The molecular weight was determined by the cryoscopic method in benzene. Calcd: 251.7. Found: 253.

Preparation of B-Tricyanoborazole.—Eastman Kodak "white label" acetonitrile was purified carefully according to the procedure reported by Wawzonek and Runner.[16] If the acetonitrile was not treated in this fashion, highly colored by-products usually were formed during the subsequent reaction. A 50% excess of vacuum dried silver cyanide was placed in a round bottom flask with several grams of glass beads. To this was added an acetonitrile solution of B-trichloroborazole. Since silver cyanide is nearly insoluble in acetonitrile (although more soluble than silver chloride), the flask was shaken for approximately one week to bring the reaction to completion. Shorter reaction times resulted in products still containing chlorine. Care was taken to shield the flask from light during the shaking period to prevent decomposition of the silver chloride.

After the shaking period was complete the acetonitrile solution was filtered from silver chloride and excess silver cyanide. The precipitate was extracted several times with acetonitrile. The combined fractions were subjected to a vacuum distillation to remove the solvent. The white solid which was thus obtained was recrystallized four to six times from acetonitrile. In spite of several recrystallizations, the purest reaction product contained nearly 5% of silver by weight, possibly as a silver cyanide complex. The solubility of silver cyanide is much too small to account for the silver present and the high molecular weight of the inorganic salt would result in only slight changes in the cyanide to be expected on analysis.

Properties of B-Tricyanoborazole.—The compound is a white solid and unlike B-trichloroborazole and B-trithiocyanatoborazole it is relatively thermally stable, decomposing in vacuum only at temperatures exceeding 200°. The cyano derivative is insoluble in benzene, toluene, carbon tetrachloride and hexane. Its solubility in acetonitrile at room temperature is 0.6–0.7 g. per 100 cc. solvent. B-Tricyanoborazole is most sensitive toward moist air and in water hydrolyzes immediately to liberate hydrogen cyanide. Attempted reduction with lithium and sodium borohydride lead only to the formation of black unidentified products.

Analytical results on the purest reaction product were: B, 18.4; N(ring), 24.6; CN, 44.9; Ag, 4.8. Calcd: B, 20.8; N(ring), 27; CN, 50.0.

The ratio of boron to ring nitrogen to cyanide thus was 0.99: 1.01:1.00.

Reaction of B-Trichloroborazole with Silver Nitrate and Silver Nitrite.—In a typical experiment 2.9 g. of B-trichloroborazole and 8.5 g. of silver nitrate were dissolved separately in purified acetonitrile and the solutions cooled overnight at −10°. The silver nitrate solution then was added to the B-trichloroborazole solution under a blanket of dry nitrogen maintaining the low temperature. Immediately all three halogens of the B-trichloroborazole were precipitated as silver chloride. After filtration and partial removal of solvent, well formed white crystals were deposited in the flask. Vacuum distillation of the filtrate at 0° produced a white solid that tenaciously retained some acetonitrile. Upon warming to room temperature the solid partly redissolved in the retained solvent and liberated copious quantities of nitrogen dioxide over a period of 12 hr. leaving a pale yellow solid. In one reaction which had been kept slightly above 0° the recovered solvent was subjected to a fractional distillation on the vacuum line. The acetonitrile was trapped in a −63.5° trap whereas a more volatile material was stopped in a liquid nitrogen trap. The vapor pressure, 84 mm. at −112° and the molecular weight, determined by gas density measurement as 44, identified this volatile material as nitrous oxide.

Extractions of the original reaction product with dry diethyl ether below 0° yielded a solid which retained ether but appeared stable toward the evolution of nitrogen dioxide at room temperature. The ether adduct reacted explosively with water with ignition. Although it is apparently not shock sensitive, the ether adduct (and presumably the original product) should be treated most cautiously since it exploded violently on one occasion in contact with toluene below room temperature. Further studies of this reaction would be interesting to determine whether the adduct behaved as a nitrating agent or is itself unstable.

The reaction of B-trichloroborazole with silver nitrite appears to be similar to the reaction with silver nitrate. Solutions were prepared of 12.2 g. of silver nitrite and 5 g. of B-trichloroborazole each dissolved in 50 ml. of purified acetonitrile. The solution of silver nitrite cooled to 0° was added to the cooled B-trichloroborazole solution. An immediate reaction took place as shown by the formation of a white precipitate of silver chloride and evolution of nitrogen dioxide. The solution was filtered and the filtrate vacuum distilled, but the remaining white solid continued to evolve nitrogen dioxide below room temperature and no relatively pure product could be isolated.

Acknowledgments.—Gerald L. Brennan and Gerd H. Dahl gratefully acknowledge the generous financial support of this work by fellowships awarded by the Stauffer Chemical Company. Support of this work at Indiana University by NSF Grant G-6224 is also gratefully acknowledged.

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[16] S. Wawzonek and M. E. Runner, *J. Electrochem. Soc.*, **99**, 457 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN]

The Preparation and Structure of the Diammoniate of Tetraborane[1]

BY G. KODAMA AND R. W. PARRY

RECEIVED JULY 14, 1960

The reaction between ammonia and tetraborane has been examined under a variety of conditions. The pure compound $B_4H_{10}\cdot 2NH_3$ has been isolated and evidence to support the structure $[H_2B(NH_3)_2{}^+][B_3H_8]$ is presented. The "diammoniate of tetraborane" resembles the "diammoniate of diborane" in many of its reactions. Available evidence suggests that the unstable "compounds" $B_4H_{10}\cdot 2.5NH_3$ and $B_4H_{10}\cdot 4NH_3$ reported in an earlier study are complex mixtures.

In their initial study of the reaction between tetraborane and ammonia Stock, *et al.*,[2] reported two unstable compounds, $B_4H_{10}\cdot 4NH_3$ and $B_4H_{10}\cdot 2.5NH_3$. In a careful study of the same system made in this Laboratory neither the formula $B_4H_{10}\cdot 4NH_3$ nor $B_4H_{10}\cdot 2.5NH_3$ could be verified. A modification of the experimental procedures resulted, however, in the isolation of a pure "*diammoniate* of tetraborane," $B_4H_{10}\cdot 2NH_3$, which is stable at room temperature. A preliminary description of this solid has been given.[3] In this

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[1] (a) This research was supported by the United States Air Force, under Contracts No. AF 33(616)-3343 and AF 33(616)-5874 monitored by the Aeronautical Resarch Laboratory, Wright Air Development Center, Ohio. (b) Received in the original form April 8, 1959.

[2] A. Stock, E. Wiberg and H. Martini, *Ber.*, **63B**, 2927 (1930); A. Stock, E. Wiberg, H. Martini and A. Nicklas, *ibid.*, **65B**, 1711 (1932).

[3] (a) G. Kodama and R. W. Parry, THIS JOURNAL, **79**, 1007 (1957); (b) G. Kodama and R. W. Parry, Paper presented before the Inorganic Section of the Sixteenth International Congress of Pure and Applied Chemistry, Paris, France, 1957, p. 483; (c) G. Kodama, Ph.D. Dissertation, University of Michigan, 1957.

paper a more complete account of the investigation is recorded, and evidence is presented in support of the belief that the original "compounds" described by Stock and his coworkers, were indeed complex and unstable mixtures.

The Preparation and Properties of $B_4H_{10}\cdot 2NH_3$.—When ammonia was added slowly to a cold (−78°) ether solution of tetraborane, the ammonia was absorbed completely. An excess of tetraborane (in relation to ammonia) was always used. If the system were aged at low temperature (4 days at −78°, 12 hours at −45°) then the solution were filtered and the solvent removed from the filtrate at −45°, a white, dry, microcrystalline solid, identified by analysis as $B_4H_{10}\cdot 2NH_3$, was obtained. The molecular weight of the product as determined by vapor pressure depression in liquid ammonia was 81.[3c] In diethyl ether, values obtained by vapor pressure depression ranged from 150 to 250. The theoretical value for $B_4H_{10}\cdot 2NH_3$ is 87. The marked discrepancy between results in liquid ammonia and in ether would suggest that $B_4H_{10}\cdot 2NH_3$ is an ionic type of solid.[4,5]

The compound $B_4H_{10}\cdot 2NH_3$ undergoes no visible decomposition in air at room temperature. It dissolves in cold water with only very slow hydrogen evolution although both acid and platinized platinum accelerate gas evolution in water. The compound is soluble in liquid ammonia and, judging from its X-ray powder pattern, it is unchanged upon recovery from the liquid ammonia solution. If perfectly dry, the compound will dissolve in anhydrous diethyl ether to give a stable solution at room temperature; the compound can be recovered unchanged by evaporation of the solvent. If, however, the solid has been handled in moist air prior to its solution in ether, a precipitate slowly forms.

TABLE I

INTERPLANAR SPACINGS AND RELATIVE INTENSITY DATA FOR $B_4H_{10}\cdot 2NH_3$

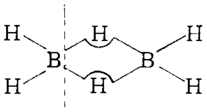
Intensity[a]	d(Å).	Intensity	d(Å.).
w	6.50	w	2.36
w	6.10	mw	2.29
m	4.63	w	2.18
s	4.10	w	2.03
m	3.69	vw	1.97
w	3.48	vw	1.89
m	3.29	vw	1.84
w	3.06	vw	1.81
ms	2.88	vw	1.78
m	2.78	vw	1.74
w	2.62	vw	1.60
m	2.57	vw	1.54
m	2.52	vvw	1.50
w	2.46		

[a] s = strong, m = medium, w = weak, v = very.

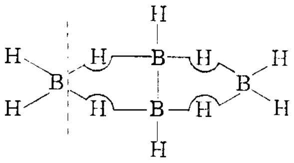
The pure compound appears to form an etherate at low temperatures. At −78° well formed, clear crystals were separated out from a diethyl ether solution of the diammoniate of tetraborane. This solid melts quite readily to form a clear ethereal solution. The diammoniate of tetraborane is insoluble in aromatic as well as in aliphatic hydrocarbons.

The crystalline nature of the material is indicated by the X-ray powder data. The interplanar spacings and relative intensities of the reflections are given in Table I. A single crystal X-ray study is being conducted in the laboratory of Dr. C. E. Nordman of this Department.

Chemical Evidence for the Structure of $B_4H_{10}\cdot 2NH_3$.—Although no unequivocal physical evidence for the structure of $B_4H_{10}\cdot 2NH_3$ is yet available, it is possible to assign a structure with a high degree of certainty on the basis of chemical evidence. Diborane and tetraborane can be represented in planar projections as



and



It is significant to note that the end borons of tetraborane are bound to the rest of the molecule *only* by double bridge bonds. This feature resembles rather closely, but is not identical with the double bridge bond structure of diborane. Nonsymmetrical cleavage of the double bridge bond of *diborane* by ammonia (see dotted lines in formula) results in the structure $[H_2B(NH_3^+)_2][BH_4^-]$. An application of the same argument to tetraborane suggests for the diammoniate of *tetraborane* the structure $[H_2B(NH_3^+)_2][B_3H_8^-]$. Such a model immediately suggests a number of discriminating chemical reactions which should be of structural significance. These are outlined below.

(1) The reaction of $B_4H_{10}\cdot 2NH_3$ with sodium.

The reaction between sodium and the diammoniate of *diborane* can be written as[6]

$$[H_2B(NH_3)_2]BH_4 + Na \xrightarrow[-78^\circ]{\text{liq. }NH_3} {}^1/_2H_2 + NaBH_4 + H_2BNH_2 + NH_3$$

If the proposed structure were correct for the diammonaite of *tetraborane*, the reaction would be

$$[H_2B(NH_3)_2]B_3H_8 + Na \xrightarrow[-78^\circ]{\text{liq. }NH_3} {}^1/_2H_2 + NaB_3H_8 + H_2BNH_2 + NH_3$$

A solution of $B_4H_{10}\cdot 2NH_3$ in liquid ammonia will react with dissolved metallic sodium at −78° to liberate one half mole of hydrogen per mole of $B_4H_{10}\cdot 2NH_3$. This reaction is complete in 20 minutes; further hydrogen evolution proceeds more slowly.[7] If the reaction is stopped after the initial rapid hydrogen evolution process has been completed, NaB_3H_8 can be extracted in 60 to 70% yield from the solid residues by leaching them with di-

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(4) Ionic solids in liquid ammonia frequently appear as ion pairs in the concentration range of interest here. The same solids in ether appear as ion clusters.[5]

(5) A. B. Burg and G. W. Campbell, Jr., THIS JOURNAL, **74**, 3744 (1952); R. W. Parry, G. Kodama and D. R. Schultz, *ibid.*, **80**, 24 (1958).

(6) D. R. Schultz and R. W. Parry, *ibid.*, **80**, 4 (1958).

(7) These data together with other data available in this Laboratory suggest that the rate *and stoichiometry* of hydrogen evolution may be of more significance in indicating compound purity rather than compound structure. A more complete account will be reported later.

TABLE II

THE REACTION OF B_4H_{10} AND NH_3 IN DIETHYL ETHER

B_4H_{10} (mmole)	NH_3 (mmole)	Ether (ml.)	NH_3/B_4H_{10}	Temp. (°C.)	Time	Yield $B_4H_{10}\cdot 2NH_3$ Based on NH_3 (pct.)	Yield $B_4H_{10}\cdot 2NH_3$ Based on B_4H_{10} (pct.)	Remarks
4.18	7.56	3	1.81	−78 to −70	30 min.	0	0	[a]
4.20	1.91	2	0.455	−78 to 0	1 hr.	54[b]	12	
2.18	3.35	3	1.54	−95	1 hr.	Trace	Trace	
3.08	5.55	5	1.8	−78	4 hr.	40	37	[c]
2.05	3.84	10	1.88	−78	3 days	54	51	[c]
2.37	4.25	10	1.8	−78	4 days	87	78	[c]
				−45	12 hr.			

[a] Product became liquid at room temperature. [b] Purity of product in doubt because methods of purification were not well developed at the time of the run. [c] Solvent ether removed at room temperature.

ethyl ether. The NaB_3H_8 was identified by comparing its X-ray powder pattern with that of an authentic pattern for NaB_3H_8 which was kindly furnished by Dr. L. J. Edwards of Callery Chemical Co. NaB_3H_8 was characterized earlier in an excellent independent study by Hough, Edwards and McElroy.[8]

(2) The reactions of $B_4H_{10}\cdot 2NH_3$ with HCl and HBr.

The reaction of HCl with the diammoniate of diborane is characteristic of the general reaction between borohydrides and HCl[6,9] and can be represented as

$$[H_2B(NH_3)_2][BH_4] + HCl \longrightarrow [H_2B(NH_3)_2]Cl + H_2 + {}^1/_2B_2H_6$$

An extrapolation of such an argument to the structure proposed for $B_4H_{10}\cdot 2NH_3$ gives the equation

$$[H_2B(NH_3{}^+)_2][B_3H_8{}^-] + HCl \longrightarrow [H_2B(NH_3)_2]Cl + H_2 + B_3H_7$$

The B_3H_7 group would immediately undergo further reaction unless stabilized by coördination with a suitable base.

The interaction of HCl with a stoichiometric quantity of $B_4H_{10}\cdot 2NH_3$ in diethyl ether solution at −78° gave rapid liberation of the expected mole of hydrogen and immediate precipitation of the ether insoluble solid $[H_2B(NH_3)_2]X$ where X is Cl^- or Br^-. The complex chloride and bromide salts were shown to be purer forms of the salts first prepared earlier from the diammoniate of *diborane*.[6] Indeed the reaction between $B_4H_{10}\cdot 2NH_3$ and HCl or HBr in diethyl ether at −78° is the best method currently available for preparing *pure* samples of the chloride and bromide salts of the dihydrido-diammineboron(III) cation. A single crystal X-ray study of the chloride salt by Nordman and Peters[10] removes all doubt as to the structure of the cation.

(3) The preparation of ammonia-triborane from $B_4H_{10}\cdot 2NH_3$.

When diethyl ether was used as the solvent at −78°, the B_3H_7 fragment, resulting from the action of HCl on $B_4H_{10}\cdot 2NH_3$, was stabilized at −78° through formation of the etherate, $(C_2H_5)_2OB_3H_7$. If such a solution were warmed, the etherate dissociated and the B_3H_7 group decomposed. If, however, ammonia were added to the cold (−78°), ether solution, ammonia, being a stronger base than ether, displaced it to give the stable solid $H_3NB_3H_7$.

$$NH_3 + (C_2H_5)_2OB_3H_7 \xrightarrow[Et_2O]{-78^\circ} (C_2H_5)_2O + H_3NB_3H_7$$

The ammonia adduct was identical in all respects with the product prepared by other methods and described elsewhere.[11] Recovered yields of $H_3NB_3H_7$ were about 45% based on the above equation.

The System Ammonia–Tetraborane without Solvent.—In their original study Stock and his collaborators froze excess ammonia and tetraborane together using liquid air; they then held the system at −75° for 1 hr. When excess ammonia was removed, the composition of the residue corresponded to the formula $B_4H_{10}\cdot 4NH_3$. The solid decomposed when warmed to room temperature; gaseous boron compounds, hydrogen and ammonia were liberated and the "salt-like solid turned to a liquid." When excess tetraborane was used in the reaction instead of an excess of ammonia, an unstable solid residue of composition $B_4H_{10}\cdot 2.5NH_3$ resulted. Similar experiments conducted in this Laboratory indicated that many hours of aging were required for apparent equilibration of the B_4H_{10}–NH_3 system both with and without solvent (Tables II and III). This fact, plus the reported instability of Stock's products, and the identification of the $B_3H_8{}^-$ ion in the solid reaction product (see below) indicate that Stock's original solid material was a complex mixture.

In a typical experiment, patterned after that of Stock, an excess of ammonia was frozen with a measured quantity of tetraborane; then the system was equilibrated at −78° for 5 hr. The reaction vessel next was opened to a trap cooled with liquid nitrogen, and excess ammonia was removed. The over-all composition of the B_4H_{10}–NH_3 adduct was followed as a function of time. Data are shown in Fig. 1. Comparable data of the earlier workers for a sample without the preliminary 5 hr. aging period are shown for comparison. Under the conditions described above the composition of the residue at −78° corresponds to the formula $B_4H_{10}\cdot 7NH_3$. When no change in composition was detected at −78°, the temperature was raised to −63.5°. At this higher temperature ammonia was lost without significant hydrogen evolution. The composition of the residue appeared to be approaching

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[8] W. V. Hough, L. J. Edwards and A. D. McElroy, THIS JOURNAL, **78**, 689 (1956).

[9] H. I. Schlesinger and H. C. Brown, *ibid.*, **62**, 3429 (1940).

[10] C. E. Nordman and C. Peters, *ibid.*, **81**, 3551 (1959).

[11] G. Kodama, R. W. Parry and J. C. Carter, *ibid.*, **81**, 3534 (1959).

TABLE III

SUMMARY OF RUNS OF B_4H_{10} AND NH_3, NO SOLVENT

B_4H_{10} (mmole)	NH_3 at start (mmole)	Reaction temp. (°C.)	Reaction time (hr.)	NH_3 Removal		NH_3/B_4H_{10} ratio approached by system	H_2/B_4H_{10} mmole ratio
				(°C.)	(hr.)		
Data from this study							
1.04	12.58	−196 to −78	5	−78	8.5		
				−63.5	6.00	7.05	Nil
1.12	8.34	−165 to −65	12+	−63.5	..	3 to 3.2	Nil
						3.2	0.053
0.325	4.66	−78	1	−78	24	3.2	.15
				−63	6	2.91	.15
				−45	3	2.83	.15
				−23	8	2.34	.17
				0	25	2.16	.70
				25	6	2.16	.76
0.337	5.17	−78	24	−23	3.3	3.03	.016
				25	18	2.14	.72
Comparable data from Stock, Wiberg and Martini							
0.445	4.7	−75	1	−75	[a]	4.0	[b]
.455	4.8	−75	1	−75	[a]	4.0	[b]
.442	4.6	−75	1	−75	[a]	4.0	[b]

[a] About 3. [b] Not reported.

$B_4H_{10}\cdot 3NH_3$, although the agreement was rather poor (Fig. 1). At temperatures above −63.5° additional ammonia was evolved and the ratio NH_3/B_4H_{10} slowly approached 2. It is significant that in systems of this type H_2 evolution became quite vigorous above 0°, and the ratio H_2/B_4H_{10} became as large as 0.82 on some samples after several days.

A pressure-composition diagram then was constructed for the system B_4H_{10}–NH_3. A sample of B_4H_{10} was placed in a tube and a measured *excess* of ammonia was added. The apparent equilibrium pressure above the solid adduct was measured at −78, −63, −45 and −35°. Part of the ammonia was removed and the pressure measurements were repeated. Many days were required to reach a steady pressure at each temperature-composition point. Data are presented in Fig. 2. At temperatures above −78° the highest definite ammoniate appears to be $B_4H_{10}\cdot 6NH_3$. At −78° the data do not exclude the composition $B_4H_{10}7\cdot NH_3$ shown in Fig. 1. It is also of interest to note that the data of Fig. 1 are not in conflict with the existence of $B_4H_{10}\cdot 6NH_3$ at −63.5° but simply imply that such a hexammoniate has a measurable dissociation pressure at that temperature; thus ammonia can be removed to a trap cooled with liquid nitrogen.

Stock's observations on the instability of the above product at temperatures above −23° were confirmed. The adduct of B_4H_{10}–NH_3, prepared without solvent, evolved gaseous boron compounds, ammonia and hydrogen and became liquid when warmed to room temperature. In fact even stable $B_4H_{10}\cdot 2NH_3$ lost hydrogen and ammonia and turned to a liquid *when it was added to the viscous liquid residues from the above system.* Thus even if $B_4H_{10}\cdot 2NH_3$ were formed by the direct reaction of B_4H_{10} and ammonia, the unstable and catalytically active by-products formed in the same reaction would complicate the isolation of pure $B_4H_{10}\cdot 2NH_3$.

Some evidence for $[H_2B(NH_3{}^+)_2][B_3H_8{}^-]$ was indeed found in the product resulting from the reaction described by Fig. 1 and in related processes. If B_4H_{10} and ammonia were frozen together with liquid nitrogen then warmed to −78°, aged for 3 days at this temperature, dissolved in liquid ammonia and treated with metallic sodium, hydrogen gas was evolved and NaB_3H_8 could be extracted from the solid product in yields up to 60%. Such an observation suggests that the solid product resulting from the prolonged interaction of tetraborane and *excess* ammonia at −78° is largely an ammonia addition compound or an ammonia solvate of $[H_2B(NH_3)_2][B_3H_8]$.

There is also evidence for other products in such a system which appear to result from the uncontrolled cleavage of the B_4H_{10} molecule. When the clear ammonia solution of the B_4H_{10}–NH_3 adduct was treated with an ammonia soluble Mg-salt, $[Mg(NH_3)_6(AsF_6)_2]$, a small quantity of $[Mg(NH_3)_6](BH_4)_2$ was formed. Liquid ammonia solutions of pure $[H_2B(NH_3)_2{}^+]B_3H_8{}^-$ and NaB_3H_8 do not give any precipitate at all when treated with $Mg(NH_3)_6(AsF_6)_2$; thus the foregoing constitutes strong evidence for the borohydride ion as a contaminant in this obviously impure diammoniate of tetraborane. The problem of higher ammoniates is still being studied.

Discussion

The foregoing observations suggest that the use of a solvent is important in the isolation of a stable tetraborane–ammonia adduct. It is equally clear that the choice of the solvent is of great importance in determining the nature of the product formed. If one uses an ether which is a moderately strong electron donor, such as tetrahydropyran, it will cleave the double bridge bond of the tetraborane molecule symmetrically to give one half mole of B_2H_6 and the etherate of B_3H_7. Addition of ammonia to this system then results in the displacement of the ether by the stronger base to give the compound $H_3NB_3H_7$.[11] On the other hand if the ether is a weak electron donor such as diethyl ether, it does not attack the tetraborane molecule under

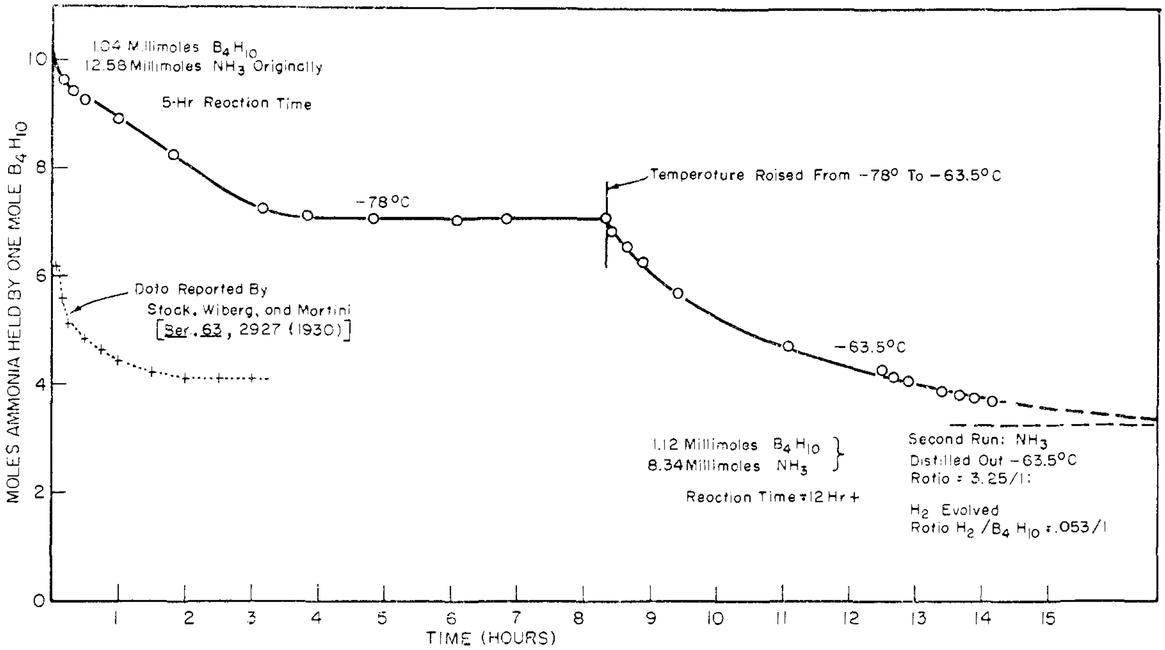


Fig. 1.—The system B_4H_{10}–excess ammonia; the composition of the residue as a function of time.

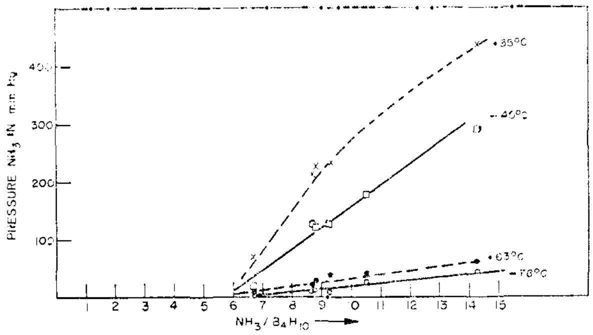
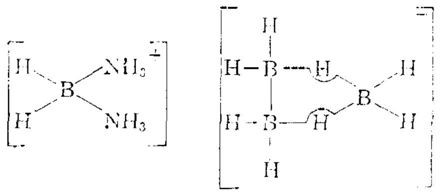


Fig. 2.—The system B_4H_{10}–excess ammonia; pressure composition diagram.

the conditions used; it will simply serve as diluent and heat transfer medium to minimize localized overheating. Under such conditions the ammonia attacks the tetraborane molecule directly in the ether solution and effects non-symmetrical cleavage of the double bridge bonds without further decomposition. It is clear that B_4H_{10} is not attacked by the diethyl ether at low temperature since it was found in this and other laboratories[12] that B_2H_6, the normal decomposition product, is not evolved and B_4H_{10} can be separated unchanged by fractionation.

The resemblance between the chemistry of diborane and tetraborane is indeed striking. Nearly every diborane reaction finds a predictable and verifiable counterpart in tetraborane chemistry if proper conditions are established. Such analogies are apparent in this and an earlier paper. It is also significant that the analogy between diborane and tetraborane serves as a tool for predicting the structure of the $B_3H_8^-$ ion; the resulting model differs markedly from two earlier models postulated for this species.[13,14] If the $B_3H_8^-$ ion is considered as a fragment resulting from the non-symmetrical cleavage process, the structure suggested for $B_4H_{10}\cdot 2NH_3$ may be represented as



Experimental

1. **Reagents.**—The reagents were identical with those described previously.[11]

2. **The Preparation of $B_4H_{10}\cdot 2NH_3$.**—The method of preparation and data for characterization have been given.[3ac] Representative data are shown in Table II.

3. **The Reaction of $B_4H_{10}\cdot 2NH_3$ with Sodium in Liquid Ammonia.**—A sample of $B_4H_{10}\cdot 2NH_3$ (0.856 mole) was placed in a dried nitrogen-filled tube and an excess of sodium in a bulb was crushed into the tube. The tube was attached to the vacuum line and 2 ml. of liquid ammonia was condensed onto the sample. The temperature was raised to −78° rapidly. In 5 min. 0.358 mmole of H_2 was liberated. On standing for an additional 15 min. at −78°, 0.101 mmole of H_2 gas was evolved (total H_2 = 0.459 mmole = 0.53 moles $H_2/B_4H_{10}\cdot 2NH_3$). The excess sodium was eliminated by shaking the ammonia solution with mercury and filtering at −35°. H_2 gas evolved during this operation was 0.027 mmole. Most of the solvent ammonia could be removed at −35° by distillation. Warming the solid residue to room temperature resulted in rapid evolution of H_2 gas. (Total H_2 then equaled 1.35 mmoles.) The solid residue was leached with dry diethyl ether at room temperature in the vacuum line extraction system. From the filtrate NaB_3H_8 was obtained by evaporation of the ether at room temperature. The yield of recovered NaB_3H_8 was 69% based on the equation

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[12] H. I. Schlesinger, University of Chicago, Navy Contract, N173 S-9820, Final Report (1946–1947). Abstracted in W. H. Schechter, R. M. Adams and C. B. Jackson, "Boron Hydrides and Related Compounds," Callery Chemical Co., Callery, Pa., 1954, p. 18.

[13] L. Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1960, p. 378.

[14] W. D. Phillips, H. C. Miller and E. L. Muetterties, This Journal, 81, 4499 (1959).

$$[H_2B(NH_3)_2][B_3H_8] + Na \longrightarrow H_2NBH_2 + NH_3 + NaB_3H_8 + 0.5H_2$$

4. The Reactions of $B_4H_{10}\cdot2NH_3$ with HCl and HBr. The Formation of $[H_2B(NH_3)_2]Cl$ and $[H_2B(NH_3)_2]Br$.—In a typical run 1.84 mmoles of $B_4H_{10}\cdot2NH_3$ was placed in a reaction tube and dissolved in about 2 ml. of diethyl ether. The solution was frozen with liquid nitrogen and an almost stoichiometric quantity (1.78 mmoles) of HCl was condensed into the tube. When the temperature was raised to −78°, 1.74 mmoles of hydrogen gas was evolved in 15 minutes and a white precipitate formed. The precipitate was separated in the vacuum line filtration assembly; the solid was washed through the filter disc with liquid ammonia and the solvent ammonia was distilled from the filtrate at −45°. A sample of $[H_2B(NH_3)_2]Cl$ weighing 119 mg. remained (yield was 79%). Analytical data showed B, 13.2; N, 33.9; hydridic H, 2.41; Cl^-, 42.7. The theoretical values for $[H_2B(NH_3)_2]Cl$ are: B, 13.1; N, 34.0; hydridic H, 2.43; Cl^-, 43.05. The molecular weight was determined by vapor pressure depression in liquid ammonia using standard methods.[4] The value obtained by extrapolation to infinite dilution was 95, which is in only fair agreement with the theoretical value of 82.3, but the deviation is in the range of uncertainty of the method for certain substances. The X-ray powder pattern was the same as that for $[H_2B(NH_3)_2]Cl$ made in an earlier study[6] and is identical with the powder pattern calculated from the single crystal data of Nordman and Peters.[10]

The compound $[H_2B(NH_3)_2]Br$ could be obtained by a similar procedure if HBr were substituted for HCl. Analysis of the bromide salt gave: B, 8.46; N, 22.15; Br^-, 62.5; hydridic H, 1.56. Values calculated for $[H_2B(NH_3)_2]Br$ are: B, 8.53; N, 22.10; Br^-, 63.02; hydridic hydrogen, 1.58. The molecular weight in liquid ammonia was about 120 as compared to a theoretical value of 127. Detailed data are available in dissertation form[3c]; the powder pattern is given elsewhere.[6]

When a large excess of the acid (4- to 6-fold excess) was used in this reaction, gas evolution proceeded very rapidly. One mole of hydrogen per mole of $B_4H_{10}\cdot2NH_3$ was evolved in a few minutes; then the rate of gas evolution dropped almost to zero even when the temperature was raised to −63°. Yields of $[H_2B(NH_3)_2]Cl$ or $[H_2B(NH_3)_2]Br$ were unaffected by using a reasonable excess of acid.

5. The Preparation of $H_3NB_3H_7$ from $B_4H_{10}\cdot2NH_3$.—The filtrate obtained from the reaction between $B_4H_{10}\cdot2NH_3$ and HCl (see run described in previous section) was agitated constantly at −78° and a 1.44 mmole sample of ammonia gas was introduced slowly into the system. It was absorbed completely. The solvent ether was removed at room temperature and from the viscous liquid left in the tube, $H_3NB_3H_7$ was sublimed at 40 to 50° in the vacuum sublimation system. The yield was 36.5 mg. or 45% on the basis of ammonia added.

6. The System Ammonia–Tetraborane without Solvent.—The proportion obtained for the direct reaction of tetraborane and ammonia without solvent was strongly dependent upon experimental conditions. The two cases differentiated by Stock were: (a) reaction systems containing an excess of ammonia and (b) those containing an excess of tetraborane.

(a) **Excess Ammonia Present.**—A measured amount of B_4H_{10} was condensed with liquid nitrogen at the bottom of a reaction tube and a measured amount of ammonia condensed in a ring above it. The system was allowed to warm slowly to the reaction temperature. Data for a typical run are plotted in Fig. 3 and several runs under different conditions are summarized in Table III. Examination of runs 1 and 3 indicates that the formula approached by the resulting residue is strongly dependent upon the aging period provided at −78° and upon the temperature of the sample during removal of excess ammonia. The marked time dependence strongly suggests that the reaction mixture had not reached its equilibrium condition.

(b) **Excess Tetraborane Present.**—The reactants were frozen together as indicated previously. Excess B_4H_{10} was distilled from the mass. Typical data are shown in Table IV. In run 2 a small amount of solid, stable at room temperature, apppeared on the wall of the tube above the decomposing residue. The X-ray powder pattern of the solid was that of $B_4H_{10}\cdot2NH_3$.

TABLE IV

THE ADDITION OF EXCESS B_4H_{10} TO AMMONIA

NH_3 (mmole)	B_4H_{10} (mmole)	Temp., (°C.)	Time at temp. listed (min.)	Ratio NH_3/B_4H_{10}	Remarks
1.62	5.53	−196 to			
		−126	20		Unstable at room
		− 95	30	2.25	temp.
		− 78	90		
2.46	8.37	−196 to			Mostly unstable at
		− 95	20 min.		room temp. but
		− 78	30 min.	1.8	some $B_4H_{10}\cdot2$-
		− 35	150 min.		NH_3 isolated

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π-Complexes of the Transition Metals. XIII. Acetylenic Condensations on Nickel(II) and Chromium(II)[1]

BY M. TSUTSUI AND H. ZEISS

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The formation of dimesitylnickel(II) by the addition of mesitylmagnesium bromide to nickel(II) bromide in tetrahydrofuran is deduced from its reactions with diphenyl- and dimethylacetylene and the analogous formation and reactions of dimesitylchromium(II). The possibility of the existence of a π-complexed cyclobutadiene intermediate in the reaction between dimesitylnickel and tolane is considered and discussed within the framework of the cyclobutadiene problem.

The origin of the π-bis-arene concept in 1954 and the specific examples of the Hein compounds having two aromatic rings bound to chromium by π-bonds led to an extension of our structural proposals to nickel and its eight π-electron requirement for a stable krypton configuration.[2] On this basis the prediction of the eventual capture of cyclobutadiene in the form of a complex, such as bis-cyclobutadiene-nickel(0) or the nickel cation, was made. Reppe's synthesis of cycloöctatetraene from acetylene on a nickel catalyst[3] together with the Longuet-Higgins and Orgel molecular orbital treatment of the matter[4] permitted an optimistic view of this problem.

The low temperature, cyclic condensation of 2-butyne on triphenylchromium(III), yielding hexamethylbenzene and 1,2,3,4-tetramethylnaphthalene

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(1) A portion of this paper was presented in Chicago, Sept., 1958; Abstracts, 134th Meeting, Am. Chem. Soc., p. 59-P. Paper XII, THIS JOURNAL, **81**, 6090 (1959).

(2) H. Zeiss and M. Tsutsui, *ibid.*, **79**, 3062 (1957).

(3) See M. W. Bigelow and J. W. Copenhaver, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Co., New York, N. Y., 1949.

(4) H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1969 (1956).