4.96×10^{-13}, respectively,[30,36a,b,c] we obtain K_{AgSCN} equal to 1.05 and 0.93×10^{-12}. These values, based on limited but perhaps the most reliable comparative data in the literature, agree well with our value (1.01×10^{-12}). Cave and Hume[12] by direct analysis found 1.06×10^{-6} *M* for the solubility at 25°, using a nephelometric method; however, it is quite possible that even at such low concentrations, silver thiocyanate is not completely dissociated.

The most reliable criteria of reversible cell behavior are the reproducibility of e.m.f. using electrodes of different types and methods of preparation, and the agreement of the cell data with related calorimetric data. To the extent that such data are available for comparison, those criteria are met for this system.

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[36] (a) B. B. Owen, THIS JOURNAL, **60**, 2229 (1938). (b) B. B. Owen and S. R. Brinkley, Jr., *ibid.*, **60**, 2233 (1938). (c) B. B. Owen and E. J. King, *ibid.*, **63**, 1711 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ST. LOUIS UNIVERSITY]

On the Alkali Metal Salts Derived from the Diammoniate of Diborane[1]

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The reaction of an alkali metal with an ammonia solution of the diammoniate of diborane, $B_2H_6\cdot2NH_3$, gives upon removal of the solvent the alkali metal borohydride and aminoborine: $M + B_2H_6\cdot2NH_3 = \frac{1}{2}H_2 + NH_3 + MBH_4 + BH_2NH_2$. During removal of the solvent, the aminoborine undergoes ammonolysis. The extent of this secondary reaction is dependent upon the metal employed, increasing from potassium through lithium.

The arguments which first led to the assignment of the ammonium salt structure,[3] $NH_4BH_3NH_2BH_3$ to the diammoniate of diborane, $B_2H_6\cdot2NH_3$, depend in part on the supposed replacement of the ammonium ion with the sodium ion by reaction of the diammoniate of diborane with sodium metal in liquid ammonia. The reaction assumed may be represented by the equation

$$Na + NH_4BH_3NH_2BH_3 = NaBH_3NH_2BH_3 + NH_3 + {}^1/_2H_2 \quad (1)$$

Upon removal of the solvent ammonia, a residue possessing the empirical formula expected from a simple replacement was obtained and the material was therefore assumed to be the sodium salt corresponding to the monoammonium salt formulation of the diammoniate of diborane. In view of recent observations[4] which suggest that the ion $BH_3NH_2BH_3^-$ either does not exist or is unstable with respect to disproportionation into the borohydride ion and aminoborane, it becomes of interest to examine closely the nature of the products that may be isolated from the metal–$B_2H_6\cdot2NH_3$ reaction and to determine their relationship to the diammoniate of diborane.

To this end, the reactions of solutions of the diammoniate of diborane $B_2H_6\cdot2NH_3$ in liquid ammonia with lithium, sodium and potassium were examined, and the isolation and identification of the reaction products were attempted. Without exception the products were found to be the metal borohydride, polymeric aminoborane and ammonolysis products of aminoborane. The over-all process can be represented by the following two equations: first, the reaction of the metal with the ammonia solution of the diammoniate[5]

$$Li(soln.) + B_2H_6\cdot2NH_3(soln.) = LiB_2H_8N(soln.) + {}^1/_2H_2 + NH_3 \quad (2)$$

followed by the removal of the solvent

$$LiB_2H_8N(soln.) = LiBH_4(solid) + BH_2NH_2(polymeric) \quad (3)$$

In the case of lithium and sodium borohydride, it was possible to separate the borohydride from the excess metal and the polymeric aminoborane by use of an appropriate ether solvent. The borohydride was identified by analysis and the composition of the ether-insoluble fraction was inferred by difference and confirmed by direct analyses to be aminoborane. In the cases of sodium and potassium, the identity of the borohydrides was confirmed by X-ray diffraction.

Unless the solvent ammonia was removed at the lowest possible temperatures, ammonolysis of the aminoborane with the production of hydrogen, empirically represented by the following equation, occurred

$$BH_2NH_2 + XNH_3 = BH_{2-x}(NH_2)_{1+x} + XH_2 \quad (4)$$

That the reaction which produced hydrogen was indeed ammonolysis of the aminoborane was indicated by the following observations: (a) the mole ratio of hydrogen produced to ammonia retained was always one; (b) regardless of the extent of the reaction, the diffraction pattern of the borohydride remained unchanged; (c) under comparable conditions, alkali metal borohydrides do not react with ammonia; and (d) the extent of ammonolysis does not appreciably affect the amount of borohydride which can be recovered.

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[1] Presented at the 128th Meeting of the American Chemical Society, Minneapolis, Minnesota, September, 1955.

[2] Taken from theses presented by Max D. Adams in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1955, and by the Rev. Francis J. Koenig, S.J., in partial fulfillment of the requirements for the degree of Master of Science, February, 1955, to the Graduate School of St. Louis University.

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

[4] G. W. Schaeffer and L. J. Basile, *ibid.*, **77**, 331 (1955).

[5] The formula "LiB_2H_8N" is written only in accord with the stoichiometry and does not imply a structure or a particular species.

Experimental

Apparatus.—The usual high vacuum apparatus[6] for the handling of volatile substances was employed throughout the investigation.

Materials.—Ammonia was dried over metallic sodium, v.p. 125–128 mm. at −63.5° (lit. 125 mm.); diborane was prepared by the reaction of lithium aluminum hydride and diethyl ether–boron trifluoride[7] and purified by fractional condensation, v.p. 225 mm. at −112° (lit. 225 mm.); diethyl ether was dried over lithium hydride and stored *in vacuo* until used; lithium, sodium and potassium metals were cut from the commercial analytical reagent quality material and manipulated in a nitrogen-filled dry box.

Preparation of the Diammoniate of Diborane.—Because the behavior of the product obtained by the reaction between ammonia and diborane is strikingly dependent upon the conditions of preparation, the procedure will be given in considerable detail.

The diammoniate of diborane was prepared following closely the method of Schlesinger and Burg.[3] About 100 cc. of ammonia was measured in a calibrated system and then transferred to the sides of the reaction tube provided with a side addition tube for later addition of alkali metal, as a thin film covering about 500 cm.^{2} of the tube wall. Best control of the coating was achieved if the ammonia was slowly transferred at a low pressure (below 10 mm.) into the reaction tube while a −196° bath was gradually raised around the reaction tube. Formation of the diammoniate, with the ammonia confined to a small volume, was tried but greater difficulty was met in the complete removal of the excess ammonia. After the introduction of the ammonia, the level of the −196° bath was raised 3 to 5 cm. above the ammonia film and a measured amount of diborane (about 25 cc. or one-fourth of the ammonia taken) was condensed onto the upper portion of the reactor. A bath of −140° was placed around the tube and was allowed to warm slowly, over two to four hours, to −80°. A −78° bath was then substituted and the reaction mixture was allowed to stand at this temperature from 2 to 15 hours. Rapid formation of the diammoniate takes place beginning at about −128°, but unless the mixture is allowed to stand at the higher temperature for several hours, unreacted diborane, which then reacts with ammonia elsewhere in the apparatus, will be removed along with the excess ammonia.

After allowing the mixture to stand, the reactor is opened to the high vacuum through a −196° trap to collect the excess ammonia. The ammonia is measured from time to time and when the ratio of retained ammonia to diborane is two, no more ammonia can be removed and the diammoniate is considered formed. The quantity of diammoniate is taken as the quantity of diborane used in the preparation and is so recorded in column 2 of Table I.

TABLE I

REACTION OF ALKALI METALS WITH $B_2H_6\cdot 2NH_3$ IN LIQUID AMMONIA

Metal	$B_2H_6\cdot 2NH_3$, mmoles taken	H_2, mmoles produced	$H_2/B_2H_6\cdot 2NH_3$
Li	1.83	0.86	0.47
	1.99	1.13	.57
	1.67	0.79	.47
	1.97	1.05	.53
Na	1.38	0.72	0.52
	1.29	.56	.44
	1.51	.72	.48
	2.73	1.36	.50
K	0.84	0.44	0.52
	1.52	.77	.51
	1.18	.65	.55
	1.03	.57	.55

Reaction of the Diammoniate of Diborane with the Alkali Metals.—A measured volume of ammonia (about 100 cc.) was condensed into the tube containing the diammoniate and, under cover of dry nitrogen, an equivalent amount of alkali metal was added. While the reactants were maintained at −196°, the addition tube of the reactor was closed and the reactor was evacuated. The reactor temperature was then brought to −80° and maintained at this temperature for approximately one-half hour. After this time, the reactor was again cooled to −196° and the hydrogen removed and measured. The reactor was again brought to −80° and the cycle repeated until the rate of production of hydrogen was negligible. Within experimental error, regardless of the alkali metal employed or its amount, one-half mole or one equivalent of hydrogen was produced for each mole of diammoniate taken, in agreement with earlier observations.[3] The rate of production of the equivalent of hydrogen appears to be determined by the rate of mixing, and the cessation of hydrogen production is abrupt after one equivalent. Table I summarizes the data so obtained.

Removal of the Solvent.—After the reaction between the alkali metal and the solution of $B_2H_6\cdot 2NH_3$ was deemed complete, the solvent was removed by sublimation at the lowest possible temperature. Not all of the solvent ammonia could be removed at −78° at which temperature the solvent is readily volatilized. This retention of ammonia is attributed to the formation of stable ammoniates of the alkali metal borohydrides, which salts are a principal product of the reaction. As the temperature is raised to increase the dissociation pressure of the ammoniate, some hydrogen may be produced, the amounts depending upon the alkali metal borohydride present. For instance, in the presence of potassium borohydride only traces of hydrogen were produced and all of the solvent ammonia was recovered at temperatures slightly higher than −78°, whereas in the presence of sodium borohydride about 15% hydrogen was produced and an equivalent amount of ammonia was unrecovered, while in the presence of lithium borohydride, over 50% hydrogen was produced with the same per cent. of ammonia remaining unrecovered. This hydrogen-producing reaction is attributed to the ammonolysis of aminoborine.

Borohydride Ammoniates.—To explain the retention of ammonia by the reaction products, the mole ratios of retained ammonia to lithium borohydride were compared to the mole ratios of retained ammonia to the reaction products of lithium and the diammoniate of diborane under identical conditions of solvent removal. The averages for three such experiments are recorded in Table II and *suggest* the formation of at least four ammoniates, each identical in both systems. Consistent with the conclusion that the retention of ammonia by the reaction products was due to the formation of stable ammoniates, the vapor tension–composition isotherm of the ammonia–lithium system[8] at 20° indicates the existence of at least four stable ammoniates. The low dissociation pressure of lithium borohydride monoammoniate (0.2 mm. at 20°) accounts for the fact that some of the solvent ammonia could not be recovered from the reaction products at lower temperatures.

TABLE II

MOLE RATIO OF RETAINED AMMONIA TO LITHIUM BOROHYDRIDE AND OF RETAINED AMMONIA TO REACTION PRODUCTS

NH_3/BH_4	−80°	−64°	−45°	−22°	0°
$LiBH_4$	3.99	3.12	2.71	1.75	0.75
Reaction products	4.25	3.26	2.53	1.11	1.03

Ammonolysis Reactions.—Evidence for the ammonolysis of the aminoborane is had by the fact that, after the ammonia is removed as completely as possible from the reaction products, the hydrogen produced during the removal of the solvent is equivalent to the amount of ammonia unrecovered. The data, Table III, are in accord with the postulated equation 4. To confirm the conclusion that the hydrogen is not produced by a reaction of ammonia with the alkali metal borohydride, pyrolytic studies of the lithium borohydride–ammonia system, which is the system most sensi-

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[6] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y, 1948.

[7] I. Shapiro, *et al.*, THIS JOURNAL, **74**, 901 (1952).

[8] D. J. Hunt, unpublished results. The dissociation pressures of the ammoniates of lithium borohydride at 20° are: monoammoniate, 0.2 mm.; diammoniate, 9.8 mm.; triammoniate, 34.5 mm.; and tetraammoniate, 74.3 mm.

tive to ammonolysis, were conducted.[9] At room temperature, a stable lithium borohydride monoammoniate is formed, but no hydrogen is produced either upon standing or upon removal of the ammonia from the borohydride ammoniate. Only at temperatures well above room temperature does lithium borohydride react with ammonia to give hydrogen.

TABLE III

AMMONOLYSIS REACTIONS

Metal	$B_2H_6 \cdot 2NH_3$, mmoles taken	NH_3 mmoles consumed	H_2, mmoles produced	Ratio $H_2/B_2H_6 \cdot 2NH_3$	Ratio H_2/NH_3
Li	2.64	1.78	1.75	0.66	0.99
	1.67	0.89	0.89	.53	1.00
Na	1.09	0.56	0.54	.50	0.97
	1.91	1.16	1.20	.63	1.03
	2.68	0.80	0.80	.30	1.00
K	0.69	0.00	0.00	.00	0.00
	1.52	0.36	0.09	.06	0.25

Extent of Ammonolysis.—By inspection of the data of Table III, column 5, it can be seen that the extent of ammonolysis of aminoborane is greatest in the presence of lithium borohydride and least in the presence of potassium borohydride. This difference can be accounted for by a consideration of the relative stabilities of the borohydride ammoniates. Because lithium borohydride monoammoniate is more stable than potassium borohydride monoammoniate, a higher temperature is required to remove the ammonia from lithium borohydride monoammoniate. Thus, if the rate of reaction of aminoborane with ammonia were temperature dependent, the extent of ammonolysis of aminoborane would be expected to be greatest in the presence of lithium borohydride and least in the presence of potassium borohydride.

The data for the lithium system given in Table III represent cases in which the ammonia was removed with extreme care at the lowest possible temperature. If less caution were exercised, extensive and complex ammonolysis occurred[10] with the production of up to four moles of hydrogen for each mole of diammoniate originally taken and several different volatile boron–nitrogen compounds were indicated but these were never recovered in amounts sufficient to establish conclusively homogeneity or to allow positive identification. The data obtained do suggest B_2H_7N (B/N, 0.99/0.50; v.p. 0°, 33 mm.) and $B(NH_2)_3 \cdot NH_3$ (B/N, 0.82/3.34; v.p. 0°, 54 mm.).

Separation and Identification of Lithium Borohydride and Aminoborane.—Because lithium borohydride is soluble and aminoborane is insoluble in diethyl ether, it is possible to separate these substances by extraction with that solvent.

After the reaction of lithium metal with the diammoniate of diborane was complete and the solvent ammonia had been removed, about 10 ml. of diethyl ether, which had been previously dried and degassed over lithium hydride, was condensed into the reactor which had been previously fitted to the usual filtration unit.[11] The filtration unit was removed from the vacuum line and the reaction products were extracted eight times to assure complete separation of the lithium borohydride from the aminoborane. Lithium borohydride was recovered from the ether solution and the two portions were identified by analysis. Hydrogen was determined by acid hydrolysis; boron by titration and nitrogen by the standard Kjeldahl method. The data are recorded in Tables IV and V.

TABLE IV

ANALYSIS OF THE ETHER-SOLUBLE FRACTION

$B_2H_6 \cdot 2NH_3$, mmoles taken	B, mmoles found	N, mmoles found	H, mmoles found	Ratio H/B
1.83	1.12	0.00	4.21	3.76
1.98	0.87	.00	3.75	4.20
1.67	1.16	.14	4.65	4.00
1.95	0.98	.36	3.90	3.97

TABLE V

ANALYSIS OF THE ETHER-INSOLUBLE FRACTION

$B_2H_6 \cdot 2NH_3$, mmoles taken	B, mmoles found	N, mmoles found	H, mmoles found	Ratio H/B	Ratio N/B
1.67	1.49	1.65	2.88	1.93	1.11
1.95	2.62	2.98	4.35	1.66	1.14

The hydrogen to boron ratios for the soluble fraction are close to the theoretical four to one and only minor amounts of nitrogen were found, thus demonstrating the material[12] to be lithium borohydride. In the case of the insoluble material, the hydrogen to boron ratios are somewhat lower than the theoretical two to one (only two hydrogens are hydrolyzable) expected for aminoborane, BH_2NH_2, while the nitrogen ratios are high. These low hydrogen and high nitrogen ratios can be explained by the presence of the ammonolysis product of aminoborane, $BH(NH_2)_2$, in the insoluble residue.

Separation of Sodium Borohydride and Aminoborane.—Sodium borohydride, which is soluble in ethylene glycol dimethyl ether,[13] was separated from the reaction residue by extraction. X-Ray diffraction patterns (see below) were obtained for both the soluble and insoluble portions. Sodium borohydride was found to be the only crystalline substance present in the soluble fraction and no crystalline substance was found to be present in the insoluble material. In another experiment, a similar separation was carried out and the residues were analyzed for boron[14] using the usual NaOH titration in the presence of mannitol but employing a *p*H meter to follow the titration. For the insoluble residue 1.25 meq. of boron was found and for the soluble material 1.32 meq. of boron. The total milliequivalents of boron titrated were 2.57 while the total boron present in the original sample was 3.02 meq. Evidently the products were separated into two nearly equivalent fractions of soluble sodium borohydride and insoluble aminoborane, or its ammonolysis products.

A similar extraction was attempted with the reaction products of potassium and the diammoniate of diborane. After eleven extraction cycles, no soluble material had been separated and the experiment was abandoned.

X-Ray Identification of Sodium and Potassium Borohydrides.—After the solvent ammonia had been removed from the reaction products, samples of the products were removed from the vacuum line, and X-ray diffraction patterns were taken. The *d*-values were calculated and found to be identical with those calculated from the reported[15] crystal constants for sodium and potassium borohydrides. The *d*-values calculated from authentic samples of the borohydrides and typical residues are compared in Table VI. No peaks were observed in any sample other than those for sodium or potassium borohydride, strongly suggesting that

TABLE VI

X-RAY DATA FOR SODIUM AND POTASSIUM BOROHYDRIDE

hkl	Authentic $NaBH_4$	Typical sample	Authentic KBH_4	Typical sample
111	3.56 m	3.56 m	3.88 m	3.87 m
200	3.08 vs	3.08 vs	3.36 s	3.35 s
220	2.17 s	2.17 s	2.37 s	2.37 s
311	1.86 m	1.86 m	2.03 m	2.03 m
222	1.78 m−	1.78 m−	1.94 m−	1.94 m−
400	1.54 m	1.54 m−	1.68 w	1.68 w
331	1.41 w	1.41 w	1.54 w	1.54 w
402	1.38 m	1.38 m	1.50 w+	1.50 w
422	1.26 w+	1.26 w+	1.37 w	1.37 w
333–511	1.18 vw	1.18 vw	1.29 w	1.29 w

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[9] P. A. Cowie, unpublished results.

[10] Reactions of this type were never observed in the sodium and potassium systems.

[11] A. C. Stewart, Doctoral Dissertation, St. Louis University, 1952.

[12] Interpretation of the data for the insoluble phase is complicated by the insolubility of lithium borohydride monoammoniate in diethyl ether. This would result in higher boron and nitrogen in the insoluble phase and low boron in the soluble phase. This effect is evident in the second experiment, Table V.

[13] "Merck Index," Sixth Ed., p. 875.

[14] L. J. Basile, Doctoral Dissertation. St. Louis University, 1954.

[15] S. C. Abrahams and J. Kalnajs, *J. Chem. Phys.*, **22**, 434 (1954)

these materials under all experimental conditions used were the only crystalline substances present.

Although the X-ray investigation of the products is the only direct evidence presented in support of the assumption that equations 3 and 4 represent the reaction in the potassium system, these results taken together with the data of Table I and the behavior of the system during the removal of the solvent support such a supposition.

Discussion

That the alkali metal borohydrides and aminoborane are obtained upon removal of the solvent after reaction of the solution of $B_2H_6 \cdot 2NH_3$ with the alkali metal regardless of the metal taken strongly suggests that these species are present in the solution before removal of the solvent. In the case of lithium such evidence is particularly strong, for even at −78° lithium borohydride tetraammoniate (Table II) appears as the solid phase immediately upon removal of the solvent and it does not seem reasonable that a precursor species would disproportionate into the borohydride and aminoborane under such mild conditions. If it is assumed that the borohydride ion exists in the solution before removal of the solvent, the reaction of $B_2H_6 \cdot 2NH_3$ with an alkali metal should be written

$$B_2H_6 \cdot 2NH_3(\text{soln.}) + M(\text{soln.}) = {}^1/_2H_2 + BH_2NH_2(\text{soln.}) + M^+(\text{soln.}) + BH_4^-(\text{soln.}) + NH_3 \quad (5)$$

and the removal of the solvent would be represented by

$$BH_2NH_2(\text{soln.}) + M^+(\text{soln.}) + BH_4^-(\text{soln.}) = MBH_4 \cdot \text{solvate} + BH_2NH_2\ (\text{polymeric}) \quad (6)$$

It should be noted that no information concerning the manner of existence of $B_2H_6 \cdot 2NH_3$ in the solution prior to reaction with the metal is provided by this investigation, but if the species in the solution were those postulated by Schlesinger and Burg,[3] it would be necessary to assume that upon reaction with the metal and replacement of the ammonium ion with the metal ion, equation 1, a hydride shift[16] within the anion would occur

$$BH_3NH_2BH_3^- = BH_4^- + NH_2BH_2. \quad (7)$$

It is, however, difficult to see why the reaction with the metal should induce such a rearrangement, and it seems more probable that the borohydride ion exists in the ammonia solution prior to the reaction with the metal.

In view of the foregoing, the *chemical behavior* of $B_2H_6 \cdot 2NH_3$ might best be represented by the formula $NH_4 \cdot BH_2NH_2 \cdot BH_4$. But such a representation must not be taken to imply uniquely a structure for a number of unresolved problems remain.

(a) Although the reaction of the ammonia solution of $B_2H_6 \cdot 2NH_3$ with sodium is most simply interpreted by postulating the cationic species to be NH_4^+, any cation which is a strong protonic acid and which upon reaction with the metal yields ammonia and aminoborane is consistent with the observation.

(b) It is known[17] that NH_4BH_4 is unstable above −10° but that solid $B_2H_6 \cdot 2NH_3$ is reasonably stable to 80°, thus stabilization of the NH_4^+–BH_4^- system by separation with BH_2NH_2 groups must be postulated if the above formulation is taken to represent the structure of the compound.

(c) The relationship between the solid $B_2H_6 \cdot 2NH_3$ and the solution of this substance in ammonia has not been established.

(d) Reactions such as that represented by equation 7 have not been conclusively eliminated and, indeed, tautomerism between structures related by such reactions is possible.

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[16] A similar hydride shift has been postulated in the reaction of diborane with carbonyl compounds (H. C. Brown, H. I. Schlesinger and A. B. Burg, THIS JOURNAL, **61**, 673 (1939)) and in the reaction $(CH_3)_2BNH_2 + BF_3 = (CH_3)_2BF + NH_2BF_2$ (R. E. Moore, Master's Thesis, The University of Chicago, June, 1949) the fluoride ion undergoes a similar shift.

[17] D. R. Schultz, Doctoral Dissertation, University of Michigan, Ann Arbor, Michigan, June, 1953.