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

Chemical Evidence for the Structure of the "Diammoniate of Diborane." I. Evidence for the Borohydride Ion and for the Dihydro-diammineboron(III) Cation

BY D. R. SCHULTZ AND R. W. PARRY

RECEIVED NOVEMBER 3, 1956

New chemical evidence is cited to support the following points: (1) the proposed existence of an ammonium in the "diammoniate of diborane" is inconsistent with its chemical properties; (2) there is strong chemical evidence for the borohydride ion in the "diammoniate of diborane"; (3) data available are consistent with the formula $[H_2B(NH_3)_2][BH_4]$.

The most widely accepted present day structure for the "diammoniate of diborane," $B_2H_6 \cdot 2NH_3$, is the ammonium model of Schlesinger and Burg,[1] $[NH_4][H_3BNH_2BH_3]$. After discovery of the borohydride ion by Schlesinger and his co-workers[2] a new structure was equally plausible, $[H_2B(NH_3)_2](BH_4)$. This moiety was mentioned briefly in the literature of 1947 but was rejected without serious examination.[3] More recently a third possibility has been suggested by Schaeffer, Adams and Koenig.[4] The ions of both previously suggested formulas are included along with BH_2NH_2 groups, $[NH_4]BH_2NH_2[BH_4]$. Since NH_4BH_4 is known to be unstable,[5] it is assumed that the compound is stabilized by separation of NH_4^+ and BH_4^- ions with BH_2NH_2 groups. In this paper additional chemical evidence for the structure of the "diammoniate" is examined in relation to each of the foregoing models.

It has been found that the "diammoniate of diborane" will react with solid NH_4Cl or NH_4Br to give hydrogen gas and new compounds which have been assigned the formulas $[H_2B(NH_3)_2]Cl$ and $[H_2B(NH_3)_2]Br$. These new compounds react with sodium in liquid ammonia to liberate H_2 gas. The reaction is comparable to that of $B_2H_6 \cdot 2NH_3$ with sodium in liquid ammonia.

Sodium borohydride, under conditions comparable to those used for the NH_4Cl reaction, is without effect on the "diammoniate of diborane." Finally when magnesium thiocyanate is added to a liquid ammonia solution of the "diammoniate of diborane," solid $[Mg(NH_3)_6](BH_4)_2$ is precipitated.

Details of the experiments are summarized below.

Experimental

a. **Reagents.**—1. Ammonia—The Matheson Co., Inc.,—stored over and distilled from sodium before use. 2. Sodium borohydride—Metal Hydrides, Inc.—recrystallized from liquid ammonia. 3. Diborane—prepared by reaction between boron trifluoride etherate and lithium aluminum hydride.[6] 4. Boron trifluoride etherate—Baker and Adamson, technical grade BF_3 etherate—was distilled just before use and the middle fraction used. 5. Lithium aluminum hydride—Metal Hydrides, Inc. 6. Magnesium (II) thiocyanate. Reactions (a), (b) and (c) were employed in synthesis[7]

$$MgCO_3 + 2HI \longrightarrow MgI_2 + H_2O + CO_2 \quad (a)$$

$$AgNO_3 + NH_4SCN \longrightarrow Ag(SCN) + NH_4NO_3 \quad (b)$$

$$2AgSCN + MgI_2 \longrightarrow Mg(SCN)_2 + 2AgI \quad (c)$$

An excess of AgSCN in step (c) produced the soluble complex $Mg[Ag(SCN)_2]_2$. The complex was broken and the silver removed from solution by saturating the system with H_2S. Ag_2S was filtered off and excess H_2S removed by boiling. Thiocyanic acid remaining in the solution was neutralized with $MgCO_3$. The $Mg(SCN)_2$ was crystallized from neutral solution by evaporating the water at 35° in a current of air. The product was recrystallized from distilled water and dried at about 50° in the air. The air-dry product was very soluble in liquid ammonia; coördinated water around the Mg(II) cation was replaced by ammonia in the solution. The water in the system resulted in some H_2 evolution when the $Mg(SCN)_2$ solution was added to an ammonia solution of borohydride, but this side reaction did not interfere with the precipitation of $[Mg(NH_3)_6](BH_4)_2$. Theory for $Mg(SCN)_2 \cdot 5H_2O$: Mg, 10.45. Found: Mg, 10.45–11.05. 7. "The diammoniate of diborane"—the procedure of Schlesinger and Burg[1] was used, except that known variations in the product could be introduced by removing excess ammonia at temperatures other than −78.5°.

b. **Reaction of the "Diammoniate of Diborane" with Sodium Borohydride or Ammonium Halide.**—A mixture of the "diammoniate of diborane" and $NaBH_4$, NH_4Br or NH_4Cl was dissolved in about 5 cc. of liquid ammonia and held for 2 hr. with continuous stirring, at low temperatures ranging from −78.5 to −33° (−63.5° was used in most runs). Hydrogen evolution was negligible. Solvent ammonia was then sublimed from the mixture and the temperature was raised slowly to the reaction temperature indicated in Table I. Hydrogen was removed with a Toepler pump; the residue was redissolved in ammonia; after stirring, ammonia was again removed, the system warmed up, and H_2 was measured. This cycle was repeated 3 to 5 times. An exactly comparable reaction was run between $NaBH_4$ and NH_4Cl. Details of all experiments are summarized in Table I.

c. **Characterization of the Products Obtained in the Reactions between the "Diammoniate of Diborane" and Ammonium Salts.**—The white microcrystalline solids from the diammoniate–ammonium halide reactions gave definite X-ray powder patterns which were distinctly different from those of the parent ammonium salts. Characteristic Debye–Scherrer powder pattern data are given in Table II. The similarity of the patterns indicates that the chloride and bromide salts are isostructural. The bromide salt has a slightly larger unit cell. Neither product as obtained above was of high purity, but the patterns are for the pure salts. Dr. C. Nordman is studying the structures.

Arguments given later suggested for the residue the general formula $[H_2B(NH_3)_2]X$, where $X = Cl^-$ or Br^-. Analytical data for the bromide salt are as follows: $N_{obs} = 22.1\%$, $N_{theor} = 22.1$, $Br^-_{obs} = 62.3\%$, $Br^-_{theor} = 63.0$; for the chloride salt values are: $N_{obs} = 34.0$, $N_{theor} = 34.0$, $Cl^-_{obs} = 41.8$, $Cl^-_{theor} = 43.2$.

Analytical values for boron and hydridic hydrogen were low due to incomplete hydrolysis of the samples but the ammonia and halide results provide evidence for the formulas.[8]

---

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

[2] H. I. Schlesinger, R. J. Sanderson and A. B. Burg, *ibid.*, **61**, 536 (1939); **62**, 3421 (1940); A. B. Burg and H. I. Schlesinger, *ibid.*, **62**, 3425 (1940); H. I. Schlesinger and H. C. Brown, *ibid.*, **62**, 3429 (1940).

[3] A. B. Burg, *ibid.*, **69**, 747 (1947).

[4] G. W. Schaeffer, M. D. Adams and F. J. Koenig, S.J., *ibid.*, **78**, 725 (1956).

[5] R. W. Parry, D. R. Schultz and P. R. Girardot, *ibid.*, **80**, 1 (1958).

[6] J. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik and G. B. L. Smith, *ibid.*, **74**, 901 (1952).

[7] D. R. Schultz, Ph.D. dissertation, Univ. of Mich., Ann Arbor, 1954.

[8] NOTE ADDED AFTER ACCEPTANCE: The compounds $[H_2B(NH_3)_2]Cl$ and $[H_2B(NH_3)_2]Br$ have been synthesized more recently in pure

TABLE I

A. REACTION OF THE "DIAMMONIATE OF DIBORANE" WITH SODIUM BOROHYDRIDE OR AMMONIUM HALIDE

	1	2	3	4	5
Temp. at which excess NH_3 removed after compd. prepn., °C.	−45	−78.5	−45	−78.5	−78.5
$B_2H_6 \cdot 2NH_3$,[a] mmoles	0.97	2.11	1.735	4.18	2.30
$NaBH_4$ used, mmoles	2.7	4.35	0	0	0
NH_4X used, mmoles	0	0	3.47 (Br^-)	8.56 (Cl^-)	4.60 (Cl^-)
Reaction temp., °C.	25	45	25	25	25
Total reaction time (hr.)	5	3	5	[b]	[b]
H_2 evolved, mmoles	0.69	0.166	3.41	8.27	4.99
H_2, mmoles/ $B_2H_6 \cdot 2NH_3$, mmoles	0.071	0.079	1.96 [c]	1.98	2.17

[a] The ratio of B_2H_6 to NH_3 in each sample was always within 2.00 ± 0.02. [b] About same rate as others but time not followed carefully. [c] Reaction with NH_4Br and authentic $B_2H_6 \cdot 2NH_3$ has been repeated many times but all details of stoichiometry not recorded.

B. SODIUM BOROHYDRIDE AND AMMONIUM BROMIDE CONTROL

3.98 mmoles $NaBH_4$	temp., 25°
6.95 mmoles NH_4Br	H_2 evolved = 6.70 mmoles +
5 ml. liq. NH_3	$H_2/NaBH_4$ = 1.68 +

TABLE II

INTERPLANAR SPACINGS AND RELATIVE INTENSITY DATA FOR $[H_2B(NH_3)_2]Cl$ AND $[H_2B(NH_3)_2]Br$

$[H_2B(NH_3)_2]Cl$ Intensity[a]	d(Å.)	$[H_2B(NH_3)_2]Br$ Intensity[a]	d(Å.)
ms	5.08	s	5.22
w,D	4.36	w,D	4.47
m	3.60	ms	3.69
vs	3.31	vs	3.42
w	3.01	vw	3.09
s	2.77	s	2.85
w	2.69	vw	2.78
s	2.54	ms	2.61
ms	2.28	ms	2.33
mw	2.18	ms	2.26
ms	2.02	s	2.08
w	1.85	w	1.93
w	1.80	w	1.83
vw	1.69	vw,D	1.75
m	1.66	m	1.71
w	1.61	w	1.65
m	1.58	m	1.62
vw	1.53	vw	1.59
w	1.51	w	1.55

[a] S, strong; m, medium; w, weak; v, very; D, diffuse.

d. **Reaction of the "Diammoniate of Diborane" with Sodium in Liquid Ammonia.**—The reaction vessel was a 25 mm. Pyrex tube with a 14/35 ₸ joint sealed at right angles near the top of the tube. A side arm making about a 60° angle with the lower side of the tube had a 24/40 ₸ inner-outer joint combination so materials could be placed in the side arm. A glass bulb (about 15 mm. in diameter) containing about 230 mg. of Na was placed in the side arm together with a magnet in a heavy glass case. After evacuation and drying of the system, the "diammoniate" was prepared in the conventional fashion; ammonia was removed to check the stoichiometry; ammonia was returned to the system and frozen; then the reaction tube was tipped around the 14/35 ₸ joint until the sodium bulb fell into the reaction vessel. The magnetic hammer, magnetically controlled from the outside, was held back, then was used to break the sodium bulb; the ammonia was allowed to melt and the reaction conducted at −78.5°. The stoichiometry obtained with this system is extremely sensitive to experimental conditions. Results of a more detailed study are given elsewhere.[9] Results of all earlier workers could be reproduced at will by proper control of conditions.

e. **The Reaction of the Compound $[H_2B(NH_3)_2]Br$ with Sodium in Liquid Ammonia.** (See Section c, above.)—The reaction between sodium and $[H_2B(NH_3)_2]Br$ was carried out in the apparatus described in Section d. The same general technique was employed. In the low temperature reaction at −78° 1.04 mmoles of $[H_2B(NH_3)_2]Br$ reacted with 1.04 milligram atoms of Na to liberate 0.52 millimole of hydrogen in 60 minutes. The stoichiometry and reaction rate were comparable to those observed in the reaction between $B_2H_6 \cdot 2NH_3$ and Na. NaBr was identified in the solid product by an X-ray powder pattern. At room temperature ammonia reacted with the residues from both the bromide salt and "diammoniate" reactions to liberate up to one mole of excess hydrogen per mole of $B_2H_6 \cdot 2NH_3$ or per mole of $[H_2B(NH_3)_2]Br$ used.

f. **The Reaction between $B_2H_6 \cdot 2NH_3$ or $NaBH_4$ and Magnesium Thiocyanate in Liquid Ammonia.**—Attempts to scale-up the preparation of the "diammoniate" by increasing the amounts of reagents were generally unsuccessful. Accordingly, four batches of the compound were prepared (−78.5°) and stored under an atmosphere of dry nitrogen at −78.5 for from 4 to 48 hr. The combined sample (0.768 mmole) was loaded by means of a dry box into one arm of an inverted Y-tube reactor; magnesium thiocyanate (2.5 mmoles) was placed in the other leg and the reactor was attached to a special vacuum-line filter assembly. Dry ammonia was then condensed in each leg and stirred; the solutions were mixed; then the precipitate was filtered off and washed eight times in the vacuum system with liquid ammonia. About 0.2 g. of precipitate was obtained from the "diammoniate." Analysis of the precipitate showed

$$[Mg_{1.19}(NH_3)_{6.24}][BH_{4.07}]_2$$

The slightly high value for Mg indicated that some of the $Mg(SCN)_2$ or some basic Mg(II) salt was contaminating the product, but the X-ray data left no doubt that the product was identical to the material obtained from $NaBH_4$ and $Mg(SCN)_2$ which gave an analysis indicating: $[Mg(NH_3)_{5.7}][B_{1.91}H_{8.0}]$. The pattern also checked with a sample of $[Mg(NH_3)_6]BH_4)_2$ generously supplied by Callery Chemical Co.[10]

g. **Analytical Methods.**—Magnesium was precipitated from ammoniacal solution using 8-hydroxyquinoline.[11] Boron was determined by titrating boric acid with sodium hydroxide in the presence of mannitol. Evolved hydrogen

---

form by two completely independent methods. These samples have been characterized by complete analysis and by molecular weight measurements in liquid ammonia. The X-ray powder patterns are the same as those described above. Details will be given in a subsequent publication; see G. Kodama, Ph.D. Dissertation. Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 1957.

[9] R. W. Parry and S. G. Shore, THIS JOURNAL, **80**, 15 (1958).

[10] The authors are indebted to Dr. A. D. McElroy of Callery Chemical Co. for pointing out that $Mg(NH_3)_6(BH_4)_2$ is insoluble in liquid ammonia and might be precipitated as a test for BH_4^- ion.

[11] W. D. Hillebrand, G. E. F. Lundell, W. A. Bright and J. J. Hoffman, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1953.

was always identified by gas density. Nitrogen was determined by the Kjeldahl method.

h. X-Ray Methods.—Specimens were sealed into thin-walled glass capillaries of 0.3 mm. diameter (supplied by the Cain Specialties Co. of Chicago). A 5.7 cm. Debye–Scherrer camera with nickel filtered copper Kα radiation was used for routine analyses. Exposures were of the order of 1–2 hr. at 30 kv. and 15 ma. For the characterization of $[H_2B(NH_3)_2]X$ and the examination of complex patterns produced by reaction mixtures, high-resolution, 11.4 cm. Debye–Scherrer camera was used. Exposures with this camera were of the order of 5–7 hr. at 30 kv. and 15 ma.

Discussion

The relationship of each of the foregoing observations to the structure assigned to the "diammoniate of diborane" will now be considered.

1. Evidence for the Cation Present in the Solid.—The principal evidence for the ammonium ion in the model of Schlesinger and Burg,[1] $[NH_4][H_3BNH_2BH_3]$ was the reaction of the "diammoniate" and sodium in liquid ammonia. The equation assumed was

$$Na + [NH_4][H_3BNH_2BH_3] \longrightarrow \tfrac{1}{2}H_2 + NH_3 + Na[H_3BNH_2BH_3]$$

Although the observation is indeed consistent with the presence of an ammonium ion in the compound, it is important to note that the reaction is definitely *not* proof of the existence of an ammonium ion in the solid "diammoniate." Rather it is evidence for the presence of *any* Brönsted–Lowry acid which can oxidize the active sodium metal in liquid ammonia solution. For example $(CH_3)_3BNH_3$ and monomeric H_3BNH_2 both react with sodium in liquid ammonia yet contain no NH_4^+ in the solid. One might also compare the reaction of acids such as $Al(H_2O)_6^{+++}$ in water systems. The acid character of $Al(H_2O)_6^{+++}$ solutions is not evidence for H_3O^+ in solid aluminum sulfate hydrate, but is, instead, evidence for the existence of water molecules whose proton donor qualities have been enhanced by coördination to an ion of relatively high field strength. Similar arguments apply to ammonia molecules coördinated to the boron of $[H_2B(NH_3)_2]^+$. The reaction with sodium may be written

$$[H_2B(NH_3)_2]X + Na \xrightarrow[NH_3,\ 78°]{liq.} NaX + H_2BNH_2 + \tfrac{1}{2}H_2 + NH_3$$

No direct evidence for an ammonium ion in the "diammoniate" of diborane ever has been presented. On the other hand, direct evidence against the presence of this ion is now available. It is known that ammonium borohydride is unstable at room temperature,[5] and mixtures containing $NaBH_4$ along with authentic ammonium salts such as NH_4Cl or $(NH_4)_2SO_4$ react rapidly to give off H_2 (Table IB). Since the "diammoniate of diborane" does not react with excess $NaBH_4$ under comparable conditions, the presence of an ammonium ion can be rationalized only by assuming that something in the solid (H_2BNH_2 has been suggested)[4] renders the NH_4^+ ion inactive toward BH_4^-. The mechanism of such stabilization without formation of the cation $[H_2B(NH_3)_2]^+$ remains obscure.

In contrast, evidence for the complex cation, $[H_2B(NH_3)_2]^+$, is provided by isolation of its chloride and bromide salts. These are isostructural. The bromide salt gives a reaction with sodium in liquid ammonia which is comparable to that of the "diammoniate of diborane." Hence all evidence cited for the ammonium ion is equally good for the ion $[H_2B(NH_3)_2]^+$ and evidence against the ammonium ion does not apply to the complex cation.

It was noticed in these studies, and has been observed by others, that approximately two thirds of the hydridic hydrogen in the "diammoniate of diborane" hydrolyzes easily near room temperature while the remaining third is hydrolyzed with greater difficulty (sealed tube, 6 M HCl; temp., 150°). It is also significant that complete hydrolysis of the salt $[H_2B(NH_3)_2]Br$ was difficult to effect. These observations are now easily correlated if the model $[H_2B(NH_3)_2]BH_4$ is assumed. The four borohydride hydrogens of the "diammoniate" would hydrolyze easily, whereas the two hydrogens on the $[H_2B(NH_3)_2]^+$ cation would be released more slowly.

Finally, brief mention should be made of an earlier argument of Burg[3] to the effect that in $[H_2B(NH_3)_2]^+$ "the strong proton–donor character of the quaternary nitrogen atoms should render the proton-sensitive BH_4^- incapable of existence." Coördination theory indicates that the proton–donor characteristic of the nitrogen in $[H_2B(NH_3)_2]^+$ should be less marked than that in NH_4^+. Furthermore, the existence of quaternary nitrogens in the stable compound $[Cr(NH_3)_6](BH_4)_3$ offers experimental contradiction to the above argument. It is also significant that $[Cr(NH_3)_6]Cl_3$ reacts with Na in liquid NH_3 to liberate H_2 initially. Finally, sodium borohydride was crystallized from liquid NH_3 with $[H_2B(NH_3)_2]Br$ and no hydrogen was evolved. Comparable experiments with NH_4Br resulted in rapid H_2 evolution.

2. Evidence for the Anion Present in the Structure.—The first evidence for the borohydride anion was obtained by Schaeffer, Adams and Koenig[4] when they showed that the reaction of sodium with $B_2H_6\cdot 2NH_3$ produces sodium borohydride rather than the complex salt, $Na[H_3BNH_2BH_3]$, of Schlesinger and Burg.[1] Their observations are consistent with the equation

$$[H_2B(NH_3)_2]BH_4 + Na \longrightarrow NaBH_4 + \tfrac{1}{2}H_2 + H_2BNH_2 + NH_3$$

They are *not* consistent with the earlier equation

$$NH_4[H_3BNH_2BH_3] + Na \longrightarrow Na[H_3BNH_2BH_3] + \tfrac{1}{2}H_2 + NH_3$$

Additional direct evidence for the borohydride is found in the fact that $B_2H_6\cdot 2NH_3$ will react with authentic ammonium salts to liberate hydrogen. The equation for the formation of the dihydridodiammineboron(III) salts may be written as

$$[H_2B(NH_3)_2]BH_4 + 2NH_4X \longrightarrow 2[H_2B(NH_3)_2]X + 2H_2$$

An authentic metal borohydride such as $NaBH_4$ reacts with NH_4X to give both NaX and the salt $[H_2B(NH_3)_2]X$.

At this point it should be noted that in arguments wherein the structure $NH_4(H_2BNH_2)BH_4$ is assumed, it is postulated that the H_2BNH_2 group stabilizes NH_4BH_4 by an unspecified mechanism.

In view of the observations here recorded, one must now postulate that H_2BNH_2 can stabilize the NH_4^+ (if present in the "diammoniate") against attack by excess BH_4^- (*i.e.*, no reaction with $NaBH_4$) but *cannot* stabilize BH_4^- (as found in the "diammoniate") against attack by NH_4^+ (*i.e.*, NH_4Cl reacts with $B_2H_6 \cdot 2NH_3$). The most reasonable explanation for such conflicting observations would be to assume the existence of the cation $[H_2B(NH_3)_2]^+$ rather than NH_4^+ in the original $B_2H_6 \cdot 2NH_3$.

The precipitation of $[Mg(NH_3)_6](BH_4)_2$ from a liquid ammonia solution of the "diammoniate" offers further simple and direct evidence for the presence of the borohydride ion in the liquid ammonia solution. Unnecessary, and in some cases unreasonable, equilibrium shifts would be required to support any argument denying the presence of the borohydride ion.

Finally the Raman spectral data of Taylor, Schultz and Emery[12] offer firm support for the presence of the borohydride ion.

3. A Resumé of Earlier Structural Arguments.—In 1947 Burg[3] mentioned the model $[H_2B(NH_3)_2]BH_4$ for the "diammoniate" but rejected it unequivocally on the basis of "a formidable array of facts." An objective reëxamination of the structural problem now demands that all of the earlier[1] arguments be examined carefully in light of current information.

Five arguments were originally cited in support of the ammonium model.[1] Each of these (italicized below) can now be shown to be consistent with the borohydride representation.

1. *The product ("diammoniate of diborane") reacts with sodium in liquid ammonia at −77° to produce one equivalent of hydrogen per mole of diborane involved; it thus seems to contain one ammonium ion per pair of boron atoms.*

It has been shown that oxidation of sodium metal in liquid ammonia solution with liberation of hydrogen is not a specific test for the ammonium ion. Tests on the compound $[H_2B(NH_3)_2]Br$ show that the dihydro-diammine boron(III) cation is likewise capable of reaction with sodium in an exactly analogous fashion. The compound $H_2B(NH_2)(NH_3)$ formed in the reaction loses ammonia to give polymeric (H_2BNH_2). This explains the analytical results of Schlesinger and Burg on their product and is consistent with all X-ray evidence.

2. *A slow secondary reaction of the product with ammonia and sodium, yielding barely 40% more hydrogen, is explained easily by assuming that ammonia removes a BH_3 group from the above structure (ammonium model) by a reversible reaction, producing $(NH_4)(BH_3NH_2)$. This explanation is supported by the fact that trimethylamine reacts with the "diammoniate of diborane" to give borine trimethylamine. Neither reaction is explained easily by other structures (i.e., structures other than the ammonium model).*

The question of excess hydrogen evolution is considered elsewhere[9] and is explained easily and quantitatively on the basis of the borohydride model.[9] On the other hand, recent isolation of the compound H_3BNH_3,[13] which presumably gives a small amount of $(NH_4)(BH_3NH_2)$ in liquid ammonia, shows definitely that it does not exist in labile equilibrium with the "diammoniate"; the postulated equilibrium is untenable.

The fact that trimethylamine reacts with the "diammoniate of diborane" to give low yields of H_3BNH_3 does not support the ammonium model, particularly when one realizes that the supposed salt $Na(H_3BNH_2BH_3)$ gives no reaction with trimethylamine. It is known that $NaBH_4$ and H_2BNH_2, the actual components of this mixture, do not react with $N(CH_3)_3$. On the other hand, the BH_4^- ion in the field of the weakly acidic, polarizing cation $[H_2B(NH_3)_2]^+$ should react slowly with $N(CH_3)_3$ to give low yields of H_3BNR_3. Such an argument is eminently reasonable when one considers the effect of cation field strength on the reactions of borohydrides. Both beryllium and aluminum borohydrides react with trimethylamine. The borohydride of the complex cation $[H_2B(NH_3)_2]^+$ would probably fall in between the beryllium and alkali metal borohydrides in terms of borohydride polarization.

3. *The reaction of the new compound $(CH_3)_2OBH_3$ with ammonia and sodium produces the salt $NaBH_3NH_2$. The negative ion of this salt is considered to be an intermediate step in the formation of the above structure (ammonium structure).*

This compound has no bearing on the structure since it is a substituted borohydride comparable to $NaBH_3(OCH_3)$. It presumably results from NH_3BH_3 and sodium in liquid ammonia; it has been shown that NH_3BH_3 is not in labile equilibrium with the "diammoniate" in anhydrous liquid ammonia,[13] hence this salt has little relationship to the structure of $B_2H_6 \cdot 2NH_3$.

4. *The salt $NaBH_3NH_2$ strongly absorbs diborane. This fact justifies the assumption that the negative ion of the above structure is easily formed by the addition of BH_3 to the $BH_3NH_2^-$ ion and is capable of existence.*

The reaction involved in this argument is not one of formation of $(H_3BNH_2BH_3^-)$ but rather it appears to be similar to the acid–base reaction between diborane and $NaBH_3OCH_3$.[14]

$$NaBH_3(OCH_3) + {}^1/_2B_2H_6 \longrightarrow NaBH_4 + BH_2(OCH_3) \quad (6)$$

$$NaBH_3NH_2 + {}^1/_2B_2H_6 \longrightarrow NaBH_4 + 1/n(BH_2NH_2)_n \quad (7)$$

It has been shown[4] that the supposed salt $Na(BH_3NH_2BH_3)$ is in reality a mixture of $NaBH_4$ and BH_2NH_2. There is absolutely no evidence at the present time for the ion $(H_3BNH_2BH_3^-)$.

5. *The new compound B_2H_7N, having a structural skeleton B–NB, is easily prepared from the "diammoniate of diborane."*

The linear structure originally attributed to B_2H_7N is now known to be incorrect. There is strong evidence[15] for a bridge structure, which could easily result from the interaction of the complex cation $[H_2B(NH_3)_2]^+$ with BH_3 groups or B_2H_6 molecules at the known high temperature (60°) of the reaction. Alternatively, NH_3 might be dis-

---

[12] R. C. Taylor, D. R. Schultz and A. R. Emery, This Journal, **80**, 27 (1958).

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

[14] H. I. Schlesinger and H. C. Brown, *et al.*, *ibid.*, **75**, 186 (1953).

[15] K. Hedberg and A. J. Stosick, *ibid.*, **74**, 954 (1952).

placed at high temperatures to react directly with B_2H_6. The original argument is equally good for the borohydride formulation and in no sense supports the ammonium model.

The new borohydride model also permits easy rationalization of earlier disturbing observations of Stock.[16] He found that gaseous HCl reacted with the "diammoniate" of diborane to yield hydrogen and diborane. Although these products were isolated in relatively large yield, they were considered as products of a side reaction since they were inconsistent with models of the "diammoniate" then available. The products are those expected from the borohydride model and have a formal resemblance to the reaction with the acid NH_4Br in liquid ammonia. The reaction is directly analogous to the reaction of alkali metal borohydrides with HCl

$$2[H_2B(NH_3)_2](BH_4) + 2HCl \longrightarrow B_2H_6 + 2H_2 + 2[H_2B(NH_3)_2]Cl \quad (8)$$

$$2M(BH_4) + 2HCl \longrightarrow B_2H_6 + 2H_2 + 2MCl \quad (9)$$

All of the foregoing properties of the "diammoniate" offer strong support for a structure containing a borohydride ion. The known instability of ammonium borohydride as well as other chemical properties of the "diammoniate" argue strongly against inclusion of ammonium and borohydride ions in the same molecule. A proposed[4] stabilizing effect due to H_2BNH_2 has no experimental support. On the other hand, the new cation $[H_2B(NH_3)_2]^+$, which can be considered as an ammonia complex of boron(III), explains all properties formerly attributed to the ammonium ion and is itself consistent in every detail with the chemistry of the "diammoniate."

Acknowledgment.—This research was conducted under Contract AF33(616)-8 with the United States Air Force, the sponsoring agency being the Aeronautical Research Laboratory of the Wright Air Development Center, Air Research and Development Command.

ANN ARBOR, MICH.

---

(16) A. Stock, "Hydrides of Boron and Silicon," Cornell Univ. Press, Ithaca, N. Y., 1933.

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

Chemical Evidence for the Structure of the "Diammoniate of Diborane." II. The Preparation of Ammonia–Borane

BY S. G. SHORE AND R. W. PARRY

RECEIVED NOVEMBER 3, 1956

The monomeric compound ammonia–borane, H_3NBH_3, has been prepared from the "diammoniate of diborane" and from lithium and sodium borohydrides. The reactions provide additional support for a borohydride formulation of the "diammoniate," $[H_2B(NH_3)_2][BH_4]$. Ammonia–borane was also prepared from dimethyl ether–borane, $(CH_3)_2OBH_3$. The "diammoniate of diborane" and ammonia–borane exist as separate entities. They do not exist in labile equilibrium. The striking contrasts in the properties provide unequivocal evidence against all attempts to formulate the "diammoniate" as H_3NBH_3.

In a previous paper[1] of this series chemical evidence was provided in support of a borohydride structure $[H_2B(NH_3)_2][BH_4]$ for the "diammoniate of diborane." By making use of the fact that ammonium borohydride which has been prepared in liquid ammonia decomposes with evolution of hydrogen, bromide and chloride salts of the "diammoniate" cation were prepared (*i.e.*, $[H_2B(NH_3)_2]X$).

As an alternative synthetic route to the chloride salt of the "diammoniate," the heterogeneous, room-temperature reaction between ammonium chloride and the "diammoniate of diborane" in a diethyl ether suspension seemed to offer interesting possibilities, especially since such a reaction would be less tedious to undertake than the ones indicated above. The results were entirely unexpected, for the reaction in ether suspension led to the synthesis of the monomeric compound ammonia–borane, H_3NBH_3.

The Preparation of Ammonia–Borane from "Diammoniate of Diborane."—Under strictly anhydrous conditions and in the absence of all extraneous proton sources, the "diammoniate" in diethyl ether suspension, decomposed only very slowly at room temperature. When anhydrous ammonium chloride was added to such a system, hydrogen evolution was still negligible. It was found, however, that by altering the ether environment through the addition of a small quantity of anhydrous ammonia, the rate of hydrogen evolution increased markedly. The rate for one run is indicated in Fig. 1. The abrupt break in the curve which resulted from the addition of ammonia is proof of the efficacy of the catalyst. Data from several runs are summarized in Table I. It is significant that even a twofold excess of ammonium chloride in the ether slurry did not produce much more than one mole of hydrogen per mole of "diammoniate."

After the ether slurry was filtered, the previously described[2] crystalline compound ammonia–borane, H_3NBH_3, was isolated from the filtrate in yields up to 80% based upon the borohydride content of the "diammoniate."

The reaction of the "diammoniate" with ammonium chloride has been written as[2]

$$[H_2B(NH_3)_2][BH_4] + NH_4Cl \xrightarrow[\text{small amt. of } NH_3]{\text{diethyl ether}} [H_2B(NH_3)_2]Cl + H_3NBH_3 + H_2$$

---

(1) D. R. Schultz and R. W. Parry, THIS JOURNAL, **80**, 4 (1958).

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