[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

Hydrides of Boron. VIII. The Structure of the Diammoniate of Diborane and its Relation to the Structure of Diborane

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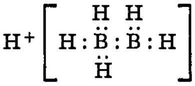
The structure of diborane (B_2H_6) is a problem of very general interest because it raises the important question of the occurrence, in simple compounds, of covalent bonds involving less than a pair of electrons.[1] Such bonds are not required by the structure advocated by Wiberg—a structure in which the two boron atoms are considered to be joined by a double bond, while two hydrogen nuclei are held by some unusual kind of electrostatic linkage.[2] The considerable amount of credence which this idea has received, as well as the importance of the question involved, has led us to consider very carefully the evidence relating to its validity.

Of the numerous arguments employed by Wiberg, the most frequently cited is the one concerning the so-called "diammoniate of diborane" ($B_2H_6 \cdot 2NH_3$),[3] which he considers to be the diammonium salt of the potential acid (diborane) formulated as $(H^+)_2(H_2B{=}BH_2)^{=}$.[4] The evidence advanced for this interpretation does not, however, uniquely demand the conclusions drawn,[5] and there are many facts which are difficult to reconcile with such a formulation. Thus a solution of a true diammonium salt in liquid ammonia, would be expected to produce a greater lowering of the vapor tension and a greater electrical conductivity than were actually observed.[5,6] These and other logical difficulties show the need of more experimental evidence bearing on the subject.

Some years ago, we undertook a further test of Wiberg's interpretation, through a study of the action of sodium upon a solution of the diammoniate of diborane in liquid ammonia. One mole of a true diammonium salt should react with two gram atoms of sodium to liberate two equivalents of hydrogen. Actually we found that the diammoniate, prepared at the lowest feasible temperature (−120°) and allowed to react with excess sodium in liquid ammonia just above its freezing point (−77°), produced only one equivalent of hydrogen per mole of diborane used. The reaction appeared to be quite complete at this point, which was reached in twenty to thirty minutes. In experiments in which the quantity of sodium was just one equivalent per mole of diborane, a stable salt having the empirical formula NaB_2H_8N could be obtained by subliming away the ammonia after the reaction was complete.

These results appear at first glance to favor the structure  $H^+\left[\begin{array}{ccccccc} & & H & & H & & \\ H & : & \ddot{B} & : & \ddot{B} & : & H \\ & & \ddot{H} & & & & \end{array}\right]^-$, proposed for diborane by Böeseken[7] and by Wahl,[8] for a molecule so constituted might bind one molecule of ammonia by coördination with the unsatisfied boron atom, and the other by the formation of the ammonium ion whose presence is indicated by the reaction with sodium.

There are, however, several objections to this interpretation. A minor logical difficulty, although not an insuperable one, is the fact that four hydrogen atoms are replaced readily by alkyl groups as the result of interaction of diborane and boron alkyls;[9] no further substitution

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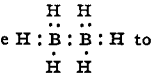
[1] The various suggestions for structures having such electron deficiencies, range from the use of a non-polar bond involving no electrons specifically, through several applications of the single electron bond, to the idea of a 6/7 electron pair bond, considered by S. H. Bauer, THIS JOURNAL, **59**, 1100 (1937). The molecular orbital treatment of the problem by Mulliken, *J. Chem. Phys.*, **3**, 635 (1935), also may be placed in this class.

[2] E. Wiberg, *Z. anorg. allgem. Chem.*, **173**, 210 (1926); *Ber.*, **69**, 2816 (1936), and other papers cited in the latter publication.

[3] Prepared by A. Stock and E. Kusz, *ibid.*, **56B**, 807 (1923); A. Stock and E. Pohland, *ibid.*, **59B**, 2213 (1926).

[4] Although Wiberg does not rely upon this argument alone, for the support of his theory, all of his other arguments are easily met by alternative explanations of the facts. For example, he explains the reaction of sodium (amalgam) with diborane as an addition to the assumed double bond. This reaction may equally well be interpreted as the result of the tendency of the electronically unsaturated molecule  $\begin{array}{ccccccc} & & H & & H & & \\ H & : & \ddot{B} & : & \ddot{B} & : & H \\ & & \dot{H} & & \dot{H} & & \end{array}$ to gain electrons; in either case the result would be the saturated compound $Na_2B_2H_6$.

[5] For example, the experiments by Stock, Wiberg, Martini and Nicklas [*Ber.*, **65**, 1711 (1932)] have been used to justify Wiberg's formulation of the diammoniate. It is true that the production of hydrogen before any nitrogen is liberated during the electrolysis of liquid ammonia solutions of this compound, suggests the presence of ammonium ions in such solutions. Nevertheless, the possibility that at least a part of the production of hydrogen is due to the cathodic reduction of ammonia (during which anodic oxidation of the boron hydride occurs instead of liberation of nitrogen) renders it impossible to estimate the quantity of ammonium ion furnished by the original salt.

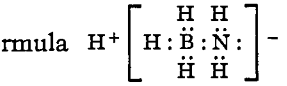
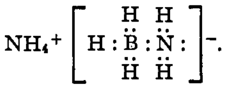
[6] A. Stock and E. Pohland, *ibid.*, **58**, 657 (1925).

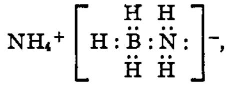
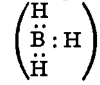
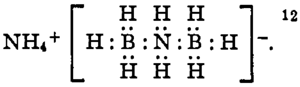
[7] J. Böeseken, *Verslag Akad. Wetenschappen Amsterdam*, **31**, 591 (1922).

[8] W. A. Wahl, *Z. anorg. allgem. Chem.*, **146**, 230 (1925).

[9] H. I. Schlesinger and A. O. Walker, THIS JOURNAL, **57**, 621 (1935); see also Schlesinger, Horvitz and Burg, *ibid.*, **58**, 407 (1936).

occurs, however great the excess of boron alkyl. This behavior is not forecast, nor even explained, by the structure suggested by Böeseken and by Wahl. A more serious objection has arisen from a further study of the reaction of the diammoniate with sodium in liquid ammonia. If the temperature is allowed to rise, a very slow secondary reaction leads to the evolution of additional hydrogen. It is significant, however, that the total quantity of hydrogen obtained never exceeds 1.4 equivalents per mole of diborane.[10] It is still more important that the exposure of the liquid ammonia solution to temperatures near −40°, before any sodium has been added, leads to the almost immediate production of 1.25 equivalents of hydrogen by reaction with sodium at −77°. This means that the evolution of hydrogen beyond one equivalent is an indirect result of a secondary reaction of ammonia with the diammoniate. Such a secondary reaction is difficult to explain by any formulation of the diammoniate based upon the Wiberg idea of diborane, or upon the structure proposed by Böeseken and by Wahl. On the other hand, it is accounted for easily by the formulation of the diammoniate to be proposed later in the present paper.

The reaction of sodium with the diammoniate thus makes clear the need for a new approach toward the solution of the problem of its structure. The basis for such an approach has been given by our recent work on borine carbonyl (BH_3CO) and borine trimethylammine.[11] The direct formation of the latter compound, by the action of trimethylamine upon diborane at temperatures as low as −110°, suggests that the product of the action of ammonia at similar temperatures also may be a complex compound of borine. Another clue to the problem is found in the fact that borine trimethylammine, dissolved in liquid ammonia, does not react with sodium. This observation suggests that the hydrogen produced by the action of sodium upon the diammoniate of diborane, comes not from the BH_3 group now assumed to be present in that compound, but rather from ammonia involved in the original reaction with diborane. By the same argument, the ionization of the hypothetical borine ammine, $BH_3 \cdot NH_3$, should occur as indicated by the formula  $H^+\left[\begin{array}{ccccc} & H & & H & \\ H: & \ddot{B} & : & \ddot{N} & : \\ & \ddot{H} & & \ddot{H} & \end{array}\right]^-$, and in liquid ammonia solutions should lead to the formation of the salt  $NH_4^+\left[\begin{array}{ccccc} & H & & H & \\ H: & \ddot{B} & : & \ddot{N} & : \\ & \ddot{H} & & \ddot{H} & \end{array}\right]^-$.

It is quite evident, however, that $B_2H_6 \cdot 2NH_3$, the final product of the low-temperature reaction of diborane with ammonia, can be neither borine ammine nor the ammonium salt postulated above. The latter is excluded by the percentage composition of the diammoniate; the former by its reaction with sodium, in which only one-half gram equivalent of hydrogen is liberated per gram atom of boron. Nevertheless, further consideration of the structure  $NH_4^+\left[\begin{array}{ccccc} & H & & H & \\ H: & \ddot{B} & : & \ddot{N} & : \\ & \ddot{H} & & \ddot{H} & \end{array}\right]^-$, leads to a formulation of the diammoniate consistent in every respect with its reaction with sodium and with all of its other known properties. Thus it is noticed that the negative ion of this salt contains a coördinatively unsaturated nitrogen atom, to which the borine molecule  $\left(\begin{array}{l} H \\ \ddot{B}:H \\ \ddot{H} \end{array}\right)$ could add itself, and produce the final result  $NH_4^+\left[\begin{array}{ccccccc} & H & & H & & H & \\ H: & \ddot{B} & : & \ddot{N} & : & \ddot{B} & :H \\ & \ddot{H} & & \ddot{H} & & \ddot{H} & \end{array}\right]^-$.[12] According to this formula, *the "diammoniate of diborane" is a mono-ammonium salt having a B–N–B skeleton, rather than a direct derivative of diborane.*[13]

A direct proof of this structure through a study of borine ammine or of its ammonium salt is not feasible, for all attempts to prepare these compounds have failed,[14] evidently because they either are unstable or undergo secondary reactions. However, very convincing indirect evidence supporting the proposed structure for the diammoniate, has been obtained from two entirely distinct types of experiment.

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[10] If the time is greatly extended, and the temperature allowed to rise above −40°, more hydrogen is obtained, but at such a rate that its formation may be attributed mainly to amide formation and to ammonolysis.

[11] Anton B. Burg and H. I. Schlesinger, THIS JOURNAL, **59**, 780 (1937).

[12] Such a reaction could occur in any mixture in which the activity of the ammonia is low and in which much of the diborane therefore would not react immediately with the ammonia. The borine molecules needed to form the final product thus would be available from the excess of diborane.

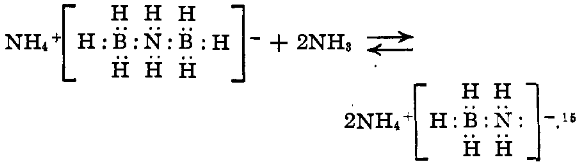
[13] In the present paper we shall nevertheless continue to use the term "diammoniate of diborane," or more simply, "the diammoniate," as a convenient, empirically derived name for the compound.

[14] In addition to the reaction of ammonia with diborane itself, and with borine carbonyl (as described in the preceding paper of this series), these attempts have included the action of ammonia upon two hitherto undescribed, very unstable compounds formed by the low-temperature addition of diborane to two volumes of phosphine and of methyl ether, respectively.

The first of these involves the use of the very unstable compound formed by the reaction of diborane with methyl ether at low temperatures. Although this substance, of as yet unknown molecular weight, might be formulated either as $B_2H_6{\cdot}2(CH_3)_2O$ or as $BH_3{\cdot}(CH_3)_2O$, analogy with borine trimethylammine favors the latter formula. As an unstable borine derivative, it might react with liquid ammonia to give borine ammine and from that, the salt $NH_4BH_3NH_2$. When the etherate actually is left for some time in liquid ammonia, and the resulting solution tested by sodium, the yield of hydrogen is considerably less than that expected from the salt $NH_4BH_3NH_2$. On the other hand, if sodium is dissolved in liquid ammonia simultaneously with the etherate, the predicted quantity of hydrogen (0.5 H_2 per B) is obtained. At the end of the process, the original quantity of methyl ether can be recovered from the solution. Furthermore, the rate of evolution of hydrogen follows the first order equation, just as expected if the rate determining process (presumably the displacement of methyl ether from the etherate by ammonia) involves the solvent and proceeds in one step. Finally, the analysis of the residue, after the solvent ammonia has been removed as thoroughly as possible, shows the presence of one atom of nitrogen per atom of boron, in agreement with the formula $NaBH_3NH_2$. It thus appears that the removal of the ammonium ion as rapidly as it is formed in the solution makes possible the indirect demonstration of the presence of the $(BH_3NH_2)^-$ ion.[15] The major assumptions of the theory leading to the new formulation of the diammoniate of diborane, are thus substantiated.

The second indirect line of evidence deals with the hitherto undescribed volatile compound B_2H_7N, a substance which is formed in good yields when diborane is passed over its diammoniate at 80°.[16] The conditions for the formation of this compound suggest that its structural skeleton is similar to that of the diammoniate of diborane. Unlike the diammoniate, the compound is sufficiently volatile for investigation by the method of electron diffraction in the gas phase; accordingly a pure sample of it was sent to Dr. Simon H. Bauer, then working by that technique at the California Institute of Technology. The results which he obtained are consistent only with structures involving the B–N–B skeleton,[17] and are therefore a striking confirmation of the views expressed in this paper.

Finally we may point out that the structure here proposed for the diammoniate accounts satisfactorily for all aspects of its reaction with liquid ammonia solutions of sodium. As a mono-ammonium salt, the diammoniate yields one equivalent of hydrogen by a relatively rapid reaction; production of additional hydrogen is explained by the reversible reaction



$$NH_4^+\left[\begin{array}{c}\mathrm{H\ \ H\ \ H}\\ \mathrm{H:\ddot{B}:\ddot{N}:\ddot{B}:H}\\ \mathrm{\ddot{H}\ \ \ddot{H}\ \ \ddot{H}}\end{array}\right]^- + 2NH_3 \rightleftarrows 2NH_4^+\left[\begin{array}{c}\mathrm{H\ \ H}\\ \mathrm{H:\ddot{B}:\ddot{N}:}\\ \mathrm{\ddot{H}\ \ \ddot{H}}\end{array}\right]^-.^{15}$$

In the absence of sodium, this equilibrium seems to lie toward the left. Sodium, however, destroys the ammonium ion, displacing the equilibrium to the right at a rate which steadily decreases as the reaction proceeds, until observation of its further progress no longer is feasible.[18]

The theory leading to the formulation of the diammoniate of diborane as the salt

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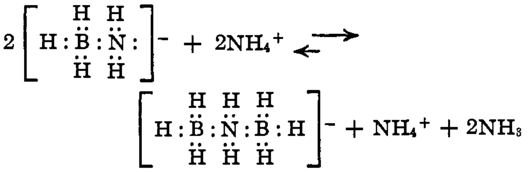
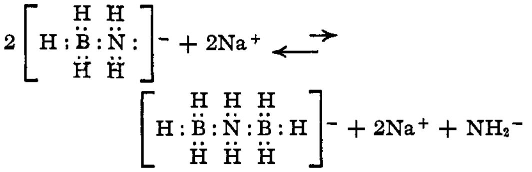
(15) The following equations, representing hypothetical but very probable reactions, show how the removal of ammonium ions might stabilize the $(BH_3NH_2)^-$ ion.

(1) 

$$2\left[\begin{array}{c}\mathrm{H\ \ H}\\ \mathrm{H:\ddot{B}:\ddot{N}:}\\ \mathrm{\ddot{H}\ \ \ddot{H}}\end{array}\right]^- + 2NH_4^+ \rightleftarrows \left[\begin{array}{c}\mathrm{H\ \ H\ \ H}\\ \mathrm{H:\ddot{B}:\ddot{N}:\ddot{B}:H}\\ \mathrm{\ddot{H}\ \ \ddot{H}\ \ \ddot{H}}\end{array}\right]^- + NH_4^+ + 2NH_3$$

(2) 

$$2\left[\begin{array}{c}\mathrm{H\ \ H}\\ \mathrm{H:\ddot{B}:\ddot{N}:}\\ \mathrm{\ddot{H}\ \ \ddot{H}}\end{array}\right]^- + 2Na^+ \rightleftarrows \left[\begin{array}{c}\mathrm{H\ \ H\ \ H}\\ \mathrm{H:\ddot{B}:\ddot{N}:\ddot{B}:H}\\ \mathrm{\ddot{H}\ \ \ddot{H}\ \ \ddot{H}}\end{array}\right]^- + 2Na^+ + NH_2^-$$

In reaction (1), the formation of slightly ionized ammonia favors the production of $(BH_3)_2NH_2^-$ ions, whereas in reaction (2), the formation of the amide ion favors the reverse reaction. The actual completion of (1) when the concentration of ammonia is low, is suggested by the reaction of the etherate with gaseous ammonia, to form the diammoniate of diborane, as described in the experimental part.

(16) Unpublished work of H. I. Schlesinger, D. M. Ritter and A. B. Burg. It is expected that the details of this work at present available only in thesis form (Ritter), will be published in the near future.

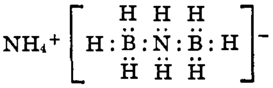
(17) This conclusion was given to us by a private communication from Dr. Bauer, whose detailed report is now in the course of publication.

(18) It is yet too soon to decide whether the equation here given is alone sufficient to describe the system. It is possible that the equilibrium is appreciably modified by such extensions of the reverse reaction as

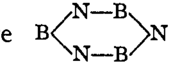
$$NH_4BH_3NH_2 + NH_4(BH_3)_2NH_2 \rightleftarrows (NH_4)_2(BH_3)_3NH + 2NH_3$$

and

$$NH_4BH_3NH_2 + (NH_4)_2(BH_3)_3NH \rightleftarrows (NH_4)_3(BH_3)_4N + 2NH_3$$



$$\mathrm{NH_4^+}\left[\begin{array}{ccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ \mathrm{H} & : & \mathrm{\ddot{B}} & : & \mathrm{\ddot{N}} & : & \mathrm{\ddot{B}} & : & \mathrm{H} \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \end{array}\right]^-$$

is in better agreement with the previously known facts concerning this substance, and with the new reactions here described, than are any of the ideas suggesting that it contains some type of boron to boron linkage. Thus the new interpretation explains the stability of the diammoniate, for compounds containing B–N linkages generally are more stable than those involving B–B bonds; it shows why the diammoniate behaves as a mono- rather than a diammonium salt; it accounts for all of the facts concerning the action of liquid ammonia and sodium upon the diammoniate as well as on the methyl etherate of diborane; it predicts the existence of a B–N–B skeleton in the compound B_2H_7N, and makes it easy to understand the formation of the structure  (found in the compound $B_3N_3H_6$), by the heating of the diammoniate of diborane.[19]

Whether or not one considers the indirect evidence sufficiently cogent for the acceptance of the structural formula here proposed, the arguments presented make it evident that the structure of the "diammoniate of diborane" cannot properly be used for the support of hypothetical structures of diborane, since the present work has shown that the diammoniate is not necessarily a direct derivative of diborane. The tendency of diborane to yield the transitory molecules of borine, the chemical evidence of its unsaturation, and the electron diffraction pattern which it produces,[20] all seem best in accord with formulas containing bonds involving less than two electrons.

Experimental Part

Apparatus and Technique.—The technical requirements of the present work were met by adaptations of the high vacuum methods described by Stock.[21] The technique of obtaining and using small, accurately weighed samples of pure sodium for the reactions discussed in the preceding sections, deserves more detailed description.

Capsules containing sodium are made by drawing the molten metal into a length of 3-mm. glass tubing, and cutting out short pieces just before use. Such a capsule is put into a carefully dried and weighed tube of the design indicated in Fig. 1. The capillary portion of this tube is 1 mm. in diameter; the bulb at its lower end is 3 to 5 mm. wide, and very thin walled. After the introduction of the capsule, the tube is connected immediately to the high vacuum pump by means of a Piceïn joint, and thoroughly evacuated. The sodium is melted by immersing the tube in an oil-bath at 200°; air is now admitted in order to force the molten metal into the bulb. After cooling, the tube is again evacuated; next the bulb is immersed just to its neck in water and sealed off; for a good seal, it is necessary to distil the excess sodium out of the capillary, by careful use of the hand torch. The bulb and the remainder of the tube are now cleaned, dried, and weighed. The total weight, minus the original weight, is the weight of the sodium in the bulb, within 0.2 mg.[22]

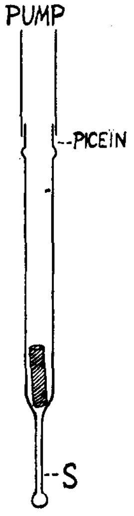


Fig. 1.

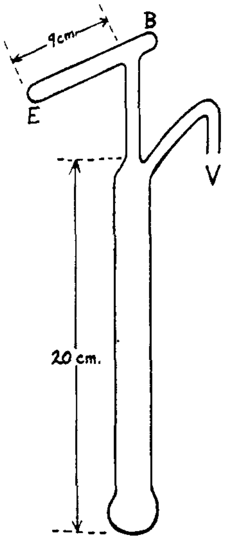


Fig. 2a.

Fig. 2b.

The design of the reaction tube used for work with sodium in liquid ammonia is shown in Fig. 2a. It is connected at V to a mercury float valve attached to the vacuum apparatus. The material whose behavior toward sodium is to be investigated, is prepared in the lower part of this tube. The 2 to 3 cc. of solvent ammonia is introduced before or after the introduction of sodium; in either case, the contents of the reaction tube are held at −196° during the latter process. The cooled tube is filled with dry hydrogen, and the lower end of the slanting portion BE is opened. The hydrogen streams down the slant, preventing access of air or moisture, which cannot rise against the lighter gas. The bulb containing the sodium is placed in the special breaking tool[23] (Fig. 2b) and in-

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[19] Other properties of the diammoniate of diborane have been recorded, but these do not appear to be uniquely related to any particular hypothesis concerning its structure. Thus its reaction with hydrogen chloride at −80°, quickly evolves two moles of hydrogen per mole of diborane originally used; further reaction is extremely slow. Wiberg assumes that the first step in this reaction is the addition of hydrogen chloride to the assumed double bond. But borine trimethylammine, in which there cannot be any double bond, reacts with hydrogen chloride in perfectly analogous fashion (unpublished results). The assumption of a double bond between boron atoms therefore is not necessary for an explanation of the behavior of the diammoniate toward hydrogen chloride.

[20] S. H. Bauer, THIS JOURNAL, **59**, 1096 (1937).

[21] Stock, "Hydrides of Boron and Silicon," Cornell University Press, 1933; *Ber.*, **54A**, 142 (1921). See also the first, second, and fourth papers of the present series, and Burg, THIS JOURNAL, **56**, 499 (1934).

[22] As shown by experiments in which all of the sodium reacted to produce hydrogen.

[23] This instrument consists of a small metal block, with a hole to receive the capillary stem of the bulb, and a long metal handle provided with spot-welded wire loops to guide the glass rod which acts as a holder and breaker of the sodium bulb.

serted to the point B, where it is crushed and then allowed to drop upon the frozen material at the bottom of the reaction tube. After withdrawal of the breaking tool, the open end of the tube is melted and drawn to a capillary; the hydrogen stream is stopped after a few minutes, and the rounded end is restored by sealing off the capillary. After thorough evacuation, the tube is warmed to a temperature just above the melting point of ammonia, in order to start the reaction. The course of any such reaction can be followed by pumping off and measuring the hydrogen at intervals; the solution is held at −196° during the pumping.

Blank tests of the technique here described, showed that the quantity of hydrogen which might be attributed to the introduction of water never exceeded 0.03 cc.[24] Such blank tests also permitted us to estimate what part of the hydrogen obtained from a reaction mixture might have been due to the reaction between sodium and ammonia, and to judge the extent of side reactions. The value of the method itself, for the determination of ammonium ions, was investigated by an experiment with hydrogen sulfide.[25]

The Reaction of Diborane with Ammonia at −120°.—Diborane was allowed to react with an excess of solid ammonia in the manner described by Stock and Pohland.[3] The sodium-dried ammonia was condensed as a thin layer upon the walls of the reaction tube, and the diborane was condensed upon it. The temperature was then set at −130° (alcohol–ether bath) and allowed to rise during four hours to −110°. The diborane was wholly absorbed at temperatures between −123 and −118° in all cases in which the ratio of ammonia to diborane was greater than 4:1. When the ratio was smaller, completion of the reaction required temperatures as high as −85°. The excess of ammonia could be sublimed off at temperatures below −80°, leaving a residue of the formula $B_2H_6{\cdot}2NH_3$, as shown by the data presented in Table I.

TABLE I

THE LOW-TEMPERATURE AMMONIATION OF DIBORANE

Volume of			
Diborane, cc.	Ammonia, cc.	Ammonia regained, cc.	Empirical formula of the residue
20.3	59.4	18.6	$B_2H_6{\cdot}2.01NH_3$
20.8	74.0	32.1	$B_2H_6{\cdot}2.01NH_3$
19.5	109.6	70.5	$B_2H_6{\cdot}2.00NH_3$
18.6	214.0	176.6	$B_2H_6{\cdot}2.01NH_3$
21.2	124.8	81.4	$B_2H_6{\cdot}2.04NH_3$

It appeared possible that a tetrammoniate might exist, but the evidence was not clear: in those experiments in which the ammonia had been in excess of four moles per mole of diborane, it became suddenly more difficult to remove when the four-mole point was reached, but the process always could be completed within five or six hours.

The Reaction of the Diammoniate with Sodium.—Several samples of the material prepared as described above, were treated with sodium in liquid ammonia just above its melting point (−77°) for fifteen to thirty minutes. The quantities of hydrogen so formed are given in Table II. After each experiment, there remained a blue color, indicating an excess of sodium at the end of the process. Only negligible quantities of hydrogen were evolved when the reaction mixtures were kept at the same temperature for an hour or two longer.

TABLE II

THE REACTION OF $B_2H_6{\cdot}2NH_3$ WITH SODIUM

Expt.	Diborane, cc.	Sodium, mg.	Temp., °C.	Time, min.	Hydrogen, cc.	Ratio of H-atoms to B_2H_6
1	22.6	excess	−77	30	11.9	1.05
2	20.3	excess	−77	20	9.95	0.98
3	20.8	22.8	−77	30	10.2	.98
4	19.5	21.0	−77	30	9.65	.99
5	37.8	85.2	−75	15	19.1	1.01
6	42.6	58.9	−64	30	21.6	1.01

The Preparation of the Salt NaB_2H_8N.—From the products of experiments 3 and 4 (Table II), the solvent ammonia was removed by distillation, followed by pumping at room temperature. In later experiments, in which the sodium was equivalent to the diborane, the solvent ammonia was removed by sublimation at temperatures below −80°, leaving an extremely light, porous solid showing a considerable tendency to adsorb ammonia. In all cases, the last traces of free ammonia were removed by pumping at −40°; the residues gave off no more ammonia *in vacuo*, even when warmed to 70°, a temperature which seemed to have no effect of any kind.[26] Analysis of these residues showed one atom of nitrogen per pair of boron atoms.

The analyses were made by distilling concentrated hydrochloric acid upon each residue, pumping off the resulting hydrogen, neutralizing the hydrochloric acid by sodium hydroxide, and distilling the ammonia and water into a bulb for titration. The actual data are presented in Table III. The deviations from the simple ratio of two boron

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(24) All gas volumes in this paper refer to standard conditions.

(25) A 21.8-cc. sample of pure hydrogen sulfide was dissolved in dry liquid ammonia and treated with 50 mg. of sodium at −45°. The reaction produced 10.8 cc. of hydrogen during the first five minutes, and a further 0.3 cc. during the following ten hours. This result is in full agreement with the entirely different evidence, due to Scheflan and McCrosky, THIS JOURNAL, **54**, 193 (1932), that hydrogen sulfide forms mainly NH_4SH in liquid ammonia, with but little tendency to form secondary ammonium ions.

(26) At higher temperatures, hydrogen began to be evolved slowly.

atoms to one nitrogen, are to be attributed to errors due to the small scale of the work.

TABLE III

ANALYSES OF THE RESIDUAL SODIUM SALTS

Experiment	3	4	(later)
Diborane originally used, cc.	20.8	19.5	21.6
Ammonia, cc. of gas	21.5	20.8	19.8
Ratio of B to N	1.94	1.88	2.18

The Secondary Reaction.—Of the experiments listed in Table II, the last two were continued in order to determine the effect of longer times and higher temperatures. The details for experiment 5, which was carried farther than experiment 6, are given in Table IV.

TABLE IV

EXTENSION OF EXPERIMENT 5 OF TABLE II

Temperature, ° C.	−75	−70	−65	−60	−60	−60	−59	−59
Total time, hrs.	0.25	0.50	1.5	5.5	25	47	72	120
Total vol. of hydrogen, cc.	19.1	19.6	20.7	21.0	22.2	22.8	23.2	23.4
Ratio H to B_2H_6	1.01	1.04	1.10	1.11	1.17	1.21	1.23	1.24

At the end of the five days which this experiment required, the reaction had become so slow that any further evolution of hydrogen might be attributed largely to the direct action of sodium upon the solvent ammonia. The apparent approach toward a limit far short of a second equivalent of hydrogen per mole of diborane, could not be explained as the behavior of a diammonium salt undergoing secondary ionization; on the contrary, it seemed far more reasonable to attribute the excess hydrogen to some further reaction of the salt with ammonia, by which the appropriate number of ammonium ions were formed.

In order to test this suggestion further, a sample of the diammoniate made from 18.6 cc. of diborane (fourth experiment of Table I) was dissolved in 3 cc. of liquid ammonia and allowed to remain for some twenty hours at −40°. The product reacted with sodium in the manner indicated by the data of Table V. The reaction was discontinued after thirty hours, because it was recognized that any further results would be complicated by the possibility of amide formation. The rapid production of 1.25 equivalents of hydrogen at −75° showed that the long treatment with ammonia at −40° had resulted in the formation of an extra quarter equivalent of ammonium ions, by a reaction which certainly was too slow to be explained as a simple secondary ionization.

Further evidence of a secondary reaction of the diammoniate with ammonia, came from a study of the decomposition pressures in the system $B_2H_6{\cdot}2NH_3$-NH_3 at −40°. The pressures involved were low enough to allow the use of the mercury float valve as the manometer. In order to aid the approach toward equilibrium, a small drop of mercury was allowed to flow into the bottom of the tube containing the sample; by shaking the tube, the mercury could be made to act as a pestle for breaking up the crystals. The essential results of this experiment, which involved 21.2 cc. of diborane (fifth experiment of Table I), are given in Table VI. The pressure changes abruptly as the ratio of ammonia to diborane is decreased to 3.34; a less sharp change occurs in the range 2.6 to 2.3. If the action of ammonia upon the diammoniate were a simple addition, the pressure changes would occur only when the ratio is simple; actually it appears that the original diammoniate has undergone a partial conversion to a radically different material, whose ammoniates exhibit decomposition pressures different from those of the ammoniates of the original material.

TABLE V

SODIUM REACTION OF THE SECONDARY AMMONIATE

Temperature, °C.	−74	−75	−67	−50	−40	−39
Total time, hrs.	0.17	0.42	0.57	1.57	9.5	30
Total hydrogen, cc.	11.3	11.7	11.8	12.0	12.5	13.0
Ratio H to B_2H_6	1.22	1.26	1.27	1.29	1.35	1.40

TABLE VI

PRESSURES IN THE SYSTEM $B_2H_6{\cdot}2NH_3$-NH_3 at −40°

Temp., °C.	Ammonia in the condensed phase, cc. gas	Ratio of NH_3 to B_2H_6	Pressure, mm.	Remarks
−39	77.3	3.64	40	Completely liq.
−39	74.9	3.54	35	
−40	71.5	3.38	33	
−40	70.7	3.34	27.5	Crystals appear
−40	68.3	3.22	27	
−40	64.3	3.03	27	
−40	62.2	2.94	26	
−40	59.5	2.80	25	Completely solid
−40	58.4	2.75	24	
−39	56.2	2.65	22	
−39	54.6	2.58	21.5	Pressure read after 5 hrs.
−40	53.8	2.54	18	
−40	52.3	2.46	15	
−40	51.9	2.44	13	
−38	50.8	2.40	9	
−40	48.8	2.30	6	
−39	47.9	2.26	4	
−39	47.2	2.22	2.5	
−40	44.5	2.10	2	

Still other evidence supports the conclusion that ammonia attacks the original diammoniate of diborane to produce a fundamental change. The diammoniate formed at −120° is easily freed from ammonia at −80°, but it requires eight hours at −37° to remove a 5% excess of ammonia from a mixture which has been kept at −40 to −50° for some time before the attempt. Furthermore, the removal of excess ammonia from the original diammoniate ceases sharply when the composition $B_2H_6 \cdot 2NH_3$ is attained, but the altered material continues to yield small additional quantities of ammonia at 0°, and this change is accompanied by the evolution of a trace of material less volatile than ammonia.[27] Finally, the altered material evolves hydrogen rather rapidly at room temperature, in contrast to the relatively inert character of the original diammoniate.

That the altered material is responsible for the evolution of hydrogen in excess of one equivalent, in the reaction with sodium, is shown by an actual experiment in which the residue after extensive deammoniation (material resulting from an extension of the experiment recorded in Table VI) was treated with liquid ammonia and sodium at −77°. The rate and quantity of hydrogen production by the deammoniated, altered material were almost precisely parallel to the data recorded in Table V.

The Action of Trimethylamine upon the Diammoniate of Diborane.—In our explanation of the action of ammonia upon the diammoniate of diborane,[28] it is assumed that ammonia seizes a BH_3 group, thus removing it from its combination in the diammoniate. Experimental evidence that such a transfer of a BH_3 group can occur at temperatures comparable to those at which the diammoniate is attacked by ammonia, is found in the action of trimethylamine upon the diammoniate, described as follows.

The diammoniate was formed in the usual manner from 19.05 cc. of diborane. After complete removal of the excess ammonia, the solid was treated with 87.2 cc. of pure trimethylamine, at gradually rising temperature. Although the first evidence of reaction (an increase of the vapor tension over that of pure trimethylamine) appeared at −35°, the reaction tube was warmed to room temperature in order to allow extensive reaction within a reasonable time. The reaction evidently was practically complete after twelve hours at room temperature, for very little change occurred when the repurified trimethylamine was allowed to act for twenty hours longer. The volatile products were 10.8 cc. of hydrogen, 30.8 cc. of ammonia, and 10.0 cc. (gas at S. C.) of a slightly volatile solid; there remained 55.2 cc. of trimethylamine. The solid showed a melting point slightly higher than 90° and a vapor tension of 80 mm. at 99°; these values would be expected for a slightly impure sample of borine trimethylammine (m. p. 94°; v. t. 84 mm. at 99°). Its identity with that substance is scarcely to be questioned, for the shapes of individual crystals, as well as the aggregational habits of the crystal masses, corresponded very well. The yield of this product, representing only 26% of the borine groups assumed to be present in the diammoniate, evidently was greatly impaired by the side reaction (presumably ammonolysis) which produced the hydrogen.

An attempt to obtain a cleaner reaction of the same sort, by treating the salt NaB_2H_8N with trimethylamine, led only to very small yields of borine trimethylammine, possibly because the sodium salt is considerably less reactive than the ammonium salt. Such a difference of reactivity appeared when the rate of attack by dry hydrogen chloride upon each substance was studied.

The Reaction of Diborane with Methyl Ether.—The behavior of methyl ether toward diborane is like that of ammonia or trimethylamine, in that two moles of the ether react with one of diborane, at temperatures below −80°. Thus when 25.3 cc. of pure methyl ether and 9.15 cc. of diborane were condensed together at −196°, and then warmed to −80°, there appeared at once a new substance, solid and fairly stable even at the higher temperature. In order to ensure adequate contact between the gaseous reactants, the temperature was varied several times between −80 and −196°; then the excess gas was removed and found to be 7.0 cc. of practically pure methyl ether. The solid residue therefore contained 18.3 cc. of methyl ether and 9.15 cc. of diborane—a ratio of two moles to one.

The Decomposition of the Etherate.—During four or five hours at −78.5°, the product developed a final pressure of 18 mm. The vapor was drawn off and fractionated (by passing the diborane through a U-tube at −130°, in which the methyl ether condensed completely): it consisted of 0.65 cc. of diborane and 1.3 cc. of methyl ether. The same proportions always were found after the decomposition of any fraction of a sample of the solid etherate. It is thus evident that the formation of the etherate is easily and cleanly reversible. The rate of decomposition at −78.5° was studied by connecting the container to a vacuum trap at −196°, and measuring the condensed gases at intervals. Throughout the process of decomposing 71% of a sample derived from 15.2 cc. of diborane, the rate of destruction varied between 1.4 and 1.6% per hour: the reaction evidently is first order. The process was discontinued at that point, except that the residue was allowed to remain for several hours at −78.5°, in a closed system, where it finally registered the previously observed decomposition pressure of 18

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[27] The nature of this volatile material has not been determined. It might be the hypothetical $BH_3 \cdot NH_3$, but it is equally possible that it is B_2H_7N, whose formation would involve the production of a quantity of hydrogen equal to that actually observed (0.25 cc.).

[28] This explanation appears near the end of the introductory discussion, where it is used to account for the secondary production of hydrogen from the liquid ammonia-sodium reaction.

mm. Some notion of the dependability of this value is gained from the fact that an approach from the other direction led to a value of 20 mm. for the pressure of the residual gases.

The Reaction of the Etherate with Ammonia and Sodium.—A measured sample of diborane was allowed to react with an excess, measured quantity of methyl ether at −80°, in a reaction tube of the sort shown in Fig. 2a. The residual gases were measured, in order to determine the quantity of the etherate. Then a sample of sodium-dried ammonia (some 3 cc. of liquid) was condensed upon the etherate at −196°, and an excess of pure sodium (more than two gram atoms per mole of diborane involved) was introduced in the manner previously described. The evacuated tube was warmed to −75°, in order to melt the ammonia, which at once dissolved both the etherate and the sodium. The reaction was then carried forward, in one case at −78.5° (by direct immersion in a mixture of solid carbon dioxide with ether), and in the other, at −76° (maintained by holding a large test-tube, filled with solid carbon dioxide and ether, in the bath surrounding the reaction tube). At appropriate intervals, the reaction was stopped by freezing the solution, and the hydrogen was drawn off through a trap and measured.

TABLE VII

REACTION OF THE ETHERATE WITH AMMONIA AND SODIUM

(a) Sample derived from 9.43 cc. of diborane; temperature −78.5°

Time, min.	Total H., cc.	C	Ratio C/C_0	$-\log_{10} C/C_0$
0	0.00	18.85	1.000	0.000
4	.46	17.9	0.95	.020
13	.83	17.2	.913	.039
30	1.32	16.2	.860	.065
60	1.92	15.0	.796	.099
210	3.85	11.15	.592	.228
306	4.86	9.13	.484	.315
475	6.05	6.75	.358	.446
700[a]	7.00	4.85	.257	.590
950[b]	8.15	2.55	.135	.870
1190	8.90	1.05	.056	1.25
1400	9.20	0.45	...	...
1950	9.28	.29	...	...

(b) Sample derived from 14.8 cc. of diborane; temperature −76°

Time, min.	Total H., cc.	C	Ratio C/C_0	$-\log_{10} C/C_0$
0	0.00	29.6	1.000	0.000
10	1.1	27.4	0.926	.033
40	2.4	24.8	.838	.077
70	3.4	22.8	.770	.113
100	4.4	20.8	.702	.154
160	5.8	18.0	.608	.216
170	6.0	17.6	.594	.226
510	10.65	8.3	.281	.551
570	11.23	7.1	.240	.620
700	12.1	5.4	.183	.737
900[a]	12.9	3.8	.128	.893

The data from two such experiments are given in Table VII, which includes also the values calculated for plotting the curves shown in Fig. 3.

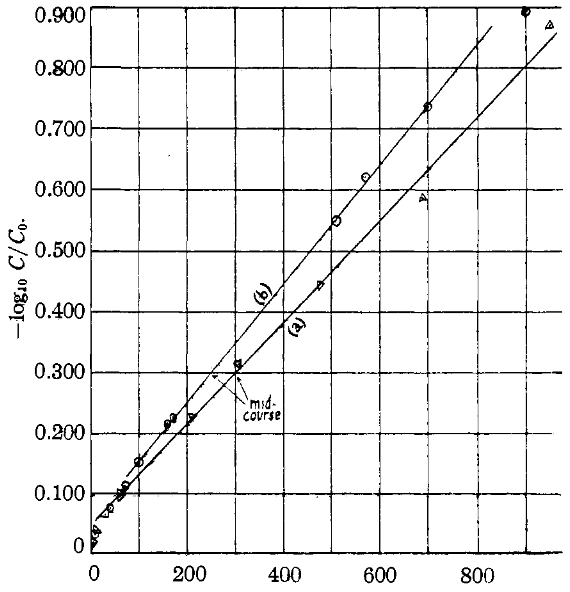

Fig. 3.

The quantity C, appearing in this table, was computed by subtracting the doubled volume of hydrogen from the doubled volume of diborane involved in the original etherate. According to the assumed equation $(CH_3)_2OBH_3 + NH_3 + Na \rightarrow Na^+BH_3NH_2^- + 0.5H_2$, the resulting value is a direct measure of the quantity, and hence of the concentration, of the etherate at the corresponding point in the reaction.

At the end of each of these experiments, the solvent ammonia was distilled away, and the solid residue was freed from the last traces of uncombined ammonia by long standing *in vacuo* at gradually rising temperatures. The process seemed to be complete after twenty-four hours at

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[a] During the time interval preceding this measurement, the temperature was lower than usual, on account of the addition of some undercooled solid carbon dioxide. This point therefore falls low on the graph.

[b] From this point on, the temperature rose very slowly to −60°. The corresponding points therefore tend to fall above the line. In any case, these points should not be considered important, because the value of the ratio C/C_0 could not be estimated accurately in this region.

$-40°$, for only negligible additional quantities of ammonia could be removed during another eighteen hours at $-15°$. At the higher temperature there was some tendency toward formation of hydrogen. After the experiments on the absorption of diborane by these residues (described in the following section), one of them, derived from experiment (b) of Table VII, was analyzed for ammonia nitrogen by the method described previously for the salt NaB_2H_8N. The result was 28.9 cc. of ammonia, or 0.98 mole per gram atom of boron. This result agrees with the formula $NaBH_3NH_2$ for such residues.

The displaced methyl ether was carried away with the solvent ammonia, during the distillation mentioned in the preceding paragraph. The quantity of this methyl ether was determined by absorbing the ammonia in dilute sulfuric acid; the unabsorbed gas was freed from water vapor by passage through a trap at $-80°$; its vapor tension, 35 mm. at $-78.5°$, showed it to be pure methyl ether. The quantity of the ether thus regained after the experiment involving 14.8 cc. of diborane was 29.2 cc. This result, together with the analysis for ammonia nitrogen and the quantity of hydrogen produced, completes the experimental check of the equation $(CH_3)_2OBH_3 + NH_3 + Na \longrightarrow Na^+BH_3NH_2^- + 0.5H_2$.

The Absorption of Diborane by $NaBH_3NH_2$.—It was assumed in the introductory discussion that the $BH_3NH_2^-$ ion would absorb a borine molecule (derived from diborane) rather easily to form the stable complex ion $(BH_3)_2NH_2^-$. It is therefore significant that the salt $NaBH_3NH_2$ actually does absorb diborane, presumably to form $NaBH_3NH_2$. The experiments are described below.

The residues derived from the reaction of the etherate with ammonia and sodium (after thorough removal of the excess ammonia, as described above), were treated with diborane, first at temperatures below $-80°$, which led to no reaction, and then at room temperature. The sample which originally involved 14.8 cc. of diborane, and whose later analysis showed that it contained 28.9 cc. of ammonia nitrogen, absorbed 9.9 cc. of diborane (from a 19.0-cc. sample) in the course of forty-two hours, after which further absorption was negligible. The sample derived from 9.43 cc. of diborane absorbed 5.6 cc. during twenty-two hours at room temperature. In the latter case, it was observed that the reaction began to occur appreciably at $-20°$ (3.4 cc. of diborane absorbed during nine hours). In neither case, however, was it feasible to push the reaction beyond two-thirds of the absorption required by the equation $2NaBH_3NH_2 + B_2H_6 \longrightarrow 2Na(BH_3)_2NH_2$. From the manner in which the reaction slowed down, it is reasonable to attribute its incompleteness to the heterogeneous character of the process.[29]

Although this reaction is very much slower than the assumed formation of the $(BH_3)_2NH_2^-$ ion during the reaction of diborane with ammonia, the conditions in the two cases are so different that the contrast in the rates cannot be considered significant.

The Action of Gaseous Ammonia upon Borine Dimethyl Etherate.—As mentioned in footnote 15, borine dimethyl etherate reacts with gaseous ammonia to produce the diammoniate of diborane. The experimental conditions and results are given below. It is to be noted that the displacement of dimethyl ether by ammonia occurs at a rate much greater than that of the spontaneous decomposition of the etherate. It thus appears that the ammonia attacks the etherate directly.

In one experiment, a sample prepared from 16.9 cc. of diborane and 33.8 cc. of methyl ether, was treated first with 16.6 cc. of pure ammonia, whose action was allowed to begin at $-100°$. After two and one-half hours, during which the temperature rose to $-87°$, the gaseous material was drawn off and found to consist of 17 cc. of methyl ether, containing a faint trace of diborane. A further 15.3 cc. of ammonia was added, and the mixture was left at $-80°$ for twelve hours. From the composition of the volatile material then removed at that temperature, the solid residue was estimated to consist of slightly more than 15.5 cc. of diborane with 31 cc. of ammonia. This solid was treated with 35 mg. of sodium in 3 cc. of liquid ammonia at $-77°$; it thus produced 8.1 cc. of hydrogen in fifteen minutes, and a total of 8.6 cc. in an hour. This means a total of 1.1 equivalents of hydrogen per mole of diborane estimated to be involved. Although this result was not very clear cut, it was evident that the methyl ether had been displaced completely by the ammonia, during a time which would not have been sufficient for the decomposition of more than 20% of the etherate to form diborane, and that the product was very nearly identical with the diammoniate of diborane.

A second experiment yielded a better quantitative check with this conclusion. Here the quantity of diborane was 7.8 cc., and of methyl ether, 22.4 cc. The excess of methyl ether was allowed to remain in the reaction tube (to inhibit decomposition of the etherate) during the addition of 15.6 cc. of ammonia in portions not larger than 1.5 cc. In spite of the presence of excess methyl ether, the displace-

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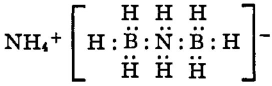
(29) In order to interpret correctly the absorption of diborane by these residues, it was of course necessary to determine whether the finely divided sodium which they contained might have been the absorbing agent. Accordingly, a sample of pure sodium was dissolved in liquid ammonia, which was next sublimed away at temperatures below $-80°$, and finally removed completely by pumping at room temperature. The resulting finely divided sodium showed not the slightest tendency to absorb diborane at room temperature. A similar negative result was obtained with the use of sodium which had been deposited by distilling the ammonia away (instead of subliming it).

ment was completed in forty hours at −80°. The entire original sample of methyl ether was then regained in pure condition, leaving a solid having the same composition as the diammoniate of diborane. Its identity with that substance was now clearly recognized by its stability at room temperature, its reaction with sodium in liquid ammonia at −75° to produce 3.97 cc. (1.02 equivalents per mole of diborane) of hydrogen during thirty minutes, and even by the characteristic formation of an exceedingly light and porous solid web when the ammonia was sublimed away after the completion of the reaction with sodium.

Acknowledgment.—We wish to express our thanks to the National Research Council and to the Research Corporation, for providing the liquid nitrogen used in this work.

Summary

The reaction of diborane with ammonia at low temperatures is interpreted as an addition of borine (BH_3) to ammonia, followed by other reactions leading to a final product having the structure  $NH_4^+\left[H:\overset{H}{\underset{H}{\ddot{B}}}:\overset{H}{\underset{H}{\ddot{N}}}:\overset{H}{\underset{H}{\ddot{B}}}:H\right]^-$. These ideas are supported by the following new experimental facts.

1. The product reacts with sodium in liquid ammonia (at −77°) to produce one equivalent of hydrogen per mole of diborane involved; it thus seems to contain one ammonium ion per pair of boron atoms.
2. A slow secondary reaction of the product with ammonia and sodium, yielding barely 40% more hydrogen, is easily explained by assuming that ammonia removes a BH_3 group from the above structure, by a reversible reaction producing $NH_4BH_3NH_2$. This explanation is supported by the fact that trimethylamine reacts with the "diammoniate of diborane" to give borine trimethylammine. Neither reaction is easily explained by other structures.
3. The reaction of the new compound $(CH_3)_2OBH_3$ with ammonia and sodium produces the salt $NaBH_3NH_2$. The negative ion of this salt is considered to be an intermediate step in the formation of the above structure.
4. The salt $NaBH_3NH_2$ strongly absorbs diborane. This fact justifies the assumption that the negative ion of the above structure is easily formed by addition of BH_3 to the $BH_3NH_2^-$ ion, and is capable of stable existence.
5. The new compound B_2H_7N, having the structural skeleton B–N–B, is easily prepared from the "diammoniate of diborane."

CHICAGO, ILL. RECEIVED NOVEMBER 29, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Solubilities of Red and Yellow Mercuric Oxides in Water, in Alkali, and in Alkaline Salt Solutions. The Acid and Basic Dissociation Constants of Mercuric Hydroxide

BY A. B. GARRETT AND ALFRED E. HIRSCHLER[1]

This investigation had its inception in an effort to obtain data for mercuric oxide similar to those obtained in this Laboratory for silver oxide[2] and for cupric oxide,[3] to establish the amphoteric character of mercuric oxide, to obtain information concerning the nature of the mercury-bearing ions in solution, to determine the dissociation constants of mercuric hydroxide, and to calculate therefrom the free energy changes in a number of reactions involving mercuric oxide.

Solutions of mercuric oxide in alkali were thought to be colloidal by Chatterji and Dhar.[4] Fuseya,[5] however, measured the solubility of red mercuric oxide in several concentrations of sodium hydroxide ranging from 0.01 to 2 *M;* the results indicated that a true chemical reaction was responsible for the solubility. Due to an obvious error, the solubilities listed by Fuseya are 100 times too great.

There is a rather serious discrepancy in the work of Fuseya, for the extrapolation of the alkali solubility to zero alkali concentration leads to a solubility value larger than the solubility of the oxide in pure water. Fuseya explains this discrepancy by supposing that the oxide is peptized by dilute alkali to finer particles, which might be

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[1] Present address: The Sun Oil Laboratories, Norwood, N. J.

[2] Johnston, Cuta and Garrett, THIS JOURNAL, **55**, 2311 (1933).

[3] McDowell and Johnston, *ibid.*, **58**, 2009 (1936).

[4] Chatterji and Dhar, *Chem. News*, **121**, 253 (1920).

[5] Fuseya, THIS JOURNAL, **42**, 368 (1920).