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.

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[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

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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]

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

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[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).

TABLE I

THE DECOMPOSITION OF THE "DIAMMONIATE OF DIBORANE" IN AN ETHER SLURRY

Run	$[BH_2(NH_3)_2][BH_4]$, mmoles	$\frac{NH_4Cl}{[BH_2(NH_3)_2][BH_4]}$	Ether, ml.	Comments	Time, hr. (cumulative)	$\frac{H_2(\text{cumulative})}{[BH_2(NH_3)_2][BH_4]}$
1	2.02	1.86	5	0.3 mmole →	22	0.25
				NH_3 added	40	1.17
2	2.17	0.99	8	0.3 mmole →	12	0.55[a]
				NH_3 added	32	.85
3	2.12	1.84	7	0.19 mmole	12	.07
				NH_3 added	32	.89
					54	1.04
					99	1.06
4	1.93	0.97	10	0.15 mmole →	36	0.99[a]
				NH_3 added	48	1.02
5	1.73	0.00	10	0.15 mmole →	12	0.05
				NH_3 added	26	.42
					43	.53
					67	.74
					115	.82

[a] Since the "diammoniate" was in excess, these values represent H_2/NH_4Cl.

According to such an equation the compound $[H_2B(NH_3)_2]Cl$ should be a principal component of the solid reaction residue. X-Ray powder examination of the reaction residues indicated the presence of relatively small quantities of $[H_2B(NH_3)_2]Cl$ and much larger quantities of unchanged ammonium chloride, even from those reactions in which the "diammoniate" and ammonium halide were in one to one molar ratio.

The presence of unchanged ammonium chloride suggested the possibility of spontaneous decomposition of an ether slurry of the "diammoniate" in the presence of a small amount of ammonia. The data which are presented in Table I and Fig. 1 indicate that such decomposition does indeed take place at a relatively rapid rate.

It is now believed that two separate and competing reactions to produce ammonia–borane took place. The first reaction was a relatively spontaneous decomposition which took place in the presence of ammonia

$$[H_2B(NH_3)_2][BH_4] \xrightarrow[\text{small amt. of } NH_3]{\text{diethyl ether}} H_2 + H_3NBH_3 + 1/n(H_2NBH_2)_n$$

and the second reaction was the previously postulated reaction 2 between the "diammoniate" and ammonium chloride to produce the chloride salt of the "diammoniate" cation. This reaction was slower than the first one since both reactants are insoluble in ether.

The Reaction between Lithium Borohydride and Ammonium Salts in an Ether Slurry.—The foregoing process for the synthesis of H_3NBH_3 from the "diammoniate of diborane" was interpreted in terms of the reaction of a borohydride ion. Such an interpretation suggests that other borohydrides should react similarly with NH_4Cl in an ether slurry

$$MBH_4 + NH_4X \longrightarrow MX + H_3NBH_3 + H_2$$

As a preliminary experiment, the reaction between sodium borohydride and ammonium chloride was studied in diethyl ether. Even when small amounts of ammonia were used to accelerate the gas evolution, the production of hydrogen was negligible. On the other hand E. R. Alton, Jr., of this Laboratory was able to prepare H_3NBH_3 in small yields through the reaction between NH_4Br and $NaBH_4$ in Ansul 141 polyether. The polyether is a solvent for $NaBH_4$. It also was found that $LiBH_4$, which dissolves in diethyl ether, will react relatively rapidly with a *diethyl ether* slurry of ammonium chloride or sulfate at about room temperature to produce H_3NBH_3. The purest product is obtained from ammonium sulfate and $LiBH_4$. Schaeffer and Anderson[3] have used a similar type of reaction to prepare $(CH_3)_3NBH_3$. Results of several experiments are summarized in Table II. Although the theoretical yield of hydrogen was produced readily in each experiment with $LiBH_4$, the yield of ether soluble ammonia–borane did not ever exceed 50% of theory. Since ammonia-

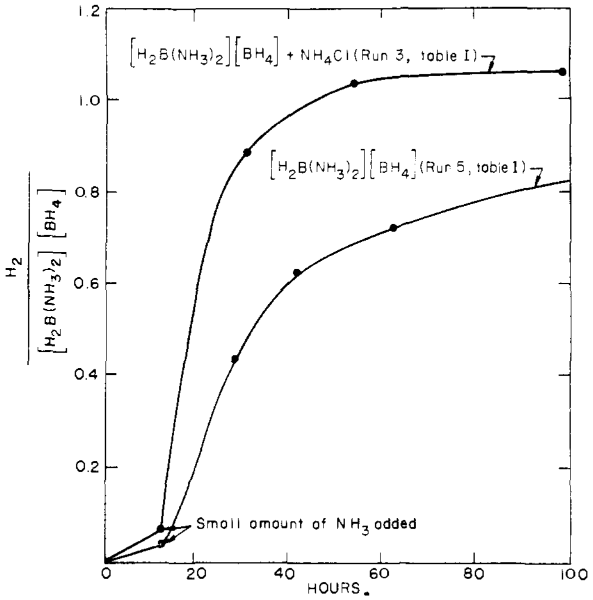

Fig. 1.—The decomposition of the "diammoniate of diborane" in an ether slurry.

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[3] G. W. Schaeffer and E. R. Anderson, THIS JOURNAL, **71**, 2143 (1949).

borane is only one of several compounds with the empirical formula $(H_3NBH_3)_n$,[4] it is probable that the ether insoluble forms, empirically $(H_3NBH_3)_n$, were alternative products. The reaction of such compounds with ammonium chloride is very slow in the absence of small amounts of ammonia.

Table II

The Reaction between Lithium Borohydride and an Ammonium Salt Slurried in Ether

Run	$LiBH_4$, mmoles	Meq. NH_4^+ Salt	Ether, ml.	Time, hr.	H_2/ $LiBH_4$	% Yield ether soluble H_3-NBH_3
1	2.08	2.10 NH_4Cl	15	2.5	0.99	33
2	14.2	16.8 $(NH_4)_2SO_4$[a]	50	6	[b]	40
3	19.1	22.4 [a]	50	4.5	0.98	44
4	23.0	26.0 [a]	50	7	[b]	47

[a] Ammonium sulfate was used in preference to ammonium chloride in later experiments because the product lithium sulfate is even less ether soluble than lithium chloride. [b] The extent of reaction was followed, qualitatively, by observing the rate of hydrogen evolution through a mercury bubbler. Analytical ratios for ether soluble product from runs 1 and 2: N/B, 0.98, 0.98; H(hydridic)/B, 2.93, 2.98. Analysis of ether soluble product from run 3. Calcd. for H_3NBH_3: H(hydridic), 9.79; B, 35.0; N, 45.4. Found: H(hydridic), 9.73; B, 35.1; N, 45.6.

The Properties of Ammonia-Borane.—Even though ammonia-borane and the "diammoniate of diborane" are both of empirical formula H_3NBH_3, their properties show striking contrasts. Illustrative data are summarized in Table III.

It was reported previously[2] that ammonia-borane is monomeric in dioxane and diethyl ether. Additional molecular weight studies by vapor pressure depression show that it is monomeric in liquid ammonia also (observed mol. wt. 33; theoretical mol. wt. 30.88). Furthermore, two independent investigations[5] of its crystal structure show that it is monomeric in the solid state.

Ammonia-borane has a negative temperature coefficient of solubility in diethyl ether from about −78 to 25°. Clear, rigorously *anhydrous* ether solutions are stable at room temperature to the extent that only a small amount of precipitate appears after standing for several days. The precipitate has the empirical composition $(H_3NBH_3)_n$. Trace quantities of hydrogen indicate that small amounts of $(H_2NBH_2)_n$ may contaminate the ether insoluble solid. In the presence of trace quantities of moisture, the ether solution becomes very unstable and solid material is precipitated quite rapidly.

Ammonia-borane is soluble and stable in anhydrous liquid ammonia. On the basis of X-ray powder pattern intensities there was no detectable conversion to the "diammoniate" when a sample stood for 30 hr. at −78° and an additional 18 hr. at −45° in liquid ammonia. Reaction of ammonia-borane with sodium in liquid ammonia liberated one equivalent of hydrogen per mole of ammonia-borane. The stoichiometry of the process suggests the reaction

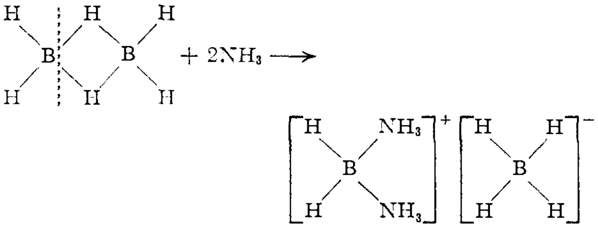
$$H_3NBH_3 + Na \longrightarrow NaH_2NBH_3 + {}^1/_2\, H_2$$

The sodium amidotrihydridoborate(III) has not been isolated from this process in pure form; its preparation by another procedure has been reported by Schlesinger and Burg.[6]

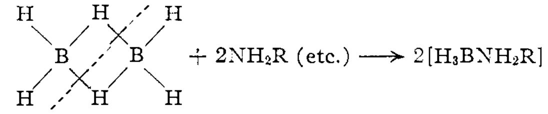
Solid ammonia-borane appears to undergo slow conversion to the "diammoniate of diborane" at room temperature. Very slow loss of hydrogen at room temperature occurs also. A sample which stands at 25° in a dry atmosphere for a period of even five minutes will not redissolve completely in ether. Solid ammonia-borane sublimes with difficulty under high vacuum at room temperature; the purity of the sublimate was not determined. The density of the solid, determined from X-ray powder data,[5] is 0.74 g./cm.[3].

Discussion

Data as summarized here and elsewhere[1,7] support the borohydride formulation for the product formed in the reaction between ammonia and diborane, $[H_2B(NH_3)_2][BH_4]$. The reaction of diborane with ammonia differs from reactions with mono-, di- and trimethylamines in that the former process appears to involve non-symmetrical cleavage of the hydrogen bridges in diborane



whereas the latter reactions involve symmetrical cleavage of the bridge to give monomeric products[8]



The conversion of the classical "diammoniate" to H_3BNH_3 through its reaction with NH_4Cl makes untenable all earlier arguments[9] which supported the hypothesis that the "diammoniate" has the structure H_3NBH_3 but shows abnormally high molecular weights in liquid ammonia as a result of dipole association. Comparative properties of H_3NBH_3 and the "diammoniate" demonstrate unequivocally that two separate compounds are being considered. The formation of H_3NBH_3 from $LiBH_4$ and from the "diammoniate" by comparable reactions adds strong support for a structure containing the borohydride ion in the solid state. Ammonia-borane, on the other hand, shows properties which are consistent with those of the methyl substituted amine-boranes.

It now becomes of interest to examine the experimental procedures of this investigation and

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(4) R. W. Parry and S. G. Shore, This Journal, **80**, 15 (1958).

(5) E. L. Lippert and W. N. Lipscomb, *ibid.*, **78**, 503 (1956); E. W. Hughes, *ibid.*, **78**, 502 (1956).

(6) H. I. Schlesinger and A. B. Burg, *ibid.*, **60**, 290 (1938).

(7) R. C. Taylor, D. R. Schultz and A. R. Emery, *ibid.*, **80**, 27 (1958).

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

(9) L. E. Agromonov, *J. Gen. Chem.* (*U.S.S.R.*), **9**, (1939); **10**, 1120 (1940); taken from *C. A.*, **34**, 1267^3 (1940), and **35**, 1333^9 (1941); E. Wiberg, A. Bolz and P. Buchheit, *Z. anorg. Chem.*, **256**, footnote 5, p. 287, and footnote 41, p. 301 (1948).

TABLE III

COMPARISON OF THE PROPERTIES OF AMMONIA–BORANE WITH THOSE OF THE "DIAMMONIATE OF DIBORANE"

H_3NBH_3	$[H_3NBH_2NH_3][BH_4]$
(1) Crystalline material which gives a definite X-ray powder pattern	(1) Apparently amorphous material which gives no X-ray powder pattern[a]
(2) Soluble in ether	(2) Insoluble in ether
(3) Mol. wt. in ammonia, ether and dioxane corresponds to above formula	(3) Mol. wt. in ammonia corresponds to above formula
(4) Not readily hydrolyzed by distilled water	(4) Readily hydrolyzed by distilled water
(5) Slowly splits out hydrogen at room temp.	(5) Stable to 80°. Splits out hydrogen very very slowly at room temp.
(6) Reacts with sodium in ammonia to produce $\frac{{}^1/_2H_2}{H_3NBH_3}$	(6) Reacts with sodium in ammonia to produce $\frac{{}^1/H_2}{[H_3NBH_2NH_3][BH_4]}$

[a] Note added in proof: A distinctive crystalline form, the "diammoniate," has been prepared recently and is now under study.

compare them with earlier procedures which have led invariably to the "diammoniate of diborane."

Other work in this Laboratory[7] indicated that the product obtained by the *solid-phase* decomposition of ammonium borohydride was the "diammoniate of diborane," rather than ammonia–borane. In an earlier study Schlesinger and Burg[6] added gaseous ammonia to *solid* $(CH_3)_2OBH_3$ in an attempt to form H_3NBH_3, but the "diammoniate" was produced instead. In the normal procedure for preparing the "diammoniate," *solid* ammonia picks up diborane. All the foregoing processes which produce the "diammoniate" have the reaction of a solid phase in the absence of solvent as a common factor. The principal feature which differentiates the process for preparing ammonia–borane is the presence of ether during the reaction between an ammonium salt and a borohydride salt. The role of a solvent in moderating or altering the course of the reaction is not unusual. The reaction of hydrazine and diborane[10] and the reaction of PCl_3 and $LiAlH_4$[11] are both strongly dependent on the presence of ether as a solvent. Although reaction takes place in the absence of solvent, products differ from those obtained in ether.

The role of ether in the present process is reasonably certain, but its mode of action is still unknown. The facts can be interpreted in terms of the following hypothesis. If the decomposition of ammonium borohydride to the "diammoniate of diborane" can be considered to take place through either of the reaction schemes

$$2NH_4BH_4 \longrightarrow 2H_3NBH_3 + 2H_2$$
$$2H_3NBH_3 \longrightarrow [BH_2(NH_3)_2][BH_4]$$

or

$$NH_4BH_4 \longrightarrow H_3NBH_3 + H_2$$
$$H_3NBH_3 + NH_4BH_4 \longrightarrow [BH_2(NH_3)_2][BH_4] + H_2$$

then the role of ether in an ether slurry of an ammonium salt and a borohydride salt might be twofold. The ether might serve as a heat transfer medium preventing localized heating at reaction sites by dissipating the heat of the initial exothermic reaction between protonic and hydridic hydrogen. Therefore, the possibility of ammonia–borane possessing the energy of activation required for conversion to the "diammoniate of diborane" is diminished. Secondly, ether is a solvent for ammonia–borane. Therefore, ammonia–borane is removed from the reaction sites as soon as it is formed and the possibility of participating in conversion to the "diammoniate" is diminished due to dilution. These reasons are consistent with the observation that the reaction of ammonium and borohydride salts in an ether slurry produces ammonia–borane, while the decomposition of solid ammonium borohydride does not produce ammonia–borane.[7]

The Synthesis of Ammonia–Borane from Dimethyl Ether–Borane.—The foregoing discussion suggests that by using an appropriate modification of the procedure of Schlesinger and Burg,[6] ammonia–borane can be synthesized from dimethyl ether–borane. This was confirmed. Ammonia, in large excess, reacted with a solution of dimethyl ether–borane in liquid dimethyl ether at − 78°. Yields of ammonia–borane were about 70% of theoretical.

$$(CH_3)_2OBH_3 + NH_3 \longrightarrow H_3NBH_3 + (CH_3)_2O$$

Experimental

a. Materials.—1. Ammonia—commercial tank NH_3 was dried and stored over sodium metal in the vacuum system. 2. Ammonium chloride and ammonium sulfate—Reagent grade NH_4Cl and $(NH_4)_2SO_4$ were dried at 80° for at least 2 hr. prior to their introduction into the vacuum system.

3. Diborane—B_2H_6 was prepared and purified by standard techniques.[2] 4. Dimethyl ether—Commercial tank $(CH_3)_2O$ was dried and stored over calcium hydride in the vacuum system. 5. Diethyl ether—reagent grade $(C_2H_5)_2O$ was dried and stored over lithium aluminum hydride in the vacuum system. 6. Lithium borohydride and sodium borohydride—$LiBH_4$ and $NaBH_4$ (supplied by Metal Hydrides, Inc.) were purified by extraction with liquid ammonia at −65 to −75°. The extractor was similar to the vacuum-line filter described by Schultz[12] and was operated in the same manner. The bulk of the solvent ammonia was removed by sublimation as the system was slowly warmed from −78 to −40°. Remaining traces of ammonia were pumped away at room temperature. 7. "Diammoniate of diborane"—$[H_2B(NH_3)_2][BH_4]$ was prepared according to standard techniques.[4]

b. The Reaction between the "Diammoniate of Diborane" and Ammonium Chloride in an Ether Slurry.—The apparatus in which this work was carried out has been described elsewhere. All the stopcocks and joints in the system which had to be rotated were greased with Dow-

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(10) H. I. Schlesinger and M. J. Steindler, THIS JOURNAL, **75**, 756 (1953).

(11) J. T. Yoke, III, G. Kodama and R. W. Parry, to be published.

(12) D. R. Schultz, Ph.D. Dissertation, University of Michigan, 1954; R. W. Parry, D. R. Schultz and P. R. Girardot, THIS JOURNAL, **80**, 1 (1958).

Corning High Vacuum Grease. All the joints which did not have to be rotated were sealed with DeKhotinsky cement.

In a typical run, "diammoniate of diborane" was prepared and isolated in the reaction tube of the apparatus. The system was then filled with dry nitrogen and the tube was removed from the line; the reactor tube was charged with a known amount of ammonium chloride and returned to its original position as rapidly as possible. The vacuum system was evacuated and ether was distilled into the reaction tube. A small quantity of anhydrous ammonia was distilled in also. Hydrogen evolution was initiated by maintaining the reaction tube at about room temperature and stirring its contents vigorously. In order to prevent the condensation of ether in other parts of the system, the temperature of the reactor tube was actually maintained at just below room temperature by immersing it in a beaker of water.[13] The extent of reaction was determined at various intervals by quenching the reaction tube in liquid nitrogen and measuring volumetrically the quantity of hydrogen produced. Upon completion of the reaction the contents of the reactor tube were filtered and extracted with ether. The filtration and extraction were carried out at about −75° in order to take advantage of the negative temperature coefficient of solubility of ammonia–borane. Crystalline ammonia–borane was obtained from the filtrate by distilling away the ether as the receiver tube was warmed from −70° to −20°.

c. **The Reaction between Lithium Borohydride and Ammonium Salts in an Ether Slurry.**—The reaction with ammonium chloride was carried out in the apparatus mentioned above. The reaction with ammonium sulfate was carried out on a ten-fold larger scale, and it was therefore necessary to modify the apparatus slightly. In this case the reactor consisted of a 100-ml. round-bottom flask which was fitted with a standard taper 24/40 drip-tip. This reactor flask was charged with a magnetic stirring bar and weighed quantities of lithium borohydride and ammonium sulfate in the protective atmosphere of the "dry box." The flask was then transferred to the vacuum system as rapidly as possible. After thoroughly evacuating the system, anhydrous ether was distilled into the flask. Hydrogen evolution was initiated by maintaining the flask at about room temperature and stirring its contents vigorously. The extent of reaction was followed either by measuring, at various intervals, the quantity of hydrogen produced or by qualitatively observing the rate of hydrogen evolution through a mercury bubbler. After the theoretical amount of hydrogen had been produced, or after the rate of hydrogen evolution had decreased appreciably, the contents of the flask were filtered and extracted with ether at −75°. Crystalline ammonia–borane was isolated by distilling the bulk of the ether from the filtrate as it was warmed slowly from −70 to −40°. The remaining traces of ether were pumped from the solid as it was warmed slowly from −40 to −20°. For further purification, samples of solid ammonia–borane were placed on the frit of the vacuum-line filter and re-extracted with ether at −75°.

d. **The Preparation of Ammonia–Borane from Dimethyl Ether.**—In a typical run a 6 millimole sample of diborane was condensed upon a 2-ml. quantity of frozen dimethyl ether in a reaction tube which was connected to a vacuum line filtering device. The tube was then warmed to −78° and thermostated for 0.5 hr. Then the tube was immersed in liquid nitrogen and 3 ml. of ammonia was condensed directly on top of the frozen dimethyl ether, dimethyl ether–borane system. The system was thermostated at −78° for 2 hr. Then the excess dimethyl ether and ammonia were distilled away at −78°, leaving behind a white solid. This solid was extracted with 20 ml. of diethyl ether at −75°. The ether was removed, as described above, from the extract. Pure ammonia–borane was left behind.[14]

e. **The Reaction between Ammonia–Borane and Sodium in Liquid Ammonia.**—Through the use of standard techniques,[4] a 0.96 mmole sample of ammonia–borane was allowed to react with a large excess of sodium in about 5 ml. of liquid ammonia at −78°. The reaction produced 0.96 H/H_3NBH_3 in 16 hr. Just a trace quantity of hydrogen was produced within the next 10 hr. at −78°.

f. **Molecular Weight Determinations.**—The determination of the molecular weight of ammonia–borane by vapor pressure depression in ammonia and in ether[2] was carried out in equipment similar to that described by Parry, Kodama and Schultz,[8] except that a mercury-filled differential manometer was used. The determination of the molecular weight of ammonia–borane in dioxane,[2] by freezing point depression, was carried out in a Beckmann-type freezing point apparatus.

g. **Analytical.**—Chemical and X-ray methods of analysis have been described elsewhere.[1]

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.

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[13] All the reactions in this investigation which are described as carried out at room temperature were actually carried out at slightly below room temperature through this technique.

[14] If dimethyl ether is used in the extraction, the extracted material is not pure ammonia–borane, some $(H_3NBH_3)_n$ is present.

ANN ARBOR, MICH.

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

Chemical Evidence for the Structure of the "Diammoniate of Diborane." III. The Reactions of Borohydride Salts with Lithium Halides and Aluminum Chloride

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

RECEIVED NOVEMBER 3, 1956

It is shown that LiBr, LiCl and $LiBH_4$ bring about *slow* evolution of H_2 from a diethyl ether suspension of $B_2H_6 \cdot 2NH_3$. Results are interpreted in terms of polarization of the borohydride by the Li(I). A diethyl ether solution of $AlCl_3$ will react with an ether suspension of $B_2H_6 \cdot 2NH_3$ to give hydride–halide interchange.

One of the important pieces of evidence pertinent to the structure of the "diammoniate of diborane," empirically $B_2H_6 \cdot 2NH_4$, is the unstable nature of ammonium borohydride. Such instability justifies the reaction between the "diammoniate" and ammonium salts if a borohydride ion is assumed in the formula. By the same token, the reported absence of reaction between the "diammoniate" and sodium borohydride argues against the presence of an ammonium ion in the "diammoniate."[1] In connection with reactions of the latter type, an observation of Schaeffer[2] to the effect that $LiBH_4$ in ether reacted very slowly with an ether slurry of "diammoniate" to give off hydrogen seemed to merit additional study.

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

[2] G. W. Schaeffer, private communication.