

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.<sup>9</sup> 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.<sup>5</sup> 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.<sup>10</sup> 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.<sup>11</sup> 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.<sup>1</sup>

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.<sup>8</sup>

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°.<sup>12</sup>

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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, H<sub>2</sub>BO<sub>3</sub>, CO<sub>2</sub> and B<sub>2</sub>H<sub>6</sub> have been studied. The complexity of the system increases in the order given. The sensitivity of the B<sub>2</sub>H<sub>6</sub>-NH<sub>3</sub> 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

sodium in liquid ammonia to produce one equivalent of hydrogen per mole of diborane in a short period of time. A slow secondary process yields small quantities of additional hydrogen with time.<sup>1</sup> However, if the "diammoniate" has been "mis-treated," either through the rapid addition of diborane to ammonia or by maintaining an ammonia solution of carefully prepared "diammoniate" at relatively high temperatures near  $-40^{\circ}$ , then the resulting material has been shown to react with sodium to produce up to 1.3-1.4 equivalents of hydrogen per mole of diborane in a short period of time.<sup>1,2</sup> These observations contrast sharply with early observations in this Laboratory<sup>3</sup> in which a procedure that seemingly followed carefully the method of Schlesinger and Burg<sup>1</sup> did not yield much more than one-half of an equivalent of hydrogen per mole of diborane. Furthermore, it was observed that sodium was used up (blue color discharged) without further hydrogen evolution.

From these observations it is obvious that the ammonia-diborane-sodium reaction is very complex. In order to obtain a better understanding of the system, it was thought that a study of the generalized reaction between sodium and Lewis acids in liquid ammonia would be in order. The acids chosen in addition to diborane were hydrogen cyanide, boric acid and carbon dioxide.

### Experimental

**A. Materials.**—1. Ammonia—commercial tank  $\text{NH}_3$  was dried and stored over sodium metal in the vacuum system. 2. HCN—anhydrous HCN from laboratory stock was distilled in the vacuum system before use. 3. Boric acid—reagent grade  $\text{H}_3\text{BO}_3$  was dried for several hours at room temperature under high vacuum. 4. Carbon dioxide— $\text{CO}_2$  gas, obtained from Dry Ice, was dried by passing it several times through a trap packed with glass helices and cooled to  $-112^{\circ}$ . 5. Diborane— $\text{B}_2\text{H}_6$  was prepared by the reaction between  $\text{LiAlH}_4$  and excess  $\text{BF}_3$  etherate in ether solution. 6. Sodium—sealed, evacuated, thin-walled glass bulbs 1.5-2 cm. in diameter and containing 0.5-0.75 g. of sodium metal were prepared by standard techniques.<sup>4</sup>

**B. Procedures.**—A thin walled glass bulb containing sodium metal was placed in the reactor tube of the vacuum system. The system was evacuated and the solution of acid in ammonia was prepared (described below) in the tube. The bulb was then crushed *in vacuo* and the reaction with sodium was initiated.

1. **Hydrogen Cyanide.**—Hydrogen cyanide (2.04 mmoles) was distilled into the reaction tube. Excess ammonia (*ca.* 5 ml.) was condensed into the reactor. The reaction with excess sodium produced one equivalent of hydrogen per mole of hydrogen cyanide.

2. **Boric Acid.**—In a preliminary experiment the action of ammonia on boric acid was explored. About 5 ml. of ammonia was condensed upon a small, finely divided sample of boric acid and maintained at  $-45^{\circ}$  for 1.5 hr. Excess ammonia was distilled away at  $-78^{\circ}$ ; the final trace of ammonia was removed at room temperature. Analysis of the remaining solid indicated the formula  $\text{NH}_4\text{HB}_3\text{O}_7$ .

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

(2) W. L. Jolly, Univ. of Calif. Radiation Laboratory, Livermore Site, Livermore, Calif., Contract No. W-7405-eng-48, UCRL-4504, 1955.

(3) R. W. Parry, P. R. Girardot, *et al.*, "Final Report, Chemistry of Boron Hydrides and Related Hydrides," Univ. of Mich., Eng. Res. Inst., Project M966, U. S. Air Force, Contract AF 33(616)-S, E.O.R.-464, Br-1, 1952.

(4) A detailed description of experimental techniques and procedures is given elsewhere: S. G. Shore Doctoral Dissertation, Univ. of Mich., Ann Arbor, Mich., 1956.

$5/2\text{H}_2\text{O}$ . Calcd. for  $\text{NH}_4\text{HB}_3\text{O}_7 \cdot 5/2\text{H}_2\text{O}$ : N, 6.39; B, 19.73. Found: N, 6.40; B, 19.6.

Ammonia (*ca.* 5 ml.) was condensed upon a sample of boric acid (1.61 mmoles) and the system was maintained at  $-52^{\circ}$  for 2 hr. prior to the addition of sodium. Reaction with a large excess of sodium at  $-52^{\circ}$  produced 1.81 equivalents of hydrogen per mole of boric acid in 10 hr. A negligible quantity of hydrogen gas was produced within the next 10 hr. at  $-52^{\circ}$ . In order to avoid the possibility of secondary reactions, another experiment was carried out at a lower temperature. Ammonia (*ca.* 5 ml.) was condensed upon boric acid (1.87 mmoles) and the system was maintained at  $-64^{\circ}$  for 0.5 hr. prior to the addition of sodium. Reaction with a large excess of sodium at  $-64^{\circ}$  produced 1.74 equivalents of hydrogen per mole of boric acid in 18 hr. Further hydrogen evolution was negligible at this temperature.

3. **Carbon Dioxide in Ammonia.**—A known amount of carbon dioxide was condensed an inch or so above an excess of frozen ammonia which was at the bottom of the reaction tube, and the system was warmed from about  $-140$  to  $-80^{\circ}$  in a period of about 8 hr. In other experiments the positions of the ammonia and carbon dioxide were reversed. The excess ammonia was sublimed away at  $-78^{\circ}$  when the formation of ammonium carbamate was desired. Data are given in Table I.

A subtle point of experimental technique is emphasized in Table I. In run 1 ammonia in excess was added to solid carbon dioxide and allowed to melt. When the excess ammonia was sublimed away at  $-78^{\circ}$ , solid ammonium carbamate was isolated. Upon returning the ammonia to the solid and introducing sodium metal, reaction was relatively rapid.

In run 2 ammonia in excess was added to frozen carbon dioxide and in run 3 carbon dioxide was added to frozen ammonia in excess. In both cases the excess ammonia was never removed, so the solid carbamate was never really isolated. In both cases hydrogen evolution was very slow compared to run 1 in which the solid was isolated prior to reaction.

4. **Diborane in Ammonia.**—Since the nature of the product from the diborane-ammonia reaction is extremely sensitive to details of experimental procedures, it is necessary to describe first the simple, but specific, procedure for preparing pure "diammoniate of diborane." The effect of variations in this procedure will then be considered.

A thin film of ammonia was condensed along the walls and bottom of a cylindrical reactor tube of 25 mm. diameter. A band of diborane was then condensed from one to several inches above the ammonia and the entire reactor was warmed slowly from  $-140^{\circ}$  to about  $-80^{\circ}$  in a period of about 8 hr. During this time the diborane vaporized and added to the surface of the solid ammonia at a temperature near  $-120^{\circ}$ . Addition was evidenced by a marked decrease in the pressure of diborane in the system. Since the addition depends on the surface available, the ammonia was in excess by at least a four-to-one mole ratio. When the temperature of the system had reached  $-80^{\circ}$ , the ammonia was allowed to melt and run down the walls to the bottom of the reactor tube. The tube was then thermostated in a Dry Ice-isopropyl alcohol slush at  $-78^{\circ}$  and all of the excess ammonia was sublimed away, leaving behind solid "diammoniate of diborane." In most cases the exact amount of ammonia which was put in and removed from the reactor tube was known. In each such case it was found that ammonia and diborane had reacted in a two-to-one mole ratio. Ammonia was then returned to the system by condensing it, in rings, along the wall of the reactor tube. By allowing the ammonia rings to melt, any solid "diammoniate" on the walls was washed down to the bottom of the tube. As a preliminary experiment, "diammoniate," prepared and isolated in the foregoing fashion, was redissolved in liquid ammonia (*ca.* 5 ml.) and allowed to react with sodium ( $\text{Na}/\text{B}_2\text{H}_6 = 2$ ) at  $-78^{\circ}$ . In less than 1 hr. one equivalent of hydrogen per mole of diborane had been produced.

In a second study three variations in the above procedure were introduced: (1) the ring of diborane was condensed at least three inches above the frozen ammonia; (2) after the diborane had combined with the ammonia and the system had warmed to  $-78^{\circ}$ , the system was aged for an additional 5 to 8 hr. at  $-78^{\circ}$ ; (3) most important of all, the excess ammonia was never removed from the system prior to addi-

TABLE I  
THE REACTION OF AMMONIUM CARBAMATE WITH SODIUM IN LIQUID AMMONIA

Run <sup>a</sup>	Comments	CO <sub>2</sub> , mmoles	Na CO <sub>2</sub>	Reaction temp., °C.	Reaction time (cumulative), hr.	H Evolved (cumulative) CO <sub>2</sub>
1	Excess NH <sub>3</sub> was sublimed away to isolate NH <sub>4</sub> CO <sub>2</sub> NH <sub>2</sub> . Then the NH <sub>3</sub> was returned	2.57	10-15	-78	3	1.06
				-64	6	1.06
2	Excess NH <sub>3</sub> was never removed	1.03	10-15	-78	1	0.19
				-78	3	.48
				-78	7	.53
				-78	17	.58
				-78	39	.71
				-78	51	.86
				-78	75	.91
3	Excess NH <sub>3</sub> was never removed	24.2	1.01	-78	24	.35
				-78	48	.60
				-78	72	.78
				-78	96	.88
				-78	120	.89
				-64	126	.92
				-64	132	.95
-64	144	1.00				

<sup>a</sup> All reactions were carried out in about 5 ml. of solution.

tion of sodium. The reaction with sodium (Na/B<sub>2</sub>H<sub>6</sub> = 1.7) in 5 ml. of liquid ammonia at -78° produced 0.58 of an equivalent of hydrogen per mole of diborane in 1 hr. The total amount of hydrogen which was given off at the end of the second hour was 0.72 of an equivalent per mole of diborane. The slow rate of gas evolution in this case is reminiscent of the observation on the carbon dioxide-ammonia system.

In order to follow the evolution of hydrogen more carefully, the reactions were slowed down by using a 10-15-fold excess of sodium.<sup>5,6</sup> The new results are presented in Tables II and III. For "diammoniate" prepared according to the standard procedure one equivalent of hydrogen per B<sub>2</sub>H<sub>6</sub>·2NH<sub>3</sub> was liberated in about 3 hr. (Table II). For "diammoniate" prepared according to the modified procedure more than 30 hr. were required for liberation of one equivalent of hydrogen (Table III). If all three of the modifications in procedure were not carefully imposed, the results were erratic giving slow or rapid gas evolution unpredictably.

TABLE II  
THE REACTION OF THE "DIAMMONIATE OF DIBORANE" WITH SODIUM IN LIQUID AMMONIA

Run <sup>a</sup>	Comments	B <sub>2</sub> H <sub>6</sub> , mmoles	Reaction time (cumulative), hr.	H Evolved (cumulative) B <sub>2</sub> H <sub>6</sub>
1	In all cases NH <sub>3</sub> was removed to identify [H <sub>2</sub> B(NH <sub>3</sub> ) <sub>2</sub> ]-[BH <sub>4</sub> ]. The NH <sub>3</sub> was then returned	1.69	1	0.73
			2	0.89
			3	0.99
			16	1.00
2		1.90	3	0.97

<sup>a</sup> In all cases the ratio Na/B<sub>2</sub>H<sub>6</sub> was 10-15. Used about 5 ml. of solution at -78°.

All the above conditions which appear to be conducive to consistent results are designed to avoid localized heating effects. The effect of sudden warming was demonstrated in one particular experiment in which diborane had been apparently taken up by ammonia, but the temperature of

(5) The stability of a sodium-ammonia solution increases with increasing concentration of alkali metal,<sup>11</sup> which indicates a decrease in the reducing action of the dissolved metal. The slowing of the reaction by using a large excess of sodium probably is due to the properties of the concentrated solution and to the fact that reaction could be initiated at a slightly lower temperature in the lower melting system.

(6) C. A. Kraus, THIS JOURNAL, **43**, 749 (1921); W. C. Johnson and A. W. Meyer, *ibid.*, **54**, 3624 (1932); J. F. Dewald and G. Lepoutre, *ibid.*, **76**, 3369 (1954).

TABLE III  
THE REACTION OF SODIUM WITH DIBORANE-AMMONIA SYSTEMS FROM WHICH AMMONIA WAS NEVER REMOVED

Run <sup>a</sup>	Height of B <sub>2</sub> H <sub>6</sub> above NH <sub>3</sub> , in.	Time system was aged at -78° after B <sub>2</sub> H <sub>6</sub> had been taken up by NH <sub>3</sub>	B <sub>2</sub> H <sub>6</sub> , mmoles	Reaction time (cumulative), hr.	H Evolved (cumulative) B <sub>2</sub> H <sub>6</sub>
1	3	8	2.02	1	0.43
				2	.51
				12	.63
				21	.71
				33	.72
2	3	8	2.02	1	.66
				3	.76
				7	.82
				17	.90
				41	.96
3	6	6	1.21	1	0.71
				3	.82
				7	.87
				20	.93
4	5	8	1.40	1	0.72
				3	.80
				7	.87
				16	.92

<sup>a</sup> In all cases the ratio Na/B<sub>2</sub>H<sub>6</sub> was 10-15. Used about 5 ml. of solution at -78°.

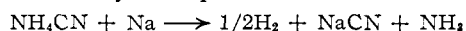
the system had not been above -100°; upon suddenly thermostating this system at -78°, a vigorous reaction occurred during which solid products were scattered throughout the reactor. This observation plus the slow evolution of hydrogen in the reaction with sodium suggests that the mere taking up of diborane by ammonia, if heating effects are carefully avoided, does not necessarily result in the formation of the "diammoniate of diborane."

The condition that diborane be condensed several inches above the ammonia facilitates gas-phase addition of diborane

and avoids or lessens the possibility of liquid diborane coming in contact with ammonia to cause localized heating. The aging process at  $-78^\circ$ , once the diborane has been added to solid ammonia, maintains the system at just below its freezing point ( $-77.7^\circ$ ), where ammonia has a vapor pressure of about 45 mm. Under such circumstances the slow solvation or solution of adsorbed diborane can take place with the heat evolved being properly dissipated so that the possibility of bond rupture to form the "diammoniate" is diminished. Once the system is properly aged in this manner, it apparently can become liquid without conversion to the "diammoniate" taking place. However, if the system is not aged, inconsistent results in the reaction with sodium are obtained.

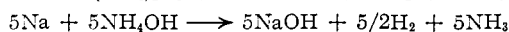
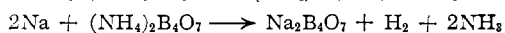
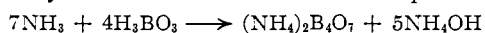
### Discussion

**A. The Behavior of Hydrogen Cyanide, Boric Acid and Carbon Dioxide with Sodium in Liquid Ammonia.**—Hydrogen cyanide reacts with ammonia to form ammonium cyanide. The reaction with sodium produces one equivalent of hydrogen per mole of cyanide, in accord with an earlier study,<sup>7</sup> and may be expressed as



This is a typical<sup>8</sup> result for ammonium salts in that one equivalent of hydrogen is liberated per equivalent of ammonium ion.

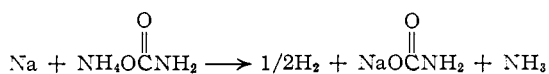
The observations from the boric acid-ammonia-sodium system are consistent with the equations



The above equations indicate that 1.75 equivalents of hydrogen should be liberated for each mole of boric acid used ( $7\text{H}/4\text{H}_3\text{BO}_3$ ). The experimental ratios of 1.82 and 1.74 are in good agreement with the demands of the above reaction sequence.

The observations from the carbon dioxide-ammonia-sodium system show a pronounced dependence upon experimental details. Such relationships are apparent in observations of earlier workers.<sup>9,10</sup>

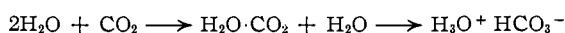
Carbon dioxide is normally assumed to react readily with ammonia to form ammonium carbamate. The reaction with sodium has been written<sup>9</sup> as



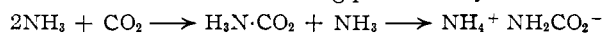
On the other hand, it has been found that if ammonia and carbon dioxide are thoroughly dried, not the faintest sign of interaction occurs, even after the gases have been in contact with each other for 24 hr. at room temperature.<sup>10,11</sup> Since the experiments of the present investigation were carried out under anhydrous conditions, the very slow hydrogen evolution in runs 2 and 3 of Table I suggests that incomplete reaction to form ammonium carbamate had occurred at the time that sodium was added to the ammonia solutions. Rengade,<sup>9</sup> who first studied this system, also noted the very slow evolution of hydrogen from a sodium-

ammonia solution into which he introduced carbon dioxide under anhydrous conditions. He assumed that ammonium carbamate had formed but did not react since it is only slightly soluble in ammonia. However, his explanation seems to be inapplicable here since once the carbamate is isolated as the solid (run 1), it reacts relatively rapidly with sodium in ammonia, even though its solubility is low.

Although the nature of carbon dioxide in ammonia is unknown, it could well be analogous to carbon dioxide in water. It has been reported that for the most part carbon dioxide is simply dissolved in water. According to Mills and Urey,<sup>12</sup> only about 1% is hydrated. Furthermore, it is well known that the reaction between water and carbon dioxide is not instantaneous.<sup>12</sup> The rate of hydration is dependent on catalysts which affect the pH of the solution. From available information,<sup>12</sup> one may represent the formation of carbonic acid as



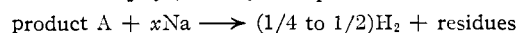
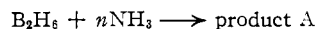
in which the slow step is considered to be hydration. Similarly then, in the absence of catalysts, it is conceivable that carbon dioxide may be simply dissolved in liquid ammonia, with conversion to ammonium carbamate taking place slowly.



The experimental observation that removal of excess ammonia from the carbon dioxide-ammonia system seems to facilitate ammonium carbamate formation (run 1) might be attributed to the concentration of trace quantities of catalytic material such as water. Rengade<sup>9</sup> found it necessary to remove excess ammonia to be certain that the reaction with sodium would take place properly, although he did not identify solvent removal as the important variable in his work.

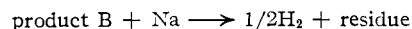
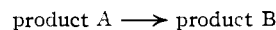
**B. Reactions of the System Diborane-Ammonia-Sodium.**—Observations from this system can be summarized under three headings:

Case 1:



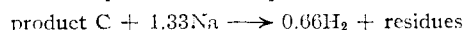
Special conditions for the formation of "product A" are: (a) special provisions taken to prevent localized overheating (see experimental modifications of preparative procedure); (b) excess ammonia never removed from the system.

Case 2:



The condition for conversion of "product A" to "product B" appears to be the removal of excess ammonia at  $-78^\circ$ ; solid B is left behind. The reaction of "product B" with sodium in liquid ammonia is more rapid than the reaction of "product A."

Case 3:



The conditions for the preparation of "product C" are: (a) maintaining "product B" near  $-40^\circ$

(12) G. A. Mills and H. C. Urey, *ibid.*, **62**, 1019 (1940).

(7) H. H. Frank and C. Freitag, *Z. angew. Chem.*, **39**, 1430 (1926).

(8) G. W. Watt, *Chem. Revs.*, **46**, 289 (1950).

(9) E. Rengade, *Bull. soc. chim., Paris*, **31**, 565 (1904).

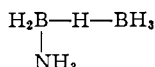
(10) R. E. Hughes and F. Soddy, *Chem. News*, **69**, 138 (1894).

(11) In the same way, a dry mixture of HCl and NH<sub>3</sub> is slow to form solid NH<sub>4</sub>Cl: H. B. Baker, *J. Chem. Soc.*, **73**, 422 (1898); W. H. Rodebush and J. C. Michalek, *THIS JOURNAL*, **51**, 748 (1929).

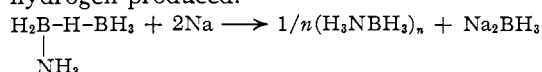
for 20 or more hours; (b) or allowing diborane to react rapidly with ammonia.<sup>2</sup> The reaction of "product C" with sodium in ammonia is more rapid than the reaction of "product A."

It is believed that the initial slow, low temperature addition of diborane results in the adsorption of diborane on the surface of solid ammonia without cleavage of the hydrogen-bridged bonds in diborane. Evidence for this hypothesis is offered by the fact that in one experiment after the initial low temperature addition of diborane to ammonia below  $-100^\circ$  (indicated by decrease in pressure to essentially zero mm.), the sudden raising of the temperature to  $-78^\circ$  caused a violent reaction to take place. White solid was scattered throughout the system. Furthermore, evidence is offered in the observations of Schaeffer and co-workers<sup>13</sup> (confirmed in this laboratory), who report that upon the addition of diborane to ammonia, if the system is warmed from  $-140$  to  $-80^\circ$  in 4 hr. instead of 8 hr. as in this investigation, it is then necessary to age the system at  $-78^\circ$  for at least an additional 2 hr.; otherwise it is possible to distil small quantities of diborane from the system.

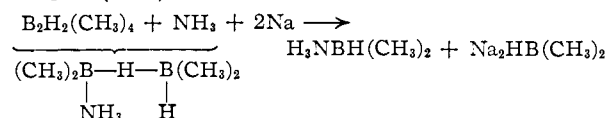
After the initial low temperature adsorption of diborane by ammonia, it is believed that the aging process at  $-78^\circ$  permits slow solvation or solution without the rupture of both of the hydrogen-bridged bonds. One attractive possibility for an intermediate would be a compound with only one hydrogen bridged bond



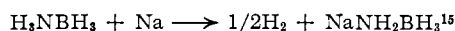
This structure is suggested for at least part of "product A." Such a model could be used to rationalize the earlier observation in this Laboratory<sup>3</sup> that in the reaction with sodium the equivalents of sodium used up exceeded the equivalents of hydrogen produced.



Such a reaction would be analogous to that by which Burg and Campbell<sup>14</sup> prepared the base  $\text{Na}_2\text{BH}(\text{CH}_3)_2$ .



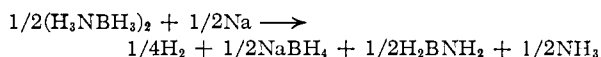
The volatility and comparatively high stability of  $\text{H}_3\text{NBH}(\text{CH}_3)_2$  permitted its removal by Burg and Campbell and the isolation of  $\text{Na}_2\text{HB}(\text{CH}_3)_2$ . The low volatility of  $(\text{H}_3\text{NBH}_3)_n$ , either monomer, dimer, or polymer, made its removal by sublimation impossible in this study. The initial reaction of "product A" with sodium to produce about one-half an equivalent of hydrogen per mole of diborane originally used could well arise from the reaction of  $\text{H}_3\text{NBH}_3$  and/or  $(\text{H}_3\text{NBH}_3)_2$  with sodium in the conventional fashion



(13) G. W. Schaeffer, M. D. Adams and F. J. Koenig, *THIS JOURNAL*, **78**, 725 (1956).

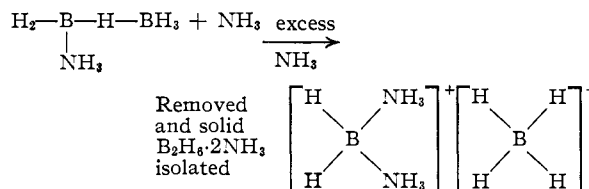
(14) A. B. Burg and G. W. Campbell, Jr., *ibid.*, **74**, 3744 (1952).

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

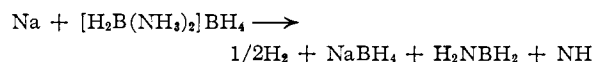


A combination of the above two processes would produce between one-half and one equivalent for each mole of diborane originally used. Such values were found experimentally.

It is suggested that "product A" undergoes further reaction with  $\text{NH}_3$  when excess ammonia is removed.



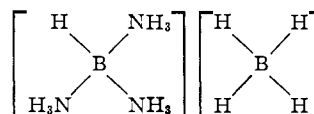
and that "product B" is the "diammoniate of diborane,"  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BH}_4$ , the structure of which has been discussed in the previous papers of this series.<sup>16</sup> Its reaction with sodium in ammonia is represented as



The role of solvent removal in the formation of ammonium carbamate from ammonia and carbon dioxide already has been noted and tentatively attributed to the concentration of trace quantities of a catalyst; water or hydrolysis products are possibilities. A similar explanation might be invoked in the present situation, especially since traces of water, or hydrolysis products, cause ammonia-borane to precipitate from ether solution empirically as  $(\text{H}_3\text{NBH}_3)_n$ .<sup>15</sup> It should be emphasized, however, that if such substances are truly responsible for the conversion, then only a very minute quantity is sufficient for catalysis, because the experiments with carbon dioxide and diborane were carried out under anhydrous conditions. None the less the nuclear magnetic resonance experiments of Ogg<sup>17</sup> show that unless extreme efforts are made to dry ammonia systems, the liquid contains sufficient water to affect, markedly, the NMR spectrum of ammonia. Recent observations in this Laboratory indicate that ammonia which was handled by methods used in this study did not produce the spectrum of Ogg's rigorously dried ammonia.

"Product C" is empirically  $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$ . It has been labeled "mistreated diammoniate" by Jolly<sup>2</sup> but is called "diammoniate of diborane II" in this series of papers.

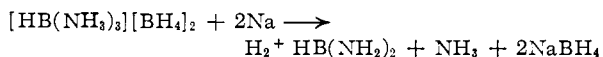
An extension of Werner's coordination theory in the ammonia-diborane system suggests the following possibility for the structure of "diammoniate of diborane II."



(16) Parry, *et al.*, *ibid.*, **80**, 1-27 (1958).

(17) R. A. Ogg, Jr., *Disc. Faraday Soc.*, **17**, 215 (1954).

Such a compound should retain ammonia more strongly than the "diammoniate" because the hydrogens of its ammonias are more acidic than those of the "diammoniate." For the same reason it should split out hydrogen more readily than the "diammoniate." The reaction of such a compound with sodium in ammonia would be represented as



The hydrogen produced is equal to 1.33 equivalents per mole of diborane. All of the foregoing properties have been reported for the "diammoniate II."<sup>1,2</sup> Furthermore its molecular weight in liquid

ammonia is consistent with the above formula.<sup>18</sup> However, no direct physical evidence for the structure of the "diammoniate II" is yet available and its nature must still be regarded as subject to revision.

**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.

(18) R. W. Parry, G. Kodama and D. R. Schultz, *THIS JOURNAL*, **80**, 24 (1958).  
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

## Chemical Evidence for the Structure of the "Diammoniate of Diborane." V. A Tracer Study of the Reaction between Sodium and the "Diammoniate of Diborane"

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A tracer study of the reaction between sodium and the "diammoniate of diborane" in liquid ammonia, using deuterium as the labeling element, showed that in the low-temperature reactions with sodium only nitrogen-hydrogen bonds were broken; no boron-hydrogen bonds were ruptured. In the room-temperature ammonolysis reaction involving the residues of the sodium reaction, a boron-hydrogen and a nitrogen-hydrogen bond were broken. A rather high separation factor for the isotopes of hydrogen is suggested by the data.

In the preceding paper of this series<sup>1</sup> it was pointed out that the formation of the "diammoniate of diborane" is assured only by a very specific preparative method. Under slightly different conditions it appears to be possible to prepare what might be termed a solution of diborane in ammonia. Under relatively vigorous conditions a material of the same empirical formula as the diammoniate,  $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$ , but possessing different chemical properties appears to be formed. This material is named "diammoniate of diborane II."

In an exchange study of the "diammoniate" in ammonia, using deuterium as a tracer, Burg<sup>2</sup> demonstrated that H-D exchange between the solute and solvent occurs only between those hydrogens which were originally bound to nitrogen. His results indicate that the hydrogens which are bound to boron in the "diammoniate" are not sufficiently acidic to form an ammonium salt, since it is known<sup>3</sup> that rapid proton exchange takes place between an ammonium ion and ammonia, even at  $-60^\circ$ . Burg's work refutes the early diammonium formulation,  $(\text{NH}_4)_2\text{B}_2\text{H}_4$  of Stock.<sup>4</sup>

Insofar as exchange experiments can be accepted as a criterion for acidic character, Burg's evidence is convincing; however, his experimental conditions were mild. Of somewhat greater importance in evaluating the models proposed here is information concerning the source of the hydrogen which arises during various phases of reaction. A tracer study of the reaction between sodium and

the various forms of the "diammoniate" has been conducted in order to determine whether H-B or H-N bonds are broken during hydrogen evolution.

**A Tracer Study of the Reaction of the "Diammoniate of Diborane" with Sodium in Liquid Ammonia.**—Since Burg<sup>2</sup> has demonstrated that hydrogen which is bound to boron does not exchange with hydrogen which is attached to nitrogen, the following species of the "diammoniate" may be regarded as being stable in liquid ammonia- $h_3$  or liquid ammonia- $d_3$ :  $\text{B}_2\text{D}_6 \cdot 2\text{NH}_3$ ,  $\text{B}_2\text{D}_6 \cdot 2\text{ND}_3$  and  $\text{B}_2\text{H}_6 \cdot 2\text{ND}_3$ .<sup>5</sup>

When the classical "diammoniate of diborane" has been prepared under carefully prescribed conditions and when its ammonia solution has been always maintained at  $-78^\circ$  or below, it will react with sodium in liquid ammonia to produce one equivalent of hydrogen per mole of "diammoniate."<sup>1</sup> The species which are listed above were allowed to react with sodium in liquid ammonia; the results are summarized in Table I.

The complete absence of deuterium<sup>6</sup> in the gas evolved from the reaction between sodium and  $\text{B}_2\text{D}_6 \cdot 2\text{NH}_3$  in ammonia- $h_3$  (run 2) confirms Burg's contention that the hydrogens which are bound to boron in the "diammoniate" have no acidic character. Even under the comparatively vigorous conditions of this reaction, no boron-hydrogen bonds were broken. However, the reaction between  $\text{B}_2\text{H}_6 \cdot 2\text{ND}_3$  and sodium in ammonia- $d_3$  (run 3) produced gas which was only 77% deuterated. This result could not have arisen from contamina-

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

(2) A. B. Burg, *ibid.*, **69**, 747 (1947).

(3) C. J. Nyman, Si-Ghang Fung and H. W. Dodgen, *ibid.*, **72**, 1033 (1950).

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

(5) For the sake of simplicity, isotopically substituted "diammoniate" will be represented by its empirical formula.

(6) In discussing the tracer studies, the term hydrogen will refer to the elements of atomic number one. Protium and deuterium will refer to its isotopes of mass one and two, respectively.