RECENT DEVELOPMENTS IN THE CHEMISTRY OF THE BORON HYDRIDES

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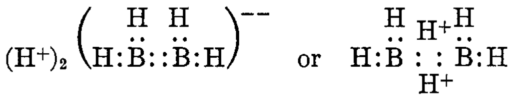
I. INTRODUCTION AND DISCUSSION OF NOMENCLATURE

The hydrides of boron have long been of interest because of their unusual chemical properties, and because of their bearing on the problem of valence and of the nature of the chemical bond. According to older valence concepts, current before the introduction of the electron theory, a trivalent element such as boron should form hydrides conforming to the generic formula B_nH_{n+2}. But the simplest such compound, BH_3, although it may have transitory existence as an intermediate in certain reactions, cannot be isolated; it is known only as a dimer, B_2H_6, and in complex compounds in which it is associated with other molecules, such as those of trimethylamine or dimethyl ether. The higher hydrides also fail to conform to the formula B_nH_{n+2}; those the molecular weights of which have been determined have the formulas B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and $B_{10}H_{14}$.

The development of the electron theory of valence did not immediately aid in clarifying the difficulty. In the case of diborane, B_2H_6, for example, it is evident that there are only twelve valence electrons; for an ethane-like structure with the usual electron-pair bonds, fourteen valence electrons are required. The same sort of electron deficiency is to be recognized in the higher hydrides.

The problem thus briefly outlined gave rise to numerous suggestions. Some writers took the view that positively charged boron atoms are associated with negatively charged hydride ions; others assumed both trivalent positive and pentavalent negative boron and both positive and negative hydrogen to be present in the structures of these compounds. These earlier hypotheses usually had no experimental basis other than the molecular formulas of the hydrides. On this account, most of them are not discussed in this review; a full set of references has been compiled by Wiberg (62).

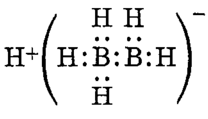
Four of these earlier suggestions have, however, received so much attention as to require special mention. One of these, put forward by Wiberg (62), describes diborane as a weak dibasic acid, in which the two boron atoms are joined by a double bond, thus:



$$(H^+)_2\left(H:\overset{\overset{H}{\cdot\cdot}}{B}::\overset{\overset{H}{\cdot\cdot}}{B}:H\right)^{--}\quad\text{or}\quad H:\overset{\overset{H}{\cdot\cdot}}{B}\;\overset{H^+}{\underset{H^+}{:\;:}}\;\overset{\overset{H}{\cdot\cdot}}{B}:H$$

(the second formula is intended to convey the idea that the two hydrogen ions are not entirely free). Numerous arguments for this formulation have been advanced, but there are no experimental facts pointing uniquely in that direction. The behavior of diborane toward ammonia once seemed to yield favorable evidence, but later studies contradicted the earlier interpretation (see pages 23). The parachor is cited by Wiberg as evidence favoring this formulation, but this interpretation also has been criticized by later workers (16).

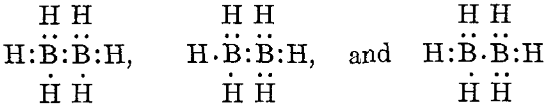
Another formulation, proposed in slightly different forms by Boeseken, by Wahl, and by Henstock (62), pictures diborane as a monobasic acid, in which one boron atom is coördinatively saturated and the other unsaturated, as shown by the formula



$$H^+\left(H:\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{B}}:\overset{\overset{H}{\cdot\cdot}}{B}:H\right)^{-}$$

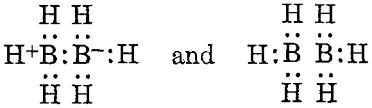
This idea once seemed useful for the interpretation of the reaction of diborane with ammonia, but here, also, facts obtained later are more favorable toward a different interpretation.

A third important suggestion, tending more definitely to accept as real the apparent electron deficiency already mentioned, was made by Sidgwick, who considered it necessary to assume that two of the hydrogen atoms in diborane are attached by single electrons, instead of doublets (33). With the development of the concept of resonance, this suggestion was generalized to include all of the structures represented by the formulas



$$\begin{array}{ccccccc} & & H & & H & & \\ & & \cdot\cdot & & \cdot\cdot & & \\ H & : & B & : & B & : & H, \\ & & \cdot & & \cdot & & \\ & & H & & H & & \end{array} \qquad \begin{array}{ccccccc} & & H & & H & & \\ & & \cdot\cdot & & \cdot\cdot & & \\ H & \cdot & B & : & B & : & H, \\ & & \cdot & & \cdot\cdot & & \\ & & H & & H & & \end{array} \qquad \text{and} \qquad \begin{array}{ccccccc} & & H & & H & & \\ & & \cdot\cdot & & \cdot\cdot & & \\ H & : & B & \cdot & B & : & H \\ & & \cdot & & \cdot\cdot & & \\ & & H & & H & & \end{array}$$

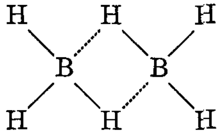
to which more recently were added (19) structures such as



$$\begin{array}{ccccccc} & & H & & H & & \\ & & \cdot\cdot & & \cdot\cdot & & \\ H^{+} & & B & : & B^{-} & : & H \\ & & \cdot\cdot & & \cdot\cdot & & \\ & & H & & H & & \end{array} \qquad \text{and} \qquad \begin{array}{ccccccc} & & H & & H & & \\ & & \cdot\cdot & & \cdot\cdot & & \\ H & : & B & & B & : & H \\ & & \cdot\cdot & & \cdot\cdot & & \\ & & H & & H & & \end{array}$$

Similar types of resonance are to be considered also for the other boron hydrides.

In the formulas so far discussed, the boron atoms are regarded as directly linked to each other. According to the fourth general viewpoint requiring discussion here, these atoms are indirectly linked, through hydrogen atoms forming a bridge, as represented by the following formula:



This suggestion, originally made by Dilthey and later somewhat modified by Core (62), has been reviewed and extended by Nekrasov (18), who has, however, not advanced decisive evidence in its favor. It is to be recognized that this formulation easily accounts for many of the chemical properties of diborane; it also accounts for the diamagnetism of this substance, and, as pointed out recently by Stitt, it offers one interpretation of the relatively high potential barrier to internal rotation which is indicated by specific-heat measurements (35). The results derived from the Raman spectrum (1) also seem compatible with this picture. Nevertheless, the picture drawn here is not in agreement with the results of electron-diffraction studies (2).

All of the ideas here discussed, as well as some not specifically mentioned, have had value in the development of the subject and are supported by some observations. Nevertheless, it must be recognized that no single picture of diborane is in satisfactory agreement with either the total chemical behavior of the substance or deductions from the various physical properties so far studied.

Numerous structures have been proposed for the higher boron hydrides, but knowledge of their chemical properties is still too meagre to give support to any of these suggestions. Since Bauer in the following review (2) discusses in detail the physical data bearing upon the structure of diborane and of the higher hydrides, structural problems will not be further discussed in this review, except as they are directly related to the chemical aspects of the subject.

Quite aside from these structural problems, the chemistry of the boron hydrides is so unusual as to be a matter of considerable interest in itself. The unique behavior of these substances may be briefly indicated by listing some of the better-known reactions of diborane, the simplest and most thoroughly studied member of the group:

$$5B_2H_6 \rightarrow 2B_5H_{11} + 4H_2$$

$$2B_5H_{11} + 2H_2 \rightarrow 2B_4H_{10} + B_2H_6$$

$$B_2H_6 + 2Na \rightarrow Na_2B_2H_6$$

$$B_2H_6 + HCl \rightarrow B_2H_5Cl + H_2$$

$$5B_2H_6 + 2B(CH_3)_3 \rightarrow 6B_2H_5CH_3$$

$$\underline{B_2H_6} + 2CO \rightarrow \underline{2BH_3CO}$$

$$B_2H_6 + 2N(CH_3)_3 \rightarrow 2BH_3N(CH_3)_3$$

$$B_2H_6 + 2NH_3 \rightarrow B_2H_6 \cdot 2NH_3$$

$$B_2H_6 + 4CH_3OH \rightarrow 2BH(OCH_3)_2 + 4H_2$$

$$B_2H_6 + 4CH_3CHO \rightarrow 2BH(OCH_2CH_3)_2$$

$$6B_2H_6 + Al_2(CH_3)_6 \rightarrow 2AlB_3\underline{H_{12}} + 3B_2H_4(CH_3)_2$$

$$3B_2H_6 + 2LiC_2H_5 \rightarrow 2\underline{LiBH_4} + 2B_2H_5C_2H_5$$

The preceding equations are not always to be taken as complete representations of the reactions; for example, the equilibria involving diborane and hydrogen include hydrides other than the tetraborane and pentaborane shown in the equations. Similarly, the reaction between diborane and trimethylboron yields not only monomethyldiborane, but three higher methyl derivatives as well. The same is true of other reactions in which specific alkyl derivatives of diborane are shown as reaction products. Indeed, one of the striking characteristics of the boron hydrides and their derivatives is their extreme lability: thus, nearly all of the other boron hydrides can be obtained from diborane by reactions proceeding under mild conditions of temperature and pressure; furthermore, the methyldiboranes readily disproportionate into each other, yielding also diborane or trimethylboron.

Such reactions are reminiscent of the cracking and alkylation of hydrocarbons. In the case of the boron hydrides, however, reactions of this type usually proceed at low temperatures and without catalysts. It is possible, therefore, that a study of the mechanisms of these reactions will throw light upon the analogous reactions of carbon chemistry. There are other directions in which the future study of the boron hydrides may prove valuable in leading to a better understanding of the mechanisms of reactions in which boron itself is not involved. Thus, an investigation of the interaction of diborane with aldehydes, ketones, and esters has thrown light on the mechanism by which other reactions of these organic substances may proceed. Another possibility is found in the striking parallelism between the chemical and physical properties of borine carbonyl,

BH_3CO, and those of the carbonyls of the transition elements—a parallelism which suggests that a full understanding of the structure of borine carbonyl may prove to be of importance in elucidating the more complex metal carbonyls. Finally, we call attention to the most recent development in the field of borane chemistry, the discovery of the metallo borohydrides. Some of these are highly volatile and therefore of particular interest to those engaged in the study of metallic elements. These and other matters of general interest justify a review of the hydrides of boron at the present time, although there are still many unexplored aspects of their behavior, and hypotheses concerning their structures are likely still to undergo considerable modification.

Before the detailed discussion of the subject under review is undertaken, it should be pointed out that no thoroughly uniform and consistent nomenclature has been adopted for the hydrides themselves, or for several new types of compounds discovered in the course of investigations of the hydrides. Although the name "diborane" is in general use for the compound B_2H_6, divergence in nomenclature occurs in the case of the higher hydrides. Thus it has been proposed to designate as boranes those hydrides to which the generic formula B_nH_{n+4} is applicable and to designate as dihydroboranes those (B_4H_{10} and B_5H_{11}) which may be represented by the formula B_nH_{n+6}. Since there is only one instance in which the latter term has any advantage of convenience, and since it corresponds to no established structural characteristic, we shall use in this review only names derived from "borane" for the hydrides containing more than one boron atom. The hypothetical molecule BH_3 is called borine.

For substances formally to be considered as substitution products of the boranes, a nomenclature derived from the practise in organic chemistry is followed: e.g., B_2H_5Cl is called chlorodiborane, and the symmetrical dimethyl derivative, $B_2H_4(CH_3)_2$, is named 1,2-dimethyldiborane. The term "borane salts" is employed for compounds formed by addition of metals to the boranes, whereas other salts containing the same constituents, but in different proportions, are designated as metallo borohydrides, for reasons discussed later in the review.

The most difficult problems of nomenclature arise in connection with substances considered to be "addition compounds" of borine and of its derivatives. According to the point of view adopted in this review, these compounds are the result of the union of a borine type of molecule, which lacks an electron pair, with a molecule containing an unshared electron pair. In other words, the "addition compounds" are the products of an acid–base reaction in the sense in which G. N. Lewis uses this term. In products of this type, the basic constituent is usually named first; consequently, we shall use such terminology as trimethylamine-borine and dimethyl ether-borine for the compounds originally named borine trimethylammine and borine etherate, respectively. Their composition will be represented by formulas such as $(CH_3)_3N:BH_3$ and $(CH_3)_2O:BH_3$. The use of a single dot will be limited to cases in which there is considerable doubt about the structure.

In a number of instances no names have been as yet assigned to compounds the structures of which are unknown or not finally determined with respect to all details. In other instances, we have accepted the names used in the original publications. For example, the substance BH_3CO is designated borine carbonyl, in order to call attention to its similarity to other carbonyls. On the other hand, the rather convenient term "diammoniate of diborane" has been retained, even though the interpretation of its structure, favored in this review, is that it is a monoammonium salt, $NH_4(H_3BNH_2BH_3)$. To indicate its unsystematic character, we enclose the term "diammoniate" in quotation marks, whenever it is used in this and similar connections. One or two other questions of nomenclature are taken up in the body of the review.

II. OLDER KNOWLEDGE OF THE BORANES

The existence of compounds of boron with hydrogen has been recognized for a long time, but the compounds are so unstable and so reactive toward air and moisture that very little progress was made in their investigation until Stock developed a special technique (36, 37) for dealing with substances possessing such properties. This technique, the early history of the compounds, and the knowledge gained about them up to the year 1932, have been reviewed by Stock in his Baker Lectures at Cornell University (36). Since that time there has been considerable development in this field, made possible largely by more efficient and convenient methods of preparation of the boranes than were available for Stock's earlier work. It therefore seems most appropriate to treat very briefly the work already so carefully reviewed by Stock, and to devote the major portion of this review to a survey of the developments since the appearance of Stock's book. Because of the close relationship between the subjects studied during the two periods, it will not always be possible to treat them quite independently.

TABLE 1

Physical constants of the boranes

NAME	MOLECULAR FORMULA	DENSITY	MELTING POINT	BOILING POINT	VAPOR TENSION	REFERENCE
			°C.	*°C.*	*mm.*	
Diborane	B_2H_6	0.577 (−183°C.) 0.447 (−112°C.)	−165.5	−92.5	225 (−111.9°C.)	(36)
Tetraborane	B_4H_{10}	0.56 (−35°C.)	−120	18	388 (0°C.)	(36)
Stable pentaborane	B_5H_9	0.61 (0°C.)	−46.6	48	66 (0°C.)	(36, 54)
Unstable pentaborane	B_5H_{11}		−123	63	53 (0°C.)	(8)
Hexaborane	B_6H_{10}	0.69 (0°C.)	−65		7.2 (0°C.)	(36)
Decaborane	$B_{10}H_{14}$	0.92 (99°C.) 0.78 (100°C.)	99.7	213	19 (100°C.)	(36)

The first boron hydride which was definitely characterized as a chemical individual was tetraborane (B_4H_{10}), which Stock and Massenez (46) obtained by the action of hydrochloric acid upon magnesium boride. Even at the outset, it was recognized that small proportions of heavier boranes were present in the volatile reaction products, but the total yields were very small (less than 3 per cent of the boron) and the presence of silicon hydrides (formed in some 30 per cent yield from the silicide impurity in the boride) made the process of purification very difficult. As a result, several years elapsed before a very stable pentaborane (B_5H_9), a less stable hexaborane (B_6H_{10}), and a trace of the especially stable decaborane ($B_{10}H_{14}$) could be definitely proved to be present in the less volatile fractions (39, 42). The difficulty of handling these substances was due chiefly to their instability and activity toward air, moisture, and the available stopcock lubricants. Stock therefore found it necessary to develop the special technique already mentioned; it involves high-vacuum low-temperature distillations, and the complete exclusion of all substances other than glass and mercury (36, 37).

Studies on the thermal decomposition of tetraborane soon led to the discovery of diborane (38) and this in turn, on long standing, gave very small yields of an unstable pentaborane having the formula B_5H_{11} (54). The latter completes the list of definitely known pure hydroborons; these are characterized physically in table 1. Other boron hydrides are capable of existence; most of these, however, are difficult to handle in the vacuum apparatus (either because they are non-volatile or because they are extremely unstable), and hence have not been recognized as chemical individuals.

A. Thermal stabilities

The least stable of the six compounds listed in table 1 is the pentaborane B_5H_{11}, which may show signs of irreversible decomposition within an hour at room temperature. When heated or allowed to stand for long periods of time, it produces diborane, tetraborane, hydrogen, the stable pentaborane, a faint trace of decaborane, and brown non-volatile liquids and solids (8). Tetraborane is slightly more stable; its decomposition leads to similar products. Both of these compounds probably are involved in the formation of numerous volatile and non-volatile materials from diborane, but it is not possible at present to assign to either a definite rôle in the process. In particular, the belief that the unstable pentaborane is a direct intermediate in the formation of decaborane appears to be unfounded (8, 54).

Diborane, the most thoroughly studied of the boron hydrides, is sufficiently stable to be stored in sealed bulbs (preferably containing some hydrogen) with losses not necessarily exceeding 10 per cent during a year. At 100°C., it rather rapidly produces non-volatile white and brown products, traces of tetraborane and the unstable pentaborane, and ultimately some of the stable pentaborane and decaborane. The formation of the last two is favored by an increase of temperature up to 150°C. A non-volatile brown solid, formulated as $(BH)_x$, has been obtained from diborane in a silent electric discharge (48).

At ordinary temperatures, hexaborane slowly undergoes complete decomposition, yielding hydrogen, a trace of diborane, and a non-volatile solid substance the hydrogen content and molecular weight (determined cryoscopically in benzene) of which suggest the molecular formula $B_{26}H_{36}$ (42). This complete decomposition of hexaborane at room temperature indicates that it is less stable than diborane; nevertheless it is not completely destroyed when passed at low pressure through a tube at 300°C. (42).

The most stable of the volatile boranes are the pentaborane B_5H_9 and decaborane. The former decomposes only very slowly at 150°C. During some years at room temperature, it produces a small quantity of non-volatile material and hydrogen. Decaborane is quite permanent at room temperature, and can be heated for considerable periods of time at 150°C. without observable change; its decomposition becomes noticeable at 170°C.

B. Chemical reactions of the boranes with other substances

(1) Oxygen: Some of the boron hydrides are very sensitive to atmospheric oxygen, while others are but little affected. Both of the pentaboranes are spontaneously inflammable in air at ordinary temperatures. Decaborane explodes in oxygen only at elevated temperatures (e.g., 100°C.), while hexaborane at room temperature reacts with air only slowly. Diborane and tetraborane seem to have flash points slightly above room temperature (36); the former may remain in intimate mixture with air for 3 to 5 days, after which the mixture explodes with great violence (24). The products of these reactions are brown or black solids of indefinite composition.

(2) Water: The rates of hydrolysis of the boron hydrides vary over a wide range. Diborane reacts almost instantaneously, according to the equation (41):

$$B_2H_6 + 6HOH \rightarrow 6H_2 + 2B(OH)_3$$

Tetraborane and the unstable pentaborane also are readily hydrolyzed, especially at slightly elevated temperatures or in acid solutions, to yield boric acid and hydrogen. It is the slightly slower rate of hydrolysis which makes possible the preparation of tetraborane by the reaction of magnesium boride with an aqueous solution of an acid,—a solution in which diborane is instantly destroyed. The hydrolysis of the stable pentaborane, of hexaborane, or of decaborane can be completed only by long heating, preferably in acid solution. In all cases, however, the hydrolysis reaction is a feasible first step in an elementary analysis of the volatile boranes or their derivatives.

Neither for the hydrolysis of magnesium boride nor for the reactions of the boranes with water has any mechanism been established. Nevertheless, certain published suggestions require discussion. To explain the former reaction, it has been assumed (62) that the boride contains a group of four boron atoms, as indicated by the formula $(B_4)Mg_6$. The first step in the reaction is supposed to be the formation of the compound $(B_4H_6)(MgOH)_6$, which then is believed to hydrolyze in two ways, yielding $[B_4(OH)_6](MgOH)_6$ in one reaction, and small proportions of tetraborane, hydrogen, and magnesium hydroxide in the other. In support of these assumptions, it is claimed that the salt $[B_4(OH)_6](NH_4)_6$ has been isolated, but the formula is based only upon analyses and a molecular weight calculated from the freezing-point depression, without regard for activity coefficients which might have been important.

For the reaction of diborane with water, ten steps are postulated (62). Of the nine compounds assumed to be formed as intermediates, five are admittedly unknown; three are hypothetical and but vaguely related to the products of the hydrolysis of magnesium boride (62, references to the work of Ray and of Travers, Ray, and Gupta), and only one, formulated as $H_2[H_2B(OH)B(OH)H_2]$, can be directly related to diborane. Even this is known only as a potassium salt, and its structure remains largely hypothetical. This salt, formed by the action of diborane upon solutions of potassium hydroxide, is discussed more fully on page 33.

A simpler interpretation of the reaction between diborane and water involves the assumption that a borine derivative, $H_2O:BH_3$, is formed as an intermediate step (18). Although the behavior of diborane toward trimethylamine and toward dimethyl ether (see pages 16 and 19) lends support to such a possibility, it seems premature, on the basis of the meagre data as yet available, to attempt a critical evaluation of this or other ideas on the subject.

(*3*) *Ammonia:* The reactions of the boron hydrides with ammonia have led to the discovery of a number of unusually interesting types of compounds, the study of which has had considerable bearing on the development of hypotheses concerning the structural principle of the hydrides. Although most of the compounds involved were discovered in the period summarized in this section of the review, many important developments occurred later. For the present, therefore, we shall review briefly these compounds, most of which have been already described in detail in Stock's book (36), and shall leave critical discussion to a later section (page 22).

At −120°C., *diborane* reacts quantitatively with two volumes of ammonia, yielding a salt-like product which is quite stable at room temperature (42, 50). *In vacuo* it melts at 90°C. and gives off hydrogen. The compound is commonly called the "diammoniate of diborane," although it is more properly to be formulated as some type of ammonium salt. This "diammoniate" reacts with additional ammonia at −50°C. The significance of this fact will be discussed later.

The ammoniates of the higher hydrides are not well understood. *Tetraborane* forms a "tetrammoniate" (53) which seems to be a diammonium salt, capable of undergoing a complicated secondary reaction with ammonia. At −40°C. *in vacuo* it is transformed by loss of ammonia into a product approximately described by the formula $B_4H_{10}\cdot 2NH_3$; at higher temperatures, hydrogen also is evolved (24). The *stable pentaborane* forms a "diammoniate," $B_5H_9\cdot 2NH_3$, in which only one of the nitrogen atoms seems to be present as ammonium ion (24). A further, slow reaction with ammonia leads to the formation of a "tetrammoniate" (53), two of the nitrogen atoms of which seem to function as ammonium ions (24). A product having the same composition as this "tetrammoniate" is formed by the reaction of ammonia with the *unstable pentaborane* (50). It is not certain, however, that any of the ammoniates of the pentaboranes are single substances, rather than mixtures of degradation products. The behavior of *hexaborane* toward ammonia has not been studied. *Decaborane* forms a "hexammoniate" which, unlike the compounds obtained from the other hydrides, is readily decomposed into the parent substances (53).

The reactions just described occur at low temperatures; at elevated temperatures, a wider variety of products may appear. Thus diborane reacts with ammonia, present in excess, to yield boron imide, $B_2(NH)_3$, which decomposes, on further heating, to form boron nitride (51). When the proportions of diborane and ammonia are those of the "diammoniate," or when this substance itself is heated, the volatile compound $B_3N_3H_6$ is obtained in yields as high as 45 per cent. A study of the conditions favoring high yields of this compound has appeared recently; for details the original article (63) should be consulted. The same compound is formed also by the action of ammonia on tetraborane or on either of the pentaboranes (36), but not from decaborane (53).

The benzene-like structure of the stable compound $B_3N_3H_6$ was recognized by Stock and Pohland (51), and was confirmed by electron-diffraction studies (2, 61) as well as by the preparation of methyl derivatives (page 29). Because of its structural similarity to benzene, the name borazole was suggested by H. Wieland (63); in spite of its unsystematic character, this designation has the advantage of brevity, and we shall use the name borazole rather than the more formal name, triborine triamine, in this review.

Another product of the reaction of diborane with ammonia is the compound B_2H_7N; both this substance and borazole will receive more detailed discussion later (pages 25 and 27).

(*4*) *Halogens:* Three of the volatile boranes are known to react vigorously with halogens, and the others undoubtedly would behave similarly if the appropriate experiments were tried. *Diborane* may be converted to chlorodiborane or bromodiborane by reaction with chlorine or bromine, smoothly only at very low temperatures (43). The action of iodine yields products difficult to isolate, but iododiborane can be prepared by the (uncatalyzed) reaction of hydrogen iodide with diborane (52):

$$B_2H_6 + HI \rightarrow B_2H_5I + H_2$$

This iodo derivative is of interest because it may be converted partially to tetraborane by treatment with sodium amalgam (52):

$$2B_2H_5I + 2Na \rightarrow B_4H_{10} + 2NaI$$

Hydrogen bromide attacks diborane in the manner of hydrogen iodide, but the corresponding reaction with hydrogen chloride usually requires the presence of a catalyst such as aluminum chloride (36) or boron chloride (24). Far more efficient for the preparation of chloro- and bromo-diboranes are the reactions of the corresponding boron halides with diborane, as illustrated by the following equation (22):

$$5B_2H_6 + 2BCl_3 \leftrightarrows 6B_2H_5Cl$$

The isolation of chlorodiborane by this method (6) is made difficult by the rapidity and extent of the reverse reaction in the absence of excess boron chloride; conditions are more favorable in the case of bromodiborane.

The reaction of *tetraborane* with hydrogen chloride proceeds very slowly even in the presence of aluminum chloride. Heating does not help, because tetraborane is too unstable. No chloro derivatives of tetraborane have been isolated; instead, only chlorinated degradation products are obtained (58).

Decaborane and the stable *pentaborane* are unaffected by either hydrogen chloride or boron chloride, but they submit to direct attack by halogens. The reaction

$$B_5H_9 + Cl_2 \rightarrow B_5H_8Cl + HCl$$

can be controlled at −80°C.; the chief product, which has the composition of a monochloro derivative, probably is a mixture of isomers differing little in volatility, but more in stability (24). The halogenation of decaborane occurs slowly at room temperature and leads to a variety of products, among which are substances formulated as $B_{10}H_{12}Br_2$ and $B_{10}H_{12}I_2$ (43, 53).

(5) Metals: Diborane reacts with sodium amalgam to produce the interesting salt-like compound $Na_2B_2H_6$; several other metals react in similar fashion (42). Although these reactions were discovered early in the history of the boron hydrides, most of the information about the compounds thus obtained is of relatively recent origin, and they are accordingly reviewed in a later section (page 33).

III. DEVELOPMENTS IN BORON HYDRIDE CHEMISTRY SINCE 1931

A. Preparation of the boranes

Previous to the year 1931, the chief obstacle to the increase in knowledge of the boron hydrides was the great difficulty and expense of preparing the hydrides by the boride–acid method in quantities sufficiently large for thorough study. The preparation of an active magnesium boride is in itself a cumbersome task; the conversion of the boride to the hydrides is a very time-consuming procedure which gives very poor yields. Although this method (as yet the only satisfactory source of hexaborane) has been materially improved by the use of phosphoric acid (34) instead of hydrochloric acid, the total yields do not exceed 11 per cent (64), and the process still is a very slow one, involving troublesome impurities.

The situation was greatly improved by the development of a new method, which consists essentially of the hydrogenation of boron chloride or bromide by the aid of a fairly powerful electric discharge. According to the original description of the procedure (22), pure hydrogen is allowed to bubble through liquid boron chloride at −40°C., and the resulting mixture (10 moles of hydrogen per mole of boron chloride) is led through a 12- to 15-kilovolt ($\frac{1}{4}$ K.V.A.) discharge at a pressure of 10 mm. The resulting hydrogen chloride, chlorodiboranes, and unused boron chloride are condensed from the excess hydrogen, and fractionated to remove the hydrogen chloride (6). The fractionating column then is operated at a pressure of 2 atm. (reflux temperature, 0°C.), in order to attain a temperature favorable to rapid decomposition of the chlorodiboranes, according to equations such as

$$6B_2H_5Cl \leftrightarrows 5B_2H_6 + 2BCl_3$$

Because of the reversibility of these reactions, it is well to remove the diborane as rapidly as it is formed, and the fractionating column does this very well (24). The fractions rich in hydrides are subjected to a further process of fractional condensation, and the diborane finally is purified by a direct vacuum distillation from a tube at −150°C.

A later improvement in this process substitutes boron bromide for the chloride (55); the advantage is due to the fact that the decomposition of bromodiboranes to diborane

$$6B_2H_5Br \leftrightarrows 5B_2H_6 + 2BBr_3$$

is more easily brought to completion than that of the chloro derivatives, because the volatility of boron bromide is such that it is relatively easy to remove this substance from the reaction mixture; also more favorable is the relative ease with which the diborane may be purified from bromine-containing impurities, rather than from the corresponding chlorine compounds. The recent development of an easy and efficient method of preparing boron bromide (14) avoids the difficulty which formerly stood in the way of its use.

A large portion of the boron halide passes through the discharge without evident change, and is readily recovered; of that reacting, 60 to 75 per cent can be converted to diborane when boron chloride is the starting material, and up to 80 per cent when the bromide is used.

The new method of preparing diborane also made other boron hydrides more readily available. Diborane, tetraborane, the unstable pentaborane, and hydrogen constitute a system involving several sets of equilibria which are attained at different rates (8). Furthermore, this system of equilibria is not entirely stable, for there is also a slow, irreversible production of the stable pentaborane and of decaborane. Consequently, by suitably controlling the temperature, the time of heating, and the relative proportions of the components, the desired borane may be obtained in yields sufficiently high to warrant its separation from the mixture. Hexaborane is involved to a slight extent in this system (47), but it is best prepared by Stock's original method (41). For a very unstable octaborane (8), apparently present as a slight trace among the products of this set of reactions, no satisfactory preparatory method has been developed.

The conditions best suited to the preparation of the four better-known higher hydrides of boron are given in the following paragraphs. For details, the original references must be consulted.

The unstable pentaborane may be prepared by allowing diborane to flow through a U-tube heated to 115°C. The rate of flow of diborane (as it evaporates from a tube at −80°C.) is controlled by a capillary tube so as to make the treatment roughly equivalent to a 2-min. heating of a stationary sample. The product is purified by fractional condensation, and the recovered diborane is put through the process repeatedly until the desired quantity of unstable pentaborane is obtained. In terms of diborane transformed, the yield is nearly 90 per cent, but the fraction of diborane undergoing change in a single passage through the heated tube is small. The product usually is contaminated with about 3 per cent of the stable pentaborane, unless milder heating is employed; tetraborane is a by-product (8).

Tetraborane is obtained by heating a mixture of hydrogen and the unstable pentaborane (molecular ratio about 10:1) for 10 min. at 100°C., in a bulb of such dimensions that the pressure rises to about 1.5 atm. In terms of the pentaborane used up (75 per cent), the yield is approximately 85 per cent, as calculated according to the equation

$$B_5H_{11} + H_2 \rightarrow B_4H_{10} + \tfrac{1}{2}B_2H_6$$

Longer heating lowers the yield because of the transformation of some of the tetraborane into diborane (8).

The simultaneous preparation of tetraborane and the unstable pentaborane from diborane has been carried out by the use of a magnetically operated circulating pump, sending diborane at an initial pressure of 140 mm., first through a furnace at 180°C., and then through a trap at -115°C. (adequate for condensing the products, but allowing diborane to go through). This method offers a certain convenience, but requires a more elaborate apparatus (47).

The stable pentaborane is prepared most efficiently by the use of the circulating-pump apparatus, employing diborane at an initial pressure of 120 mm. It passes through a 10 x 160 mm. tube in which mercury is vaporized at 250°C.; the rate of flow is 50 cc. (S.C.) per minute. Of the diborane used up during a 4-hr. operation, 56 per cent is converted to the stable pentaborane, and 26 per cent to the unstable pentaborane. Small but significant quantities of hexaborane also are obtained. Similar results are achieved in half the time if the temperature of the hot tube is 300°C., but these conditions lead to a lower yield of the unstable pentaborane (47).

A similar flow process could be operated without the special pump, but would then be far less convenient. The heating of diborane in a sealed bulb (best in the presence of a catalyst such as boron chloride) leads to yields of approximately 30 per cent of the diborane used up. This method is less efficient, but is convenient for small quantities of the product (8, 22).

Decaborane is obtained in 30 per cent yields from diborane in a sealed bulb, one side of which is heated to 160°C. (pressure slightly above atmospheric) (24). It is obtained also by heating tetraborane (39), or by the circulating-flow heating of the unstable pentaborane (38 mm., 250°C., and 12 cc. per minute) (47).

B. Preparation and properties of the alkyldiboranes

The discovery that the formation of diborane and boron chloride from chlorodiboranes is a reversible reaction (see page 12) suggested that it might be possible to prepare alkyl derivatives of diborane by the reaction of trimethylboron with diborane. Actually, when a mixture of these two reactants is left for a few hours at room temperature, it becomes possible to isolate four methyl derivatives of diborane (32). The positions of the methyl groups in these compounds have been demonstrated by hydrolytic reactions, according to the following equations:

$$CH_3B_2H_5 + 5HOH \rightarrow CH_3B(OH)_2 + B(OH)_3 + 5H_2$$

$$1,1\text{-}(CH_3)_2B_2H_4 + 4HOH \rightarrow (CH_3)_2BOH + B(OH)_3 + 4H_2$$

$$1,1,2\text{-}(CH_3)_3B_2H_3 + 3HOH \rightarrow (CH_3)_2BOH + CH_3B(OH)_2 + 3H_2$$

$$1,1,2,2\text{-}(CH_3)_4B_2H_2 + 2HOH \rightarrow 2(CH_3)_2BOH + 2H_2$$

TABLE 2

Physical constants of the alkyldiboranes

FORMULA	MOLECULAR WEIGHT		MELTING POINT	BOILING POINT	CHARACTERISTIC VAPOR TENSION		REFERENCE
	Observed	Calculated			Pressure	Temperature	
			°C.	°C.	*mm.*	°C.	
$CH_3B_2H_5$	Normal	41.7			55	−78.5	(32)
$(CH_3)_2BHBH_3$	54.3	55.7	−150.2	−2.6	10	−78.5	(32)
$(CH_3BH_2)_2$	55.6	55.7	−124.9	+4.9	7	−78.5	(25)
$(CH_3)_2BHCH_3BH_2$	68.9	69.7	−122.9	45.5	123	0	(32)
$[(CH_3)_2BH]_2$	83.95	83.75	−72.5	68.6	48	0	(32)
$C_2H_5B_2H_5$	56.1	55.7	Glassy		7	−78.5	(26)
$(C_2H_5)_2BHBH_3$	83.6	83.75	Glassy	67	42	0	(26)
$(C_2H_5)_2BHBH_2C_2H_5$		111.8	Glassy		4	0	(26)
$[(C_2H_5)_2BH]_2$		139.8	Glassy		0.5	0	(26)
$n\text{-}C_3H_7B_2H_5$	71.1	69.7	Glassy		6.2	−60	(26)
$(n\text{-}C_3H_7)_2BHBH_3$		111.8	Glassy		2.8	0	(26)

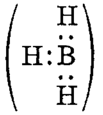
Although the symmetrical dimethyldiborane, $1,2\text{-}(CH_3)_2B_2H_4$, has not been found among the reaction products of diborane with trimethylboron, it has been prepared by a special method to be described later (page 20). Four analogous ethyl derivatives have been prepared by the reaction of diborane with triethylboron. Mono-*n*-propyl- and 1,1-di-*n*-propyl-diboranes also have been obtained by the exchange of the alkyl group for hydrogen (26). The physical constants of all of the known alkyldiboranes are summarized in table 2.

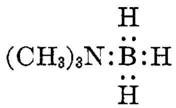
Chemical studies of these alkyl derivatives have led to a number of interesting observations. Like diborane, they react vigorously with air or with moisture, but they are far more stable against decomposition with loss of hydrogen. Thus, a mixture containing chiefly tri- and tetra-methyldiboranes, together with an excess of trimethylboron, has been kept for several years at room temperature, and has been heated to 200°C. without irreversible change (24). On the other hand, disproportionation reactions occur quite readily; because of the formation of the nearest members of its series, any one of the pure derivatives soon becomes impure if allowed to stand at room temperature. The isolation of the pure derivatives, therefore, is a fairly difficult task, achieved only by low-temperature, low-pressure fractionation; in each case the product remains pure only if the temperature is sufficiently low practically to eliminate the vapor phase.

It has been observed that derivatives in which two alkyl groups and one hydrogen atom are attached to boron are more stable than those having only one alkyl group attached to boron. Thus, symmetrical dimethyldiborane is rapidly converted at room temperature into the unsymmetrical derivative (25), a fact which explains the absence of the former among the products of the reaction of diborane with trimethylboron. Similarly, monomethyldiborane so rapidly produces diborane and dimethyldiborane that it has not been possible to measure its vapor tension with precision; trimethyldiborane, which likewise contains the CH_3BH_2 unit, somewhat more slowly produces 1,1-dimethyldiborane and tetramethyldiborane. Other chemical properties of the alkyl derivatives are described in later sections (pages 16, 19, 25 and 29).

Irrespective of the magnitude of the excess of trialkylboron employed in the preparation, not more than four of the six hydrogen atoms of diborane are replaced by alkyl groups. Furthermore, no derivative of diborane in which three alkyl groups are attached to the same boron atom ever has been obtained. These facts have been used to support two ideas: *(1)* that two of the six hydrogen atoms in diborane are bound differently from the others, and *(2)* that the presence of hydrogen is essential to the formation of such a boron-to-boron link as that in diborane. Such conclusions are, however, not necessarily valid, since other explanations (e.g., steric hindrance) are conceivable.

IV. COÖRDINATION COMPOUNDS OF BORINE

Early in his work on the boranes, Stock demonstrated that the molecule of diborane is not thermally dissociated into two borine (BH_3) molecules at temperatures as high as 150°C. (42). Nevertheless, even at relatively low temperatures, diborane reacts with substances, the molecules of which contain unshared electron pairs, to produce coördination compounds of borine. The breaking of the boron–boron bond thus occurs rather readily when it results, not in the formation of two electronically unsaturated borine  $\left(\begin{matrix} & H \\ H: & \overset{..}{\underset{..}{B}} \\ & H \end{matrix}\right)$ molecules, but in the production of coördinatively and electronically saturated substances such as trimethylamine-borine:



$$\begin{matrix} & H & \\ (CH_3)_3N: & \overset{..}{\underset{..}{B}} & :H \\ & H & \end{matrix}$$

The formation of compounds of this type is of such importance in the chemical behavior of diborane, and probably of the other boranes as well, that most of the chemical reactions of these substances cannot be adequately discussed without reference to this property. For this reason, considerable space is given to a description of the borine complexes, with special emphasis on those which have a direct bearing on other phases of boron hydride chemistry, or on the question of the possible transitory existence of borine itself.

A. *Trimethylamine-borine and related compounds*

The reaction of diborane with trimethylamine is rapid and quantitative at temperatures as low as −110°C. (10); the product is trimethylamine-borine, $(CH_3)_3N:BH_3$, a sublimable white solid which is not rapidly attacked by moist air. In the absence of air, it seems to be permanently stable; it may be heated for hours at 125°C. without appreciable decomposition, and has been observed as one of the major products of a nearly quantitative reaction occurring slowly at 200°C. (25). In the presence of hydrochloric acid at 100°C., it is completely hydrolyzed to form boric acid, hydrogen, and trimethylammonium chloride.

TABLE 3

Physical constants of trimethylamine-borine and derivatives

FORMULA	MOLECULAR WEIGHT		MELTING POINT	BOILING POINT	SAMPLE VAPOR TENSION	REFERENCE
	Observed	Calculated				
			°C.	*°C.*	*mm.*	
$(CH_3)_3N:BH_3$	74.4	72.9	94	171	0.8 (23°C.)	(10)
$(CH_3)_3N:BH_2CH_3$	88.5	86.9	0.8	177	2.3 (22°C.)	(25)
$(CH_3)_3N:BH(CH_3)_2$	102.2	101.0	−18	172	2.9 (21°C.)	(25)
$(CH_3)_3N:B(CH_3)_3$	Dissociates		120		2.1 (23°C.)	(25)

The action of dry hydrogen chloride causes the stepwise replacement of hydrogen atoms in the BH_3 part of the molecule by chlorine atoms; the first step of the reaction is completed in half an hour at −80°C. (25). The second step of this reaction occurs far more slowly at +100°C. (25), and the third with still more difficulty at 200°C. (24). The resulting chloro derivatives all are difficultly volatile, white solids which have not been investigated in detail.

Trimethylamine-borine can be obtained, not only from diborane, but also by the reaction of some of the higher boranes with trimethylamine (24). The stable pentaborane reacts with trimethylamine to give first the compound $B_5H_9 \cdot 2N(CH_3)_3$, which when heated gives trimethylamine-borine and other products not yet adequately characterized. Tetraborane and the unstable pentaborane react with trimethylamine to yield somewhat impure samples of trimethylamine-borine and a non-volatile solid residue. These reactions deserve further, more detailed study, since they may be helpful in elucidating the structure of the higher hydrides.

Methyl derivatives of trimethylamine-borine have been prepared by the action of trimethylamine upon methyldiboranes and upon trimethylboron (25).

From symmetrical dimethyldiborane the compound $(CH_3)_3N\!:\!BH_2CH_3$ has been obtained; tetramethyldiborane produces the compound $(CH_3)_3N\!:\!BH(CH_3)_2$; trimethylboron yields $(CH_3)_3N\!:\!B(CH_3)_3$. Monomethyl- and trimethyl-diboranes give mixtures apparently composed of the first two of these derivatives, which are difficult to separate from each other. The physical constants of the complex compounds mentioned here are given in table 3.

The least stable of the four compounds listed in table 3 is the last: the vapor of trimethylamine-trimethylboron is 70 per cent dissociated at 80°C. and 70 mm. pressure. The dimethylborine derivative is stable up to 70°C.; at this temperature it begins to disproportionate slowly, according to the equation

$$2(CH_3)_3N\!:\!BH(CH_3)_2 \rightarrow (CH_3)_3N\!:\!BH_2CH_3 + (CH_3)_3N + B(CH_3)_3$$

Trimethylamine-monomethylborine, although quite stable at 100°C., disproportionates at 200°C. according to the equation

$$3(CH_3)_3N\!:\!BH_2CH_3 \rightarrow (CH_3)_3N\!:\!BH_3 + (CH_3)_3N + B(CH_3)_3$$

The monomethyl and dimethyl derivatives react with dry hydrogen chloride as does trimethylamine-borine itself. At -80°C. these reactions are faster than the attack upon the parent substance; the rate increases with the number of methyl groups attached to boron (25).

B. Action of methylamine and of dimethylamine upon diborane

Two moles of methylamine add to 1 mole of diborane to form a compound (28). Unlike the salt-like "diammoniate" of diborane (see pages 9 and 22), this product is liquid at room temperature. It is not volatile at room temperature, nor can it be vaporized by heating, since even a mild increase of temperature causes it to lose hydrogen and to be converted, in good yields, into tri-*N*-methylborazole (see page 29). No other reactions of the compound are known.

Dimethylamine reacts with diborane to produce a compound, $H_2BN(CH_3)_2$, the formation of which may be preceded by an intermediate addition compound, $(CH_3)_3HN\!:\!BH_3$. The end product, $H_2BN(CH_3)_2$, has been called "inorganic isobutylene" by its discoverers, who have not yet published details concerning its preparation or properties (63). The same authors mention also the formation of the compound $[(CH_3)_2N]_2BH$. Both compounds are stable volatile substances having no tendency to disproportionate.

C. Borine carbonyl

Borine carbonyl (10), H_3BCO, is conveniently prepared by heating diborane with a large excess of carbon monoxide in a bomb tube at 100°C. For best results, the pressure should be high (e.g., 20 atm.), as might be expected from the equation

$$2CO + B_2H_6 \rightleftarrows 2H_3BCO$$

The equilibrium is established within 20 min. and is then fixed by rapid cooling. The three main components of the mixture,—borine carbonyl, diborane, and carbon monoxide,—can be isolated by a process of fractional condensation.

From the quantities found in each of a number of experiments at different pressures, the approximate average value 2.8×10^4 has been calculated for the equilibrium constant,

$$\frac{P^2_{CO} \times P_{B_2H_6}}{P^2_{H_3BCO}}$$

at 100°C. (partial pressures expressed in millimeters of mercury).

Borine carbonyl melts at -137.0°C. and boils at -64°C. (as extrapolated from the equation $\log_{10} p_{mm.} = 7.850 - 1040/T$).

At room temperature, borine carbonyl decomposes into diborane and carbon monoxide at a very rapid rate which is, however, very sharply decreased long before equilibrium is established. The inhibiting factor evidently is the carbon monoxide developed by the reaction, for a mixture of diborane with the carbonyl (either put together directly, or remaining after the removal of carbon monoxide) shows the rapid, but soon diminishing, rise of pressure characteristic of a fresh sample of the carbonyl. Particularly significant is the fact that the admixture of an equal volume of carbon monoxide to the pure borine carbonyl almost entirely prevents the decomposition.

These observations are easily explained on the assumption that the first stage of the decomposition is the rapid and highly reversible reaction

$$H_3BCO \rightleftarrows CO + BH_3$$

The second stage is assumed to be the nearly irreversible reaction

$$2BH_3 \rightarrow B_2H_6$$

A high concentration of carbon monoxide would, according to the first assumption, greatly decrease the concentration of borine (BH_3), and this would mean that the rate of the second stage would be greatly diminished, especially as this stage appears to be a second-order reaction with respect to borine.

Although this relatively simple explanation of the inhibiting effect of carbon monoxide on the rate of decomposition of borine carbonyl has not been shown to agree quantitatively with the rate curves (10), its qualitative agreement with the facts suggests strongly that borine molecules may have transitory existence. On the other hand, the failure to obtain any more direct evidence of the presence of borine indicates that it has too short a life to be isolated as a chemical individual.

The chemical reactions of borine carbonyl may depend in large measure upon its dissociation, or at least upon the displacement of carbon monoxide. Thus at -80°C., it is not attacked at once by trimethylamine (as diborane is), but at higher temperatures, such as would favor rapid dissociation, carbon monoxide is liberated and trimethylamine-borine is formed quantitatively:

$$H_3BCO + (CH_3)_3N \rightarrow CO + H_3B{:}N(CH_3)_3$$

Its hydrolysis may be an even better example: it takes place according to the equation

$$H_3BCO + 3HOH \rightarrow 3H_2 + B(OH)_3 + CO$$

at a rate comparable to the decomposition (24), and accordingly requires heating for conveniently rapid completion. It is conceivable that the hydrolysis is not direct, but is preceded by the displacement of carbon monoxide and the formation of an unstable hydrate such as $H_2O:BH_3$. Similarly, it is possible that the hydrolysis of diborane itself involves, as a first step, the formation of such a hydrate,—an interpretation which would relate the hydrolysis of diborane to its reaction with ammonia, with amines, and with organic compounds containing carbonyl groups (5).

The reaction of borine carbonyl with ammonia, in contrast to its simple reaction with trimethylamine, is a complex process: no carbon monoxide is liberated, and the product is a non-volatile solid of composition corresponding to the empirical formula $H_3BCO \cdot 3NH_3$. This material loses one-third of its ammonia at room temperature, leaving a residue of the empirical formula $(H_3BCO)_{0.9} \cdot 2.07NH_3$. When this residue is dissolved in liquid ammonia and treated with sodium, 1 gram-equivalent of hydrogen is rapidly liberated per mole of borine carbonyl; a second equivalent of hydrogen is produced far more slowly (10). It is possible that the product of the reaction of borine carbonyl with ammonia is a mixture of two ammonium salts.

Borine carbonyl is in some respects similar to the volatile metal carbonyls (4). Like them, it agrees with Sidgwick's rule in regard to effective atomic numbers; again like them, it is more volatile than any hydrocarbon of similar molecular weight; it also shows their tendency to lose carbon monoxide reversibly, or to react with tertiary amines, with displacement of carbon monoxide. The similarities may be chiefly formal, however. In particular, it seems that borine carbonyl differs rather sharply from the hydrogen metal carbonyls.

No compounds of carbon monoxide with derivatives of borine are as yet known. Trimethylboron and the boron halides are inert toward carbon monoxide. The methyldiboranes react irreversibly with carbon monoxide, producing liquids containing neither B—H nor B—B linkages. These substances deserve further study, but they are not derivatives of borine carbonyl (17). Little is known about the behavior of the higher boranes toward carbon monoxide. The only evidence that they may react to yield carbonyl compounds is the presence of a by-product in the mixtures from which borine carbonyl is obtained. This little-known by-product is even less stable than borine carbonyl; like that substance, it loses carbon monoxide at a rate which is sharply inhibited by the presence of carbon monoxide (10).

D. Dimethyl ether-borine

The solid compound $(CH_3)_2O:BH_3$ is formed by the reaction of diborane with dimethyl ether at low temperatures (23). It is very unstable, for the reverse reaction,

$$2(CH_3)_2O:BH_3 \rightarrow B_2H_6 + (CH_3)_2O$$

develops an equilibrium pressure of 18 mm. at $-78.5°C$. Since the compound is wholly dissociated in the vapor phase, values for its molecular weight cannot be obtained except by cryoscopy at unusually low temperatures, and this has not yet been attempted. The formula assigned to it (i.e., $(CH_3)_2O:BH_3$ rather than $B_2H_6\cdot 2(CH_3)_2O$) is based largely upon analogies with the behavior of diborane toward other "electron donor" molecules. In spite of its instability, the compound has proved useful in the study of the structure of the "diammoniate" of diborane, as will be described later (page 24).

Another interesting consequence of the study of the etherate (dimethyl ether-borine) was the development of a method for the preparation of symmetrical dimethyldiborane, a compound not obtained by the methods used for the preparation of the other methyldiboranes. The compound is obtained by the reaction of dimethyl ether with methyldiborane at −78.6°C. (25). This reaction is readily understood on the assumption that, whereas dimethyl ether-borine, $(CH_3)_2O:BH_3$, is sufficiently stable to be formed at −78.6°C., the corresponding derivative of monomethylborine, $(CH_3)_2O:BH_2CH_3$, is not. If this assumption is correct, the first step of the reaction is

$$B_2H_5CH_3 + (CH_3)_2O \rightarrow (CH_3)_2O:BH_3 + CH_3BH_2$$

The methylborine molecules then would associate with each other to form symmetrical dimethyldiborane, $CH_3H_2BBH_2CH_3$. The success of the method which is based upon this assumption is evidence of the correctness of the latter; further evidence is found in the relative stabilities of the derivatives of trimethylamine-borine, described on page 17.

E. Diborane and phosphine

As is the case with its analog, ammonia, phosphine reacts with diborane in the ratio of 2 moles of the former to 1 mole of the latter (13, 23). The reaction occurs slowly at −30°C. in the gas phase, but more rapidly in the liquid phase at −110°C. (13). The compound thus formed is spontaneously inflammable in air; it is readily hydrolyzed to phosphine, boric acid, and hydrogen; it reacts rather slowly with hydrogen chloride (or bromide) at −80°C. to give products formulated empirically as PH_3BH_2Cl, PH_3BHCl_2, and PH_3BCl_3, although rapid disproportionation makes difficult the isolation of the individuals (13). The original compound is rather unstable (decomposition pressure, 200 mm. at 0°C.) (13); although it can be sublimed in the high-vacuum apparatus without extensive decomposition (24), its vapor is decomposed far too rapidly for a determination of the molecular weight by vapor-density methods.

Since the molecular weight is not definitely known, there is no firm foundation on which to base hypotheses of the structure of the phosphine addition compound, but there are some suggestive experimental facts. No phosphine is liberated when the compound is dissolved in liquid ammonia at the melting point of the latter, and at −60°C. the evolution of phosphine is slow; in contrast to this behavior, true phosphonium salts rapidly evolve phosphine in liquid ammonia at −77°C. (13). It therefore seems that the formulation $(PH_4)(H_3B:PH_2:BH_3)$, an analog to that which is favored for the "diammoniate" of diborane, would not be appropriate. On the other hand, trimethylamine completely displaces the phosphine at −40°C., according to the equation

$$B_2H_6 \cdot 2PH_3 + 2N(CH_3)_3 \rightarrow 2PH_3 + 2(CH_3)_3N{:}BH_3$$

The rapid formation of trimethylamine-borine at low temperatures is a reaction characteristic of the less stable borine complexes, and consequently suggests the formulation $H_3P{:}BH_3$ for the compound.

The information at present available concerning the phosphine derivative is not adequate to establish definitely the structure $H_3P{:}BH_3$; in fact, such a structure makes necessary certain additional assumptions in order to account for the behavior of the compound toward ammonia. Unlike trimethylamine, ammonia displaces only a part of the phosphine from the compound; when the reaction occurs in liquid ammonia at −30°C. or higher temperatures, a fairly definite stopping point may be recognized after approximately 50 per cent of the phosphine has been displaced. The displacement may amount to 75 per cent if the ammonia is employed only in the gas phase, but there is always a remainder of phosphorus which can be recovered as phosphine only by complete hydrolysis (13). When the displacement has reached the halfway point in liquid ammonia, the solvent may be evaporated at −60°C., leaving a material having the empirical formula $B_2H_6 \cdot PH_3 \cdot 2NH_3$ (24). This substance loses one molecule of ammonia when pumped at −30°C., leaving an apparently pure substance, $B_2H_6 \cdot PH_3 \cdot NH_3$ (24). In liquid ammonia, this reacts with sodium to yield 1 gram-equivalent of hydrogen per mole of compound (13).

The fact that the mixed phosphine–ammonia compound does not liberate phosphine when dissolved in liquid ammonia or when treated with water (13) shows that it is not a phosphonium salt; its reaction with sodium suggests that it is a monoammonium salt. It is possible to reconcile this conclusion with the formulation of the original phosphinate as $H_3P{:}BH_3$, by assuming that this compound is transformed by ammonia into the compound $(NH_4)(H_3B{:}PH_2{:}BH_3)$. Such a reaction would be entirely analogous to the reaction which the hypothetical $H_3N{:}BH_3$ is supposed to undergo in order to produce the end product, $(NH_4)(H_3B{:}NH_2{:}BH_3)$, in the reaction between diborane and ammonia (see page 24).

F. Diborane and methyl cyanide

Methyl cyanide reacts slowly with diborane at −80°C. to form a substance of the composition CH_3CNBH_3. This is a white solid which cannot be volatilized except by dissociation, a reaction accompanied by the formation of a difficultly volatile oil. Like other complex compounds of borine, it reacts with trimethylamine to produce trimethylamine-borine, and the methyl cyanide is set free. It may be chlorinated by treatment with hydrogen chloride; this reaction is somewhat slower at −80°C. than the corresponding reaction of trimethylamine-borine. The compound and its products of thermal decomposition appear to be worthy of further investigation (24).

G. Diborane and pyridine

Diborane reacts rapidly with pyridine at 0°C., in the expected 2:1 ratio, to form a white solid (m.p., 11°C.) which is too slightly volatile to be handled conveniently in the vacuum apparatus. Trimethylamine displaces pyridine from the compound and produces trimethylamine-borine. Although the molecular weight of the pyridine compound has not been determined, there seems to be no reason for doubt that it is a borine derivative, $C_5H_5N{:}BH_3$, analogous to trimethylamine-borine (21).

V. THE REACTION OF DIBORANE WITH AMMONIA, AND RELATED TOPICS

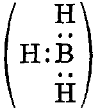
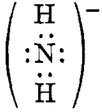
The behavior of diborane toward ammonia is far more complex than the formation of the relatively simple addition compounds discussed in the preceding section. The various products, such as the "diammoniate," $B_2H_6 \cdot 2NH_3$, the compound B_2H_7N, and the interesting inorganic analog of benzene, $B_3N_3H_6$, themselves undergo interesting reactions, have numerous derivatives, and are suggestive of possibilities even wider than those already explored.

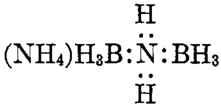
A. The "diammoniate" of diborane and related compounds

Before taking up in detail the evidence concerning the constitution of the "diammoniate"—a problem having an important relation not only to the structure of diborane but also to certain questions of reaction mechanism—it is necessary to emphasize the fact that, unless the compound is prepared with particular care, it may be contaminated with by-products, the presence of which may lead to erroneous conclusions. It is obtained in pure condition when diborane is allowed to act on solid ammonia, thinly spread on the walls of a tube at −120°C., and the excess of ammonia is removed by sublimation at −100°C. A product so obtained is stable at temperatures up to +80°C., but if the procedure outlined is not closely followed, or if the temperature is allowed to rise above −80°C. before removal of the excess ammonia, the product retains more ammonia than that required by the formula $B_2H_6 \cdot 2NH_3$, and loses hydrogen at temperatures (e.g., −10°C.) at which the pure compound is unaltered. As will be shown later, these changes, resulting from departure from the procedure outlined, also produce compounds which contain more ammonium ion than does the pure "diammoniate."

The importance of these considerations is seen from an examination of the evidence adduced by Stock, Wiberg, Martini, and Nicklas (59, 60) in favor of Wiberg's formulation (62) of the diammoniate, $(NH_4)_2(H_2B{::}BH_2)$. These authors have studied the products resulting from the electrolysis of solutions of diborane, tetraborane, and decaborane in liquid ammonia. From a study of the gaseous products liberated at the electrodes, they conclude that two processes occur: (*1*) the liberation of hydrogen unaccompanied by the formation of nitrogen, and (*2*) the production of both hydrogen and nitrogen, a reaction which seems to be essentially an electrolytic decomposition of the ammonia used as the solvent. In a number of experiments, especially those involving diborane, the amount of hydrogen obtained is considerably in excess of that required by the number of faradays passed through the solution. This fact indicates that secondary reactions, of the type described at the close of the last paragraph, had occurred.

The same authors have also analyzed the solid products obtained by evaporation of the ammonia after electrolysis had been discontinued. On account of the possible secondary reactions already mentioned, and because there is no evidence that the solid products were homogeneous, we do not believe that the results of the electrolysis experiments can be accepted as specifically indicating the formula $(NH_4)_2(H_2B::BH_2)$ for the diborane product, or the formulas assigned by these authors to the ammonia derivatives of other boranes. The same is true of all other evidence adduced in favor of these structural formulations (23, 60).

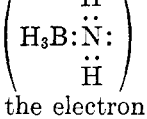
On the other hand, there is much evidence specifically favoring a different view: namely, that the compound is a borine complex in which two borine molecules  $\left(\mathrm{H}:\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{B}}}\right)$ are attached to an amide ion  $\left(:\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{N}}}:\right)^-$, as indicated by the formula



$$(\mathrm{NH_4})\mathrm{H_3B}:\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{N}}}:\mathrm{BH_3}$$

The facts and arguments leading to this conclusion may be summarized as follows (23):

(*1*) In solutions in liquid ammonia at −77°C., the compound reacts with sodium (present in excess) to produce only 1 gram-atom of hydrogen for every 2 gram-atoms of boron present. Although further hydrogen may be obtained, its evolution at this point is extremely slow. It thus appears that the compound $B_2H_6 \cdot 2NH_3$ is a monoammonium salt. If the calculated amount of sodium is used, it is possible to isolate a compound having the empirical formula NaB_2H_8N, which may well be the salt $Na(H_3B:NH_2:BH_3)$.

(*2*) Trimethylamine reacts with diborane to form only the relatively simple compound $(CH_3)_3N:BH_3$, which is inert toward sodium in liquid ammonia. It seems, therefore, that it is a proton derived from ammonia, rather than from diborane, which is responsible for the formation of an ammonium ion. This deduction is in complete accord with the formulation here proposed: it is assumed that one stage of the ammoniation involves the formation of the  $\left(\mathrm{H_3B}:\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{N}}}:\right)^-$ ion, to which a second BH_3 group becomes attached by means of the electron pair exposed by the loss of the proton.

(*3*) Evidence for the existence of the $(H_3B:NH_2)^-$ ion, mentioned in the preceding paragraph, is found in the reaction of dimethyl ether-borine, $(CH_3)_2O:$

BH_3, with sodium in liquid ammonia. If the etherate is added to a solution of sodium in liquid ammonia, 1 gram-atom of hydrogen is liberated per gram-atom of boron contained in the original etherate, and the salt $Na(H_3B{:}NH_2)$ may be obtained from the reaction mixture. These results are in agreement with the equation

$$NH_4^+(H_3B{:}NH_2)^- + Na \rightarrow NH_3 + Na^+ + (H_3B{:}NH_2)^- + \tfrac{1}{2}H_2$$

Furthermore, the interaction of the etherate, ammonia, and sodium, under the conditions specified, is of the first order, as would be expected if the rate-determining first step of the reaction (carried out in liquid ammonia solution) were

$$(CH_3)_2O{:}BH_3 + 2NH_3 \rightarrow (H_3B{:}NH_2)(NH_4) + O(CH_3)_2$$

(*4*) There is also clear evidence of an equilibrium, represented by the equation

$$NH_4(H_3B{:}NH_2BH_3) + 2NH_3 \rightleftarrows 2NH_4(H_3B{:}NH_2)$$

When the "diammoniate" (here represented by the first formula of the equation) is allowed to remain in contact with liquid ammonia for a short time at −40°C., before sodium is added, more hydrogen than corresponds to 1 gram-atom per mole of compound is liberated by the subsequent action of sodium. This result indicates that additional ammonium ions are formed, as should be observed when the reaction proceeds toward the right, approaching the equilibrium condition. If, on the other hand, the dimethyl ether-borine remains in contact with liquid ammonia for a short time before sodium is added, less than 2 gram-atoms (e.g., 1.8 or less) of hydrogen is evolved per 2 gram-atoms of boron in solution. This result indicates the reverse approach toward equilibrium,—a reaction in which $(H_3B{:}NH_2)^-$ ions react with ammonium ions to form $(H_3B{:}NH_2{:}BH_3)^-$ ions and ammonia.

It is also to be mentioned, in this connection, that the compound $Na^+(H_3B{:}NH_2)^-$ absorbs diborane to some extent, as would be expected if the $(H_3B{:}NH_2)^-$ ion were converted to $(H_3B{:}NH_2{:}BH_3)^-$ ion.

(*5*) The "diammoniate" is easily transformed into compounds which have been shown by electron diffraction and other experiments to contain a B—N—B grouping of atoms. One of these is the compound B_2H_7N (2, 29), the formation of which is discussed later; the other is the ring compound $B_3N_3H_6$, which likewise will receive further attention (pages 25 and 27).

From the point of view here developed, it is interesting that the "diammoniate" reacts with hydrogen chloride at −80°C. very much in the same way as does trimethylamine-borine; the reactions proceed at similar rates (50, 25), and in both cases the reaction ceases with the liberation of 1 mole of hydrogen per gram-atom of boron, unless the temperature is raised. In both cases chlorine is substituted for hydrogen. This similarity fits in with the hypothesis that the "diammoniate" contains two borine groups, bonded as is the one in trimethylamine-borine. It should be noted, however, that the similarity is not a proof of structure.

Also of interest at this point is the fact that the solution resulting from the treatment of the "diammoniate" with water possesses the same specific reducing properties (e.g., precipitation of Ni_2B) characteristic of the hypoborates obtained by partial hydrolysis of diborane in strong base solutions (50). This was interpreted as evidence that the "diammoniate" and diborane itself have similar structures; since neither the mechanisms nor the products of these partial hydrolyses are fully understood, this interpretation is not necessarily valid.

In view of the complexity of the reaction of diborane with ammonia, it is not possible to use the structure of the "diammoniate" as a valid basis for discussions of the structure of diborane itself. The study of the ammonia reaction nevertheless has thrown a great deal of light upon the more general chemical character of diborane.

B. Reactions of ammonia with the methyldiboranes

The methyldiboranes, like diborane itself, react with 2 moles of ammonia to produce solid, white, salt-like compounds (27). That they are similar in structure to the "diammoniate" of diborane is suggested by the fact that the product obtained by the action of ammonia on tetramethyldiborane reacts with sodium in liquid ammonia in the same manner (including rate and point of cessation) as does the diborane compound (24).

The "diammoniates" of most of the methyldiboranes lose hydrogen very readily. Especially unstable is the compound derived from tetramethyldiborane: even at $-35°$C. this is quantitatively transformed by the loss of hydrogen into dimethylboron amide, $(CH_3)_2BNH_2$. The same product results also from the heating of the "diammoniates" of 1,1-dimethyldiborane or of trimethyldiborane. More stable than these is the "diammoniate" of monomethyldiborane, which can be kept for some time at room temperature without change.

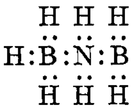
C. The compound B_2H_7N

In the original publication on the reaction of ammonia with diborane at elevated temperatures (51), it is stated that the first reaction occurs according to the equation

$$B_2H_6 + NH_3 \rightarrow B_2H_5NH_2 + H_2$$

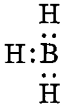
but no description of such an amide is given. Considerably later it was discovered that a substance of the composition and molecular weight corresponding to $B_2H_5NH_2$ is obtained as a by-product in the preparation of borazole (28) or, in better yields, by passing a stream of diborane over the "diammoniate" of diborane at 88°C. and at a pressure somewhat above 1 atm. (29). But this substance, which melts at $-66.4°$C. and has an estimated boiling point of 76°C., is not an amido diborane. Its electron diffraction (2) shows that it has a B—N—B skeleton, and that its structural pattern is closely similar to that of dimethylamine. Furthermore, 1 mole of the compound reacts with 1 mole of ammonia or 1 mole of trimethylamine to form fairly stable addition products, whereas diborane and all of its derivatives not otherwise attacked by ammonia (e.g., the alkyldiboranes) take up 2 moles of ammonia or amine.

Several different structural formulations of this compound might be considered. Most in accord with its known chemical properties is the formula



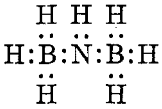
$$\begin{array}{cccc} & \mathrm{H} & \mathrm{H} & \mathrm{H} \\ & \cdot\cdot & \cdot\cdot & \cdot\cdot \\ \mathrm{H{:}} & \mathrm{B{:}} & \mathrm{N{:}} & \mathrm{B} \\ & \cdot\cdot & \cdot\cdot & \cdot\cdot \\ & \mathrm{H} & \mathrm{H} & \mathrm{H} \end{array}$$

which accounts easily for the addition of ammonia or amine in the 1:1 ratio. The chief objection to this formulation is purely theoretical: the boron atom shown on the right has only a sextet of electrons, and there is no obvious means of completing its octet; it thus would be similar to boron in a



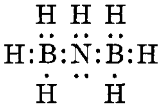
$$\begin{array}{cc} & \mathrm{H} \\ & \cdot\cdot \\ \mathrm{H{:}} & \mathrm{B} \\ & \cdot\cdot \\ & \mathrm{H} \end{array}$$

group, and accordingly might be expected to unite with another of its own kind, to form a molecule twice as large. Other formulations, however, seem less acceptable from the chemical viewpoint. Thus,



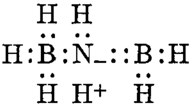
$$\begin{array}{ccccc} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \\ & \cdot\cdot & \cdot\cdot & \cdot\cdot & \\ \mathrm{H{:}} & \mathrm{B{:}} & \mathrm{N{:}} & \mathrm{B{:}} & \mathrm{H} \\ & \cdot\cdot & & \cdot\cdot & \\ & \mathrm{H} & & \mathrm{H} & \end{array}$$

and



$$\begin{array}{ccccc} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \\ & \cdot\cdot & \cdot\cdot & \cdot\cdot & \\ \mathrm{H{:}} & \mathrm{B{:}} & \mathrm{N{:}} & \mathrm{B{:}} & \mathrm{H} \\ & \cdot & \cdot\cdot & \cdot & \\ & \mathrm{H} & & \mathrm{H} & \end{array}$$

while implying the symmetry indicated by electron-diffraction studies (2), do not directly account for the behavior of the substance toward ammonia. The structure



$$\begin{array}{ccccc} & \mathrm{H} & \mathrm{H} & & \\ & \cdot\cdot & \cdot\cdot & & \\ \mathrm{H{:}} & \mathrm{B{:}} & \mathrm{N_{-}{:}{:}} & \mathrm{B{:}} & \mathrm{H} \\ & \cdot\cdot & & \cdot\cdot & \\ & \mathrm{H} & \mathrm{H^{+}} & \mathrm{H} & \end{array}$$

accounts easily for the addition of ammonia, but implies the presence of that all too active chemical entity, a proton bound only by electrostatic forces. On the whole, therefore, it seems as difficult to assign a specific electronic formulation to this substance as to diborane. Nevertheless, the various pictures here discussed may contribute usefully to resonance calculations of energy values.

The compound B_2H_7N is sufficiently stable to remain unchanged for several days at room temperature if out of contact with air or moisture. Over long periods of time, however, it undergoes gradual decomposition, ultimately yielding diborane, a residue of the composition $(BH_4N)_x$, and traces of other products. It is readily hydrolyzed in hydrochloric acid solution, to yield ammonium chloride, hydrogen, and boric acid. Gaseous hydrogen chloride also attacks it, evidently substituting chlorine for hydrogen, but the products have not been fully investigated.

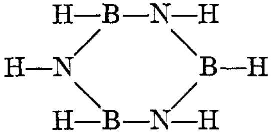
The trimethylamine and ammonia addition products are quite stable at room temperature, but can be made to undergo interesting changes on heating. The former, when heated with excess trimethylamine, yields trimethylamine-borine and a residue of the empirical formula $BH_2N \cdot 0.5N(CH_3)_3$. Sudden heating of the ammonia addition product to 200°C. in a sealed tube results in a 45 per cent yield of borazole.

At −60°C. the ammonia addition product liberates 1 gram-atom of hydrogen per mole of compound when treated with sodium in liquid ammonia for about 1 hr.; thereafter the reaction is very slow. At the end of the first stage of the reaction, a salt-like product of the composition $NaNH_2 \cdot B_2H_7N$ may be isolated.

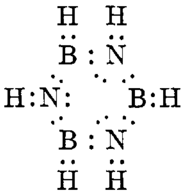
D. Borazole and its derivatives

The compound $B_3N_3H_6$, already mentioned at several points in this review, has been the subject of considerable investigation and discussion in recent years. Its resemblance to benzene has led to the designations "inorganic benzene" and "borazole" (63), the latter of which we have chosen to use in the present discussion.

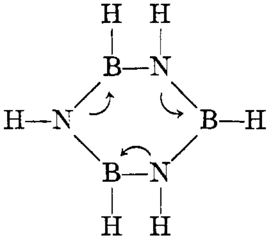
The discoverers of this compound (51) assigned to it the ring structure



and this pattern is supported by electron-diffraction data (2, 61) as well as by the preparation of methyl derivatives (see page 29). When this structural formula is rewritten in electronic terms (I), it is seen that each nitrogen atom has an unshared electron pair, and each boron atom lacks an electron pair. Obviously the unshared electron pairs assigned to nitrogen might complete the valence shells of the boron atoms, thus creating three "internal dative bonds." The analogy with benzene then is the more striking, as shown in formula II (58, 63). Resonance undoubtedly contributes to the stability of the compound.



I



II

This formal similarity is paralleled by some rather striking similarities in the physical properties shown in table 4, which is taken from a recent discussion of the subject (63). Also very striking are the similarities in infrared and Raman spectra (12).

It is, of course, not to be expected that the chemical similarity between the two substances will be as close as the physical. Catalytic hydrogenation leads not to an analog of cyclohexane, but to an evidently polymeric material concerning which little is known. In regard to other types of addition reactions, borazole is in general far more reactive than benzene. Thus 1 mole of borazole adds 3 moles of water, of methanol, of hydrogen chloride, of hydrogen bromide, or of methyl iodide, always yielding products which are not volatile without decomposition. Although these reactions occur with moderate rapidity, they are much slower than would be expected if borazole had the structure represented by formula I, rather than the more tightly bonded structure indicated by formula II, on page 27. Still slower and more difficult to complete are the additions of ammonia, trimethylamine, and dimethyl ether. Ultimately each is added in the ratio of 3 moles to 1 mole of borazole. The addition of the amine or the ether requires heating (60°–70°C.) and 2 weeks' time; each product is a gelatinous opaque mass (63).

It has been suggested (63) that these addition reactions may be strictly analogous to the double-bond additions of benzene chemistry, and that the more positive group in each adding molecule goes to nitrogen, while the more negative goes to boron. The internal dative bonds thus would be removed in favor of external bonding to both boron and nitrogen. This view seems quite reasonable for some cases, such as the addition of hydrogen halides, methyl iodide, and possibly water or ammonia. However, in the case of a molecule which is not easily split, such as trimethylamine, it seems better to assume that the intact molecule is added to boron, and the internal dative bond only suppressed. In some cases, such as that of dimethyl ether, a decision between the two interpretations is very difficult.

TABLE 4

Comparison of the physical properties of benzene and of borazole

PROPERTIES	C_6H_6	$B_3N_3H_6$
Molecular weight	78	80
Boiling point	353°K.	328°K.
Melting point	279°K.	215°K.
Critical temperature	561°K.	525°K.
Density (liquid at boiling point)	0.81 g. per cc.	0.81 g. per cc.
Heat of vaporization (at boiling point)	7400 calories	7000 calories
Molar volume (at boiling point)	96 cc.	100 cc.
Surface tension (at boiling point)	31.0 dynes per cm.	31.1 dynes per cm.
Parachor	206	208
Carbon–carbon distance	1.42 Å.	
Boron–nitrogen distance		1.44 Å.

At temperatures from 50° to 100°C., some of these addition products lose hydrogen, forming substituted borazoles. Thus the compound $B_3N_3H_6 \cdot 3HCl$, formed by addition of hydrogen chloride at lower temperatures, yields another compound, $B_3N_3H_3Cl_3$, on heating to 100°C.; analogous results are obtained with hydrogen bromide (63). In the final products of these reactions, the halogen appears to be attached to the boron atoms of the ring.

The reactions with water and methyl alcohol proceed somewhat farther. When borazole is treated with cold water, a neutral solution is obtained; although the solute is a strong reducing agent, it is not to be confused with the hypoborate obtained by alkaline hydrolysis of diborane, for the trihydrate $B_3N_3H_6 \cdot 3H_2O$ is obtainable by evaporation of the ice-cold solution. At higher temperatures, hydrolysis sets in and ammonia is liberated; the breaking of the ring thus is clearly indicated (51).

The treatment of the trihydrate $B_3N_3H_6 \cdot 3H_2O$ with hydrogen chloride leads to loss of hydrogen and the formation of a compound of the composition $B_3N_3H_3Cl_3 \cdot 3H_2O$. A similar reaction occurs with hydrogen bromide (51, 63).

The reaction of methanol is similar to that of water; the trimethanolate is broken down by heat, yielding hydrogen and a polymeric mass, $(CH_3OBNH)_x$. This material, as well as the product of decomposition of the trihydrate, seems to form boron nitride on further heating (63).

Borazole not only forms addition compounds as just described, but undergoes ring-substitution reactions as well. Thus, both chlorine and bromine attack this pseudobenzene to produce the corresponding hydrogen halides and derivatives of the type $B_3N_3H_5X$. Unlike benzene, however, borazole does not add halogens without substitution.

The direct substitution of methyl groups for hydrogen in borazole may be accomplished by treatment with trimethylboron or with dimethylaminoborine, $(CH_3)_2BNH_2$ (28), but this procedure is not very expeditious, and replaces with methyl groups only hydrogen attached to boron. The *B*-methyl derivatives are more effectively prepared by rapidly heating the "diammoniates" of the mono-, di-, or tri-methyldiboranes to 200°C. in a closed tube (27). The *N*-methyl derivatives may be obtained by heating diborane in similar fashion with methylamine or with mixtures of ammonia and methylamine (28). The *N*-methyl derivatives may be further methylated by treatment with trimethylboron in a sealed tube at 100°C., yielding compounds in which methyl groups are attached not only to nitrogen but also to boron (28).

By these methods, nine of the expected methyl derivatives of borazole have been obtained, and no unpredicted derivative could be found among the products. The physical evidence favoring the ring structure (2) thus is supplemented by very strong chemical support. An ortho- and a para-*N*-methyl-*B*-methylborazole are theoretically possible, but only one substance of this composition has been obtained.

The physical properties of borazole and of all of its known methyl derivatives are compared in table 5.

Several mechanisms for the formation of borazole and of its methyl derivatives have been proposed. Originally it was suggested (27) that the first step in the reaction is an ammonolysis to form some derivative such as $(NH_2)H_2BBH_2(NH_2)$, which then dissociates into transitory fragments such as BH_2NH_2. Condensation of three such fragments with loss of hydrogen might then result in the formation of the ring. After the discovery that trimethylamine reacts with diborane to form a borine complex, $(CH_3)_3N:BH_3$, this hypothesis was modified by the assumption that the high-temperature reaction with ammonia involves an analogous borine complex, $H_3N:BH_3$, which polymerizes with loss of hydrogen (23, 63). For the whole reaction, the following steps have been suggested (63):

$$3B_2H_6 + 6NH_3 \rightarrow 6BH_3 \cdot NH_3 \xrightarrow{-H_2} 6BH_2\text{—}NH_2 \xrightarrow{-H_2} 6BH\text{=}NH \rightarrow 2B_3N_3H_6$$

Several facts may be cited to support such an interpretation, although there is no dependable basis for deciding whether there is any ammonolysis before the B—B link is broken, or for recognizing at what point the ring formation occurs. When diborane is treated with dimethylamine, the reaction might be expected to proceed in similar fashion as with ammonia, except that only one molecule of hydrogen could be lost per borine unit, leaving the compound $H_2BN(CH_3)_2$.

TABLE 5

Physical constants of the methylborazoles

FORMULA	MOLECULAR WEIGHT		MELTING POINT	BOILING POINT	CHARACTERISTIC VAPOR TENSOION	REFERENCE
	Observed	Calculated				
			°C.	°C.	mm.	
$B_3N_3H_6$	80.2	80.5	−58.0	53	85 (0°C.)	(49)
B-$CH_3B_3N_3H_5$	94.9	94.6	−59	87*	19.5 (0°C.)	(27)
N-$CH_3B_3N_3H_5$	94.7	94.6		84*	23.5 (0°C.)	(28)
B,B'-$(CH_3)_2B_3N_3H_4$	109.3	108.6	−48	107*	6.5 (0°C.)	(27)
B,N-$(CH_3)_2B_3N_3H_4$	109	108.6		124*	8 (0°C.)	(28)
N,N'-$(CH_3)_2B_3N_3H_4$	109	108.6		108	8.2 (0°C.)	(28)
B,B',B''-$(CH_3)_3B_3N_3H_3$	124.1	122.6	31.5	129*	21 (35°C.)	(27)
N,B,B'-$(CH_3)_3B_3N_3H_3$	123.6	122.6		139	241 (100°C.)	(28)
N,N',N''-$(CH_3)_3B_3N_3H_3$	123	122.6		134	271 (100°C.)	(28)
N,B,B',B''-$(CH_3)_4B_3N_3H_2$	138	136.6		158	112 (100°C.)	(28)

* This estimate came from an extreme extrapolation of vapor-tension data.

A substance of this composition, but as yet not fully described, actually has been obtained in 100 per cent yield by the reaction in question (63). Similarly, treatment of tetramethyldiborane with ammonia should and actually does lead to the compound $(CH_3)_2BNH_2$, which is incapable of further intramolecular ammonolysis; this also is obtained in quantitative yield (27). These reactions are suggestive of one stage in the suggested mechanism, but obviously throw but little light upon the rest of the process, and do not clearly account for the large yields of by-products.

When such a simple mechanism is applied to the interpretation of the reactions by which the B-methylborazoles are formed, certain difficulties arise. Thus, the reaction of monomethyldiborane with twice its (gas) volume of ammonia would be expected to produce borazole and its mono-, di-, and tri-B-methyl derivatives, in proportions represented respectively by the numbers 1:9:9:1, if it were true that CH_3BHNH_2 and BH_2NH_2 fragments combined in a random manner. Actually, the reaction produces roughly equal quantities of borazole and its three *B*-methyl derivatives (27). Similar deviations from the simple theory occur also in other cases. The question whether the mechanism must be modified to include disproportionation at some stage of the process, or whether the difference is to be attributed to a selective process in the formation of nonvolatile by-products, cannot as yet be decided.

VI. REACTIONS OF DIBORANE WITH ALCOHOLS, ALDEHYDES, KETONES, AND ESTERS

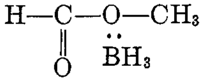
Diborane reacts with alcohols (9), as well as with certain compounds containing carbonyl groups (5), to form dialkoxyborines, such as $(CH_3O)_2BH$. There is evidence, especially in the case of the carbonyl type of compound, that such a reaction proceeds through the intermediate formation of a borine "complex"; for example,

$$2CH_3CHO + B_2H_6 \rightarrow 2CH_3CHO{:}BH_3$$

Presumably this step in the reaction is followed by rearrangement to the borine substitution derivative,—in the example cited, to $CH_3CH_2OBH_2$. By repetition of this series of reactions, the formation of the dialkoxyborine would ensue.

If this interpretation is correct, the reaction can occur only when the borine "complex" has a sufficient strength of B—O bonding. The complex must, however, not be too stable, since it must undergo rapid rearrangement. For this reason the intermediate complex cannot be isolated, but indirect evidence for the mechanism proposed was obtained through a study of the closely related addition products of boron fluoride with the organic compounds involved (5). Thus acetone, acetaldehyde, and trimethylacetaldehyde, which react rapidly with diborane even at −80°C., form moderately stable addition products, whereas chloral, carbonyl chloride, and acetyl chloride, which appear not to react at all with diborane, either do not react with boron fluoride, or form addition compounds so unstable that they exist only at low temperatures. Furthermore, the fact that trimethylacetaldehyde acts as readily as acetaldehyde with diborane shows that enolization is not involved in the reaction.

It is important to note, however, that esters such as methyl formate and ethyl acetate, which form especially stable boron fluoride addition products, react very slowly with diborane: there is no reaction at low temperatures, and at room temperature several hours are required to produce noticeable change. This effect is nevertheless readily explained in terms of a borine-complex mechanism. It is well known that boron fluoride forms very stable addition products with ethers. For this reason it is permissible to assume that the addition involves the ether oxygen atom, rather than the carbonyl oxygen atom, of the ester. Thus the borine complex of, for example, methyl formate, would have the structure



$$H-\underset{\underset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle BH_3}{\cdot\cdot}}{O}-CH_3$$

Rearrangement of this type of compound to form a borine derivative requires the rupture of a carbon–oxygen bond, a reaction presumably requiring a much higher activation energy than the wandering of a hydrogen atom (which is all that is involved in cases in which the borine is linked to the carbonyl oxygen atom).

These mechanisms involve the primary formation of monoalkoxyborines. Compounds of this type have not been isolated, but the production of unstable, solid by-products has been observed in the formation of the dialkoxyborines, and these may be polymers of the monoalkoxy derivatives. The only one of these by-products as yet subjected to study is that obtained in the reaction between methanol and diborane (9). Its composition corresponds to the empirical formula $(CH_3OBH_2)_x$. Its molecular weight has not been determined, because it is non-volatile at room temperature and slowly decomposes to yield dimethoxyborine, diborane, and methyl borate.

The compounds so far obtained by reactions of the types discussed here are the following: (*a*) dimethoxyborine, from diborane with methanol (9) or with methyl formate (5); (*b*) diethoxyborine, from diborane and acetaldehyde (5); (*c*) diisopropoxyborine, from diborane and acetone (5); (*d*) di(neopentoxy)borine, from diborane and trimethylacetaldehyde (5); and (*e*) ethylenedioxyborine, from diborane and ethylene glycol (24).

All but one of these (i.e., the neopentoxy derivative, having a vapor tension of only 3 mm. at 25°C.) are sufficiently volatile and stable during a long enough time to allow rapid determinations of their vapor densities. The results show that polymerization does not occur appreciably in the vapor state (5, 9). The liquids also appear to be normal, with the exception of ethylenedioxyborine, $C_2H_4O_2BH$, which reversibly forms a glassy polymer when condensed (24).

The only one of these derivatives as yet subjected to detailed study is dimethoxyborine (9). It is a moderately stable liquid (b.p., 26°C.; m.p., -130.6°C.) which decomposes reversibly according to the equation

$$6(CH_3O)_2BH \rightleftarrows B_2H_6 + 4B(OCH_3)_3$$

A rough determination of the equilibrium constant for the reaction has given the value 63 ± 5 at 25°C. (for concentrations expressed in partial pressures in atmospheres). The equilibrium mixture of diborane, methyl borate, and dimethoxyborine slowly undergoes decomposition to yield dimethyl ether, methane, carbon monoxide, hydrogen, and non-volatile solid material (24). Since methane, carbon monoxide, and hydrogen are the normal products of the thermal decomposition of dimethyl ether at red heat, the appearance of these products may be the result, either of a room-temperature, catalytic decomposition of the ether primarily formed, or of some preferential formation of the decomposition products. The reaction deserves fuller investigation.

Dimethoxyborine is not spontaneously inflammable in air, but it is readily hydrolyzed by water. With ammonia it forms an unstable addition product, $(CH_3O)_2BH \cdot NH_3$ (24).

One additional observation, made in the study of the reactions involving the carbonyl compounds, is worthy of mention. Acetaldehyde and acetone, which react with diborane very rapidly even at $-80°C.$ in the liquid state, react only very slowly in the gas phase at room temperature (5). It is not likely that the explanation of this phenomenon is to be found in a greater probability of formation of the intermediate complex in the liquid state, for other borine complexes, such as trimethylamine-borine, are readily formed in the vapor phase (24). A more likely explanation may be based upon the assumption that the unstable complexes, formed from acetone and acetaldehyde, have a longer life in the liquid phase.

VII. THE BORANE SALTS

One of the most significant reactions of diborane is its interaction with amalgams of highly active metals (sodium, potassium, calcium) according to equations (42, 44, 50, 56) such as

$$2Na(Hg) + B_2H_6 \rightarrow Na_2B_2H_6 + (Hg)$$

The resulting non-volatile compounds are insoluble in liquid ammonia and in the common organic solvents, and react with water; consequently the molecular formulas assigned to them are based, not upon determinations of their molecular weights, but upon their diamagnetic character (15), which rules out simpler formulas such as $NaBH_3$. That their structure is not more complex than that of diborane is a reasonable assumption, based upon an electronic interpretation of their formation.

The addition of two electrons to the electronically unsaturated diborane ($B_2H_6 + 2e \rightarrow B_2H_6^{--}$) would lead to an ion having a structure analogous to that of ethane, and therefore expected to be very stable. Actually, the diborane salts are far more stable than diborane itself. The compounds $Na_2B_2H_6$, $K_2B_2H_6$, and CaB_2H_6 are so stable that all of the mercury remaining after their formation may be distilled away, leaving the purified salts in nearly quantitative yields (44, 56). The sodium and potassium salts may actually be sublimed *in vacuo* at 400°C., without complete decomposition, although as much as two-thirds of each sample is converted to free metal and to solids such as $K_2B_4H_4$ (an ill-defined substance, believed to be derived from $K_2B_4H_{10}$) (40, 44, 56). The liberation of such active metals as those here involved is in itself evidence of the strong reducing power of these compounds; this property is further demonstrated by their explosive reaction with nitric acid and their immediate reduction of permanganate.

In spite of this marked reducing power, the compounds are permanently stable in dry air at room temperature. They are, however, hydrolyzed without difficulty to produce "hypoborates," which have been shown by x-ray studies to be identical with the hypoborates produced by the action of alkalies upon diborane (3). On the basis of its diamagnetism (15), the potassium hypoborate, which originally was formulated as $KOBH_3$, has been assigned the structure $K_2(BH_2OH \cdot BH_2OH)$ and is regarded as an hydroxyl derivative of a diborane salt. In fact, like the diborane salts, these hypoborates are powerful reducing agents: when heated *in vacuo*, they produce the free metals (and other products), and in solution, they reduce silver, bismuth, mercury, arsenic, and antimony salts to the free metals; with cupric salts they give "copper hydride" (36, 42). Their most characteristic property is the formation of a black precipitate of nickel boride, Ni_2B, from solutions of nickel sulfate.

The diborane salts are more rapidly attacked by hydrogen halides than is diborane: the reaction

$$K_2B_2H_6 + 4HBr \rightarrow K_2B_2H_2Br_4 + 4H_2$$

proceeds almost to completion during one day at room temperature (56). In some cases this reaction is accompanied by the production of diborane, potassium bromide, and hydrogen:

$$K_2B_2H_6 + 2HBr \rightarrow 2KBr + B_2H_6 + H_2$$

It is not certain that this reaction involves a reversal of the original preparation of the diborane salt (56).

Tetraborane and the stable pentaborane also react with alkali metal amalgams to give, respectively, $M_2B_4H_{10}$ (40, 44, 58) and $M_2B_5H_9$ (40, 44); there is some indirect evidence that tetraborane forms compounds other than the one mentioned, but the problem of their isolation has not been solved (58). The higher borane salts are less easily prepared in pure condition than is true of the diborane salts, since they lose hydrogen so readily that it is difficult to preserve them during the removal of mercury by evaporation. Thermal decomposition seems to proceed through steps which may be represented by the formulas $M_2B_4H_8$, $M_2B_4H_6$, and $M_2B_4H_4$ in the case of the tetraborane salt, and by $M_4B_{10}H_{16}$ and $M_4B_{10}H_6$ in the case of the pentaborane salt (40, 44). Although numerous interpretations might be placed upon these decomposition products, it seems best to regard them as mixtures of salts derivable from the numerous stable and unstable decomposition products of diborane. One reason for this opinion is the fact that both $K_2B_4H_{10}$ and $K_2B_5H_9$ give sublimates of potassium and of $K_2B_2H_6$ when heated to 400°C. *in vacuo*. Another reason is that during gentler heating, the tetraborane salt gives considerable proportions of diborane and the stable pentaborane, along with smaller quantities of tetraborane (40). There is thus every reason to believe that free boranes, capable of undergoing "cracking reactions," are present with the alkali metals in the initial products of decomposition.

The tetraborane and pentaborane salts behave toward hydrogen halides as do the diborane salts, except that the products are more numerous. Hydrogen, tetraborane, the stable pentaborane, diborane, potassium chloride, and nonvolatile materials containing the metal, boron, hydrogen, and chlorine, all are formed by the action of hydrogen chloride (44). The potassium salt of the stable pentaborane dissolves in water without evolution of hydrogen, to give a strongly reducing solution which does not, however, give the nickel boride precipitate characteristic of the hypoborates obtained from diborane or its salts (40). It is to be noted also that this nickel test is not obtained with solutions formed by dissolving the stable pentaborane in aqueous alkali.

The existence of still other salts, formulated as $K_2B_2H_4$, $K_4B_4H_6$, and $Ba_2B_4H_6$, has been postulated, and has been used by Wiberg (62) as a part of his argument in favor of the structure $H_2(H_2B{=}BH_2)$ for diborane. But the evidence—namely, the fact that solutions containing 4 moles of sodium or potassium hydroxide or 2 moles of barium hydroxide absorb 1 mole of tetraborane without immediate evolution of hydrogen—seems inadequate as a basis for the acceptance of these formulas as representing chemical individuals.

VIII. THE METALLO BOROHYDRIDES

Among the more striking results of recent investigations in the chemistry of the boron hydrides is the discovery of metal–boron–hydrogen compounds containing unusually large proportions of hydrogen. Of these, the compounds containing lithium (20), beryllium (11), and aluminum (30, 31) have been studied most. They are prepared by the action of diborane upon alkyl compounds of the corresponding metals. Thus lithium borohydride, a definitely salt-like substance formulated as $Li^+BH_4^-$, is produced in practically pure condition by the action of diborane on solid ethyllithium at room temperature, as represented by the equation

$$2LiC_2H_5 + 2B_2H_6 \rightarrow 2LiBH_4 + (C_2H_5)_2B_2H_4$$

Analogous reactions produce the highly volatile, only slightly salt-like solid, beryllium borohydride, BeB_2H_8, and the still more volatile, not at all salt-like, liquid aluminum borohydride, AlB_3H_{12}. The reactions are slightly more complex than represented by the equation for the lithium compound, inasmuch as one first obtains trialkylboron compounds and, in the later stages of the reaction, mixtures of alkyldiboranes.

The physical constants of these compounds are assembled in table 6, which contains also the corresponding data for diborane for use in a comparison of the four compounds.

It is of interest to note that the beryllium and aluminum borohydrides are the most volatile compounds of these metals. Beryllium borohydride is computed to exert a pressure of at least 5 atm. before its melting point is attained, and its heat of fusion is estimated to be at least 7800 calories per mole. On sudden condensation at low temperatures, it forms a transparent glass, which changes to the white solid form at temperatures in the neighborhood of $-10°C$.

Both the beryllium and the aluminum compounds are formed only as the final reaction products of a series of reactions; other compounds, containing methyl groups, precede them in the course of the preparation, and must be used up before either of these pure borohydrides can be isolated. There are also indications that intermediates occur in the formation of lithium borohydride. The initial stage of the reaction between diborane and (solid) dimethylberyllium at 95°C. is a non-volatile, colorless, highly mobile liquid; on further treatment with diborane, this is converted into a white solid, as volatile as BeB_2H_8, but having the empirical formula CH_3BeBH_4. During the analysis of this relatively unstable compound, it was possible to show that the methyl group is attached to beryllium; the substance thus may appropriately be named methylberyllium borohydride. This compound reacts rapidly with additional diborane to yield BeB_2H_8, along with a small amount of a non-volatile white solid which seems to be $(BeBH_5)_x$. These intermediates in the preparation of beryllium borohydride deserve further study. Also in need of further investigation are the intermediates in the preparation of aluminum borohydride; these have not yet been isolated because they are almost as volatile as the final product, aluminum borohydride.

Possibly analogous to the by-product $(BeBH_5)_x$ is a non-volatile zinc compound, $(ZnBH_5)_x$, which has been prepared by the action of diborane on dimethylzinc, but which has not been further investigated (24).

Lithium borohydride is stable in dry air, but the beryllium and the aluminum compounds inflame violently when air is allowed to enter upon them suddenly. All three compounds are readily hydrolyzed to the metal borate and hydrogen; they also react with hydrogen chloride, fairly rapidly even at −80°C., to yield 1 mole of hydrogen per gram-atom of boron. Diborane is liberated at the same time, and the (non-volatile) chloride of the metal is formed. On this account, the action of hydrogen chloride results in an analytically useful separation of boron from the metal.

TABLE 6

Physical properties of metallo borohydrides and of diborane

FORMULA	MOLECULAR WEIGHT		MELTING POINT	BOILING POINT	CHARACTERISTIC VAPOR TENSION	REFERENCE
	Observed	Calculated				
			°C.	*°C.*	*mm.*	
$LiBH_4$			275(d)		Non-volatile	(20)
BeB_2H_8	38.5	38.7	>123	91.3	5.2 (at 20°C.)	(11)
AlB_3H_{12}	71.4	71.5	−65.4	44.5	119.5 (at 0°C.)	(31)
B_2H_6	27.7	27.69	−165.5	−92.5	225 (at −111.9°C.)	(36)

Lithium borohydride reacts with methyl alcohol to give lithium methylate and trimethyl borate; an intermediate compound, lithium boromethoxide, $LiB(OCH_3)_4$, can be isolated. The discovery of this compound led to the preparation of another compound, $LiC_2H_5B(CH_3)_3$, by the action of trimethylboron upon ethyllithium. The compound is unquestionably a mixed quaternary organoboron salt, closely related to the borohydride (20).

Of special interest in relation to the problem of the structure of the metallo borohydrides is their behavior toward trimethylamine. The lithium compound is inert to this reagent, but the beryllium and aluminum compounds form addition products and react further with the amine to liberate trimethylamine-borine. Those addition products which have been definitely isolated contain 1 mole of the amine per mole of borohydride; indications that addition products with a larger proportion of the amine may exist also have been obtained. The compound $BeB_2H_8 \cdot N(CH_3)_3$ is sufficiently stable to permit determination of the molecular weight from vapor-density measurements.

The treatment of these amine addition products with an excess of trimethylamine at slightly elevated temperatures leads to the formation of almost exactly 1 mole of trimethylamine-borine per mole of the borohydride. This removal of one BH_3 group is completed rather easily in the case of the aluminum compound; in contrast to this, the reaction of the beryllium compound is highly reversible and difficult to carry to completion. The materials remaining after the amine treatment are not as yet fully understood; they may be represented by the empirical formulas $BeBH_5 \cdot N(CH_3)_3$ and $AlB_2H_9 \cdot N(CH_3)_3$, but it is not certain that they are single substances rather than mixtures. Attempts to remove all of the boron from the compounds by use of trimethylamine, and thus to form substances which might be formulated as addition compounds of aluminum hydride and of beryllium hydride, have not been successful.

In connection with this attempt to eliminate the boron, it is of interest to note that alminum borohydride seems to form a monoammoniate by an apparently complex reaction with ammonia (31), and that by treatment of the monoammoniate with trimethylamine, as much as 93 per cent of the boron could be removed. The reaction is accompanied by loss of hydrogen and leaves a non-volatile residue; the composition of this (white) material approximates the formula $(AlH_2N)_x$. Although it is improbable that this material is an analog of borazole ($B_3N_3H_6$), it may be a compound containing an aluminum–hydrogen link. It may also be mentioned that dimethyl ether forms a 1:1 addition compound with aluminum borohydride; this compound is, however, too unstable for satisfactory study. At 60°C., it slowly produces methane (31).

On comparison of diborane with the three borohydrides thus far studied, one is struck by the fact that these four compounds constitute a series with progressive changes in properties. The gradation in physical properties from the relatively high-melting, non-volatile, essentially polar lithium borohydride to the very low-melting, very volatile, non-polar diborane is clearly shown in table 6 (page 36); it appears that aluminum borohydride approaches diborane in these respects, while beryllium borohydride is more like the lithium compound. There seems to exist also a trend in solubilities in organic solvents: aluminum borohydride is readily miscible with benzene (20), in which lithium borohydride does not dissolve at all.

A similar gradation is apparent also in the chemical behavior of these substances, a gradation most strikingly illustrated by their behavior toward trimethylamine. With this reagent, diborane rapidly produces trimethylamine-borine at $-110°C.$; aluminum borohydride undergoes a corresponding reaction at temperatures above 0°C., whereas the reaction in the case of the beryllium compound is not conveniently rapid at temperatures below 90°C., and lithium borohydride does not react at all. In sum, the removal of BH_3 groups (as $(CH_3)_3N:BH_3$) from these compounds becomes progressively more difficult from diborane to lithium borohydride.

On the other hand, as the ease with which BH_3 derivatives are formed decreases, the ease of formation of derivatives of the BH_4^- ion increases. Thus diborane reacts relatively slowly with ethyllithium to produce lithium borohydride, whereas aluminum borohydride reacts in benzene solution by a relatively rapid reaction very similar to an ionic double decomposition (20):

$$6LiC_2H_5 + 2AlB_3H_{12} \rightarrow 6LiBH_4 + Al_2(C_2H_5)_6$$

It has been suggested (20) that this gradation in properties might be explained in terms of the charge densities of the lithium, beryllium, aluminum, and boron ions. The relatively large, univalent lithium ion might be expected to exert a relatively small deforming influence on the hypothetical borohydride ion, BH_4^-. The deformation would be greater under the influence of the smaller, doubly charged beryllium ion, and still greater would be the deforming effect of the trivalent aluminum ion; greatest of all would be the deforming influence of the very small, highly charged boron ion. Consequently, whereas the lithium, beryllium, and aluminum compounds have properties which might be ascribed to the presence of the borohydride ion, although to a regularly decreasing degree, these properties have practically disappeared in the boron compound. It seems very improbable that such an aggregate as $B(BH_4)_3$ could exist; it is readily understood that extensive distortion of borohydride ion in a compound of this type would lead to disruption of that ion, and to the formation of BH_3 groups which associate to diborane.

Obviously the increasing distortion of the BH_4 group, or ion, represents a transition from the essentially ionic type of bond in lithium borohydride to the covalent type of bond in diborane. Since the latter is characterized by the electron deficiency pointed out in the introduction, aluminum and beryllium borohydrides must likewise present a degree of electron deficiency which causes their properties to approach those of diborane.

Although the beryllium and aluminum compounds are thus intermediate in character between diborane and lithium borohydride and actually possess only slight ionic properties, the names aluminum borohydride and beryllium borohydride, and the formulas $Al(BH_4)_3$ and $Be(BH_4)_2$, are both convenient and useful.

IX. CONCLUSION

The foregoing review has shown that, in spite of the difficulties inherent in work with these highly unstable, very reactive substances, considerable progress has been made. The difficulties themselves had value, in that they made necessary Stock's development of the high-vacuum methods of dealing with volatile substances,—methods which have proved extraordinarily useful whenever the necessity arose for separating small quantities of mixed volatile materials, or for studying their chemical reactions on a small scale.

The study of the boron hydrides has raised, and has brought partial answer to, new problems concerning the nature of the chemical bond, and has called the attention of chemists not only to the hydrides themselves, but also to a number of compounds such as borine carbonyl, the metal boranes, and the metallo borohydrides. These interesting new types of substances may prove useful in solving problems in related fields.

There are, however, many questions still unanswered and many facts still to be discovered. Further work is needed on the reactions of carbon monoxide with alkyldiboranes, and on the behavior of diborane toward types of organic compounds other than those which have been investigated. For example, diborane undergoes with ethylene (24) what appears to be a most unusual type of autocatalytic reaction, yielding an unusually inert solid, ethane, probably trimethylboron, and other, unidentified products. Additional work is needed to elucidate more definitely the character of the hypoborates. Further studies, some of which are now under way, are needed for a better understanding of the relationships between the various borohydrides, including those which might be formed by the heavier alkali metals, and by other metals in the second and third groups of the Periodic System. Even the problem of the structure of diborane and of the nature of its chemical bonds has not yet been completely solved. These are but a few of the many directions in which further exploration of diborane chemistry might proceed. It is, as a matter of fact, difficult to forecast the future in this field, because experience has shown that each new experiment opens up new veins, rich in interest, which could not possibly have been foreseen by analogy with the compounds of any other element.

Very important would be more development of the chemistry of the higher boranes, including the non-volatile solid products which occur in the preparation of diborane by the hydrogenation of boron halides, or which are formed in the spontaneous decomposition of diborane at low and high temperatures. Some of the volatile higher boranes have been investigated by the electron-diffraction method, as described in the review by Bauer (2), but deductions about their structure, based upon such data, must be regarded as preliminary until more is known about their chemical behavior. The chemistry of even these volatile compounds is fragmentary and not very illuminating, and practically nothing is known about the non-volatile materials. The study of their reactions with trimethylamine and with metalloörganic compounds may prove to be a promising mode of attack, but because of the instability of many of the compounds, and the complexity of the others, the problem is a difficult one which will engage workers in this field for many years.

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