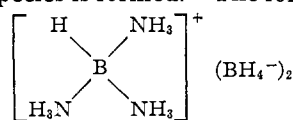


When the ammonia is removed at the higher temperature of -45° , the sodium reaction suggests that a new species is formed. The formula



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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[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

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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

(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).

TABLE I
RAMAN FREQUENCIES (IN CM.⁻¹) AND ASSIGNMENTS FOR LITHIUM, SODIUM, POTASSIUM AND AMMONIUM BOROHYDRIDES
AND FOR LITHIUM AND POTASSIUM BORODEUTERIDES DISSOLVED IN LIQUID AMMONIA

LiBH ₄	NaBH ₄	KBH ₄	NH ₃ BH ₄	LiBD ₄	KBD ₄	Assign- ment 1	Assignment 2
.....	824 ± 5	827 ± 5	ν ₁	ν ₄
1202 ± 4	1205 ± 4	1214 ± 4	1205 ± 4	854 ± 2	862 ± 10	ν ₂	ν ₂
2141 ± 5	2151 ± 5	2155 ± 5	2146 ± 5	1665 ± 2 ^a	1662 ± 2 ^a	2ν ₄	2ν ₄
.....	2239 ± 10	1695 ± 3	1692 ± 3	ν ₃	(ν ₂ + ν ₄)(for BH ₄ ⁻ only)
2260 ± 2	2264 ± 2	2269 ± 2 ^a	2264 ± 2	1566 ± 1 ^a	1568 ± 1 ^a	ν ₁	ν ₁
2394 ± 5	2402 ± 5	2404 ± 5	2400 ± 5	2ν ₂	ν ₃

^a Indicates line is strongly polarized.

below its boiling point. Suitable precautions were taken to eliminate frosting of the sample tube during transfer to the light source. Since the hydrogen in BH₄⁻ is hydridic in nature, isotopic exchange with the hydrogen of the ammonia does not occur at any detectable rate and it was possible to obtain the spectrum of the borodeuteride ion in NH₃ without difficulty.

Spectroscopic Equipment.—The Raman spectra were recorded photographically using the spectrograph and light source described previously.⁶ In general, exposure times ranged from 15 minutes to 5 hr., and several exposures were made on more than one sample of each substance. Measurements were made directly on the plates with a Mann comparator and also on enlarged tracings made with a Leeds and Northrup microphotometer. The numerical values reported represent the average of all measurements. Many of the lines were weak and rather broad and, consequently, their maxima could not be measured as precisely as desired because of the general noise level of the tracings. Figures are given for the estimated probable errors with the data.

Results and Discussion

The Borohydride Ion.—The Raman frequencies observed for lithium, sodium, potassium and ammonium borohydrides dissolved in liquid ammonia are listed in Table I, as are also the frequencies of lithium and potassium borodeuterides in the same solvent. There appears to be a small but real shift in the maxima of the bands in the different salts, which may be related to the polarizing ability of the cation. No features were observed in the spectra which suggested a specific interaction between the solute and solvent.

The following assignments are discussed in terms of a tetrahedral ion belonging to the point group T_d. This model predicts four fundamental frequencies, one totally symmetric stretching mode (a₁), one doubly degenerate bending mode (e) and two triply degenerate modes, one stretching and one bending (f₂). All fundamentals are allowed in the Raman effect, but only the f₂ fundamentals are allowed in the infrared. For purposes of the discussion, the data for the potassium salt are used; the shifts of frequencies with cation are sufficiently small so that no ambiguity results.

On the basis of its intensity and polarization properties, the a₁ mode (ν₁) can immediately be assigned to the most intense band in the Raman spectrum which occurs at 2269 cm.⁻¹ in the hydrogen case and 1568 cm.⁻¹ in the deuterium. The frequency ratio however is 1.45 instead of the harmonic value 1.41 which suggests that one of the fundamentals possibly is involved in a Fermi resonance. Examination of the polarization results shows that the band at 1662 cm.⁻¹ in the BD₄⁻ spectrum, which is nearly as intense as the 1568 cm.⁻¹ fundamental, is also strongly polarized and

consequently it is assigned as the overtone of the fundamental at 827 cm.⁻¹ resonating with the a₁ fundamental. The unperturbed value of ν₁ for BD₄⁻ on the basis of the harmonic approximation is calculated to be about 1605 cm.⁻¹.

In order to assign the band at 1214 cm.⁻¹ in the BH₄⁻ spectrum as the E mode, ν₂, it is necessary to review the infrared data, since there are two H-B-H bending frequencies to be expected in this general region. Price¹ has reported a band at 1080 cm.⁻¹ in a mull of NaBH₄, while Hornig² reports the band at 1121 cm.⁻¹ from a solid film of the same salt at liquid nitrogen temperatures. In this Laboratory, a value of 1122 cm.⁻¹ was obtained for KBH₄ by the KBr pellet technique. These data on the solid indicate that the infrared active band ν₄ lies somewhere in the neighborhood of 1100 cm.⁻¹ and that the 1205 cm.⁻¹ band consequently is most likely ν₂. Unfortunately, when liquid ammonia is used as a solvent, the region around 1100 cm.⁻¹ is completely obscured by the very strong ν₂ band of the NH₃ molecule so that the position of ν₄ in solution could not be established directly in the present work. However, the band appearing at about 2155 cm.⁻¹ can hardly be explained except as the overtone of ν₄ and its position indicates that the fundamental is probably not far from 1080 cm.⁻¹. In the spectrum of the deuterated ion, two bands were observed in the low-frequency region, one at 862 cm.⁻¹ and one at 827 cm.⁻¹. The former was quite weak but agrees with the shift expected for ν₂ and is so assigned. The latter was somewhat more intense and is assigned to ν₄.

The assignment of ν₃, the remaining f₂ fundamental of BH₄⁻, is somewhat uncertain because of the unexpected complexity of the B-H stretching region. Since this fundamental is infrared active, one might expect some help from infrared results. Price,¹ in his spectrum of solid NaBH₄, shows at least three poorly resolved bands in this region with a main maximum about 2270 cm.⁻¹. The spectrum of KBH₄ in a KBr pellet shows a moderately intense band at about 2278 cm.⁻¹, a less intense but well-resolved band at 2210 cm.⁻¹ and a shoulder at about 2340 cm.⁻¹. These bands can be assigned with a high degree of confidence to ν₃, 2ν₄ and ν₂ + ν₄, respectively. Hornig² gives a value of 2298 cm.⁻¹ with no mention of other bands. Although the shift between solid and solution is unknown, it appears that ν₃ probably lies very close to ν₁. In the Raman spectrum of the B-H stretching region (Fig. 1), at least four bands are present, including the A₁ fundamental. The band at 2155 cm.⁻¹ has already been assigned, while the band at

(6) G. L. Vidale and R. C. Taylor, *THIS JOURNAL*, **78**, 294 (1956).

2404 cm.^{-1} appears to be $2\nu_2$. The remaining band, which is present as a shoulder on the 2269 cm.^{-1} peak, is most easily explained as the ν_3 fundamental. In a spectrum of NaBH_4 taken with polarized light, the intensity of ν_1 was greatly reduced and the band in question, as near as could be determined, was depolarized with its maximum at about 2240 cm.^{-1} . Perhaps the chief objection to this assignment is the fact that in most other tetrahedral molecules, ν_3 occurs at a higher frequency than ν_1 . However, the alternative assignment (Assignment 2, Table I) implies a rather large shift between the solvent and solution for ν_3 and requires a rather large anharmonicity correction in the explanation of the 2240 cm.^{-1} band as $\nu_2 + \nu_4$.

In the borodeuteride spectrum, ν_1 is well isolated and ν_3 is assigned to the depolarized band at 1692 cm.^{-1} . The Teller-Redlich product rule ratio for the F_2 class calculated from the masses of the atoms involved is 1.77. Using the figures from Assignment 1, Table I, and an estimated value of 1085 cm.^{-1} for ν_4 of BH_4^- , the frequency product ratio is 1.74 whereas the ratio based on Assignment 2 is 1.86. The first assignment is thus clearly favored.

The Diammoniate of Diborane.—Previous work from this Laboratory⁵ has supported the structure $[\text{H}_2\text{B}(\text{NH}_3)_2]^+(\text{BH}_4)^-$ for the classical "diammoniate of diborane" rather than the currently accepted ammonium ion formulation of Schlesinger and Burg, *viz.*, $(\text{NH}_4^+)(\text{H}_3\text{BNH}_2\text{BH}_3^-)$.⁷ Since most of the evidence for the latter structure is chemical in nature, it was deemed of interest to include this substance in the present study. The Raman frequencies observed exclusive of solvent bands are listed in Table II and a tracing of the B-H stretching region is shown in Fig. 1.

TABLE II
RAMAN FREQUENCIES (IN CM.^{-1}) OF THE DIAMMONIATE OF
DIBORANE DISSOLVED IN LIQUID AMMONIA

Diammoniate of diborane	NH_4BH_4 decomposition product	Product from NH_4Br -diammoniate reaction
772 \pm 3	773 \pm 3	773 \pm 3
839 \pm 5	852 \pm 10
882 \pm 5	884 \pm 8	
1209 \pm 4	1214 \pm 4	1208 \pm 4
2140		
2265 \pm 2 s	2263 \pm 2 s	
2321 \pm 3	2322 \pm 3	2322 \pm 3
2403 \pm 3	2405 \pm 3	2407 \pm 3
2437 \pm 3	2441 \pm 3	2437 \pm 3

Comparison of the data in Table II with those in Table I shows that the frequencies of four characteristic bands of the borohydride ion agree with frequencies in the diammoniate spectrum within experimental error or the uncertainty in position caused by the effect of the cation. A more striking comparison is made if one mentally subtracts the bands at 2321 and 2437 cm.^{-1} from the diammoniate spectrum in Fig. 1 and compares the remainder with the borohydride spectrum. The very close similarity furnishes strong evidence for the presence of a borohydride ion in the liquid ammonia solution of the diammoniate of diborane.

(7) H. I. Schlesinger and A. B. Burg, *THIS JOURNAL*, **60**, 290 (1938).

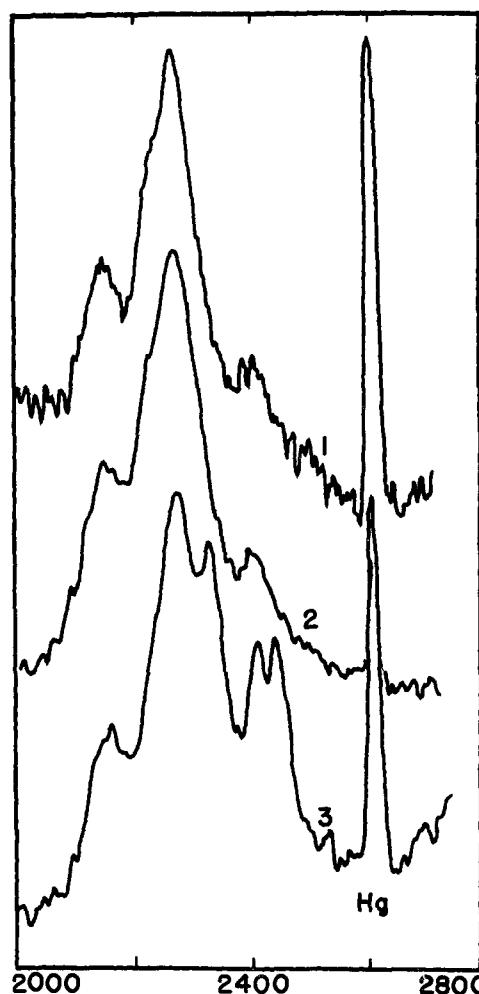


Fig. 1.—The B-H stretching region in the Raman spectra of some borohydrides dissolved in liquid ammonia (cm.^{-1}): (1) LiBH_4 ; (2) NaBH_4 ; (3) $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$.

The structure given above for the cation is iso-electronic with propane. In agreement with this formulation, only two B-H stretching frequencies not found in the borohydride ion spectrum were observed. No information could be obtained about the N-H modes due to the interference of solvent bands.

In the lower frequency region, three bands were observed at 772, 839 and 882 cm.^{-1} . The first was relatively sharp and agrees with what one might expect for a symmetrical stretching mode of the N-B-N skeleton. The latter two were weaker and much more diffuse members of a doublet. No lower frequency which might be assigned to a skeletal bending mode was observed, although this failure may have been caused by experimental difficulties. In propane, the symmetrical and unsymmetrical skeletal stretching modes occur at 867 and 922 cm.^{-1} , respectively.⁸

The recorded spectrum thus is reasonably consistent with the new formulation⁵ but, of course, does not exclude other possibilities for the cation. On the other hand, the structure proposed by Schles-

(8) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 361.

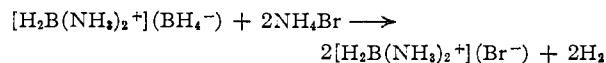
inger and Burg⁷ for the diammoniate contains six B-H bonds which, judging from the spectra of analogous molecules such as propane and dimethyl ether, would be expected to give a very complicated spectrum in the B-H stretching region. That such a pattern fortuitously would match that obtained by superimposing two additional frequencies on the borohydride spectrum seems extremely unlikely, and to this extent the spectral evidence does not agree with their proposed structure.

Decomposition Product of Ammonium Borohydride.—Chemical evidence has been given elsewhere⁹ to the effect that if liquid ammonia solutions of NH_4BH_4 are evaporated to dryness and the solid allowed to warm to room temperature, the solid evolves hydrogen and leaves a product which has the properties of the diammoniate of diborane. The spectrum of this decomposition product prepared as described was obtained in the present work largely to supply confirmatory evidence. Due to experimental difficulties, the solutions obtained were more dilute than those of the diammoniate and were not as "clean" optically. However, the frequency values in Table II match those of the diammoniate within experimental error and the band outline in the B-H stretching region also agreed very closely. The identity of the decomposition product with the diammoniate thus appears confirmed.

Product of the Diammoniate-Ammonium Bromide Reaction.—As a consequence of the instability of solid ammonium borohydride at room temperature, treatment of the diammoniate with ammonium bromide under the proper conditions can result in the destruction of the borohydride

(9) R. W. Parry, D. R. Shultz and P. R. Girardot, *THIS JOURNAL*, **80**, 1 (1958).

ion present and its replacement by the bromide ion. In terms of the structure proposed previously,⁵ the reaction can be written



Details of this reaction also have been given elsewhere⁵ and the properties of the product described. The Raman frequencies observed for this reaction product dissolved in liquid ammonia are given in Table II. Inspection shows that all values listed also appear in the diammoniate spectrum and, further, that the frequencies of the borohydride ion plus those of the NH_4Br reaction product together account for all bands observed in the diammoniate spectrum. The spectral evidence thus is strong that the reaction written above is correct. Two bands appear to be common to the spectrum of the cation and to the borohydride ion, namely, the bands at about 1210 cm.^{-1} and their overtones at about 2405 cm.^{-1} . Apparently the bending frequency of the BH_2 group in the cation occurs at almost the identically same position as ν_2 of the borohydride ion. Due to the small, and in this case unknown, effect of the cation on the borohydride frequencies plus the inherent experimental uncertainty in measuring the positions of weak and rather broad bands, the two cannot clearly be distinguished.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Reaction of Tetrasulfurtetranitride with Nickel Chloride

BY T. S. PIPER

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The reaction of nickel chloride with tetrasulfurtetranitride in alcohol solution, which has been reported to yield NiS_4N_4 , has been reinvestigated and found to produce the series of compounds $\text{NiS}_4\text{N}_4\text{H}_2$, $\text{NiS}_3\text{N}_3\text{H}$ and NiS_2N_2 .

M. Goehring and her co-workers have discovered an interesting series of compounds of transition metals to which was ascribed the type formula $\text{M}(\text{NS})_4$; compounds were reported for Ni,^{1,2} Co,^{2,3} Fe,^{2,4} Pd^{2,5} and Pt.⁵ Preliminary studies of the platinum compound by X-ray diffraction⁶ have shown the presence of two -N-S-N-S- bidentate ligands in a planar *cis* configuration. With a view to obtaining further structural information an in-

(1) M. Goehring and A. Debo, *Z. anorg. allgem. Chem.*, **273**, 319 (1953).

(2) M. Goehring, K.-W. Daum and J. Weiss, *Z. Naturforsch.*, **10b**, 298 (1955).

(3) K.-W. Daum, M. Goehring and J. Weiss, *Z. anorg. allgem. Chem.*, **278**, 260 (1955).

(4) M. Goehring and K.-W. Daum, *ibid.*, **282**, 83 (1955).

(5) E. Fluck, M. Goehring and J. Weiss, *ibid.*, **287**, 51 (1956).

(6) J. Weiss, *Angew. Chem.*, **69**, 108 (1957).

vestigation of the chemistry and spectra of the nickel compound has been undertaken.

Experimental⁷

The Preparation of $\text{NiS}_4\text{N}_4\text{H}_2$.—The reported procedure² combining S_4N_4 and anhydrous NiCl_2 in refluxing alcohol was used. Twenty grams of S_4N_4 and 25 g. of anhydrous NiCl_2 were mixed with 700 ml. of anhydrous methyl alcohol and heated to reflux under nitrogen for eight hours. The alcohol was then distilled out of the reaction flask at reduced pressures and the solid which remained behind was extracted with one liter of benzene. The benzene solution was run through a chromatographic column (55 mm. diameter) containing four pounds of acid washed alumina (Merck and Co., Inc.). A red fraction was eluted with the benzene leaving a purple band on the column. The solid

(7) I am indebted to Mr. J. Nemeth, Miss C. Higham and Mrs. M. Stingl for the carbon, hydrogen and nitrogen analyses and also to Mr. James Brader who kindly measured the infrared spectra.