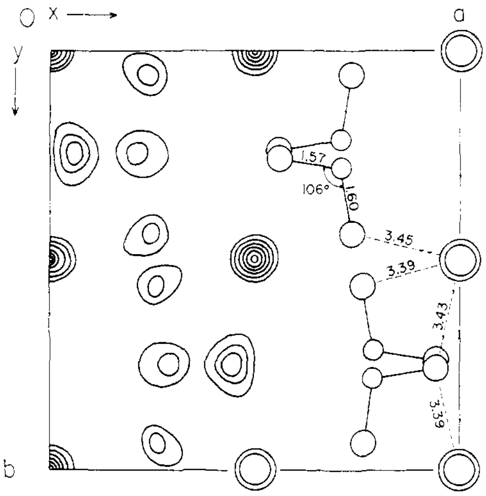


Fig. 2.—Electron density projection on (001), contours as in Fig. 1.

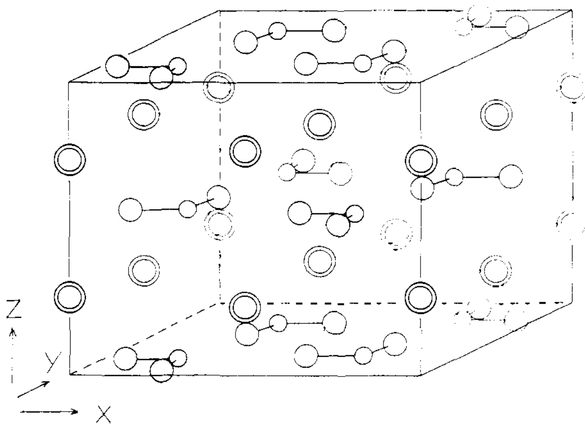


Fig. 3.—The structure of $(NH_3)_2BH_2Cl$.

indicate that the compound is ionic, namely, $[(NH_3)_2BH_2^+]Cl^-$. The four symmetrically non-equivalent distances may be compared with the N . . . Cl distances in ammonium chloride (3.36 Å.) and particularly methylammonium chloride[6] (3.18 Å.) where the coördination is more comparable to that found in $[(NH_3)_2BH_2]Cl$. The lengthening of this distance in the present case is to be expected in view of the presumably smaller charge on each of the NH_3 groups in the $(NH_3)_2BH_2^+$ ion.

The lengths of the two N–B bonds in the cation are equal within experimental error, and also equal to the N–B bond length found in ammonia-borane, NH_3BH_3,[7] and ammonia-triborane, NH_3-B_3H_7.[8] The N–B bond distance also is in close agreement with values found in the addition compounds of BF_3 with NH_3 and methyl amines.[9]

Acknowledgment.—This work was conducted, in part, under Contract AF33(616)-3343 with the U. S. Air Force, the sponsoring agency being the Aeronautical Research Laboratory of the Wright Air Development Center, Air Research and Development Command.

---

(6) E. W. Hughes and W. N. Lipscomb, This Journal, **68**, 1970 (1946).

(7) E. W. Hughes, *ibid.*, **78**, 502 (1956); E. L. Lippert and W. N. Lipscomb, *ibid.*, **78**, 503 (1956).

(8) C. E. Nordman and C. Reimann, *ibid.*, **81**, 3538 (1959).

(9) J. L. Hoard, S. Geller and T. B. Owen, *Acta Cryst.*, **4**, 405 (1951).

Ann Arbor, Michigan

[Joint Contribution from Callery Chemical Company and the Department of Chemistry of the University of Michigan[1]]

Systematics in the Chemistry of the Boron Hydrides

By R. W. Parry and L. J. Edwards

Received January 8, 1959

Stock originally recognized two groups of boron hydrides, the B_nH_{n+4} and B_nH_{n+6} series. This classification has been extended and used as a basis for the systematic arrangement of the boron hydrides. Four types of chemical reactions of the boron hydrides are recognized. These are: (1) symmetrical cleavage of the double bridge bond, (2) non-symmetrical cleavage of the double bridge bond, (3) loss of a proton from a hydrogen bridge bond, and (4) loss of molecular hydrogen from the molecule. The type of reaction expected from a given molecule is related to the position of the molecule in the systematic arrangement and to the geometry of the original boron hydride.

In his original reports on the boron hydrides Stock[2] suggested two series of compounds which he represented by the empirical formulas B_nH_{n+6} and B_nH_{n+4}. Early attempts to use these formulas as a basis for systematizing the chemistry of the boron hydrides were of limited success, since arguments based on analogies with the hydrocarbons were often misleading and little was known of the geometry of the molecules. In recent years the structures of nearly all of the known boron hydrides have been established with considerable certainty as a result of a number of very clever structural studies.[3] This structural information coupled with recently acquired chemical knowledge can now be used as a basis for a number of chemical correlations based on an extension of Stock's classification.

---

(1) The research in boron chemistry at the University of Michigan is supported by the United States Air Force under Contract AF33(616)-3343 monitored by the Aeronautical Research Laboratory, WADC. The work at Callery is supported by the Bureau of Aeronautics of the United States Navy under contracts NOa(s)52-1024c and NOa(s) 58-454.

(2) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p. 17.

(3) J. S. Kaspar, C. M. Lucht and D. Harker, This Journal, **70**, 881 (1948); M. E. Jones, K. Hedberg and V. Schomaker, *ibid.*, **75**, 4116 (1953); **73**, 3538 (1951); C. E. Nordman and W. N. Lipscomb, *ibid.*, **75**, 4116 (1953); W. J. Dulmage and W. N. Lipscomb, *ibid.*, **73**, 3539 (1951); W. N. Lipscomb, *J. Chem. Phys.*, **22**, 985 (1954); E. B. Moore, R. E. Dickerson and W. N. Lipscomb, *ibid.*, **27**, 209 (1957).

Systematic Arrangement of the Hydrides

The members of Stock's original B_nH_{n+6} series are listed in column I of Table I. The removal of a single BH_3 group from each member of the B_nH_{n+6} series gives the next lower member of the series of empirical formula B_nH_{n+4}. These compounds are listed in column II of Table I. In a similar fashion removal of $2BH_3$ groups from B_nH_{n+6} series gives the B_nH_{n+2} series and removal of $3BH_3$ groups gives a series of empirical formula B_nH_n. Numerology suggests that addition of a BH_3 to members of the B_nH_{n+6} series should give a B_nH_{n+8} series, but no stable members of such a group have been reported.

Tetraborane (B_4H_{10}) and pentaborane-11 (B_5H_{11}) are well known members of the B_nH_{n+6} group. Less common members are B_9H_{15}, identified by Lipscomb, Schaeffer and co-workers,[4] and B_6H_{12} tentatively identified by Stock.[5] The compound B_3H_9 has been postulated as an intermediate in many reactions involving hydride interconversion,[6] but no direct, unequivocal evidence for its existence has yet been presented.

Well established members of the B_nH_{n+4} group include $B_{10}H_{14}$, B_6H_{10}, B_5H_9 and B_2H_6. Triborane (B_3H_7) is well established in combination with a number of Lewis bases, such as ethers, amines, ammonia and alkylphosphines.[7] A carbon monoxide adduct of B_4H_8 has been reported.[8]

TABLE I

SYSTEMATIC ARRANGEMENT OF THE HYDRIDES OF BORON[a]

B_nH_{n+6}	B_nH_{n+4} or $[B_nH_{n+6}] - BH_3$	B_nH_{n+2} or $[B_nH_{n+6}] - 2BH_3$	B_nH_n or $[B_nH_{n+6}] - 3BH_3$
BH_7			
B_2H_8	BH_5		
B_3H_9	$\underline{B_2H_6}$	$\underset{-\,-\,-}{BH_3}$ (B_2H_6)	
$\underline{B_4H_{10}}$	$\underset{-\,-\,-}{B_3H_7}$	B_2H_4 (B_4H_8)	$\underset{-\,-\,-}{B_1H_1}$
$\underline{B_5H_{11}}$	$\underset{-\,-\,-}{B_4H_8}$	B_3H_5 (B_6H_{10})	B_2H_2
$\underline{B_6H_{12}}$	B_5H_9	$\underset{-\,-\,-}{B_4H_6}$ (B_8H_{12})	B_3H_3
B_7H_{13}	B_6H_{10}	B_5H_7 $(B_{10}H_{14})$	B_4H_4
B_8H_{14}	B_7H_{11}	B_6H_8 $(B_{12}H_{16})$	B_5H_5
$\underline{B_9H_{15}}$	B_8H_{12}	B_7H_9	B_6H_6
$B_{10}H_{16}$	B_9H_{13}	B_8H_{10}	B_7H_7
$B_{11}H_{17}$	$\underline{B_{10}H_{14}}$	B_9H_{11}	B_8H_8
$B_{12}H_{18}$	$B_{11}H_{15}$	$B_{10}H_{12}$	B_9H_9
$B_{13}H_{19}$	$B_{12}H_{16}$	$B_{11}H_{13}$	$B_{10}H_{10}$
$B_{14}H_{20}$	$B_{13}H_{17}$	$B_{12}H_{14}$	$B_{11}H_{11}$
$B_{15}H_{21}$	$B_{14}H_{18}$	$B_{13}H_{15}$	$B_{12}H_{12}$

[a] ——— = known hydride; - - = known as Lewis acid in combination with a base.

In general, all hydride units of empirical formula B_nH_{n+2} exist only when stabilized by coördination with themselves or some other species. For example, the BH_3 group can achieve stability by coördination with another BH_3 group to form B_2H_6 or by coördination with other boron hydride fragments as B_3H_7 or B_4H_8 to form B_4H_{10} or B_5H_{11}, respectively. The BH_3 group can, alternatively, be stabilized by coördination with bases such as ammonia, amines, trialkylphosphines, etc., to give rise to the lengthy series of base-borane compounds. Direct and reliable evidence for the existence of B_2H_4 has not yet been obtained, but B_4H_8, the dimer of B_2H_4, has been reported as a Lewis acid in combination with the weak base CO. The triborane and pentaborane members of this series, B_3H_5 and B_5H_7, exist in the dimeric forms as B_6H_{10} and $B_{10}H_{14}$, respectively. Although neither B_4H_6 or its dimer B_8H_{12} has been positively identified as a definite chemical entity, recent unpublished studies have shown the existence of B_4H_6 in combination with Lewis bases, and well-defined coördination compounds of B_4H_6 have been isolated and characterized. The dimer, B_8H_{12}, has been tentatively reported as one of the products obtained from the pyrolysis of diborane.[9]

In contrast to the dimeric character of the hydrides of formula B_nH_{n+2} it seems significant that the corresponding halogen–boron compounds, B_nX_{n+2}, exist as simple monomers. Thus BCl_3, BF_3, B_2Cl_4 and B_2F_4 are well defined examples.[10]

All compounds formed by the removal of $3BH_3$ groups from B_nH_{n+6} have the empirical formula B_nH_n. These materials are undoubtedly the vast group of solids of approximate composition B_nH_n reported by Stock and later workers. The schematic arrangement in Table I would suggest that the composition of the materials of the form $(BH)_n$ may vary from the case where n equals one such as is found on the sun and recognized in the discharge tube[11] to the large numbers found in polymeric boron hydride residues (*i.e.*, 36 and higher reported by Stock). The frequent appearance of $[BH]_n$ as an end product of boron hydride pyrolysis can be easily rationalized from the foregoing scheme. The variation in the composition of the solid polymers often encountered experimentally[1] could well be the result of incomplete removal of BH_3 groups.

With the exception of BH no other individual member of this series has been established.

As was observed in the earlier series, the halogen counterparts are known with lower molecular weights than the hydrides. For example, B_4Cl_4 is known as a definite chemical species[12] although the corresponding B_4H_4 has not yet been separated and identified. Structurally it is observed that B–X–B bridges, where X is a halogen, do not occur in boron compounds while the B–H–B bridge is a fundamental structural feature of the hydrides. It is also noticed that the coördination number of boron for halogen is almost invariably less than that for hydrogen, a not unexpected result in view of the size, polarizability and compressibility of the halide and hydride groups.

---

(4) R. E. Dickerson, P. J. Wheatley, P. A. Howell, W. N. Lipscomb and R. Schaeffer, *J. Chem. Phys.*, **25**, 606 (1956); **27**, 200 (1957); W. V. Kotlensky and Riley Schaeffer, THIS JOURNAL, **80**, 4517 (1958).

(5) A. Stock, ref. 1, p. 77.

(6) A. T. Whately and R. N. Pease, THIS JOURNAL, **76**, 837 (1954).

(7) L. J. Edwards, W. V. Hough and M. D. Ford, paper presented before XVIth International Congress, Pure and Applied Chemistry, Paris, France, July, 1957; also G. Kodama and R. W. Parry.

(8) A. B. Burg, "Eighth Annual Technical Report of Investigations on Water Reactive Chemical Compounds," Nov. 1, 1954, University of Southern California.

(9) J. Shapiro and B. Kirlin, THIS JOURNAL, **76**, 3864 (1954).

(10) For structural data on B_2Cl_4 see: M. Atoji, P. J. Wheatley and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 196 (1957).

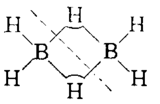
(11) H. D. Babcock, *Astrophys. J.*, **102**, 154 (1945); C. N. Challacombs and G. M. Almy, *Phys. Rev.*, **51**, 930 (1937), and others.

(12) G. Urry, T. Wartik and H. I. Schlesinger, THIS JOURNAL, **74**, 5809 (1952); M. Atoji and W. N. Lipscomb, *J. Chem. Phys.*, **21**, 172 (1953).

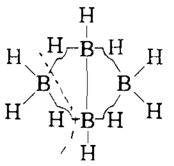
Type Reactions of the Boron Hydrides

In order to relate chemical reactivity to the foregoing tabular arrangement it is necessary to classify reactions of the boron hydrides and to correlate, where possible, the geometry of the molecule and the observed chemical process. A relatively large portion of the currently available evidence suggests that the bridge bonds in boron hydrides serve as centers of chemical reactivity. Four type reactions have been recognized; these are: (1) symmetrical cleavage of the double bridge, (2) non-symmetrical cleavage of the double bridge, (3) loss of a proton from the bridge, (4) loss of hydrogen gas from the molecule. Much of the known chemistry of the simpler boron hydrides can be considered under these four classifications.

A. Symmetrical Cleavage of the Double Bridge Bond.—Reactions in which borane groups, BH_3, are removed from the boron hydride molecule are fairly common in boron chemistry. In molecules such as diborane and tetraborane which contain two bridge bonds attached to a BH_2 unit, this is referred to as symmetrical cleavage of the double bridge, *i.e.*[13]



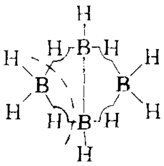
H_3B BH_3



H_3B B_3H_7

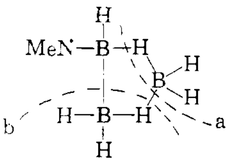
The reactions of B_2H_6 are traditionally interpreted in terms of symmetrical cleavage of the double bridge. The formation of compounds of the type $M:BH_3$ where M: represents most Lewis bases is too commonplace to warrant further discussion. In fact, bases such as ammonia, which do not react by symmetrical cleavage, have long been considered anomalous in boron hydride chemistry.

Much of the recent chemistry of B_4H_{10}[7,14] can likewise be interpreted in terms of symmetrical cleavage at the double bridge. In the following equations the processes are indicated. The resulting compounds have been isolated and characterized in every case.



$+ 2\,NMe_3 \rightarrow Me_3NBH_3 + Me_3NB_3H_7$ (1)

Triborane may also suffer symmetrical cleavage through attack by excess base; $Me_3NB_3H_7$ reacts with an excess of Me_3N to give one Me_3NBH_3 group. A second trimethylamine molecule reacts with somewhat greater difficulty to yield an insoluble residue of approximate composition $HB[N(Me)_3]_x$. Such reaction details have been completely confirmed by experiment.[15]

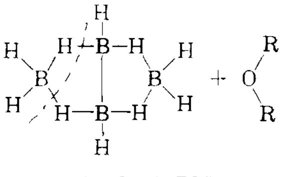


a—initial bridge cleavage
b—secondary BH_3 production; B–B bond to be broken

The over-all reaction[16] between B_4H_{10} and excess Me_3N can be represented as

$$B_4H_{10} + (3 + x)NMe_{3(\text{excess})} \longrightarrow 3Me_3NBH_3 + HB(NMe_3)_x$$

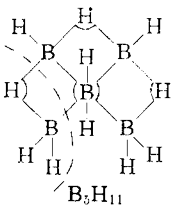
Other symmetrical cleavage processes are



$\dashrightarrow 1/2\,B_2H_6 + B_3H_7OR_2$ (2)

$$B_4H_{10} + PMe_3 \longrightarrow {}^1/_2B_2H_6 + Me_3PB_3H_7 \quad (3)$$
$$B_4H_{10} + NaH \longrightarrow {}^1/_2B_2H_6 + \underbrace{NaHB_3H_7}_{NaB_3H_8} \quad (4)$$

None of the boron hydrides other than B_2H_6 and B_4H_{10} have a BH_2 group bound by a double bridge bond, hence the term "symmetrical cleavage" can have no real meaning with these molecules; however, BH_3 groups can be removed from such structures through rupture of one or two bridge bonds and then destruction of part of the boron framework.



B_5H_{11}

$+ 2\,CO \xrightarrow[\text{(excess)}]{} B_4H_8CO + H_3BCO$

Because BH_3 is a product of such reactions the process will be considered under the term "symmetrical cleavage" even though the original geometric meaning of the term is now lost. Data covering such reactions in the higher hydrides are much less complete than the data on B_4H_{10} and B_2H_6. Nonetheless one of the few studies on B_5H_{11} indicates clearly a loss of BH_3 from the pentaborane-11 molecule and was so interpreted by Burg.[8] See Table I.

B. Non-symmetrical Cleavage of the Double Bridge Bonds in Boron Hydrides.—While the foregoing symmetrical bridge cleavage to give BH_3 groups accounts for the reactions of B_2H_6 and B_4H_{10} with most Lewis bases, it fails to account for the products formed by the interaction of these hydrides with a few bases such as ammonia. The symmetrical cleavage product H_3NBH_3 is not formed by the direct interaction of ammonia and

---

(13) The term symmetrical cleavage, originally applied [S. G. Shore and R. W. Parry, This Journal, **80**, 10 (1958)] to the symmetrical breaking of the B_2H_6 molecule, can be extended to the B_4H_{10} molecule on the basis that one of the bridge hydrogens goes to each molecular fragment.

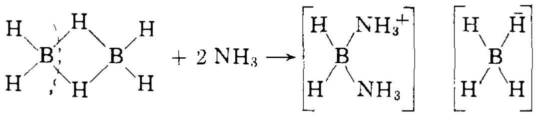
(14) G. Kodama, Doctoral Dissertation, University of Michigan, 1957; L. J. Edwards and W. Hough, unpublished data, Callery Chemical Company.

(15) W. V. Hough and L. J. Edwards, unpublished data, Callery Chemical Company.

(16) A. B. Burg and F. G. A. Stone, This Journal, **74**, 228 (1953).

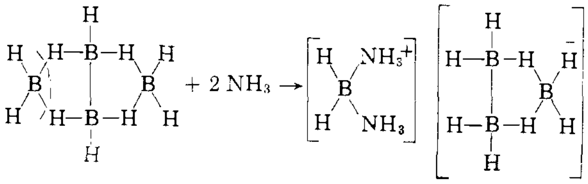
B_2H_6, and the compound $H_3NB_3H_7$ does not result from the direct reaction of ammonia on B_4H_{10}. The B_2H_6 anomaly has been interpreted recently in terms of a non-symmetrical cleavage of the double bridge to give an ionic solid as

$$B_2H_6 + 2NH_3 \longrightarrow B_2H_6\cdot 2\,NH_3$$



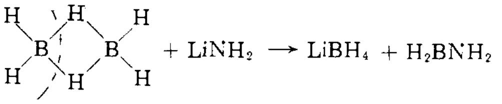
Evidence for the foregoing is summarized elsewhere[17]; additional confirmatory evidence has been presented recently by Nordman and Peters[18] in the form of a single crystal X-ray study of the salt $[H_2B(NH_3)_2]Cl$. The identity of the new ion, $[H_2B(NH_3)_2{}^+]$ is established with a high degree of certainty.

The reaction of B_4H_{10} with NH_3 also can be treated in terms of a non-symmetrical cleavage of the double bridge bond.[19]



$$B_4H_{10} + 2\,NH_3 \longrightarrow B_4H_{10}\cdot 2\,NH_3$$

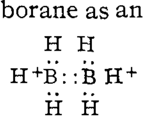
In addition to the ammonia-boron hydride reactions, one other set of data can be interpreted as a well established case of non-symmetrical bridge cleavage. Schaeffer and Basile[20] studied the reaction between B_2H_6 and $LiNH_2$ in diethyl ether slurry. Isolation of $LiBH_4$ and BH_2NH_2 as products fits well with the concept of non-symmetrical cleavage of the double bridge bond by $LiNH_2$, the basic salt of NH_3.



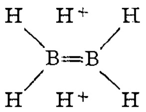
$$B_2H_6 + LiNH_2 \longrightarrow LiBH_4 + H_2BNH_2$$

Although the term non-symmetrical cleavage has little direct geometrical meaning when applied to those higher boron hydrides which have no double bridge bond, it might be possible in a few cases to split a $BH_2{}^+$ group from the molecule. By analogy such a process would be known as non-symmetrical cleavage.

C. Reactions Involving the Acidic Character of Bridge Hydrogens of the Boron Hydrides.—Many of the early attempts to account for the electron deficiency of diborane involved the suggestion that the molecule contains potentially acidic hydrogens.[21] These arguments culminated in Wiberg's[22] representation of diborane as an ethylene analog



and in Pitzer's[23] protonated bridge bond based on the now well supported bridge model.



The formation of the "diammoniate of diborane" was originally cited as evidence supporting the latent acidic character of diborane, but the exchange experiments of Burg[24] and the tracer study of Shore, Girardot and Parry[25] show conclusively that the formation of this compound in no way reflects such acidic behavior (see non-symmetrical cleavage).

On the other hand recently accumulated evidence shows quite unequivocally that the bridge hydrogens of decaborane are acidic in character. The presence of acid hydrogens in the molecule was demonstrated by Edwards and Hough in the laboratories of Callery Chemical Company through preparation of the salt $NaB_{10}H_{13}$. This work was confirmed independently by Guter and Schaeffer[26] who demonstrated that the $B_{10}H_{14}$ behaves as a strong monoprotic acid. Edwards and Grillo[27] showed using deuterium exchange followed by mass spectrometric analysis that four hydrogens exchange rapidly in the system $B_{10}H_{14}$–D_2O–dioxane. They also showed that $B_{10}H_{10}D_4 + NaH$ produces HD, indicating that the exchanged hydrogens are indeed acidic. Edwards and Grillo,[27] Atori and Kline,[28] Taylor and Parry[29] and Hawthorne and Miller[30] showed independently from infrared studies that rapid exchange with D_2O occurs through the four bridge hydrogens; one may then wonder that only one hydrogen is titrated instead of 4. Such an observation implies only that the difference between the first and second pK values is so large that only the first hydrogen is readily detectable in the above titration.

Additional evidence is available to support the belief that the acid behavior of the bridge hydrogens is not confined to $B_{10}H_{14}$ but may appear in other boron hydrides. For example when ammonia and diborane are allowed to interact slowly at about −120°, it is possible to get diborane absorption and loose compound formation as indicated by a drop in B_2H_6 pressure. It is obvious that the adduct

---

[17] D. R. Schultz, S. C. Shore, R. W. Parry, G. Kodama, P. R. Girardot, R. C. Taylor and A. R. Emery, *ibid.*, **80**, 1 (1958).

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

[19] G. Kodama and R. W. Parry, Proc. Int. Congress Pure and Applied Chem., Paris, France, July, 1957, p. 484; G. Kodama, Doctoral Dissertation, to be published.

[20] G. W. Schaeffer and L. J. Basile, THIS JOURNAL, **77**, 331 (1955).

[21] See ref. 1, p. 158.

[22] E. Wiberg, *Ber.*, **69**, 2816 (1936); ref. 1, p. 158.

[23] K. S. Pitzer, THIS JOURNAL, **67**, 1126 (1945).

[24] A. B. Burg, *ibid.*, **69**, 747 (1957).

[25] S. G. Shore, P. R. Girardot and R. W. Parry, *ibid.*, **80**, 20 (1958).

[26] G. A. Guter and G. W. Schaeffer, *ibid.*, **78**, 3546 (1956).

[27] L. J. Edwards and J. Grillo, unpublished data, Callery Chemical Company, Monthly Report, March, 1957.

[28] Atori and M. Kline, unpublished Reports, Armour Research Foundation, October, 1957.

[29] R. C. Taylor and R. W. Parry, Quarterly Report No. 5 to Wright Air Development Center Contract AF 33(616)-3343; Project No. 6-(2-3055), Task No. 70321, Eng. Res. Inst. Univ. of Mich., June, 1957.

[30] M. F. Hawthorne and J. J. Miller, THIS JOURNAL, **80**, 754 (1958).

formed under these conditions is not any of the conventional ammoniates of diborane, since it has been possible to separate some B_2H_6 and NH_3 again from this mixture by distillation. Parry and Shore[31] pictured such ammonia addition as resulting from ammonia coördination to the weakly acidic hydrogen located in the bridge. A slight rise in temperature suffices to initiate the bridge cleavage process described in the two preceding sections. It is obvious that the character of the low temperature adduct cannot be established by the earlier study on the cleavage product.[17] Kodama[14] made similar postulates for the system B_4H_{10}–NH_3. It was found that the low temperature reaction between tetraborane and ammonia in diethyl ether proceeded very slowly. The slow introduction of ammonia to the liquid B_4H_{10}–Et_2O system resulted in complete ammonia absorption and formation of a clear colorless solution as long as the NH_3/B_4H_{10} ratio did not greatly exceed 2. If an attempt were made to remove ether by vaporization from such a freshly prepared, clear, colorless solution, both NH_3 and B_4H_{10} could be distilled from the reaction mixture, despite evidence of initial absorption. Very little $B_4H_{10}\cdot 2NH_3$ ever was obtained from this solution. On the other hand when the system was aged for 4 days at −78° and for 12 hours at −45°, $B_4H_{10}\cdot 2NH_3$ was obtained in 86% yield. Kodama and Parry[14] interpreted these observations as suggesting low temperature addition of ammonia to the very weakly acidic hydrogen bridges without bridge rupture. On standing the bridge bonds opened and the new product, $B_4H_{10}\cdot 2NH_3$, was formed. Other evidence of the same type such as reversible amine addition to B_5H_9 and $B_{10}H_{14}$ under controlled conditions suggests the same phenomenon. If B_5H_9 and NMe_3 are allowed to interact at −80°, weak compound formation occurs, but, as in the system B_4H_{10}–NH_3, both of the original reactants can be separated from the system as long as the temperature is held below −45°. If the system is allowed to warm to room temperature, the reactants are no longer separable and the infrared spectrum of the product reveals the presence of H_3BNMe_3. The work of Gigatch[32] on dimethylamine adducts of B_5H_9 can be interpreted in a similar fashion. Similarly the observations of Fitch and Laubengayer[33] on the system dimethylamine–decaborane can be interpreted in terms of amine addition to the acid decaborane bridge without formation of an ionic methylammonium salt. The volatility of the product and the easy regeneration of the amine by acid indicates association of amine and borane without cleavage of the borane molecule. When the product is heated decomposition, interpretable as bridge opening, occurs.

In summary then, it is postulated that the bridge hydrogens of the boron hydrides *may* have potentially acidic character; however, one must be careful in interpreting data involving amine addition as evidence for such addition since a temperature rise above a permissible limit or long low temperature aging could well initiate bridge opening and new compound formation.

D. Reactions Involving Loss of Hydrogen from Boron Hydride Structures.—The frequent appearance of hydrogen as a product of boron hydride decompositions suggests that loss of hydrogen from hydrogen-rich structures is mandatory. It seems almost certain that at least the lower members of the B_nH_{n+8} system would be unstable and lose hydrogen at room temperatures. Similarly, the postulated intermediate B_3H_9 appears to lose hydrogen easily at low temperatures to give B_3H_7 and H_2. It does not seem unreasonable, then, to extend this to the next higher member of the B_nH_{n+6} series and postulate an equilibrium involving the loss of hydrogen at somewhat elevated temperatures.

$$B_4H_{10} \rightleftarrows H_2 + B_4H_8$$

The results of kinetic studies[34] of the thermal decomposition of tetraborane suggest at least two modes of decomposition and are consistent with the view that tetraborane may dissociate by loss of BH_3 to give B_3H_7 or by loss of hydrogen to give B_4H_8.

Type Reactions and their Relation to Systematic Hydride Arrangement

In the first section of the paper a systematic hydride arrangement was presented; in section two, common reactions of boron hydrides were classified under four headings. In the current section the systematic hydride arrangement will be used as a basis for correlating the typical reactions. Such chemical processes will be considered in reverse order from the original listing.

A. Loss of Hydrogen from the Boron Hydride.—All of the hydrides will lose hydrogen if the temperature is raised to a sufficiently high level; hence a correlation between the temperature of hydrogen loss and the location of the compound in the systematic hydride arrangement is to be sought. Available data support the following generalizations: (1) in general, hydrogen loss becomes easier as one goes from the series B_nH_n to the series B_nH_{n+6}; (2) in any given series hydrogen loss becomes more difficult as the size of the boron framework increases. Postulate one is almost self-evident. Postulate two is supported by a number of observations. For example, the first member of the B_nH_{n+6} series, B_3H_9, loses hydrogen so easily that it has been postulated as a reaction intermediate but never isolated. Its existence at low temperatures is a possibility. The next member, B_4H_{10}, appears to lose hydrogen under certain conditions to give a B_4H_8 fragment.[34] As mentioned earlier this reaction is not necessarily clean cut, but may be one of several competing processes. The direct transformation of B_5H_{11} to B_5H_9 does not take place easily. In short, hydrogen loss becomes more difficult as one goes down any series. If a member of the B_nH_{n+8} series can be isolated, the foregoing arguments along with factors of geometry suggest that it may well occur on a B_7 or B_8 framework.

B. Acidic Behavior of Boron Hydrides—Loss of Protons from the Bridge Bonds.—The known

---

(31) R. W. Parry and S. G. Shore, This Journal., **80**, 19 (1958).

(32) A. F. Gigatch, "Recherches des Propriétés Chimiques des Hydrures de Bore et Leurs Dénirés," Proceedings 16th International Congress of Pure and Applied Chemistry, Paris, France, 1957, p. 467.

(33) S. J. Fitch and A. W. Laubengayer, This Journal, **80**, 5911 (1958).

(34) R. K. Pearson and L. J. Edwards, paper presented before Division of Inorganic Chemistry, American Chemical Society, National Meeting held in New York, N. Y., Sept., 1957.

strong acidity of the protons in the bridge bonds of decaborane and the very low acidity in the bridges of B_2H_6 suggest that the acid character of the hydrogen bridges increases as one moves down any group. In the same sense the Lewis acid strength of fragments (*i.e.*, BH_3, B_3H_7, B_4H_8, etc.) should increase as one moves down any group. One method for the preparation of $Me_3NB_3H_7$ from B_4H_{10} takes advantage of the latter fact. The reaction of B_4H_{10} with a limited amount of trimethylamine may be represented in two steps as

$$B_4H_{10} + 2NMe_3 \longrightarrow Me_3NBH_3 + Me_3NB_3H_7 \quad (1)$$

$$B_4H_{10} + Me_3NBH_3 \longrightarrow Me_3NB_3H_7 + B_2H_6 \quad (2)$$

Reaction two indicates that when NMe_3 is used as a reference base the B_3H_7 group is a stronger acid than BH_3. It is also significant that the acid strength of a boron hydride fragment may be altered by replacing hydrogen with a new group such as an alkyl.

Ample precedent and theoretical justification can be found for the above generalizations on acidity. When one compares the acid character of phenol and methyl alcohol, it is customary to attribute the relatively strong proton donor qualities of phenol to the fact that electrons are withdrawn from the oxygen to the relatively low energy levels of the ring. Electronic delocalization serves to increase acid character in this organic system. A similar situation obtains in the boron hydrides. As the boron framework increases in size, more extensive delocalization of electrons increases the ability of the framework to accept electrons. In B_2H_6 with virtually no boron unit structure, the hydrogen acidity is very weak and is easily masked by bridge opening to give new products. In $B_{10}H_{14}$ with an essentially closed boron configuration, delocalization is extensive and hydrogens appear strongly acidic. Furthermore the delocalization of electrons in the boron framework makes it more difficult to split a BH_3 from the $B_{10}H_{14}$. The acid character is thus detected more easily, since masking by bridge opening is less likely.

Finally a word of caution seems desirable. One must be careful not to confuse strength of B_3H_7 as a Lewis acid with its stability against decomposition. Although B_3H_7 is a stronger acid than BH_3 it may suffer symmetrical cleavage through attack by excess base to give BH_3 adducts. Such a reaction is not a valid measure of acid strength, but measures susceptibility of the fragment to destructive cleavage processes.

C. Symmetrical and Non-symmetrical Bridge Cleavage Processes.—The nature of the bridge cleavage process is determined by both the nature of the base and the nature of the hydride. As a rather broad generalization it may be stated that cleavage becomes more difficult as one goes down a group, but geometrical factors for specific molecules frequently cause significant localized variations. Diborane and tetraborane are unique in the series in that in each case a BH_2 group is held to the rest of the molecule by two hydrogen bridge bonds. Here bridge opening and symmetrical cleavage are effected more easily than in those cases such as B_5H_9, B_5H_{11} or $B_{10}H_{14}$ where the boron framework must be altered. As a result, a striking parallel in the chemistry of diborane and tetraborane involving both symmetrical and non-symmetrical cleavage is clearly apparent.[7]

For molecules such as B_5H_9 and $B_{10}H_{14}$ containing a boron structure which must be broken to liberate BH_3 groups, symmetrical cleavage requires more vigorous conditions with a greater possibility of destructive secondary reaction. This fact serves as a complicating factor in the study of those preparative aspects of the chemistry of higher hydrides which depend upon simple stepwise cleavage processes. The most straightforward example of stepwise cleavage of a B_5 framework is found in the isolation of B_4H_8CO. Apparently, because of the weakness of CO as a base, further attack upon the B_4H_8 framework by excess base did not destroy the complex during the preparative procedure. Stronger bases such as the amines have given more complicated reactions.

Whether a symmetrical or non-symmetrical cleavage process occurs in a given boron hydride is determined primarily by the base and secondarily by the experimental conditions. Non-symmetrical cleavage of diborane is well established with only two bases, ammonia and $LiNH_2$. Non-symmetrical cleavage of B_4H_{10} is well established so far with only NH_3 but logical extensions based on coördination theory promise to extend the list somewhat. "Non-symmetrical cleavage" or loss of a BH_2^+ fragment from hydrides beyond B_4H_{10} has not yet been established, but such an extension seems reasonable. The non-symmetrical cleavage process is, by all odds, the more unusual type of reaction, since nearly all other bases effect symmetrical cleavage of the double bridge.

D. Analogies to Coördination Compounds of the Werner Type.—In principle, the cation $H_2B(NH_3)_2^+$ resulting from non-symmetrical cleavage can be considered as just one member of a series of boron coördination compounds in which hydride and NH_3 serve as coördinating ligands. In BH_4^- all coördination positions are occupied by hydride ions; in H_3NBH_3 one hydride ion has been replaced by an ammonia to give a neutral molecule; in $[H_2B(NH_3)_2]^+$ two hydride ions have been replaced by ammonia molecules to give a univalent cation. The next two members of this series should be $[HB(NH_3)_3]^{++}$ and $[B(NH_3)_4]^{+++}$, but they have not yet been identified. A formally analogous series of platinum coördination compounds, where Cl^- and NH_3 serve as coördinating ligands, is well known, and recently Chatt, Duncanson and Shaw[35] have announced a platinum complex which contains "hydride" as a coördinated ligand—$[Pt(PEt_3)_2HCl]$.

An application of general coördination theory to boron compounds is rather fruitful. In Table II is a listing of ligands which are common in the chemistry of boron hydrides. It will be noticed that these same ligands appear in any generalized discussion of the Werner coördination theory. Furthermore, differences in coördinating behavior between ligands such as ammonia and trimethylamine are not unexpected in coördination theory, but have ample precedent in the chemistry of metals. For exam-

---

[35] J. Chatt, L. A. Duncanson and B. L. Shaw, *Proc. Chem. Soc.*, 343 (1957).

ple, $CoCl_2$ will absorb 6 molecules of NH_3 readily to give $[Co(NH_3)_6]Cl_2$ while the salt will absorb only one triethylamine.[36] The ease of preparing $[Co(NH_3)_6]Cl$ and the difficulties associated with the introduction of non-chelate monoalkylamine molecules into the coördination sphere of cobalt(III)[37] are very well known to coördination chemists.

TABLE II

Ligand	Boron compd. containing ligand	Formally analogous Werner coördination compd.
H^-	$NaBH_4$, H_3NBH_3, NaB_3H_8	$[Pt(PR_3)HCl]$
NH_3	$[H_2B(NH_3)_2]Cl$, H_3NBH_3	$[PtCl_2(NH_3)_2]$
$-OCH_3$	$NaB(OCH_3)_4$	
NR_3	H_3BNMe_3	$CoCl_2 \cdot NEt_3$
NHR_2	H_3BNHMe_2	$[Co(en)_2NHR_2X]^{++}$
NH_2R	H_3BNH_2Me	$Cd(NH_2Me)_2{}^{++}$
PR_3	$H_3BPMe_3PB_3H_7$	$[Pt(PMe_3)_2Cl_2]$
PF_3	H_3BPF_3	$[Pt(PF_3)_2Cl_2]$
CO	H_3BCO	$[Pt(CO)_2Cl_2]$

If one accepts the premise that $H_2B(NH_3)_2{}^+$ and $H_3B(NMe_3)$ can be treated as true coördination compounds, the difference between symmetrical and non-symmetrical cleavage processes reduces to a determination of the optimum coördination pattern for boron with different ligands or different combinations of ligands. The general topic of coordination number has received extensive theoretical and experimental study and the arguments are summarized elsewhere.[38] It is obvious that the configuration of groups which lies lowest in energy will be favored. Replacement of a small and easily distorted group such as hydride by a larger group such as ammonia or an alkyl amine can lead to steric readjustment of the ligands. Unless the increase in energy due to steric factors can be offset by a decrease in energy of the system due to the strength of the boron–ligand bond, substitution of hydride by the new ligand will not occur. In short, the most stable coördination pattern represents a delicate balance between steric factors and bond strength and these factors vary with both ligand and the nature of the central atom.[38] The question of symmetrical and non-symmetrical cleavage then becomes, at least in part, a problem in basic coördination theory in which steric hindrance plays a major role.

E. Borane Fragments as Operational Bases—Reaction Mechanisms—Hydrolysis.—The coördination analogy in boron hydrides may be carried somewhat farther with profit by an operational extension of the definition of a base. It is customary to consider borane fragments such as BH_3 or B_3H_7 as Lewis acids since they accept electrons easily from normal electron donors. On the other hand, the originally unexpected ability of these fragments to combine with other borane fragments (Lewis acids) suggests that the borane groups may be considered as operational "electron deficient" bases as well as Lewis acids. In such interaction the formation of bridge bonds replaces the conventional donor acceptor bond of classic coördination theory. In such a sense the borane fragments are amphoteric. For example diborane can be regarded as a coördination compound resulting from the combination of two BH_3 groups which serve as both an acid and a base; tetraborane can be pictured as a coördination compound formed by the interaction of the "acidic" B_3H_7 and "basic" BH_3 groups. It is then convenient to consider diborane as just one member of a series of base borane coordination compounds; if the premise is accepted, the BH_3 group itself can be placed in any series of bases which form coördination compounds with the Lewis acid BH_3. One could then write a series representing increasing strength of the bases coördinating with BH_3. Data now available suggest the following arrangement for a few selected bases: CO, PF_3, BH_3, H_2O, NH_3, etc. It is significant to note that the ease of hydrolysis of the borane adduct and the apparent hydridic character of the hydrogens attached to boron decrease as the strength of the base increases.[39] For example, $COBH_3$ and PF_3BH_3 react vigorously and violently with water while H_3BNH_3 can float on water at 0° with only slow hydrogen evolution. If one assumes that arguments of hydrolysis mechanism, frequently applied to coördination compounds,[40] can be applied to boron chemistry, mechanisms such as that proposed independently from experimental studies by Weiss and Shapiro[41] result. In such a process, dissociation of the coördination compound is an initial step which is followed by coordination of water and loss of H_2 or HX. It is to be expected that a strong base would reduce dissociation of the complex thus making coördination of water and release of H_2 difficult. The electron distribution around the hydrogen bound to boron is an unknown variable of secondary importance.

Finally, a suitable combination of the four reaction types can be used profitably as a basis for mechanistic speculation in complex reactions such as the pyrolysis of boron hydrides. The systematic arrangement of hydrides and hydride fragments provides a basis for selecting reaction processes. Unfortunately this complex and important area is still not understood with certainty but systematic classification may offer some help in the outlining of mechanism schemes.

ANN ARBOR, MICHIGAN

---

(36) J. T. Yoke, III, Ph.D. Dissertation, Dept. of Chemistry, Univ. of Michigan, 1954.

(37) J. C. Bailar, Jr., "Chemistry of the Coördination Compounds," Reinhold Publ. Corp., New York, N. Y., 1956, p. 63.

(38) Parry and Keller in "The Chemistry of the Coördination Compounds," Edited by J. C. Bailar, Jr., Reinhold Publ. Corp., New York, N. Y., 1956, p. 143.

(39) The term hydridic character as used here refers to the classical definition as measured by the vigor of the reaction with a proton donor. As such it is strongly mechanism dependent. See T. C. Bissot, D. H. Campbell and R. W. Parry, THIS JOURNAL, **80**, 1549 (1958), for further discussion.

(40) R. D. Pearson and F. Basolo, *ibid.*, **78**, 4878 (1956); F. Basolo, W. R. Matoush and R. G. Pearson, *ibid.*, **78**, 4883 (1956); H. M. Dess and R. W. Parry, *ibid.*, **79**, 1950 (1957).

(41) H. D. Weiss and J. Shapiro, *ibid.*, **75**, 1221 (1953).