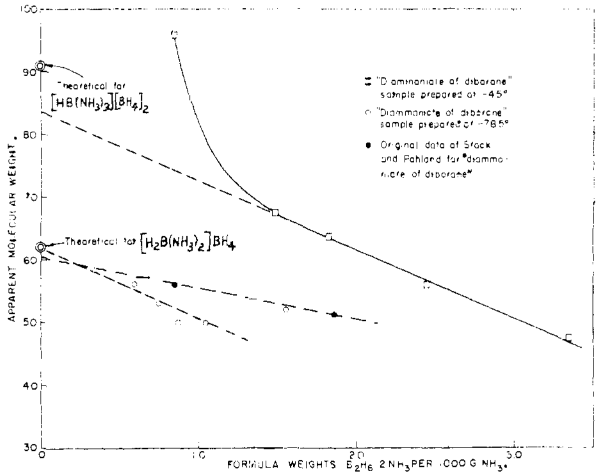
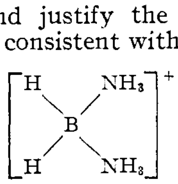


Fig. 3.—Molecular-weight measurements on the "diammoniate of diborane."

of two samples of the "diammoniate." In one case ammonia was removed at −78.5° to give the so-called classical diammoniate of Schlesinger and Burg.[12] Although the values show uncertainty characteristic of this solute, they check fairly well with the earlier measurements of Stock and Pohland[1] and justify the simple dimeric formulation and are consistent with the structure



(BH_4^-) for this species.

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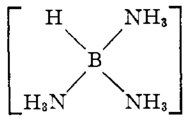
[10] These data do not preclude the possibility of forming a dimeric species $(R_2NBH_2)_2$ by other techniques.

[11] J. T. Yoke, III, and R. W. Parry, to be published.

[12] H. I. Schlesinger and A. B. Burg, This Journal, **60**, 290 (1938).

When the ammonia is removed at the higher temperature of −45°, the sodium reaction suggests that a new species is formed. The formula



has been tentatively assigned to this compound to account for the stoichiometry of hydrogen liberation.[3] Molecular-weight measurements on a sample from which ammonia was removed at −45° showed a higher value than the −78.5° product. An extrapolation of data for the −45° case shows a molecular weight of about 82 as compared to a value of 92 expected for the formula written above. Within the limits of accuracy of the evidence, the molecular-weight data support the postulates made to explain the data on the stoichiometry of the sodium reaction.

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ANN ARBOR, MICH.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Raman Spectroscopy in Liquid Ammonia Solutions. The Spectrum of the Borohydride Ion and Evidence for the Constitution of the Diammoniate of Diborane

BY R. C. TAYLOR, D. R. SCHULTZ AND A. R. EMERY

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Raman spectra of the borohydride and borodeuteride ion have been obtained in liquid ammonia solution below −35°. The results establish satisfactorily all the fundamental frequencies of these ions although precise values for two of the fundamentals cannot be given. The spectrum of the diammoniate of diborane gives strong evidence for the presence of a borohydride ion in solutions of this substance in liquid ammonia and agrees with the formulation which has been proposed in this Laboratory for the cation. Data on the decomposition product of ammonium borohydride and the product of the reaction of the diammoniate with ammonium bromide confirm conclusions based on chemical work.

Introduction

Investigators using liquid ammonia as a solvent long have been handicapped by experimental difficulties in obtaining vibrational spectra of dissolved substances. Solvent absorption presents an almost insurmountable barrier to the use of infrared methods, at least in the fundamental region, but this difficulty is minor in Raman spectroscopy. The problem in the latter case, that of removing traces of colloidal and fluorescent material, can be overcome by development of suitable experimental techniques. Very few papers have appeared on the Raman spectra of liquid ammonia solutions, and those which are available deal almost entirely with substances whose solutions have less than one atmosphere vapor pressure at room temperature.

The present paper reports the vibrational spectra of the borohydride and borodeuteride ions and, in addition, discusses the results of a spectroscopic study of the diammoniate of diborane, the decomposition product of ammonium borohydride and the product of the reaction between the diammoniate of diborane and ammonium bromide. All spectra were obtained in liquid ammonia solution at temperatures below −35°. Previous spectroscopic work on these compounds has been limited to the borohydride ion. The infrared spectrum of solid $NaBH_4$ has been published in two instances[1,2] while quite recently the position of the most intense Raman band of $NaBH_4$ dissolved in liquid ammonia has been reported.[3] The nature of the diammoniate of diborane has been controversial and the present results supply, as far as it is known, the first piece of purely physical evidence as to its structure.

Experimental

Materials.—Sodium and lithium borohydrides were obtained from Metal Hydrides, Inc., and purified by removing all ammonia insoluble material before use. Potassium borohydride was prepared by the method published recently[4a] and purified as above while lithium and potassium borodeuterides were prepared by the methods given by Schlesinger and Brown[4b] using the appropriate deuterated reagents instead of hydrogen compounds. Typical analyses are as follows: Calcd. for KBH_4: B, 20.07; H, 7.47. Found: B, 20.37; H, 7.50; H/B, 3.96. Calcd. for $LiBD_4$: B, 41.91; D, 31.21. Found: B, 41.99; D, 30.96; D/B, 3.96. Calcd. for KBD_4: B, 18.89; D, 13.90. Found: B, 18.82; D, 13.90; D/B, 3.96.

The method of preparation of the diammoniate of diborane and the other compounds studied is described elsewhere.[5] The ammonia used was the standard Matheson product dried over metallic sodium before use.

Preparation of Samples.—The volumes of the samples examined varied from about 1 to 12 ml. and the concentrations from about 1 to 5 molar depending on the amount of substance available. No significant effects of concentration on band shapes or positions were noted. Samples were prepared by dissolving weighed amounts of solute in liquid ammonia, adjusting to the desired volume and filtering the solution directly into the Raman tube through an ultrafine bacteriological-type sintered glass filter disc. Those samples suspected of being contaminated by traces of stopcock grease, which fluoresced badly, were allowed to flow through a two cm. column of Norite prior to the ultrafine filter. The system was completely closed to the air during all operations and was opened only for a second at the end when the Raman tube was removed and capped. The design of the apparatus was such that negligible amounts of sample were lost by mechanical hold-up in transfer operations and the solution could at all times be maintained

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[1] W. C. Price, *J. Chem. Phys.*, **17**, 1044 (1949).

[2] D. F. Hornig, *Disc. Faraday Soc.*, **9**, 120 (1950).

[3] L. A. Woodward and H. L. Roberts, *J. Chem. Soc.*, 1170 (1956).

[4] (a) M. D. Banus, R. W. Bragdon and A. A. Hinckley, THIS JOURNAL, **76**, 3848 (1954); (b) H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, *ibid.*, **75**, 199 (1953).

[5] D. R. Schultz and R. W. Parry, *ibid.*, **80**, 4 (1958).