

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

(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.

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/H₂NBH₃ 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 ether² 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.

(14) If dimethyl ether is used in the extraction, the extracted material is not pure ammonia-borane, some (H₂NBH₃)_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

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It is shown that LiBr, LiCl and LiBH₄ bring about *slow* evolution of H₂ from a diethyl ether suspension of B₂H₆·2NH₃. Results are interpreted in terms of polarization of the borohydride by the Li(I). A diethyl ether solution of AlCl₃ will react with an ether suspension of B₂H₆·2NH₃ to give hydride-halide interchange.

One of the important pieces of evidence pertinent to the structure of the "diammoniate of diborane," empirically B₂H₆·2NH₃, 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 Schaeffer² to the effect that LiBH₄ in ether reacted very slowly with an ether slurry of "diammoniate" to give off hydrogen seemed to merit additional study.

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

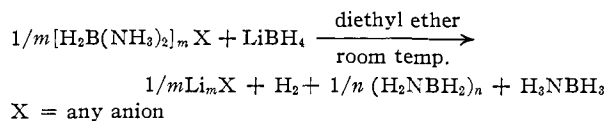
(2) G. W. Schaeffer, private communication.

The Decomposition of the "Diammoniate of Diborane" in the Presence of Lithium Salts.—

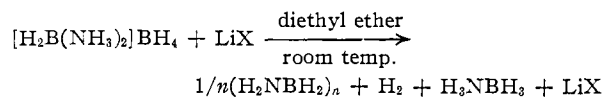
One of the interesting features of the "diammoniate of diborane" is the fact that it is described as relatively stable to 80°,³ even though its most likely structure is $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$. The chromium salt $[\text{Cr}(\text{NH}_3)_6]\text{BH}_4$ is stable up to 60°.⁴ The stability of both compounds can be related to the relatively low polarizing power of the cation since the complex chromium cation is sufficiently large to compensate for its high charge while the dihydridodiammineboron(III) cation is of intermediate size and is only singly charged.

It is well known that the proton sensitivity of the borohydride ion increases with the polarizing character of its associated cation. Thus, potassium borohydride can be crystallized from the protonic solvent water; but lithium borohydride reacts vigorously with the protons of water; and aluminum borohydride reacts explosively with water.

From arguments of this type one might rationalize hydrogen evolution from the ether slurry of the "diammoniate" and lithium borohydride on the basis of a reaction between the proton-sensitive borohydride ion in lithium borohydride and the protonic hydrogens attached to the nitrogens in the dihydridodiammineboron(III) cation. In other words, the lithium(I) influences the borohydride to such an extent that its hydridic hydrogens react with the protons of the cation, *e.g.*



If the foregoing arguments are valid, the "diammoniate of diborane" should evolve hydrogen in the presence of any lithium salt, since the presence of the Li(I) would increase the proton sensitivity of the borohydride ion in the "diammoniate."



An experimental study proved to be in accord with this supposition. It was found that the addition of a lithium halide to an ether slurry to the "diammoniate of diborane" caused decomposition of the "diammoniate." Of the several experiments carried out, the most significant were those in which it was first established that a given sample of the "diammoniate" is only slightly decomposed upon slurrying in ether at room temperature but that upon addition of a lithium halide to the slurry, the rate of decomposition, evidenced by hydrogen evolution, is increased very markedly. The results of such experiments are summarized in Fig. 1.

To avoid complications in the preceding study, it was important to exclude, rigorously, protonic substances such as water or ammonia. Extreme precautions were taken in the drying and handling

(3) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p. 124.

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

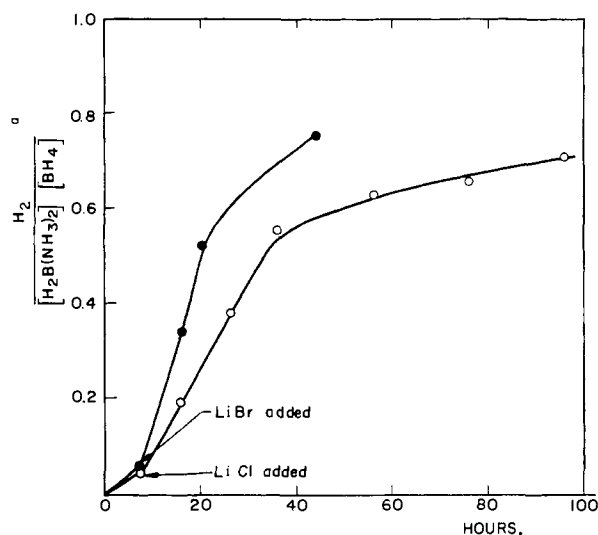


Fig. 1.—The decomposition of the "diammoniate of diborane" in the presence of a lithium halide. ^a In all the experiments about 7 ml. of ether, about 0.3 g. of lithium halide and about 2 mmoles of "diammoniate" were used.

of the lithium salts. That such precautions were successful in avoiding contamination is supported by the fact that ammonia-borane and hydrogen were produced in almost a one-to-one ratio as demanded by the equation above. If traces of water had been present, the ether soluble ammonia-borane would have formed an ether insoluble precipitate, thereby giving a much smaller yield of ammonia-borane.⁵

Since the "diammoniate" is quite insoluble in ether and since the lithium salts used are only slightly soluble in ether, the rate of decomposition of the "diammoniate" is probably dependent in part on the surface areas of the salts used. It seems probable, however, that the somewhat greater catalytic activity of lithium bromide as compared to lithium chloride is related to the greater solubility in ether of the former compound.

The Reactions of Borohydrides with Anhydrous Aluminum Chloride in Diethyl Ether.—On the basis of the foregoing arguments and results it was thought that the strongly polarizing aluminum(III) ion of aluminum chloride would be more effective than the lithium(I) of a lithium halide in accelerating hydrogen evolution from $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$. However, contrary to the original expectation, the production of hydrogen was negligible when traces of water and ammonia were scrupulously avoided. Results of two representative runs are summarized in Table I.

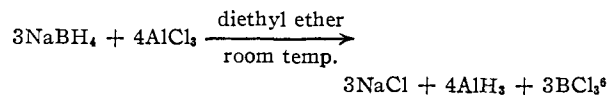
TABLE I
THE REACTION BETWEEN THE "DIAMMONIATE OF DI-BORANE" AND ALUMINUM CHLORIDE IN ETHER

Run	$\text{H}_2\text{B}(\text{NH}_3)_2\text{BH}_4$, mmoles	Ether, ml.	AlCl_3 , mmoles	Time, hr.	$\frac{\text{H}_2}{[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4}$
1	1.93	10	ca. 6	0.3	0.09
				12	.11
2	2.88	5	ca. 10	0.3	.01
				36	.05

(5) S. G. Shore and R. W. Parry, *ibid.*, **80**, 8 (1958).

In each run reaction took place as soon as the aluminum chloride was added to the ether slurry and within 20 minutes all of the ether insoluble "diammoniate" had been converted into ether soluble compounds. The resulting clear solution proved to be unstable, for within 8 hr. the presence of a fine gelatinous precipitate became noticeable. The precipitate, which was isolated by filtration, proved to be amorphous (determined by X-ray powder techniques); it contained only aluminum, hydrogen and ether and was assumed to be aluminum hydride etherate. An X-ray powder examination of the solid obtained by removal of ether from the filtrate revealed the absence of familiar materials such as ammonium chloride, $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{Cl}^1$ and ammonia-borane. It was possible, however, to sublime with difficulty from the residue a small amount of solid boron trichloride etherate.

The experimental facts strongly suggest that the borohydride ion of the "diammoniate of diborane" was destroyed through hydride-chloride interchange. If this were the case, a simpler borohydride such as sodium borohydride might act similarly under comparable conditions.



Schlesinger and co-workers⁷ already have established that the high temperature reaction between solid sodium borohydride and dry aluminum chloride produces aluminum borohydride, but the experimental conditions of the present study were completely different. The more significant differences were (a) the use of an ether slurry, (b) reaction was carried out at room temperature and (c) the rigorous exclusion of all traces of moisture from the starting materials and the reaction system.

In a typical experimental test a five-to-one molar excess of aluminum chloride was added to an ether slurry of sodium borohydride at room temperature. The reaction mixture was stirred for about 38 hr. to ensure complete reaction; only a trace of hydrogen was evolved during this period. The precipitate from the reaction mixture contained sodium chloride and polymerized aluminum hydride etherate. The residue obtained by evaporating ether from the filtrate contained boron trichloride etherate, which was removed for identification by vacuum sublimation at room temperature. The results strongly favor the equation shown above.

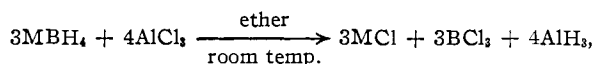
Discussion

Although the lithium halides followed the reaction pattern which was expected from theoretical arguments, the reaction of aluminum chloride was anomalous in the sense that little hydrogen was produced; hydride-chloride exchange took place much more rapidly than hydrogen evolution. The strong solvation of aluminum chloride probably plays an important role in determining the

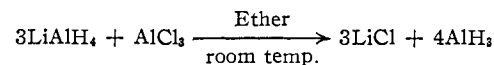
(6) AlH_3 , AlCl_3 and BCl_3 are actually etherates, but for the sake of simplicity the ether is omitted from the formulas.

(7) H. I. Schlesinger, H. C. Brown and E. K. Hyde, *THIS JOURNAL*, **75**, 209 (1953).

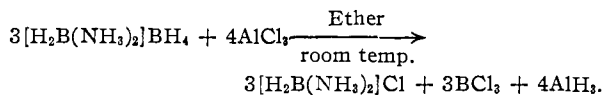
ultimate course of the reaction



which simply parallels the well-known reaction between lithium aluminum hydride and aluminum chloride.⁸

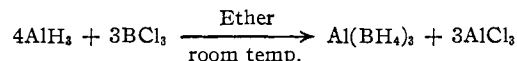


Thus for the reaction involving the "diammoniate of diborane" one would expect



Further exchange between the chloride of AlCl_3 and the hydridic hydrogens in the complex cation would convert the cation to BCl_3 . The absence of patterns for $\text{H}_2\text{B}(\text{NH}_3)_2\text{Cl}$ and NH_4Cl (determined by X-ray powder techniques) in the solid residue indicates that exchange involving the cation also occurred.

Finholt, Bond and Schlesinger⁸ have shown that the following reaction takes place



Thus the results of this investigation indicate that the reaction may be reversed if a large excess of AlCl_3 is used.

Experimental

a. Materials.—1. Diethyl ether and sodium borohydride—the purification of these substances is described elsewhere.⁹ 2. Aluminum chloride—the preparation of extremely pure and dry AlCl_3 was basic to this investigation. The unusual precautions taken are described in some detail because of their importance to the result obtained.

Reagent grade aluminum chloride was placed in a 25 mm. tube attached horizontally to one arm of a U-trap; the other arm of the U was fastened to a small three arm manifold, each arm of which contained a small glass bulb. The entire apparatus could be connected to the vacuum system by means of a Standard Taper joint and stopcock combination which was sealed to the top of the manifold. Two thin glass wool plugs in the horizontal tube separated AlCl_3 from the U-trap. After insertion of the AlCl_3 , the horizontal tube was sealed. By pumping on the system continuously and applying a yellow flame to the tube, pure aluminum chloride was sublimed past the thin glass wool plugs into the U-trap which was immersed in ice-water. After the AlCl_3 condensed in the trap, the horizontal tube containing the residues was sealed off from the U-trap.

About 8 ml. of anhydrous ether was vacuum distilled into the U-trap, which was then cooled to about -78° . The stopcock was closed and the apparatus was removed from the vacuum system. The U-trap was warmed slowly to room temperature and through appropriate tipping of the apparatus the ether was allowed to dissolve small portions of aluminum chloride at a time. Care was taken to prevent the vigorous solution of aluminum chloride since this can result in ether cleavage. After the aluminum chloride was dissolved completely, the apparatus was tilted so that a portion of the solution was poured into one of the bulbs. The solution in the bulb and the solution remaining in the U-trap were then frozen and the bulb was sealed off. In the same manner the remaining bulbs were filled and sealed off, one at a time. The amount of aluminum chloride in each of the bulbs was determined, approximately, by analyzing the contents of one of the bulbs.

3. Lithium chloride and lithium bromide— LiCl and LiBr are very hygroscopic materials. In order to ensure the

(8) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *ibid.*, **69**, 1199 (1947).

complete removal of all traces of water, they were first heated in an oven for at least 20 hr. at a temperature of at least 150°. They were then transferred to the vacuum system and were maintained at 150° *in vacuo* for 12 hr.

b. **The Decomposition of the "Diammoniate of Diborane" in the Presence of a Lithium Halide.**—The apparatus in which these experiments were carried out consisted of a conventional 25 mm. diameter reaction tube to which a side vessel was attached through a 14/35 $\frac{1}{8}$ joint. When desired, solids contained in the side vessel could be added to the reactor tube by rotating the side vessel around the standard joint. All the stopcocks and joints which had to be rotated were greased with Dow-Corning High Vacuum Grease. All the joints which did not have to be rotated were sealed with DeKhotinsky Cement. Initially, the side arm containing the lithium halide was placed in an oven and a standard taper cap was put in its place on the apparatus. The system was thoroughly evacuated and the "diammoniate of diborane" was prepared and isolated in the reactor tube, according to the standard procedure.⁹ Since the purpose of these experiments was to cause interaction between the protonic and hydridic hydrogens of the "diammoniate," great care was taken to remove all traces of excess ammonia from the system. After the apparent removal of all of the ammonia, the solid "diammoniate" was pumped on for an additional 12 hr. at room temperature. Then dry nitrogen gas was flushed through the system at atmospheric pressure and the tube containing the lithium halide was transferred, while it was still warm, from the oven to its position on the apparatus. The system was then re-evacuated and the halide was dried at 150° under vacuum for 12 hr.; anhydrous ether now was vacuum distilled into the reactor tube. Through appropriate manipulation of the apparatus, the lithium halide was dropped upon the "diammoniate"-ether slurry. The decomposition was carried out under vigorous stirring just below room temperature.⁵ The rate of decomposition was followed by measuring the amount of hydrogen given off. After appreciable decomposition had taken place, the solution was filtered at -75°. Ether soluble ammonia-borane was isolated by vacuum distilling ether from the filtrate.

c. **The Reactions of Borohydrides with Aluminum Chloride in Diethyl Ether.**—"Diammoniate of diborane" was prepared and isolated in the reactor tube. After the apparent removal of all the ammonia, the solid "diammoniate" was pumped on for an additional 12 hr. at room temperature. Then anhydrous ether was vacuum distilled into the reactor. Sublimed aluminum chloride in ether solution was contained in a bulb suspended above the ether slurry. By rotating the arm of a special bulb crusher, the glass bulb was crushed and its contents dripped into the ether slurry which was maintained at about room temperature. Details are given elsewhere.¹⁰ Immediate reaction ensued and with vigorous stirring all of the solid "diammoniate" disappeared within 20 minutes. After 8 hr. of continuous stirring at room temperature, a fine gelatinous precipitate, assumed to be polymerized aluminum hydride etherate (see below), appeared. The reactor tube was cooled to about

-70° and the bulk of the ether was distilled away as the reactor was warmed slowly from -70 to -40°. The remaining traces of ether were pumped away as the system was warmed to room temperature. It was possible to sublime, with difficulty at room temperature, small quantities of boron trichloride etherate *in vacuo* into a receiver tube for identification. The system was then flushed with dry nitrogen, and the reactor tube, containing the remaining residue after distillation and sublimation, was transferred as rapidly as possible to a vacuum filter such as the one depicted earlier.¹¹ The system was re-evacuated and 5 ml. of anhydrous ether was vacuum distilled in upon the residue, most of which dissolved at room temperature. The slurry was filtered and the precipitate of polymerized aluminum hydride etherate was extracted with ether at room temperature and removed from the system for identification.

The same procedure was employed for the reaction between sodium borohydride and aluminum chloride in ether, except that the sodium borohydride was added to the reactor tube in the protective atmosphere of a "dry box." The tube was then transferred to the vacuum system as rapidly as possible.

d. **Analytical.**—1. X-Ray powder analyses—reaction products were examined for the presence or absence of known crystalline materials such as ammonia-borane, ammonium chloride, dihydridodiammineboron(III) chloride and sodium chloride. The equipment and techniques are described elsewhere.¹

2. Chemical analyses—the products aluminum hydride etherate and boron trichloride etherate which were formed in the reactions involving aluminum chloride did not lend themselves to physical analyses and, because only small quantities of material could be isolated from the complex reaction mixtures, could not be identified by direct quantitative analysis. It was necessary to rely on observations of the characteristic properties of these compounds.

In this investigation it was shown that the fine gelatinous material which precipitated slowly from ether solution was amorphous. Qualitative analysis showed that it contained only aluminum and hydridic hydrogen. It is known that aluminum hydride etherate in ether solution slowly precipitates, forming a material of indefinite composition.⁸

The product which was sublimed *in vacuo* from the aluminum chloride reaction mixtures slowly split out ethyl chloride and melted at about 55°. Qualitative analysis showed that it contained boron and chlorine. It is known that boron trichloride etherate can be sublimed *in vacuo* at room temperature and that it slowly splits out ethyl chloride. It has a melting point of 56°.¹²

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, MICHIGAN

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

(10) S. G. Shore, Doctoral Dissertation, Univ. of Mich., Ann Arbor, 1956.

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

(12) E. Wiberg and W. Sutterlin, *Z. anorg. Chem.*, **202**, 22 (1931).

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

Chemical Evidence for the Structure of the "Diammoniate of Diborane." IV. The Reaction of Sodium with Lewis Acids in Liquid Ammonia

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

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The reactions between sodium and four Lewis acids in liquid ammonia HCN, H₃BO₃, CO₂ and B₂H₆ have been studied. The complexity of the system increases in the order given. The sensitivity of the B₂H₆-NH₃ system to experimental details is interpreted by appropriate molecular models.

Past investigations have demonstrated that the stoichiometry of the reaction of the "diammoniate of diborane" with sodium in liquid ammonia is

very sensitive to the conditions imposed. Only "diammoniate" which has been carefully prepared under a specific set of conditions will react with