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THE CHEMISTRY OF THE B_3–B_9 BORON HYDRIDES

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I. INTRODUCTION

The boron hydrides occupy a special place among the various classes of boron compounds, being typical representatives of electron deficient compounds. The study of their structure and reactivity has been the largest contribution to the theory of the chemical bond. The boron hydrides also find practical application as fuel additives, lubricants, neutron absorbers, intermediates in the production of polymers with special properties, selective reductants, etc. The first series of boron hydrides were obtained by Stock at the beginning of the XXth century after his development of special apparatus suitable for work with thermally unstable compounds sensitive to moisture and air. The chemistry of the boron hydrides has begun to develop extremely rapidly in the last decade, and now about 50 years after their discovery, the structure and chemical properties of a series of stable and unstable boron hydrides and their derivatives have been rather well studied.

The present article is a brief review of most of the investigations on the structure and chemical reactions of the boron hydrides containing from three to nine boron atoms in the molecule, the main attention being directed to the chemical properties of these compounds. The literature cited is mainly up to 1st July 1964. The problem of the structure of the boron hydrides received detailed discussion in Lipscomb's book[1], in which the chemical reactions of individual boron hydrides received comparatively little attention. The structure and chemical properties of diborane were reviewed by Mikhailov[2] and the chemistry of decaborane by Stanko and coworkers[3]. Some problems of boron hydride chemistry have been briefly discussed in the book by Samsonov and coworkers[4].

II. GENERAL CONSIDERATIONS ABOUT THE NATURE OF THE BONDS IN BORON HYDRIDES

Lipscomb proposed and developed the modern theory of the structure of boron hydrides, explaining their special properties on the basis of the concept of three-centre bonds. As is well known, with the usual covalent (two-centre) bond the two atoms have two orbitals (one bonding and one antibonding) in common and one electron from each atom; the pair of electrons fill the bonding orbital and form a two-centre bond. In the formation of a three-centre bond three atoms

have three orbitals in common use, in the interaction of which one bonding and two antibonding orbitals are formed. A pair of electrons fills only the bonding orbital. These types of bond are instances of the general type of multi-centre bonds. In considering the structure of the boron hydrides studied by him and other investigators, Lipscomb arrives at the following fundamental conclusions.

1. The hybrid orbitals of the boron atoms belong to the usual types of hybridisation: tetrahedral sp^3 or trigonal planar sp^2. The nature of the hybridisation is determined by energetic factors favourable to the formation of the most stable bonds. The hydrogen atoms use only the 1*s*-orbitals.

2. Each terminal B–H bond is a "normal" two-centre bond; on account of the very small difference in electronegativity of the boron and hydrogen atoms these bonds are considered non-polar. Each boron atom has not more than two terminal B–H bonds.

3. For the formation of the skeleton of the boron hydride molecule, bonds of four types are used in addition to the terminal B–H bonds; (a) B–H–B bridging three-centre bonds of "open" type; the electron density in this type of bond is concentrated along the lines joining the atoms; (b) two-centre covalent B–B bonds; (c) "open" three-centre B⟨B⟩B bonds, in which the π-orbital of the central boron atom and two σ-orbitals of the outer boron atoms are used; (d) the "central" three-centre bond B⟨B, B, B⟩, using the σ-orbitals of all three boron atoms; the electron density is concentrated near the centre of the triangle connecting the boron atoms.

4. The orbitals and electrons of the boron atoms are so distributed as to first satisfy the requirements of the terminal B–H bonds and bridging B–H–B bonds. The remaining orbitals and electrons are used for bonds with the other boron atoms, which form the molecular skeleton. The molecules of the boron hydrides are constructed from a few "structural units" and for a given empirical formula the number of possible structural units and bonds is strictly limited and can be determined by use of the topological theory developed by Lipscomb.

5. The following are the most apparent principles in the geometry of most boron hydride molecules: the arrangement of the boron atoms as fragments of octahedra or icosahedra; the presence of hydrogen bridge atoms in the open parts of the molecule; coordination numbers of 5 or 6 for the boron atoms; and a marked tendency to the formation of triangles of boron atoms. Triangles formed by a bridge hydrogen and the two boron atoms adjacent to it, and triangles of boron atoms, can replace one another on going from one member of the series to another.

III. TRIBORANE

1. Structure

Triborane itself, B_3H_9, has not been obtained, owing to its instability. In several studies[5-8] the formation of B_3H_9 or B_3H_7 as intermediates in the conversion of diborane into higher boron hydrides is assumed, and also in the action of HCl on NaB_3H_8.[9] The B_3H_9 molecule contains 18 electrons and 21 orbitals. Lipscomb[10,11] has proposed the most satisfactory structure for B_3H_9, in which each boron atom forms two terminal B–H bonds; three BH_2 groups are connected by bridging hydrogen atoms, forming a ring, similar to cyclopropane (Fig. 1; one of the terminal hydrogen atoms of the BH_2 groups is not shown).

Triborane derivatives in the form of complexes of neutral, $B_3H_7.L$ (where L is a Lewis base), or ionic, $X^+B_3H_8^-$, type have been isolated and studied in detail. Their structure was established by X-ray diffraction and by NMR spectra.

Nordman and Reimann[12,13] showed that the complex $NH_3.B_3H_7$ has two crystalline modifications: low-temperature (monoclinic crystals with group symmetry $P2_{1/n}$, unit-cell parameters a = 10.40, b = 4.824, c = 9.997 Å, β = 115.2°), which is converted at 297.0°K into the high-temperature form with partly disordered crystals (tetragonal with unit-cell parameters a = 6.11, c = 6.57 Å). The low-temperature modification of $NH_3.B_3H_7$ has been studied in sufficient detail and the positions of the B, N, and H (bound to B) atoms have been accurately determined; those of the H atoms bound to N have not, probably because of their rapid random motion in relation to the B–N bond. These authors, and also Kodama and Parry[14], ascribed to the complex $NH_3.B_3H_7$ the structure shown in Fig. 2.

The following interatomic distances have been determined (in Å): $B_{(1)}-B_{(2)}$ = 1.744 ± 0.005, $B_{(1)}-B_{(3)}$ = 1.820 ± ± 0.006, $B_{(2)}-B_{(3)}$ = 1.803 ± 0.006, $N-B_{(3)}$ = 1.581 ± 0.003, $B-H_{terminal}$ = 1.13 ± 0.07, $B_{(1)}-H_{(3)}$ = 1.23 ± 0.03, $B_{(2)}-H_{(3)}$ = = 1.39 ± 0.05, $B_{(3)}-H_{(6)}$ = 1.12 ± 0.03, $B_{(2)}-H_{(6)}$ = 1.75 ± 0.03; the angles between bonds are: $\angle NB_{(3)}B_{(1)}$ = 111.0° ± 0.5°, $\angle NB_{(3)}B_{(2)}$ = 115.3° ± 0.5°, $\angle NB_{(3)}B_{plane}$ = 117.2° ± 0.5°.

The B_3H_7 group is considered to be a fragment of a tetraborane molecule, formed from it in the symmetrical splitting of a bridge bond. A triangle of boron atoms forms two bridge bonds $B_{(1)}H_{(3)}B_{(2)}$ and $B_{(2)}H_{(6)}B_{(3)}$ and one covalent bond $B_{(1)}B_{(3)}$, and the NH_3 group is connected with the $B_{(3)}$ atom and located at an angle of 65° to the plane formed by the boron atoms.

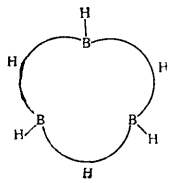


Fig. 1.

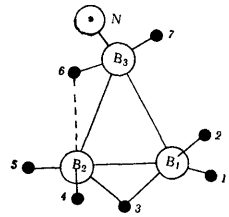


Fig. 2.

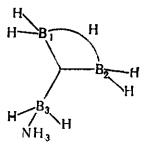


Fig. 3.

Muetterties and coworkers [15], on the basis of the ^{11}B-NMR spectrum of $B_3H_7.O(C_2H_5)_2$ and NaB_3H_8, which showed the identity of all three boron atoms, ascribed to $B_3H_8^-$ and B_3H_7 another type of structure, in which three identical boron atoms are connected by six bridging hydrogen atoms. Furthermore, the molecule contains two hydrogen atoms of another type, each of which is joined to all three boron atoms. Such a structure does not agree with the results of the X-ray analysis of $NH_3.B_3H_7$ [12] and $N(CH_3)_3.B_3H_7$, [10] which show that these molecules do not possess a third-order axis of symmetry. The results on the geometry of $NH_3.B_3H_7$ also agree rather well with the structure shown in Fig. 3. Here the $B_{(3)}-H_{(6)}$ bond is a terminal B–H bond and the $B_{(2)}$ atom is not connected to the $H_{(6)}$ atom. All three boron atoms are connected to one another by a central three-centre bond and each boron atom has two terminal hydrogen atoms. The atoms $B_{(1)}$ and $B_{(2)}$ are linked by hydrogen bridge bonds and a vacant orbital of the atom $B_{(3)}$ is used for a coordinate bond with the nitrogen atom. This structure is supported by the following facts: (1) the length of the $B_{(1)}-B_{(3)}$ bond is appreciably greater than the length of the B–B covalent bond in B_4H_{10} (1.712 Å); (2) the distance between the atoms $B_{(1)}$ and $B_{(2)}$ (1.744 Å) is less than that between the boron atoms joined by hydrogen bridging atoms (1.84 Å); (3) the B_3H_6 distance equals the mean of the terminal B–H bonds whereas B_2H_6 is 0.4 Å greater than the length of the usual bridging bond.

The structure of the ion $B_3H_8^-$ was found by X-ray diffraction and NMR spectra. The X-ray structural analysis [16] of the "diammoniate of tetraborane" $[(NH_3)_2BH_2]^+.[B_3H_8]^-$ at 25° and -100°C shows that the boron atoms in the anion form a triangle of icosahedra with a base of 1.80 Å and sides of 1.77 Å. On the basis of these results the structure shown in Fig. 4 is proposed. $B_{(1)}-B_{(3)}$ = 1.80 Å, $B_{(1)}-B_{(2)} = B_{(2)}-B_{(3)}$ = 1.77 Å, $B-H_{terminal}$ = 1.05–1.20 Å, $B_{(2)}-H_{bridge}$ = 1.5 Å, $B_{(1)}-H_{bridge} = B_{(3)}-H_{bridge}$ = 1.2 Å.

In the ion $B_3H_8^-$ there is a tautomerism of the hydrogen atoms [10,17] which is facilitated by the increase in the interatomic distances and the presence of a negative charge. This exchange explains the ^{11}B- and ^{1}H-NMR spectra of NaB_3H_8 [15] and $(CH_3)_4NB_3H_8$ [18] leading to the conclusion that all the boron atoms are equivalent and connected to the same hydrogen atoms, as in $Al(BH_4)_3$, where all the hydrogen atoms are identical.

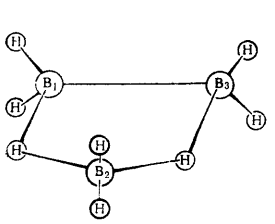


Fig. 4.

2. The Compounds $B_3H_7.L$

The triborane derivative which has been studied in most detail is triborane ammine, $NH_3.B_3H_7$, first obtained by Kodama and coworkers [14] by the action of NH_4Cl on an ethereal solution of NaB_3H_8: [19]

$$NaB_3H_8 + NH_4Cl \xrightarrow[25°]{(C_2H_5)_2O} NH_3.B_3H_7 + H_2 + NaCl\downarrow.$$

However, the compound is obtained in small yield (20–30%) and insufficiently pure; therefore Kodama and coworkers [14,20] also developed a method by which $NH_3.B_3H_7$ is obtained from B_4H_{10} by a series of reactions analogous to those for preparing $NH_3.BH_3$ from B_2H_6. In the action of NH_3 on an ethereal solution of B_4H_{10} at -78°C, the tetraborane undergoes unsymmetrical splitting with the formation of tetraborane diammine, $[(NH_3)_2BH_2]^+[B_3H_8]^-$. On treating this compound with dry HCl in an ethereal solution at low temperature, the reaction:

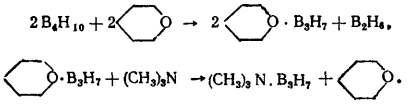
$$[(NH_3)_2BH_2]^+[B_3H_8]^- + HCl + (C_2H_5)_2O \xrightarrow[-78°]{} [(NH_3)_2BH_2]^+Cl^-\downarrow + B_3H_7\cdot(C_2H_5)_2O + H_2,$$

occurs. When the triborane–ether product is treated with ammonia $NH_3.B_3H_7$ is obtained:

$$NH_3 + B_3H_7\cdot(C_2H_5)_2O \xrightarrow[-78°]{(C_2H_5)_2O} NH_3.B_3H_7 + (C_2H_5)_2O.$$

When tetrahydropyran is used instead of ether, pure $NH_3.B_3H_7$ is obtained in 70–94% yield [14]. Triborane–ammonia is a white, crystalline substance, which melts at 73–75°C with weak liberation of hydrogen, and sublimes slowly in a high vacuum. It does not decompose in air and is stable to hydrolysis: the substance is completely hydrolysed only after heating with 6 *N* HCl for several days; the compound dissolves readily in ether, liquid ammonia (at -75°C), and benzene, and is also soluble in acetone and alcohol. The vapour pressure–temperature relation [21], heat capacity, and other thermodynamic constants [22] of $NH_3.B_3H_7$ have been measured, and some of its chemical properties have been studied [14]. It has been found that it does not react with trimethylamine at -78°C, but at 25°C they form $N(CH_3)_3.BH_3$ and an unidentified solid substance, which probably has the composition $HB[N(CH_3)_3]$. [23] NH_3 could not be replaced by $(CH_3)_3N$. When sodium in liquid ammonia acts on $NH_3.B_3H_7$, the B_3H_7 is again destroyed, an equimolecular quantity of hydrogen being released and $NaBH_4$ formed.

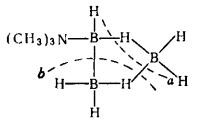
Trimethylamine–triborane $(CH_3)_3N.B_3H_7$ was obtained [24] by a method analogous to that for $NH_3.B_3H_7$:



The yield of $(CH_3)_3N.B_3H_7$ was 65–70%. The compound resembles $NH_3.B_3H_7$ in its properties: when pure it is stable to hydrolysis (for complete hydrolysis heating with 10% HCl for 100 h at 150°C is necessary), it does not decompose on heating to 300°C, does not dissolve in water, is sparingly soluble in ether, and can be recrystallised from alcohol and toluene without decomposition. Crystals of $(CH_3)_3N.B_3H_7$ have two modifications with a transformation point at 209.6°K. The thermodynamic functions of this compound have been determined [24].

Some chemical properties of $(CH_3)_3N.B_3H_7$ have been studied and the instability of the B_3H_7 fragment has been demonstrated. An excess of $(CH_3)_3N$ leads to the splitting of the compound with the formation of $(CH_3)_3N.BH_3$ and $H[B(CH_3)_3]_x$. [25]

A mechanism has been proposed for this reaction[23,26], according to which in the presence of an excess of $(CH_3)_3N$ there is "symmetrical" splitting of the B_3H_7 skeleton, during which the B–H–B bridge bond is broken first (a) with liberation of a BH_3 group and then splitting of the B–B bond occurs with the formation of another BH_3 group (b):



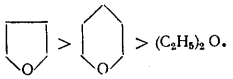
$$\xrightarrow{(CH_3)_3N} 2(CH_3)_3N\cdot BH_3 + HB[N(CH_3)_3]_x.$$

$(CH_3)_3N.B_3H_7$ is also split by triphenylphosphine[27], but there is then incomplete splitting of the triborane skeleton:

$$3(C_6H_5)_3P + (CH_3)_3N.B_3H_7 \xrightarrow[50°]{C_6H_6} [(C_6H_5)_3PBH_2]_2 + (C_6H_5)_3P\cdot BH_3 + N(CH_3)_3.$$

The triborane addition compounds with phosphine Lewis bases were made by a method developed for making $NH_3.B_3H_7$. When $(C_6H_5)_3P$ acts on the addition compound of B_3H_7 with tetrahydrofuran (THF), the THF is displaced and the complex $(C_6H_5)_3P.B_3H_7$ is formed in 54% yield[27]; when $(C_6H_5)_3P$ reacts with $(CH_3)_2S.B_3H_7$ a little $(C_6H_5)_3P.B_3H_7$ is formed and much more $(C_6H_5)_3P.BH_3$. It has been shown that the direction of the reaction depends on the strength of the bond between the ligand and the boron atom in the original complex $B_3H_7.L$: the stronger this bond the greater the destruction of triborane and the quantity of $(C_6H_5)_3P.BH_3$ formed – the strength diminishes in the sequence $(CH_3)_3N > (CH_3)_2S > C_4H_8O$. The displacement of the comparatively weak base tetrahydropyran (THP) from the complex $B_3H_7.THP$ also takes place under the action of a bicyclic phosphite – 4-methyl-2,6,7-trioxa-1--phosphabicyclo[2,2,2]octane, $CH_3C(CH_2O)_3P$, in which the complex $CH_3C(CH_2O)_3P.B_3H_7$ is formed with almost quantitative yield[28].

The strength of the B–P dative bond in the coordination compounds of B_3H_7 is less than that of the B–N bond in $(CH_3)_3N.B_3H_7$. Study of the B_3H_7 complexes with various Lewis bases (ethers, NH_3, amines, substituted phosphines, sulphides, etc.) showed that the stability of the $B_3H_7.L$ complexes depends on the coordination capacity of the base. The weaker Lewis bases, such as $(C_2H_5)_2O$, $(CH_3)_2S$, and thiophen, form unstable complexes with B_3H_7, stable only at low temperatures. Strong Lewis bases – pyridine, $(CH_3)_3N$, $(n\text{-}C_3H_7)_3N$ – form stable complexes, but an excess of the amine destroys them, with the formation of BH_3 and polymeric compounds[26]. It has been shown[14] that the stability of the $R_2O.B_3H_7$ complexes decreases in the order:



$$> (C_2H_5)_2O.$$

B_3H_7 is a stronger Lewis acid than BH_3 [26] and displaces the latter from its complexes; therefore under the action of tetraborane the BH_3.amine complexes are converted into B_3H_7.amine complexes with subsequent slow decomposition of the latter into B_2H_6, B_5H_9, and H_2.

3. Properties of Compounds of the Type $X^+.B_3H_8^-$

Triborane compounds with an ionic structure which have been obtained are NaB_3H_8, $(CH_3)_4NB_3H_8$, and $[BH_2(NH_3)_2]^+[B_3H_8]^-$.

Sodium octahydrotriborate(-1) NaB_3H_8 was first obtained by Hough and coworkers[19,29] in yields up to 80% by reaction of sodium amalgam with diborane(6) in ether at room temperature:

$$2Na + 2B_2H_6 \rightarrow NaBH_4 + NaB_3H_8.$$

NaB_3H_8 was the first representative of triborane(9) derivatives of ionic type. It is thermally stable up to a temperature as high as 200°C, readily soluble in ether, methanol, water, and liquid ammonia; it is more stable to hydrolysis than $NaBH_4$; it is solvated in ether, poly- and mono-ether addition compounds having been identified. Dissolution in water and aqueous HCl is accompanied by partial hydrolysis, but complete hydrolysis requires heating with water at 100°C for some days.

NaB_3H_8 is readily formed also by the action of sodium on a solution of "diammoniate of tetraborane" in liquid ammonia[20]:

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

The yield reaches 60–70%. This reaction is analogous to the reaction for producing $NaBH_4$ from "diborane diammine". NaB_3H_8 is obtained in yields of up to 90% by the reaction of $NaBH_4$ with diborane in dimethoxyethane[30].

A neutral triborane complex, $B_3H_7.NH_3$, is formed by the action of ammonium chloride in ether on NaB_3H_8 at 25°C.[14] The behaviour of NaB_3H_8 in this reaction is also analogous to $NaBH_4$, from which $NH_3.BH_3$ is formed under the same conditions.

Gaines and coworkers[31] proposed a rapid and convenient method for preparing $X^+.B_3H_8^-$ compounds by the hydroboration with diborane of the products of the addition of alkali metals to triphenylboron or naphthalene, or by the reaction of metal hydroborates with B_2H_6 in ethereal solution at 100°C. The salt $(CH_3)_4NB_3H_8$ was obtained in high yield. The mechanism of the reaction is unexplained. An interesting path for the preparation of compounds with the $B_3H_8^-$ anion has been proposed, consisting in the stepwise decomposition of decaborane by methanol under strictly controlled conditions[18]:

$$B_{10}H_{14} + 2(C_2H_5)_2S \xrightarrow[80°]{C_6H_6} B_{10}H_{12}\cdot[(C_2H_5)_2S]_2 + H_2; \quad (1)$$

$$B_{10}H_{12}\cdot[(C_2H_5)_2S]_2 + 3CH_3OH \xrightarrow{65°} B_9H_{13}\cdot(C_2H_5)_2S + H_2 + (C_2H_5)_2S + B(OCH_3)_3; \quad (2)$$

$$B_9H_{13}\cdot(C_2H_5)_2S + (CH_3)_4NOH \xrightarrow{C_2H_5OH} B_9H_{12}\cdot(CH_3)_4N + (C_2H_5)_2S + H_2O; \quad (3)$$

$$B_9H_{12}\cdot(CH_3)_4N + 18CH_3OH \xrightarrow{25°} [B_3H_8]^-[(CH_3)_4N]^+ + 6B(OCH_3)_3 + 11H_2. \quad (4)$$

The reaction takes place readily and this method of making $(CH_3)_4N.B_3H_8^-$ (35% yield) is convenient preparatively. $[(CH_3)_4N]^+[B_3H_8]^-$ is a stable, white, crystalline substance, which does not melt below 275°C and is insoluble in cold methanol. It reacts with $(CH_3)_3N.HCl$ in tetrahydrofuran at its boiling point, and forms $(CH_3)_3N.B_3H_7$ in good yield[18]:

$$[(CH_3)_4N]^+[B_3H_8]^- + (CH_3)_3N\cdot HCl \rightarrow (CH_3)_3N\cdot B_3H_7 + H_2 + (CH_3)_4NCl.$$

Hence here, as for NaB_3H_8, the anion $B_3H_8^-$ is converted into the neutral fragment of triborane B_3H_7.

IV. TETRABORANE(10) B_4H_{10}

1. Structure of Tetraborane

Tetraborane was the first of the boron hydrides to be definitely characterised as a chemical compound by Stock and Massenez[32] in 1912. The position of the boron and

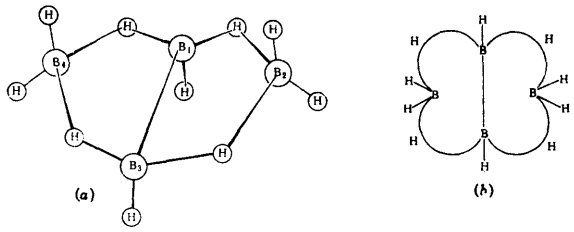


Fig. 5.

hydrogen atoms in B_4H_{10} was unequivocally established by X-ray diffraction [33-35] and electron diffraction [36], also with the aid of ^1H- and ^{11}B-NMR spectra [37]. On the basis of these results for tetraborane the structure shown in Fig. 5 was proposed [10,11]. A quantum-chemical calculation for the molecule was made [38].

The interatomic distances for B_4H_{10} determined by the electron and X-ray diffraction methods differ somewhat from one another. Lipscomb quotes [10] the X-ray results as the more accurate for the distances between the boron atoms and the molecular angles, and the electron diffraction results for the B–H distances. The main data about the geometry of the B_4H_{10} molecule are (in Å): $B_{(1)}-B_{(2)}$ = = 1.842, $B_{(1)}-B_{(3)}$ = 1.712, $B_{(2)}-B_{(4)}$ = 2.800, $B-H_{terminal}$ = = 1.19, $B_{(1)}-H_{bridge}$ = 1.16, $B_{(2)}-H_{bridge}$ = 1.37; the angles (in degrees) are: $\angle B_{(1)}-B_{(2)}-B_{(3)}$ = 56.6, $\angle B_{(1)}-B_{(3)}-B_{(2)}$ = = 61.7, $\angle B_{(2)}-B_{(1)}-B_{(4)}$ = 98, $\angle B_{(1)}-B_{(3)}-H_{(1)}$ = 118; angle between the $B_{(1)}-B_{(3)}-B_{(2)}$ and $B_{(1)}-B_{(3)}-B_{(4)}$ planes = 118.1.

The B_4H_{10} molecule contains two types of boron atom. Each atom of type I forms one two-centre B–H bond and two bridging three-centre B–H–B bonds; furthermore, these two boron atoms are connected to one another by a covalent bond making use of the remaining orbitals and electrons of each atom. The atoms of type II form two two-centre B–H bonds and two three-centre B–H–B bridge bonds, these using all four sp^3-orbitals and all three electrons of the boron atom. The planes of the two triangles formed by the boron atoms are disposed at an angle of 118.1°. The framework formed by the boron atoms of B_4H_{10} can be considered as a fragment of an octahedron or icosahedron as the $B_{(2)}-B_{(1)}-B_{(4)}$ valence angle (98°) is the mean between the angles for an octahedron (90°) and an icosahedron (108°).

Williams and coworkers [37] made a detailed study of and interpreted the ^1H- and ^{11}B-NMR spectra of B_4H_{10}, which confirmed the structure of the molecule shown in Fig. 5. The ^{11}B-NMR spectrum contains a triplet in the weak field region corresponding to the BH_2 groups, and a doublet in the strong field region, corresponding to BH groups; the interpretation of such a doublet structure as a consequence of the $^{10}B-^{11}B$ interaction [37] seemed incorrect, as such interaction is not observed in ^{11}B-NMR spectra of deuterated tetraborane [39]. The ^1H-NMR spectrum of tetraborane shows the presence in it of two types of terminal hydrogen atoms and bridging hydrogens.

The determination of the dipole moment of B_4H_{10}, [38,40] 0.56 ± 0.1 D (in benzene) shows that all the boron atoms are electrically neutral; the slight polarisation of the molecule is due to second-order effects.

2. Preparation of Tetraborane

Tetraborane(10) was first obtained by the action of HCl on magnesium boride [32]:

$$Mg_3B_2 + HCl \rightarrow B_4H_{10} + MgCl_2.$$

This method gives a negligible yield (~ 1%) of a contaminated product. Subsequently several other methods for preparing it were developed. Stock and his coworkers studied the decomposition of several metal borides with various mineral acids [41] and found [42] that the yield is somewhat better in the decomposition of beryllium boride by hydrochloric acid (~ 1.5–2%) and pure B_4H_{10} is obtained (it does not contain silicon hydrides as impurity). Wiberg and Schuster [43] found that when magnesium boride (or a mixture of magnesium and boron trioxide) is decomposed by 8 N H_3PO_4 tetraborane is obtained in ~ 11% yield:

$$B_2O_3 + Mg \rightarrow Mg_3B_2;\ Mg_3B_2 + H_3PO_4 \rightarrow B_4H_{10} + Mg_3(PO_4)_2.$$

In later work [44] it was shown that in this way B_4H_{10} can be obtained in yields of up to 14.5%. Tetraborane was prepared [45] from B_2H_5I and sodium amalgam in 30% yield:

$$2\,B_2H_5I + 2\,Na \xrightarrow[-35^\circ]{} B_4H_{10} + 2\,NaI.$$

However, the method is not very suitable for obtaining comparatively large amounts of tetraborane on account of the instability of B_2H_5I.

After the development of a method of making diborane from boron halides and hydrogen in an electric discharge [46], tetraborane began to be made by the pyrolysis of B_2H_6, initially through the intermediate stage of converting it into B_5H_{11} (100°C, 10 min) and the pyrolysis of the latter [47], and later by direct pyrolysis of B_2H_6 at 180°C and reduced pressure (450 mmHg). [48] Pyrolysis of diborane at elevated pressure (50 atm, 50–75°C) leads to the production of B_4H_{10} in yields of 20–35%. [49] All these methods had various drawbacks. In 1958 a convenient laboratory method for obtaining B_4H_{10} or B_5H_{11} (depending on the reaction conditions) by the pyrolysis of B_2H_6 was proposed [50], and made these compounds accessible. The novelty in this method was the construction of the reactor, which consisted of two tubes, nesting one within the other. The outer tube is cooled and the inner is heated to the required temperature. The reaction zone is the space between the tubes. This reactor ensures that the removal of the unstable boron hydrides from the reaction zone is as fast as possible. Low-temperature, high-vacuum fractionation [41], or gas chromatography [51] is used to isolate pure B_4H_{10} from the mixture of boron hydrides; the yield of B_4H_{10} reaches 83%. Tetraborane is also formed in the reduction of diboron tetrachloride by metal tetrahydroborates at low temperature [52]:

$$B_2Cl_4 + 4\,LiBH_4 \xrightarrow[-45^\circ]{} B_4H_{10} + B_2H_6 + 4\,LiCl.$$

The reaction is complex, and a mixture of boron hydrides is formed.

Kreyl and Marcus [53] studied the photochemical conversion of B_2H_6 into B_4H_{10} and showed that the mechanism of this reaction is different from the thermal process. The authors think that the reaction proceeds by a free radical path with the intermediate formation of B_2H_5:

$$B_2H_6 + h\nu \rightarrow B_2H_5^{\cdot} + H^{\cdot};\ 2\,B_2H_5^{\cdot} \rightarrow B_4H_{10};\ 2\,H^{\cdot} \rightarrow H_2.$$

An analogous mechanism was proposed for the mercury-sensitised conversion of B_2H_6 into higher boron hydrides [54]. Several patents were taken out on the production of B_4H_{10}:

from B_2H_6 in a silent electric discharge[55] (yield of B_4H_{10} 43–97% in the conversion of 7–36% of the B_2H_6); from B_5H_{11} by its partial hydrolysis at 0°C, 15–50 mmHg pressure, and a time of contact of B_5H_{11} with ice of 1 min.[56,57] The yield of B_4H_{10} reaches 95%.

3. Physical and Chemical Properties of Tetraborane

Tetraborane is a mobile liquid, b.p. 18°C, f.p. -120°C, vapour pressure at 0°C 388 mmHg, density 0.56 at -35°C.[41] It exhibited a high toxicity[58]. As Stock showed[41], B_4H_{10} is unstable at room temperature and slowly breaks down into B_2H_6, B_5H_9, H_2, and involatile boron hydrides. A prolonged experiment, which lasted 340 h,[41] in which B_4H_{10} was put in the cell of an infrared spectrograph at 20° and its infrared spectrum periodically recorded showed that equilibrium is reached between B_4H_{10} and its decomposition products. Study of the kinetics of the conversion of B_4H_{10} into B_5H_{11} [59,60] showed that the reaction proceeds in two stages, the first of which determines the rate of the process:

$$1)\ B_4H_{10} \rightleftarrows B_4H_8 + H_2; \quad 2)\ B_4H_8 + B_2H_6 \rightarrow B_5H_{11} + BH_3.$$

The conversion of B_4H_{10} into B_5H_{11} depends only on the B_4H_{10} concentration; the activation energy of the reaction is 23.4 kcal mole^{-1}. Proof of this course of the reaction is provided by the formation of B_4H_8CO from a mixture of B_4H_{10} and CO in the temperature range 80–110°C.[60] Mass-spectrometric study of the pyrolysis of B_4H_{10} showed[61] that the radicals BH_2 and BH_3 are formed.

In studying the kinetics of deuterium exchange between B_2D_6 and B_4H_{10} at 25–45°C it was found[62] that the exchange can proceed by two different paths. In the first reaction, which has the greater rate at this temperature, two hydrogen atoms are exchanged, with formation of $B_4H_8D_2$; the activation energy is 25.5 kcal mole^{-1}. The exchange is explained by a series of bimolecular reactions in which two hydrogens in the B_4H_{10} molecule which have greater reactivity under ordinary conditions are excited. It is suggested[63] that these are the terminal atoms connected with boron atoms 1 and 3. Under the conditions of the experiment apparently B_4H_8 is not formed, as is confirmed by the lower rate of deuterium exchange between B_4H_{10} and D_2 in comparison with the reaction of B_4H_{10} with B_2D_6:

$$B_4H_{10} + B_4H_{10} \rightleftarrows B_4H_{10}^* + B_4H_{10},$$

$$B_4H_{10} + B_2D_6 \rightleftarrows B_4H_{10}^* + B_2D_6,$$

$$B_4H_{10}^* + B_2D_6 \rightleftarrows B_4H_8D_2 + B_2D_4H_2.$$

At higher temperatures[60,64] loss of the two most mobile hydrogen atoms and the formation of B_4H_8 probably takes place.

In the second path[62] of the deuterium exchange between B_4H_{10} and B_2D_6, eight (or all ten) hydrogen atoms are exchanged. The reaction has an activation energy of 14.1 kcal mole^{-1}, and the rate of this reaction is less temperature-dependent than the first type. The rate-determining stage is the reaction of BD_3 with B_4H_{10}:

$$^{10}B_2D_6 \rightleftarrows 2\,^{10}BD_3,$$

$$^{10}BD_3 + B_4H_{10} \rightarrow {}^{10}BD_3B_3H_7 + BH_3,$$

$$BH_3 + {}^{10}BD_3 \rightarrow BH_3{}^{10}BD_3.$$

The exchange of the atoms ^{10}B–^{11}B between $^{10}B_2H_6$ and B_4H_{10} takes place at one-third of the rate of deuterium exchange[62,64]. The presence of this exchange shows the instability of the B_4H_{10} skeleton. The rate-determining stage is the dissociation of B_4H_{10} into BH_3 and B_3H_7.

In the mass-spectrographic study of the fragments obtained in the bombardment of B_4H_{10} and B_4H_8 by fast electrons (energy 70 eV), Fehlner and Koski[63,65] found that the greatest intensity in the mass spectra was possessed by ions arising as a result of the loss of two atoms of hydrogen or deuterium from the tetraborane molecule: a considerable number of metastable ions obtained by loss of three hydrogens or three deuteriums from the tetraborane molecule was also observed. The authors state that two hydrogen atoms bound to the same boron atom (that is, a terminal and a bridge hydrogen) are lost, leading to the formation of a two-centre B–B bond instead of a B–H–B bridging bond and the liberation of a molecule of H_2. The same authors[8] pyrolysed B_2H_6 and B_4H_{10} in the presence of H_2 in a reactor with a pulsating heater, making possible the isolation of unstable intermediates. It was shown that B_4H_{10} is a precursor of B_5H_{11} in the pyrolysis of B_2H_6, and B_4H_8 is an intermediate. The following equations represent the mechanism:

$$B_4H_{10} \rightleftarrows B_4H_8 + H_2, \qquad B_6H_{12} \rightleftarrows B_6H_{10} + H_2,$$

$$B_4H_{10} \rightleftarrows B_3H_7 + BH_3, \qquad n\,B_4H_8 \rightarrow m\,(\text{solid}) + H_2,$$

$$B_4H_8 + B_2H_6 \rightleftarrows B_5H_{11} + BH_3, \qquad B_3H_7 + H_2 \rightleftarrows B_3H_9,$$

$$B_4H_8 + B_2H_6 \rightarrow B_6H_{12} + H_2, \qquad B_3H_9 + B_2H_6 \rightarrow B_5H_9 + 3\,H_2,$$

$$B_5H_{11} \rightleftarrows B_4H_8 + BH_3.$$

B_2H_6, B_5H_9, B_5H_{11}, B_6H_{10}, and higher boron hydrides have been observed in the pyrolysis products. An increase in the hydrogen concentration has been shown to retard the formation of B_4H_8 as the amount of B_5H_{11} then decreases and the amount of B_5H_9 increases. Schaeffer and Tebbe[9] made boron-labile tetraborane containing three ^{10}B atoms and one ^{11}B atom from $^{10}B_3H_8Na$ and $^{11}B_2H_6$, and also $^{10}B_4H_{10}$, and they showed with the aid of ^{11}B-NMR spectra that ^{11}B is present in four (or two) positions of the tetraborane molecule (the triplet in the weak field region in the $^{10}B_3H_7{}^{11}BH_3$ spectrum corresponding to the BH_2 group has a greater intensity than in the $^{10}B_4H_{10}$ spectrum). The reaction is represented by the following equations:

$$Na^{10}B_3H_8 + HCl \rightarrow NaCl + {}^{10}B_3H_9,$$

$$\tfrac{3}{2}\,{}^{10}B_2H_6 \leftarrow {}^{10}B_3H_9 \rightarrow {}^{10}B_3H_7 + H_2,$$

$${}^{10}B_3H_7 + {}^{11}B_2H_6 \rightarrow {}^{10}B_3{}^{11}BH_{10} + {}^{11}BH_3.$$

This synthesis is the first example of the preparation of a boron hydride with an isotopic boron atom in a definite position and demonstrates the different mobilities of the boron atoms in the B_4H_{10} molecule.

Tetraborane is slowly hydrolysed by water according to the equation[41,66]:

$$B_4H_{10} + 12\,H_2O \rightarrow 4\,H_3BO_3 + 11\,H_2.$$

The hydrolysis is accelerated on heating or stirring the mixture; the slowness of the hydrolysis is explained by the poor solubility of B_4H_{10} in water. Hydrolysis by dilute acids follows an analogous path. B_4H_9Cl is formed by the action of dry HCl on B_4H_{10}:[66]

$$B_4H_{10} + HCl \rightarrow B_4H_9Cl + H_2.$$

The reaction at room temperature is very slow even in the presence of $AlCl_3$. The reaction product is unstable and breaks down into B_4H_{10} and BCl_3. B_4H_{10} is decomposed

by HCl at 50°C. Reaction of alkali metal amalgams with an excess of B_4H_{10} at 170°C leads to the formation of salts of B_4H_{10} of the composition $K_2B_4H_6$ (or $Na_2B_4H_8$) and the release of hydrogen[67]; on further heating, the mixture gives off hydrogen and $M_2B_4H_6$ and $M_2B_4H_4$ are formed. Under the action of HCl, H is replaced by Cl in the salt[67]. The reaction of NaCN with B_4H_{10} [68] leads to splitting of the latter and the formation of salts with mixed anions:

$$B_4H_{10} + \xrightarrow{NaCN} NaB_3H_7CN + NaB_2H_6CN.$$

In reaction with C_2H_5OH at -78°C, tetraborane is partly (13%) converted into a colourless polymer containing ethoxy--groups but forms mainly $HB(OC_2H_5)_2$ and $B(OC_2H_5)_3$, and also traces of B_2H_6; during the course of the reaction an equimolecular amount of hydrogen is liberated[25]. Shapiro and Weiss[69] studied the alcoholysis of B_4H_{10} by deuterated ethanol at 20°C and showed that the reaction is somewhat different from that for B_2H_6 on account of the presence of B–B bonds. The intermediates in the reaction are $DB(OC_2H_5)_2$ and $HB(OC_2H_5)_2$, that is, the B–B bonds are destroyed simultaneously with the breaking of the B–H bonds. The final product of the reaction is $B(OC_2H_5)_3$.

When iodine in methanol acts on B_4H_{10} there is a rapid exothermic decomposition of the latter with release of hydrogen. This reaction has been proposed for the analytical determination of B_4H_{10}:[70]

$$B_4H_{10} + 9\,I_2 + 12\,CH_3OH \rightarrow 4\,B(OCH_3)_3 + 18\,HI + 2\,H_2.$$

In addition to the above reactions of B_4H_{10}, leading to breakdown of its molecule, it has characteristic reactions in which there is "symmetrical" double bridge splitting, leading to formation of BH_3 and B_3H_7, and "unsymmetrical" double bridge splitting in which BH_2^+ and $B_3H_8^-$ ions are formed. Both these reactions occur when bases act on B_4H_{10}. Fig. 6 shows the decomposition schemes and also the "symmetrical" decomposition of the B_2H_6 molecule for comparison.

Most Lewis bases bring about the symmetrical breakdown of B_4H_{10};[23,25,26,71] this shows a similarity between tetraborane and diborane chemistries.

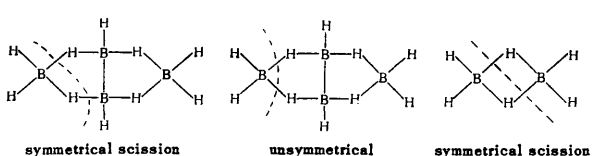
On treating B_4H_{10} with ethers, amines, or organic sulphides, $B_3H_7.L$ complexes are formed:

$$B_4H_{10} + THF \rightarrow B_3H_7 \cdot C_4H_8O + {}^1/_2\,B_2H_6,$$

$$B_4H_{10} + 2(CH_3)_3N \rightarrow B_3H_7 \cdot (CH_3)_3N + BH_3 \cdot (CH_3)_3N.$$

A second product of the reaction is B_2H_6 or the complex BH_3L, depending on the coordination capacity of the base; the stability of the complex B_3H_7L which is formed also depends on this[26]. As symmetrical decomposition of B_3H_7L also takes place in the presence of an excess of the amine, the reaction of B_4H_{10} under these conditions is by the equation[25]:

$$B_4H_{10} + (3+x)(CH_3)_3N \rightarrow 3(CH_3)_3N \cdot BH_3 + BH[(CH_3)_3N]_x.$$



symmetrical scission of B_4H_{10} | unsymmetrical scission of B_4H_{10} | symmetrical scission of B_2H_6

Fig. 6.

An excess of B_4H_{10} decomposes the complex B_3H_7L into B_2H_6, B_5H_9, and H_2.

The reaction of tetraborane with NH_3 follows the path of "unsymmetrical" splitting of the molecule. Stock[66,72] has shown the formation of two unstable compounds of tetraborane with ammonia, $4NH_3.B_4H_{10}$ and $2.5NH_3.B_4H_{10}$. On repeating and studying in greater detail the reaction of B_4H_{10} with NH_3 under various conditions, Kodama and Parry[20,73] established that the substances obtained by Stock are not individual compounds, but a mixture of several. They isolated in the pure state a new compound, "diammoniate of tetraborane" as a stable, white, finely crystalline powder and studied its physical and some of its chemical properties:

$$B_4H_{10} + 2\,NH_3 \xrightarrow[-78°]{(C_2H_5)_2O} B_4H_{10} \cdot 2\,NH_3.$$

A necessary condition for obtaining "diammoniate of tetraborane" is a low temperature and the constant presence of an excess of B_4H_{10}. On the basis of the chemical reactions, an ionic structure was advanced for the compound, $[H_2B(NH_3)_2]^+ . [B_3H_8]^-$, confirmed by the results of X-ray diffraction[16]. It reacts with sodium by the equation:

$$[H_2B(NH_3)_2]^+[B_3H_8]^- + Na \xrightarrow[-78°]{NH_3} NaB_3H_8 + H_2BNH_2 + NH_3 + {}^1/_2\,H_2$$

In this, NaB_3H_8 is obtained in 60–70% yield. This reaction reveals the structure of the anion. Proof of the structure of the cation is provided by reaction with HCl, as a result of which diammineboronium chloride and triborane(7)–ether were produced:

$$[H_2B(NH_3)_2]^+[B_3H_8]^- + HCl \xrightarrow[-78°]{(C_2H_5)_2O} [H_2B(NH_3)_2]Cl + B_3H_7 \cdot O(C_2H_5)_2 + H_2.$$

It was also established that the compounds $6NH_3.B_4H_{10}$ and $7NH_3.B_4H_{10}$ are formed in the prolonged reaction of tetraborane with an excess of NH_3 at -78°C without a solvent[20]. It was shown that in the reaction of NH_3 with B_4H_{10} the solvent plays an important part. When a solvent with considerable coordination capacity (THF, THP) is used there is symmetrical splitting of B_4H_{10} and $B_3H_7.NH_3$ is formed, whereas when a weak Lewis base is used as solvent — $(C_2H_5)_2O$, which does not react with B_4H_{10} at a low temperature (-78°C) — unsymmetrical decomposition of the molecule under the action of ammonia takes place. In these reactions there is an analogy between the chemistries of B_4H_{10} and B_2H_6.

An interesting reaction, leading to greater complexity in the skeleton of the B_4H_{10} molecule, was discovered by Boone and Burg[57]. In the action on B_4H_{10} of bis(dimethylamino)borane at -78°C an addition product of empirical formula $[(CH_3)_2N]_2BH.B_4H_{10}$ is formed, which on heating to -15°C decomposes with formation of B_5H_9, B_4H_{10}, B_2H_6, $[(CH_3)_2N]_2BH$, and $(CH_3)_2NBH_2$. The reaction of B_4H_{10} with 1,2-dimethyldiborane(6) gives a derivative of B_5H_{11}:[74]

$$B_4H_{10} + {}^1/_2(BH_2CH_3)_2 \rightleftarrows B_5H_{10}CH_3 + H_2.$$

The next type of B_4H_{10} reactions are those in which hydrogen atoms are replaced without decomposition of the skeleton of the molecule. $B_4H_9CH_3$ is obtained by the action of $CH_3B_2H_5$ on B_4H_{10}:[74]

$$B_4H_{10} + B_2H_5CH_3 \overset{45°}{\rightleftarrows} B_4H_9CH_3 + B_2H_6,$$

which was identified and characterised by the aid of infrared, NMR, and mass spectra. The infrared spectrum of $B_4H_9CH_3$ shows the asymmetry of the molecule: the principal changes are found in that part of the spectrum which characterises the vibrations of the BH_2B group; therefore the authors think that a hydrogen atom connected with a type II boron atom is replaced.

Harrison and coworkers[75] first studied the reaction of boron hydrides with unsaturated hydrocarbons in the reaction of ethylene with B_4H_{10} in the presence of aluminium chloride. They showed that here also there is replacement of the terminal B–H bonds in the BH_2 group by B–C bonds, with the formation of dimethyltetraborane (70%). The compound is more stable than B_4H_{10}:

$$B_4H_{10} + C_2H_4 \rightarrow B_4H_8C_2H_4 + H_2.$$

The infrared spectrum shows the absence of a BH_2 group and the presence of two types of B–H bonds. The authors consider that the compound has a cyclic bridging structure of unique type, unknown earlier (Fig. 7). The NMR spectra show[76] that the replacement of hydrogen atoms takes place at boron atoms 2 and 4.

The chemical properties of the compound (hydrolysis and alcoholysis) are consistent with the proposed structure[75].

Tetraborane(8)-carbonyl is a very interesting derivative of tetraborane; it was first prepared by Burg and Spielman[77] by the reaction of B_5H_{11} with carbon monoxide in a sealed ampoule at room temperature; later it was obtained[60] by heating B_4H_{10} in the presence of an excess of carbon monoxide at 80–100°C. It is an unstable liquid, which decomposes at room temperature, with liberation of carbon monoxide and higher boron hydrides, and which ignites spontaneously in air (m.p. -114°C, vapour pressure 71.2 mmHg at 0°C, b.p. 59.6°C [77]). A detailed description of the preparation of B_4H_8CO from B_4H_{10} or B_5H_{11} and CO and of its physical and chemical properties has been published[78,79]. Spectroscopic methods were used to establish its structure. The infrared spectrum shows that the molecule contains BH_2 groups, and that the B–CO bond is similar to the bond in BH_3–CO; the infrared spectrum and Raman spectrum of B_4H_8CO differ considerably from those of B_4H_{10}.[79,80] The ^{11}B-NMR spectrum of B_4H_8CO [77,79] contains a doublet in the strong field region typical of the B–H group, and a non-symmetrical triplet in the weak region, which can be ascribed to the BH_2 group. The asymmetry of the triplet is ascribed[78] to the tautomerism of the hydrogen atoms of the B–H–B bridge and terminal B–H bonds (there is a similar tautomerism in the B_5H_{11} molecule)[81]. The structure and the mechanism of formation of B_4H_8CO were not established unambiguously but it was suggested that the most probable place for the addition of CO to the B_4H_8 residue is the boron atom corresponding to the apex in B_5H_{11}, or type I in B_4H_{10}.[73] The most probable structure has the boron atoms at the corners of a trigonal pyramid; the apical boron atom is probably connected by two-centre bonds with two boron atoms of the base, to one of which the CO group is attached; the apical atom is connected with the third boron atom of the base through bridges, similar to the unique bridge in B_5H_{11}. One of the structures proposed for B_4H_8CO is shown in Fig. 8.

The chemical reactions of B_4H_8CO are characterised by rapid but incomplete loss of carbon monoxide and by strong

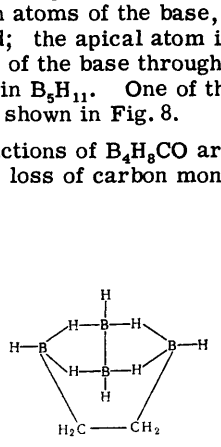


Fig. 7.

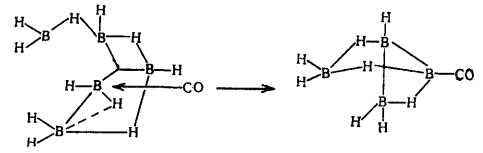


Fig. 8

electron-acceptor properties of the B_4H_8 group[78]. B_4H_8CO has two decomposition paths:

$$B_4H_8CO \rightarrow B_4H_8 + CO, \quad (1)$$

$$B_4H_8CO \rightarrow BH_3 + B_3H_3CO. \quad (2)$$

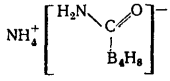
The first path is shown by the formation of B_4H_{10} in the presence of hydrogen or B_5H_{11} in the presence of B_2H_6, the second by the fact that when heated in a vacuum B_4H_8CO does not liberate carbon monoxide, but forms a high-molecular-weight substance containing boron and carbon monoxide[78].

The reactions of B_4H_8CO with electron-donor compounds – $(CH_3)_3N$, C_2H_4, and $(C_2H_5)_2O$ – have been studied[78] and it has been shown that B_4H_8CO exhibits a tendency towards hydrogen replacement reactions; the B–CO bond is rather stable. The reaction with ethylene is most unambiguous:

$$B_4H_8CO + 4\,C_2H_4 \rightarrow (C_2H_5)_4B_4H_4CO.$$

Water hydrolyses B_4H_8CO, but not quantitatively; the residue, which contains B–B bonds, has not been identified.

Parry and coworkers[82] have shown that B_4H_8CO reacts with an excess of ammonia at a low temperature (from -95° to -50°C) to form a compound of composition $B_4H_8CO.2NH_3$, to which, on the basis of its chemical reactions, infrared spectra (the presence of N–H and B–H bonds and of an amide CO bond), and also by analogy with the structure of $BH_3CO.2NH_3$ (studied by the same authors), was ascribed an ionic structure with an anion analogous to carbamate (if it is assumed that the B_4H_8 group is isoelectronic with oxygen):



The following reactions are proof of such a structure:

$$NH_4^+[B_4H_8CONH_2]^- + Na \xrightarrow[-78°]{\text{liq. } NH_3} Na^+[B_4H_8CONH_2]^- + {}^1/_2H_2, \quad (1)$$

$$NH_4^+[B_4H_8CONH_2]^- + LiBH_4 \xrightarrow[14\text{ h}]{THF} H_3NBH_3 + Li^+[B_4H_8CONH_2]^-_{\downarrow} + {}^1/_2H_2, \quad (2)$$

and the structure of the cation:

$$NH_4^+[B_4H_8CONH_2]^- + NaB(C_6H_5)_4 \xrightarrow[0°,\ 15\text{ s}]{H_2O} NH_4B(C_6H_5)_4{\downarrow} + Na^+[B_4H_8CONH_2]^-. \quad (3)$$

The precise structure of the anion $[B_4H_8CONH_2]$ has not been explained; two more probable variants have been proposed. The CO group in B_4H_8CO is readily replaced by PF_3 reversibly[78]:

$$B_4H_8CO + PF_3 \rightleftarrows B_4H_8 \cdot PF_3 + CO.$$

It was shown that when $F_2PN(CH_3)_2$ reacts with B_4H_8CO at -20°C, replacement of CO again takes place readily:

$$B_4H_8CO + F_2PN(CH_3)_2 \rightarrow (CH_3)_2NPF_2 \cdot B_4H_8 + CO.$$

In this compound B_4H_8 is coordinated with a phosphorus atom (P–B bond in the ^{34}P-NMR spectrum). The infrared spectrum is similar to the infrared spectrum of B_4H_8CO.[83]

When B_4H_8CO reacts with an excess of a strong Lewis base — $(CH_3)_3N$ or PF_3 — initially CO is replaced by H, and then B_4H_8 is destroyed and $(CH_3)_3N.BH_3$ or $PF_3.BH_3$ is formed [83,84].

V. PENTABORANE(9)

1. Structure of Pentaborane(9)

Pentaborane(9) is one of the most studied boron hydrides and the geometry of its molecule has been accurately determined by several physical methods, which give concordant results: X-ray diffraction [85,86], electron diffraction [87], and microwave spectroscopy [88]. All these results suggest that the B_5H_9 molecule has the structure shown in Fig. 9.

The most accurate data on the interatomic distances in B_5H_9, obtained from the microwave spectra [88], are: $B_{(1)}-B_{(3)} = 1.687 \pm 0.005$ Å; $B_{(3)}-B_{(4)} = 1.800 \pm 0.003$ Å; $B-H_{terminal} = 1.22 \pm 0.04$ Å; $B_{(2)}-H_{bridge} = B_{(3)}-H_{bridge} = 1.35 \pm 0.02$ Å; $\angle B_{(1)}B_{(2)}H_{(2)} = 136° 10' \pm 30'$; angle between planes $B_{(1)}B_{(2)}B_{(3)}$ and $B_{(2)}B_{(3)}H_{bridge} = 196° \pm 2°$. X-Ray diffraction [85,86] showed that B_5H_9 crystals have C_{4v} symmetry and contain two molecules in the unit cell with parameters $a = 7.16$, $c = 5.38$ Å.

On the basis of the geometry of the molecules Lipscomb and coworkers [11] proposed a structure for B_5H_9 in which the five boron atoms form a tetragonal pyramid, which is a fragment of an octahedron. Each boron atom in the base of the pyramid (type *II* in Fig. 9) forms one terminal B–H bond and two B–H–B bridging bonds. Three sp^3-orbitals and two electrons of the base boron atoms are used in these bonds; the remaining sp^3-orbital and electron of each B_{II} atom is used for a bond with an apical boron atom (type *I* in Fig. 9), which forms one terminal B–H bond directed along the axis of symmetry of the molecule. The remaining three orbitals and two electrons of the apical boron atom are used for bonds with the basal boron atoms. It is assumed that one of these orbitals has sp-hybridisation and is directed along the axis of symmetry towards the centre of the molecule; two other orbitals are "pure" p-orbitals directed perpendicularly to the symmetry axis, one of them being situated in the $B_{(2)}-B_{(1)}-B_{(4)}$ plane and directed towards $B_{(4)}$, and the other being in the $B_{(3)}-B_{(1)}-B_{(5)}$ plane and directed towards $B_{(3)}$. Rather later Lipscomb [10,89] and also Moore [90], in calculating the molecular orbitals of B_5H_9 and their overlap integrals, concluded that the apical atom

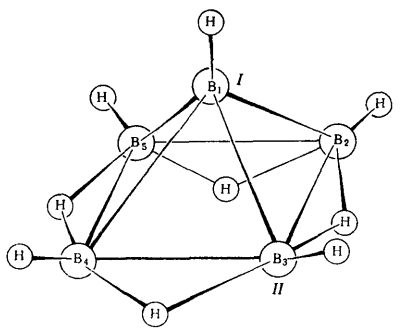


Fig. 9.

$B_{(1)}$ forms two two-centre bonds with two of the boron atoms of the base and one open three-centre bond with the other two boron atoms of the base, using in this all the remaining six electrons and seven orbitals of the boron atoms. As in this the molecule does not have C_{4v} symmetry; the authors assume that here it is possible to write two equivalent structural formulae (as in the C_6H_6 molecule) in which the open three-centre $B_{II}-B_I-B_{II}$ bond and two two-centre B_I-B_{II} bonds exchange places. Moore [90] also calculated the formal charges of the boron atoms ($B_I = -0.870$ e, $B_{II} = +0.217$ e) and from these results obtained a calculated value of the dipole moment of $B_5H_9 = 1.7–2.0$ D (with allowance for the hydride character of the bridge hydrogen atoms, -0.2 e, and apical hydrogen atom, -0.1 e). This agrees with the experimental value, 2.13 ± 0.04 D. [88]

The ^{11}B-NMR spectrum of B_5H_9 [91] shows that the molecule has four identical boron atoms (each of which is connected with one terminal hydrogen atom) and one boron atom having resonance in the region of higher field, that is, more negative, also connected with one hydrogen atom (two doublets with ratio of peak intensities 4 : 4 : 1 : 1). These results agree with the structure proposed for B_5H_9. The ^{1}H-NMR spectrum of B_5H_9, [91,92] obtained by use of the technique of "spin saturation" of ^{11}B nuclei, suggests that the terminal hydrogen atom of the apical boron atom is somewhat more negative than the terminal hydrogens on the basal boron atoms, but less negative than the bridge hydrogen atoms.

On the basis of the experimental results on the geometry of the molecule [85,87] Glockler [93] calculated the energies of the bonds in B_5H_9. The heat of formation obtained from the calculated data ($\Delta Ha_\circ = 1146.7$ kcal mole^{-1}) is considerably different from that determined experimentally (1092.73 kcal mole^{-1}).

2. Preparation of Pentaborane(9)

B_5H_9 is present in small amounts in the gas mixture obtained on decomposing metal borides with acids. Stock and Kuss first isolated pentaborane(9) from this mixture [94] but the yield of B_5H_9 in this is extremely small (< 1%), and the compound is contaminated with other boron hydrides, particularly B_5H_{11}, from which B_5H_9 is difficult to separate owing to their similar boiling points (the difference in b.p. at 100 mmHg is 4 deg). Therefore B_5H_9 was an almost inaccessible compound until Schlesinger and Burg [46] obtained it in 1931 in 20% yield by heating B_2H_6 at 120–130° with a little dry HCl or BCl_3. Somewhat later the same authors [47] increased the yield of B_5H_9 to 33%. Then Stock found [48] that a mixture of B_5H_9 (54–56%) and B_5H_{11} (10–26%) is formed in the pyrolysis of diborane over mercury at 250–300° or tetraborane at 100–200°.

A detailed study was made [95] of the kinetics of pyrolysis of B_2H_6 in the temperature range 80–120°, by three methods: (1) from the rate of increase of the total pressure in the system; (2) from the rate of formation of H_2, and (3) mass spectrometrically. The following conclusions were drawn: (1) the reaction products are H_2, B_4H_{10}, B_5H_{11}, B_5H_9, and higher boron hydrides; (2) the process has a complex path; (3) B_5H_{11} is an intermediate in the formation of most other boron hydrides from B_2H_6; (4) the formation of B_5H_9 from B_5H_{11} is a first-order reaction. It was suggested [96] that the rate-determining stage of the pyrolysis of B_2H_6 is the reaction:

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

The B_4H_{10} formed reacts with B_5H_{11}:

$$B_4H_{10} + B_5H_{11} \rightarrow B_5H_9 + 2B_2H_6.$$

These two stages were proposed to explain the conversion of B_5H_{11} into B_5H_9. Fehlner and Koski[8] showed, by pulsation heating of B_2H_6, that the reaction products are H_2, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, B_6H_{12}, B_7H_{11}, B_7H_{13}, and higher boron hydrides. Using isotopic labelling, and on the basis of the composition of the intermediate and final products of the reaction, the authors established the mechanism of the pyrolysis of diborane, which includes a series of competing reactions and equilibria. It was shown that the formation of B_5H_9 proceeds along a path different from the formation of B_4H_{10} and B_6H_{10}, namely through the formation of triborane by the reactions:

$$B_2H_6 \rightleftarrows 2BH_3,$$

$$BH_3 + B_2H_6 \rightarrow B_3H_9,$$

$$B_3H_9 + B_2H_6 \rightarrow B_5H_9 + 3H_2.$$

Confirmation is given by the fact that in the pyrolysis of B_4H_{10} in the presence of hydrogen raising the concentration of the latter increases the degree of conversion of B_4H_{10} into B_5H_9, which also proceeds through the formation of B_3H_9:

$$B_4H_{10} \rightleftarrows B_3H_7 + BH_3,$$

$$B_3H_7 + H_2 \rightleftarrows B_3H_9,$$

$$B_3H_9 + B_2H_6 \rightarrow B_5H_9 + 3H_2.$$

With the aim of finding the most favourable conditions for the conversion of B_2H_6 into B_5H_9, McCarty and Di Giorgio[97] studied the effect of temperature (in the range 175–250°), additions of hydrogen and nitrogen, and time on the reaction; they showed that the pyrolysis of diborane is exothermic and that varying the conditions makes possible the direction of the process towards the boron hydride required. Conditions were found under which B_5H_9 is obtained without B_5H_{11} as impurity, which removed one of the main disadvantages of this method of making B_5H_9 — previously the B_5H_9 was freed from B_5H_{11} by either further heating of the mixture until the B_5H_{11} had decomposed, or contacting the mixture at 0°C with Lewis bases and then distilling off the pure B_5H_9; during this the loss of pentaborane(9) was considerable. On the basis of this work[97] and that of Bragg and coworkers[95] a method for the industrial production of B_5H_9 was developed[98]. The overall pyrolysis of diborane is represented by the following schemes:

$$5B_2H_6 \rightarrow 2B_5H_9 + 6H_2, \quad (1)$$

$$5B_2H_6 \rightarrow B_{10}H_{14} + 8H_2, \quad (2)$$

$$B_2H_6 \rightarrow (BH)_x\,(\text{solid}) + H_2. \quad (3)$$

Of the B_2H_6 taken 70–85% decomposes by reactions (1) and (2); the residue consists of high-molecular-weight boron hydride of unknown composition. The conditions for obtaining B_5H_9 are: temperature of the reaction zone 240–290°C, pressure ~ 3.5 atm, time of B_2H_6 at this temperature 3 s (then the reaction gases are cooled to 35°C), and an equimolecular quantity of hydrogen is used as the reaction medium. Not less than 80% of the B_2H_6 enters into the reaction and the yield of pure B_5H_9 is 38% (purity 99.9%).

Jeffers[99] has proposed a convenient path for the preparation of pentaborane(9): pyrolysis of diborane by the method of hot (200°C) and cold (-90°C) tubes; the yield of B_5H_9 is 60% at a 90% conversion of B_2H_6.

A patent has been taken out[100] for preparing B_5H_9 by a similar method: hot zone temperature 205°C, cold -40°C, contact time 2 s, yield 80%.

3. Physical Properties of Pentaborane(9)

B_5H_9 is a colourless mobile liquid with an unpleasant odour, b.p. 58°C [41] or 60.0°C,[101] m.p. -46.6°C [41] or 226.41° ± 0.02°K.[102] Several values are given for the density of B_5H_9 at 0°C: 0.61 g ml^{-1},[41] 0.642 g cm^{-3},[103] 0.637 ± ± 0.002 g ml^{-1};[104] the last two results are evidently the most accurate; the temperature dependence of the density of B_5H_9 is $d = 0.8674 - 0.00082T$.[103] The vapour pressure of B_5H_9 at 0°C is 66 mmHg;[41] according to more recent data[102] $P_{B_5H_9} = 64.77$ mmHg at 272.99°K; the variation of the vapour pressure of B_5H_9 with temperature in the range 226–298°K is described by the equation.

$$\log p_{mmHg} = 9.96491 - \frac{1951 \times 14}{T} - 0.0036884T.$$

The viscosity of B_5H_9 at 274.1°K has been measured (η = 3.94 mP), as has the surface tension at 269.5°K (γ = 24.5 dyn cm^{-1}) and 286.2°K (γ = 22.0 dyn cm^{-1}).[103] The electrical properties of B_5H_9 have been measured[102] and it has been shown that liquid B_5H_9 has a high dielectric constant, which varies between the limits 21.1 (298°K) and 53.1 (at the melting point, 226.41°K). The apparent dipole moment of B_5H_9 varies from 3.37 D at 298°K to 4.54 D at the melting point, and in the gas phase the dipole moment is 2.13 D, that is, pentaborane(9) is a highly polar substance[102]. The value of 2.13 D for B_5H_9 has been given elsewhere[88]. Crystals of B_5H_9 have two modifications[102]: the body-centred tetragonal crystals are converted into simple tetragonal crystals in the range 130–140°K. The heat of formation of gaseous B_5H_9 from the elements[105] is 12.99 ± 0.39 kcal $mole^{-1}$ and its entropy[106] is 65.75 cal × × deg^{-1} $mole^{-1}$.

Pentaborane(9) is a highly poisonous compound[107], more toxic than diborane or decaborane. Systematic inhalation of B_5H_9 at a concentration of 0.2 parts per million by various animals leads to loss of appetite and weight, apathy, and a drop in physical and mental activity.

4. Chemical Properties of Pentaborane(9)

(a) Stability of pentaborane(9). The mass-spectrometric investigation of pentaborane(9) and deuteriopentaborane(9) [101] shows a clear tendency for these molecules to lose two or four hydrogen (or deuterium) atoms, and a much smaller tendency to lose one or three hydrogen atoms. Starting from the values of the energies of the terminal B–H and bridge B–H–B bonds (4.04 and 4.66 eV respectively) Kaufman and coworkers[108] gave reasons why, in the attack of fast electrons of 70 eV energy, the terminal B–H bonds in the B_5H_9 molecule are broken more readily, and then the molecule is reconstituted: probably a three-centre B–H–B bond is changed into B–H and B–B two-centre bonds. However, the precise path for the reconstitution of the molecule during the formation of fragment ions has not been established[88]. The authors determined the potentials for the appearance of $^{11}B_5H_9^+$ and $^{11}B_5D_9^+$, 10.39 and 9.78 eV respectively. Previously[109] the ionisation potential of B_5H_9 had been given as I = 10.8 ± 0.5 eV.

When an electric discharge acts on B_5H_9 [110] a terminal B–H bond at the apical boron atom is broken and a B_5H_8 radical is formed, which combines with a second such radical to form a $B_{10}H_{16}$ molecule. As Hall and Koski have shown[111], an analogous reaction occurs when B_5H_9 is irradiated with deuterons of 2 MeV energy. These authors

established[112] that the products of the reaction are H_2, B_2H_6, $B_{10}H_{16}$, and polymeric boron hydrides; B_5H_9 undergoes 5% decomposition. The radiochemical yields of the products were found to be: $G_{H_2} = 13.1$, $G_{B_2H_6} = 1.7$, $G_{B_{10}H_{16}} = 0.8$ mole per 100 eV. A radical mechanism for the reaction was proposed, based on experiments using D_2 as indicator, inert gases (He, Ne, Ar) as sensitisers, and I_2 as an inhibitor of the process.

NMR spectra showed[113] that in the reaction of B_5H_9 with B_2D_6 only terminal hydrogen atoms are replaced by deuterons, the bridge hydrogens not taking part in the exchange reaction. The rate of exchange of the apical hydrogen atom in this was the same as that of the terminal basal hydrogen atoms (within the limits of experimental error, ±10%). Similar results were obtained in studying deuterium exchange between B_5H_9 and B_2D_6 at 80° without a catalyst, using infrared and mass spectra[114,115].

All the hydrogen atoms are replaced by deuterium in the reaction of B_5H_9 with an excess of deuterium in the presence of a chromium–aluminium dehydrogenation catalyst ($Cr_2O_3.Al_2O_3$) at 20–25°C.[106]

Onak and Williams[116] made a directed deuterium exchange between B_5H_9 and DCl in the presence of $AlCl_3$ at 20°C: only the apical hydrogen atom is exchanged; the compound B_5H_8D which is obtained is rather stable; it is unchanged after heating for 17 h at 105°C. The H–D exchange in the presence of an electrophilic catalyst confirms the greater susceptibility to electrophilic attack of the apical hydrogen atom. The authors showed[117] that intramolecular H–D exchange takes place in the B_5H_8D molecule in the presence of 2,6-dimethylpyridine at 20°C, but without a Lewis base at elevated temperatures (145–200°C) there is intermolecular exchange. In all the reactions mentioned above there is a clear difference in the behaviour of the terminal and bridging hydrogen atoms in the B_5H_9 molecule, and also in that of the apical hydrogen and the basal hydrogen atoms.

The stability of the B_5H_9 molecule was shown by studying the exchange of ^{11}B and ^{10}B atoms: under conditions at which exchange of ^{11}B for ^{10}B takes place in diborane or tetraborane molecules there is no exchange in the pentaborane(9) molecule[118]; reaction between B_5H_9 and $^{10}B_5H_9$ does not take place up to 100°C in the liquid phase or up to 250°C in the gas phase. H–D exchange is observed between B_5H_9 and B_5D_9 at 200°C in the absence of a catalyst. Shapiro and coworkers[119] showed that in the presence of a catalyst (γ-Al_2O_3) at 90°C there is exchange of boron atoms between $^{10}B_2H_6$ and B_5H_9 through the intermediate formation of the complex $Al_2O_3.^{10}B_2H_6$, which then slowly exchanges ^{10}B atoms with the pentaborane. This reaction occurs much more slowly than for B_2H_6.

According to the results of Stock and coworkers[67], pentaborane(9) reacts with alkali metal amalgams like B_4H_{10} and B_2H_6, forming salts of composition $M_2B_5H_9$; they could not be obtained pure. However, Ford and coworkers[120] showed that B_5H_9 does not react with sodium amalgam and sodium hydride in ether at 20–25°C.

(b) Oxidation of pentaborane(9). B_5H_9 ignites spontaneously on mixing with air. The kinetics and mechanism of the oxidation of pentaborane have been studied several times to determine the conditions for the most convenient use of this reaction. A kinetic study of the B_5H_9–O_2 system[121] showed that the lower explosive limit at room temperature is at very low pressures of B_5H_9 and O_2; a B_5H_9 pressure between 1 and 5 mmHg is critical. The reaction proceeds by a type of branched-chain mechanism. Later work[122] confirmed the conclusion about the reaction type. Intermediate products were not isolated, but it was observed that $Fe(CO)_5$ has a strong inhibiting action, showing that oxygen atoms participate in the chain development. The lower explosive limits were determined for B_5H_9–O_2 mixtures at B_5H_9 pressures from 1 to 90 mmHg and temperatures of 15° and 21.5°C, and it was also shown that the final reaction product is H_3BO_3. It was shown[123] that during the slow oxidation of B_5H_9 initially H_2, B_2H_6, and a more solid substance of unknown composition are formed; the formula $B_4H_{12}O$ was proposed for the latter on the basis of its infrared and mass spectra[124]. It was concluded in a more detailed study of the partial oxidation of B_5H_9 by spectrometric methods[125] that the intermediate compound has the formula $B_2H_2O_3$ and a trigonal bipyramidal structure formed by boron and oxygen atoms with a terminal hydrogen atom at each boron. It was shown[126] that during the explosive oxidation of B_5H_9 yet another intermediate product is formed, $B_3O_3H_3$, identical with boroxole[127].

(c) Reaction of pentaborane(9) with oxygen compounds. Pentaborane(9)[41] is slowly hydrolysed by water at room temperature; for complete hydrolysis prolonged heating of it with water at 90°C is necessary. However, in aqueous dioxan solution the reaction is rather rapid and the hydrolysis rate can be measured by the increase in pressure[128]:

$$B_5H_9 + 15\,H_2O \rightarrow 5\,B(OH)_3 + 12\,H_2.$$

The first stage of the hydrolysis was studied by mass spectroscopy[129]; B_5H_9 was hydrolysed by water contained in silica gel in a combined form as OH^- ions. The mass spectrum of the product of the reaction was similar to that of B_4H_{10}. It is assumed that the first stage of the hydrolysis is the displacement by water of a boron atom from the B_5H_9 molecule (probably one of the four basal atoms) with subsequent regeneration of hydrogen. The balance in boron and hydrogen of the reaction products found on the silica gel and in the volatile products confirms this conclusion.

The interaction of B_5H_9 with alcohols[130] leads to the formation of borate esters and hydrogen:

$$B_5H_9 + 15\,ROH \rightarrow 5\,B(OR)_3 + 12\,H_2.$$

When the alcohol is added to B_5H_9 in stoichiometric proportion the borate ester is formed in quantitative yield under mild conditions; the reaction is exothermic. The intermediate product, diethoxyborane $HB(OC_2H_5)_2$, was isolated pure. Alcoholysis of the B–B bond in pentaborane was studied by using deuterated ethanol[69] and compared with the alcoholysis of diborane. It was shown that the course of the alcoholysis with B_5H_9 is different from that for B_2H_6, and similar to the alcoholysis of B_4H_{10}; during the action of alcohol on B_5H_9 there is simultaneous formation of $HB(OC_2H_5)_3$ and $B(OC_2H_5)_3$, that is, the B–B bonds are split simultaneously with the B–H bonds and not subsequently. The relative concentrations of the intermediate products $HB(OC_2H_5)_2$ and $DB(OC_2H_5)_2$ depend on the structures of the boron hydrides (B_4H_{10} and B_5H_9), and thus on the nature and number of the B–B bonds and B–H–B bridge bonds. In the splitting of the B–H–B bond by deuterioethanol only $HB(OC_2H_5)_2$ is formed; in the splitting of the B–B bonds, $DB(OC_2H_5)_2$. Pentaborane(9) reacts exothermically with acetone both at room

temperature and at -80°C.[130] The reaction is complex and the reaction mechanism is still unexplained. Isopropyl borate (25–30% yield) has been separated from the reaction mixture. When dry acetone acts on B_5H_9 hydrogen is not liberated, that is, reaction probably does not occur.

(d) Halogen derivatives of pentaborane(9). Under carefully controlled conditions B_5H_9 reacts with halogens, hydrogen halides, or BCl_3 with replacement of one hydrogen atom by halogen. Schlesinger and Burg[71] obtained B_5H_8Cl by direct chlorination of B_5H_9 at -80°C. B_5H_8Cl, B_5H_8Br, and B_5H_8I were obtained by halogenation of pentaborane(9) in the presence of $AlCl_3$ in a medium of CS_2;[131] during this B_5H_8Br (m.p. 32–34°C) and B_5H_8I (m.p. 53°C) were obtained pure with good yields; B_5H_8Cl could be obtained only in trace amounts (owing to its explosive properties) and contaminated by CCl_4. A patent had been issued earlier[132] on a method of obtaining B_5H_8Br by brominating B_5H_9 under specified conditions (yield 70%, m.p. 34–36°C, b.p. 80–82°/34 mmHg). The precise position of the halogen in the monohalogenopentaborane molecules was established by infrared and NMR spectra. The infrared spectra of B_5H_8Br [133] is similar to the spectrum of B_5H_9; the symmetry of the molecule is retained, which is possible only if the bromine replaces the hydrogen atom of the apical boron atom. The NMR spectrum of B_5H_8X [134] also shows with certainty that the substitution occurs at the apical boron atom; the ^1H–NMR spectra of B_5H_8Br and B_5H_8I contain a doublet of peaks of equal intensity, which show equal numbers of terminal and bridge hydrogen atoms; the ^{11}B-NMR spectra of B_5H_8Br and B_5H_8I do not show the doublet corresponding to the interaction of the apical boron atom with the terminal hydrogen, it being converted into a singlet of double intensity; the doublet corresponding to the basal BH groups is unchanged. The inductive influence of halogens on the ^{11}B-chemical shift in the ^{11}B-NMR spectrum of B_5H_8X (X = Br or I) is observed. The effect of a change in the shift to low field with increase in the electronegativity of the atoms bound to boron has also been shown for other boron compounds[135]. An exchange reaction between the halogen in 1-BrB_5H_8 and chlorine has also been carried out[136], in which the halogen atom is transferred from the apical boron atom to a basal boron atom. The reaction proceeds in the presence of $AlCl_3$ and is the first instance of an exchange of a halogen atom in a higher boron hydride taking place with change in bonding position. The mechanism of the reaction is not clear. Attempts to obtain 2-BrB_5H_8 by the reaction of 1-BrB_5H_8 with $AlBr_3$ or 2-ClB_5H_8 by the reaction of 1-BrB_5H_8 with BCl_3 were unsuccessful.

In a mass spectrometric study of halogenopentaboranes (1-ClB_5H_8, 1-BrB_5H_8, and 1-IB_5H_8) it was found[131] that: (1) the B–I bond is relatively easily broken; (2) the detachment of the Br (or Cl) atom from a B_5H_8X molecule occurs only when the skeleton is destroyed, that is, by loss of a BBr (BCl) group; (3) the general distribution of fragment ions in the mass spectrum of B_5H_8I (and to some extent B_5H_8Br) is similar to that in B_5H_9. From these results a sequence was derived for the relative ease of bond-breaking in the halogenopentaboranes: BI > BH > BB > BBr or BCl.

(e) Reactions of pentaborane(9) with nitrogen and phosphorus compounds. The reaction of B_5H_9 with secondary and tertiary amines has been studied in detail by Zhigach and coworkers[137]. At a low temperature (up to 0°C, usually from -3° to -5°C) B_5H_9 adds secondary amines with formation of complexes of composition $n NHR_2 \cdot B_5H_9$ (n = 2, 3, 4, or 5; R = CH_3 or C_2H_5); under the action of tertiary amines the compounds $2NR_3 \cdot B_5H_9$ are formed (R = CH_3 or C_2H_5) stable up to 0°C. At elevated temperature (100–120°C) the complexes are completely decomposed with liberation of hydrogen, splitting of the B_5H_9 molecule, and formation of alkylamino-derivatives of diborane and borane and of polymers. An increase in the proportion of amine in the original complex leads to an increase in the amount of borane derivatives and a decrease in the amount of diborane derivatives in its decomposition products.

Burg[138] showed simultaneously that $(CH_3)_3N$ at -78°C adds to B_5H_9 with formation of a complex $2(CH_3)_3N \cdot B_5H_9$, which on heating in a vacuum is partly decomposed to the initial substances and partly converted into $(CH_3)_3N \cdot BH_3$ and a polymer of composition $(BH)_x$. On heating the complex above 100°C with an excess of trimethylamine 2 moles $(CH_3)_3N \cdot BH_3$ are formed per 1 mole B_5H_9 and a polymer which exhibits thermoplastic properties[139].

In the reaction of B_5H_9 with $(CH_3)_2NH$ and also with $(CH_3)_2NBH_2$ or $[(CH_3)_2N]_2BH$ in stoichiometric amount, Burg[138] obtained a compound of low stability in air, which as X-ray analysis showed[140], is a trimer of dimethylaminoborane. Campbell and Johnson[141] came to the same conclusion, in studying the reaction of B_5H_9 with $[(CH_3)_2NBH_2]_2$ and identifying the reaction products by ^1H- and ^{11}B-NMR spectra, analysis, and molecular weight.

Hough and coworkers[142] also studied the reaction of B_5H_9 with $(CH_3)_3N$ and considered that at 20–25°C the reaction proceeds according to the equation:

$$B_5H_9 + (CH_3)_3N \xrightarrow{\text{rapid}} [(CH_3)_3N]_2 \cdot B_5H_9 \xrightarrow{\text{slow}} (CH_3)_3N \cdot BH_3 + (CH_3)_3N \cdot B_4H_8.$$

Under the action of an excess of the amine two moles $(CH_3)_3N \cdot BH_3$ and 1 mole of the polymer $[(CH_3)_3N]_x \cdot (B_3H_3)_x$ are formed per mole B_5H_9.[143] From what has been said above it is evident that the reaction of B_5H_9 with amines is complex with splitting of the B_5H_9 molecule. There has been little investigation of the reaction of pentaborane with ammonia. Schlesinger and Burg[71] state that "tetra-ammoniate of pentaborane" is formed in the reaction of B_5H_9 with NH_3; one of the nitrogens in it is in the form of an ammonium ion: further slow reaction of B_5H_9 with NH_3 leads to the formation of "tetra-ammoniate of pentaborane"; however, it was not found whether this substance was pure.

In Schaeffer's work[144] on the reaction of decaborane with CH_3CN it is stated that B_5H_9 reacts with CH_3CN with liberation of hydrogen and formation of a substitution product. The mixed salt NaB_5H_9CN is formed by the reaction of B_5H_9 with NaCN.[68]

Muetterties and coworkers[145] showed that in the reaction of B_5H_9 with *NNN'N'*-tetramethylethylenediammine (TMED) at 25°C the addition product TMED.B_5H_9 is formed, which under the action of CH_3OH at 0°C is converted into TMED.B_4H_8. The authors consider these two addition products to be derivatives of the hypothetical anions $B_5H_{11}^{-2}$ and $B_4H_{10}^{-2}$.

Burg[139] studied the reaction of B_5H_9 with phosphorus-containing Lewis bases and showed that during this the B_5H_9 molecule is split although with much greater difficulty than for B_4H_{10}. The reaction products are a cyclic trimer of composition $[R_2P-BH_2]_3$ and the tetramer $[R_2P-BH_2]_4$ in small amount and also the extremely stable boron hydride thermoplastic polymers. The polymer is unchanged on heating to 250–300°C and does not liberate H_2, $(CH_3)_3P$, or

$(CH_3)_3P.BH_3$; on heating to 400°C, there is partial liberation of hydrogen and an increase in the B : P ratio. Pentaborane(9) reacts with aminophosphines and diphosphines in a similar manner, during which it also forms the corresponding cyclic trimers and polymers. Jeffers[99] studied the reaction of B_5H_9 with $(CH_3)_3P$ and the pyrolysis of the addition compounds thus formed, as a result of which a polymer with empirical formula $BH(PR_3)_{0.2}$ is obtained. It is assumed that the polymer forms a boron hydride chain of rubber type in which are introduced molecules of the base coordinated to the boron atoms.

(f) Alkylation of pentaborane(9). The alkylation of B_5H_9 has been studied in some detail. The alkylation has been carried out under conditions of electrophilic and nucleophilic reactions using various alkylating agents. The products have been isolated and their structure determined with the aid of chromatography and infrared and NMR spectra.

In electrophilic (Friedel–Crafts) alkylation of B_5H_9 the apical hydrogen, where the charge density is greatest, is replaced. In the nucleophilic attack of alkenes on B_5H_9, the basal hydrogen atoms are replaced.

Williams and coworkers[146] carried out the reaction of ethylene with diborane at 100°C and obtained a complex mixture of products which was separated chromatographically into two homologous series: ethylpentaborane(9)s (mono-, di-, and poly-ethylpentaboranes) and ethyldecaborane(14)s (mono-, di-, and poly-ethyldecaboranes). Evidently under these conditions reaction occurred between the B_5H_9 and $B_{10}H_{14}$ formed from the diborane and the alkylating agents: C_2H_4, ethyldiboranes, and $(C_2H_5)_3B$. It was shown that the basal hydrogen atoms are replaced. Ryschkewitsch and coworkers[147] obtained a series of alkyl derivatives of B_5H_9 by the reaction of alkenes (but-1-ene, 2-methylprop-1-ene, but-2-ene, ethylene) with pentaborane(9) at 150°C. Replacement also took place at the basal boron atoms; alkenes apparently directly attack the B_5H_9 molecule at the points of least electron density. The absence of isomeric alkyl radicals attached to the boron hydride is explained by the alkene molecule's adding to the B_5H_9 at the carbon atom having the highest electron density. The reactivity of the alkenes increases in the sequence:

$$C_2H_4 < CH_2{=}CH{-}CH_2CH_3 < CH_3CH{=}CHCH_3 \leqslant CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH_3.$$

The ^{11}B-NMR spectra of RB_5H_8 contain two doublets, which shows the presence of a hydrogen atom at the apical boron. The alkylpentaboranes obtained[147] are colourless mobile liquids with a characteristic odour; in a homogeneous mixture with water they are rapidly hydrolysed; in contact with pure water they are hydrolysed slowly owing to the low solubility; they are rapidly oxidised in air and are capable of spontaneous ignition; they slowly decompose when heated in a vacuum to 150°C; they react with aliphatic amines like B_5H_9.

When pentaborane reacts with ethylene under conditions of electrophilic substitution in the presence of $AlCl_3$, ethylpentaborane is obtained[133,148]; it was shown chromatographically and with the aid of infrared and NMR spectra that under these conditions only the apical hydrogen atom is replaced. Similar results were obtained in the alkylation of B_5H_9 at 100°C by methyl chloride or ethylene in the presence of $AlCl_3$;[149] $1\text{-}CH_3B_5H_8$ is obtained in 80% yield and $1\text{-}C_2H_5B_5H_8$ in 50% yield. It was proposed[150] to use the reaction of alkenes or alkyl halides with pentaborane in the presence of $AlCl_3$, $FeCl_3$, or $SnCl_4$ as a general method for making alkylpentaboranes with an apical alkyl radical. In this way the following compounds were prepared and characterised: 1-methylpentaborane, 1-ethylpentaborane, 1-isopropylpentaborane, 1-s-butylpentaborane, and also a disubstituted product: 2-s-butyl-1-methylpentaborane. The production of a disubstituted pentaborane shows that the alkylation does not deactivate the B_5H_9 molecule in relation to further catalytic alkylation. Apical-substituted B_5H_8R derivatives are thermodynamically less stable than those substituted at a basal boron atom by 3 kcal $mole^{-1}$; therefore the direction of the substitution is determined by the mechanism of the reaction and not by the thermodynamic stability of the compounds. 1-Alkylpentaboranes are very sensitive to oxidation and hydrolysis and do not react with anhydrous HCl, but are decomposed by HCl in the presence of $AlCl_3$.

A series of patents have been taken out on methods for making alkylpentaboranes, and can be classified as follows:

1. Reaction of B_5H_9 with an alkene in the presence of catalysts — Lewis acids ($AlCl_3$, $FeCl_3$, $AlBr_3$),[151,152] the yield of 1-alkylpentaboranes being 65–68%.
2. The reaction of B_5H_9 with an alkene in the presence of basic catalysts (pyridine and alkylpyridines[153], yield of $t\text{-}C_4H_9B_5H_8$ 40.4%; tetrahydrofuran[154]; lower alkylamines[155], yield of $t\text{-}C_4H_9B_5H_8$ 43%).
3. Reaction of B_5H_9 with alkyl monohalides using Friedel–Crafts catalysts, the yield of 1-alkylpentaboranes being 80–90%.[156,157]
4. Alkyl borates, alkyl silicates, diethylborane, alkyl ester–BF_3 adducts are used as alkylating agents in the reaction with B_5H_9.[158-160]

To free alkylpentaboranes from impurities they are heated with metal oxides, the best being Fe_2O_3 or Al_2O_3.[161]

In 1961 Onak[162] observed that 1-alkylpentaborane(9) (R = CH_3 or C_2H_5) is quantitatively converted into 2-alkylpentaborane(9) in the presence of 2,6-dimethylpyridine at room temperature. The structure of the initial and final products was shown by infrared and ^{11}B-NMR spectra. The analogous conversion of 1-ethylpentaborane, obtained from B_5H_9 and C_2H_4 in the presence of $AlCl_3$, into its isomer takes place on heating to 200°C [149] but ethylpentaboranes of a higher degree of alkylation are not obtained. This rearrangement is explained by the greater thermodynamic stability of basal-substituted alkylpentaborane[150]. Hough and coworkers[163] studied such a rearrangement of $1\text{-}C_2H_5B_5H_8$ into $2\text{-}C_2H_5B_5H_8$ in the presence of $(CH_3)_3N$ at 27–28°C. Rearrangement takes place in the presence of Lewis bases (2,6-dimethylpyridine or trimethylamine), probably by intramolecular exchange of alkyl groups facilitated by the formation of an addition product of alkylpentaborane with the base. Such an addition product, $[(CH_3)_3NHB_5H_7C_2H_5]$, formed from $1\text{-}C_2H_5B_5H_8$ and $(CH_3)_3N$, was isolated at a low temperature[163]; it dissociates at 27–28°C, that is, at the temperature of formation of $2\text{-}C_2H_5B_5H_8$. To explain the mechanism of the rearrangement allowance must also be made for the recurrence of the intramolecular hydrogen exchange in B_5H_9 (as in the other boron hydrides), shown by Williams[17,81]. Onak and coworkers[117] showed that in the presence of 2,6-dimethylpyridine an intramolecular exchange takes place in 1-deuteriopentaborane(9) and intermolecular exchange does not occur; at elevated temperatures (above 145°C) exchange of H for D takes place by an

intermolecular mechanism in which di- and poly-deuteriopentaboranes are formed. With alkylpentaboranes the absence of di- and poly-alkylpentaboranes in thermal rearrangement makes more probable the hypothesis that the migration of alkyl groups proceeds by an intramolecular path. The reaction mechanism in which there is a slow "symmetrical" splitting of 1-alkylpentaborane and a rapid recombination with formation of a 2-alkylpentaborane, first proposed by Onak[149] on the basis of a theory of Parry[23], seems improbable in the light of later investigations.

A study of the thermal stability of gaseous ethylpentaborane[164] shows that it is less stable than B_5H_9. The decomposition products are H_2, CH_4, involatile boron hydrides, and traces of $B_{10}H_{14}$.

A compound derived from two B_5H_9 molecules containing a methylene bridge, bis-(1-pentaboranyl)methane $(B_5H_8)_2CH_2$, is obtained[165,166] by the reaction of B_5H_9 with alkyl halides (CH_2Cl_2, CH_2Br_2, CH_2BrCl) in the presence of $AlCl_3$. The greatest yield (~ 5%) is obtained when CH_2Cl_2 is used. Its infrared spectrum showed apical boron substitution. $(B_5H_8)_2CH_2$ is a very unstable compound, which reacts rapidly and explosively with air; in a vacuum it slowly decomposes at room temperature. Furthermore, the authors succeeded in obtaining (in insufficiently pure state) the extremely unstable dichloroborylpentabor(9)an--1-ylmethane $B_5H_8CH_2BCl_2$, in which apical substitution also takes place (as indicated by the infrared spectrum). A patent has been obtained[167] for the preparation of bispentaboranylalkanes with two B_5H_8 residues connected by an alkylene bridge by the reaction of a conjugated alkadiene with an excess of B_5H_9 at 135–145°C and elevated pressure.

VI. PENTABORANE(11)

1. Structure of Pentaborane(11)

Pentaborane(11) has been studied less than pentaborane(9). The structure of the B_5H_{11} molecule was determined by X-ray analysis and with the aid of NMR spectra. An X-ray analysis of B_5H_{11} was made by Lavine and Lipscomb[168,169], and then the calculation of the interatomic distances was refined by Lipscomb and coworkers[33]. B_5H_{11} forms monoclinic crystals with group symmetry $P2_{1/n}$, lattice parameters a = 6.76, b = 8.51, c = 10.14 Å; β = 94°3′; the unit cell contains four B_5H_{11} molecules. The B_5H_{11} molecule has a planar symmetry, the boron atoms forming a skeleton which is a fragment of an icosahedron; it can also be obtained from the B_5H_9 tetragonal pyramid by opening one B–H–B bond of the base (Fig. 10). The interatomic distances in the B_5H_{11} molecule have been determined: $B_{(1)}$–$B_{(3)}$ = 1.71 ± 0.02 Å; $B_{(1)}$–$B_{(2)}$ = 1.87 Å; $B_{(2)}$–$B_{(3)}$ = 1.76 ± 0.01 Å; $B_{(3)}$–$B_{(4)}$ = 1.77 Å; B–$H_{terminal}$ = = 1.10 ± 0.09 Å; $B_{(2)}$–H_{bridge} = 1.17 Å; $B_{(3)}$–H_{bridge} = 1.08 Å; $B_{(3)}$–H_{bridge} = 1.01 Å; $B_{(4)}$–H_{bridge} = 1.24 Å; $B_{(4)}$–H_{bridge} = = 1.37 Å; $B_{(5)}$–H_{bridge} = 1.44 Å; $B_{(1)}$–$H_{(11)}$ = 1.09 Å; $B_{(2)}$–$H_{(11)}$ = 1.77 Å; $B_{(5)}$–$H_{(11)}$ = 1.68 Å. Some contraction (by 0.1 Å) of the B–H bonds is probably explained by a systematic error in the method of calculation. The molecular angles in B_5H_{11} have also been measured[169]. The ^{1}H- and ^{11}B-NMR spectra of pentaborane(11) [92,170] confirm this structure for B_5H_{11}. The ^{1}H-NMR spectrum of B_5H_{11} [170] shows the presence of four types of hydrogen bonds: (1) the six terminal hydrogen atoms form quartets; (2) the apical terminal H_4; (3) three bridge hydrogens (multiplet); (4) the "unique" $H_{(11)}$ forms a sharp peak. The ^{11}B-NMR spectrum of B_5H_{11} shows three types of boron atom. The spectra given by Schaeffer and coworkers[92] differ somewhat from those given by Williams and coworkers[170], but they all contain peaks corresponding to three types of boron atom. The interpretation of the NMR spectra agrees with the structure of B_5H_{11}, but the distribution of charges calculated by Lipscomb[89] disagrees with some conclusions from the spectra. The ^{1}H-NMR spectrum of B_5H_{11}, specially purified by chromatography, recorded by Lutz and Ritter[74], differed slightly from the B_5H_{11} spectra mentioned above and the distribution of the charges of the boron atoms calculated from this spectrum agrees with Lipscomb's calculated data[38].

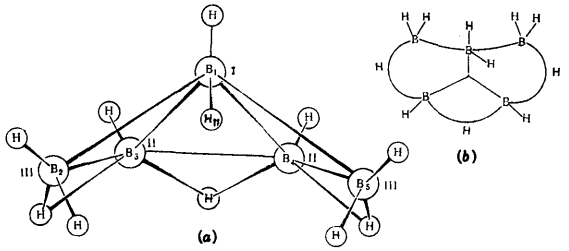


Fig. 10.

Eberhardt and coworkers showed[11] that in the B_5H_{11} molecule the apical atom $B_{(1)}$ is connected with two terminal hydrogen atoms, one of which (the "unique" $H_{(11)}$) has in addition a very weak bond with two basal boron atoms. These boron atoms (type B_{III}) are each bound by two-centre bonds with two terminal hydrogen atoms and one bridge hydrogen atom; the remaining basal boron atoms (type B_{II}) have one terminal hydrogen atom and each is bound to two bridge hydrogens. After forming these bonds, at the apical boron atom B_I there remain two orbitals and one electron; one orbital and one electron at the B_{II} atoms; one orbital and a half electron at the B_{III} atoms, that is, six orbitals and four electrons in all, which are used to form the bonds of the apical B_I atom with the basal B_{II} atoms. It is assumed that for the bonds of B_I with B_{II} atoms the sp^2-orbital of B_I and the two sp^3-orbitals of B_{II} are used, which form a central three-centre bond concentrated in the B_{II}–B_I–B_{II} triangle. For the bond of B_I with the B_{III} atoms, the p-orbital of the B_I atom and the sp^3-orbitals of the B_{III} atoms are used and by this means an open three-centre bond is formed. The formal distribution of the charges between the boron atoms was calculated[35]: $B_I = -\frac{2}{3}$, $B_{II} = +\frac{1}{3}$, $B_{III} = 0$. This charge distribution demands asymmetry of the B_{II}–H–B_{III} bridges; however, definite conclusions could not be drawn from their experimental results, measurements of greater accuracy being needed for this.

2. Preparation of Pentaborane(11)

There are several papers on the preparation of B_5H_{11} under laboratory conditions. In 1933 Burg and Schlesinger proposed a method of preparing B_5H_{11} by pyrolysis of diborane at 100–115°C,[47] a method which they subsequently improved[25].

The most convenient method of obtaining B_5H_{11} by pyrolysis of B_2H_6 was proposed by Klein and coworkers [50], using the technique of cold–hot tubes. Conditions were selected under which B_5H_{11} is obtained in 70% yield from B_2H_6: the temperature of the cold tube is -30°C, that of the hot tube +120°C, duration of the experiment 2.5 h, the B_5H_{11} and H_2 formed being removed from the reaction zone every 15 min:

$$2B_2H_6 \rightarrow B_4H_{10} + H_2;$$
$$5B_4H_{10} \rightleftarrows 4B_5H_{11} + 3H_2.$$

The conversion of B_4H_{10} into B_5H_{11} is a reversible reaction:

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

Study of the kinetics of the pyrolysis of diborane at 80–120°C [95] suggests that B_5H_{11} is an intermediate in the formation of most other boron hydrides from B_2H_6. The scheme of the reaction is:

$$B_2H_6 \rightleftarrows 2BH_3, \quad (1)$$
$$B_2H_6 + BH_3 \rightarrow \text{intermediate products}, \quad (2)$$
$$\text{intermediate products} + B_2H_6 \rightarrow B_5H_{11} + 2H_2, \quad (3)$$
$$B_5H_{11} \rightarrow B_5H_9 + H_2, \quad (4)$$
$$B_5H_{11} \rightarrow B_2H_6 \text{ — higher boron hydrides}. \quad (5)$$

The pyrolysis of diborane in a pulsation heater [8] showed that B_5H_{11} is formed through a tetraborane(10) fragment (B_4H_8):

$$B_4H_8 + B_2H_6 \rightarrow B_5H_{11} + BH_3; \; B_5H_{11} \rightleftarrows B_4H_8 + BH_3.$$

Experiment confirmed the hypothesis [95,96] that tetraborane is an intermediate in the formation of B_5H_{11} from B_2H_6.

When B_2H_6 is irradiated by light of wavelength 1849 Å a mixture of H_2, B_4H_{10}, B_5H_{11}, and, at low pressure, also the polymer $(BH)_x$ is formed [53]. On the basis of kinetic data it is assumed that B_5H_{11} and B_4H_{10} are obtained independently of one another. The condition for the formation of B_5H_{11} is the dissociation of B_2H_6 into BH_3 radicals and the reaction of the latter in an excited state. Raising the pressure lowers the rate of formation of B_5H_{11} owing to deactivation of B_2H_6 and recombination of BH_3. The mechanism of formation of B_5H_{11} is:

$$B_2H_6 + h\nu \rightarrow B_2H_6 \rightarrow 2BH_3$$
$$BH_3 \xrightarrow{M} B_2H_6 + M, \quad (M = \text{third body})$$
$$BH_3 + B_2H_6 \rightarrow B_3H_7 + H_2,$$
$$B_3H_7 + B_2H_6 \rightarrow B_5H_{11} + H_2.$$

There is a difference between the kinetics and the mechanism of thermal and photochemical conversion of B_2H_6 into B_5H_{11}.

A patent has been obtained [171] on a method for the catalytic conversion of B_2H_6 into B_5H_{11} at 175°C. The catalyst is zirconium boride and the yield of B_5H_{11} is 74.5% at a diborane conversion of 7.9%.

The preparation of completely pure B_5H_{11} was described by Spielman and Burg [78]. To purify B_5H_{11} the authors used an efficient low-temperature fractionation column, with a high reflux ratio. The B_5H_9 impurity slowly distilled into a trap (-196°C). The ^{11}B-NMR spectrum shows the complete absence of B_5H_9 impurity and other boron hydrides. B_5H_{11} has the following characteristics [78]: m.p. -122.0 ± ± 0.1°C (value given earlier -123.3°C [41]); vapour pressure 52.8 mmHg at 0°C, 103.1 mmHg at 13.5°C, 116.1 mmHg at 16.1°C. Previously a b.p. of 63°C was found for B_5H_{11} from the equation for the temperature dependence of vapour pressure:

$$\log P_{mmHg} = 7.901 - (1690.3/T).$$

Pentaborane(11) is unstable at room temperature and gradually decomposes on storage. At -78°C and prolonged storage mass spectroscopy shows that B_5H_{11} partly decomposes with formation of B_5H_9 and higher boron hydrides (B_6H_{10}, B_9H_{13}, $B_{10}H_{14}$). [172]

3. Isotopic Exchange and Pyrolysis of Pentaborane(11)

The reactions of B_5H_{11} show the instability of the molecule of this boron hydride. Koski has established [64] that when B_5H_{11} reacts with B_2D_6 or $^{10}B_2H_6$ exchange of hydrogen or boron atoms occurs, and study of the kinetics of the reaction in both instances shows that the reaction is half-order in B_5H_{11} and is first-order with respect to B_2D_6 or $^{10}B_2H_6$. Pentaborane(11) is split during this and all the ^{11}B, ^{10}B, H, and D atoms of both molecules participate in the exchange (mass spectra data) and the reaction proceeds by an intermolecular mechanism. Mass spectrometric study under mild conditions of the exchange reaction of B_5H_{11} with B_2D_6 showed that all the D atoms in B_2D_6 are exchanged at the same rate; all the B atoms also have a single rate of exchange, the exchange rate for the D and H atoms being twice that for the ^{10}B–^{11}B exchange. Similar results were obtained in studying the exchange of boron and deuterium between pentaborane(11) and diborane with infrared spectra.

The author proposes the following mechanism for the reaction:

$$B_5H_{11} \rightleftarrows BH_3 + B_4H_8$$
$$\left.\begin{array}{l} BH_3 + B_2D_6 \rightarrow B_2H_3D_3 + BD_3 \\ B_4H_8 + B_2D_6 \rightarrow B_5H_5D_6 + BH_3 \\ BH_3 + BD_3 \rightarrow B_2H_3D_3 \end{array}\right\} \text{rate-determining stages of the process}$$

The D (and ^{10}B) atoms thus introduced into the pentaborane molecule can be rapidly redistributed into the various positions of the molecule as a result of intramolecular exchange. The mass spectrum of B_5H_{11} also shows the instability of its molecule [65]. On heating (100°C), pentaborane(11) decomposes with formation of H_2, B_2H_6, B_4H_{10}, B_5H_9, and mixtures of involatile higher boron hydrides, including decaborane [46]. In the presence of hydrogen the main products of the pyrolysis of B_5H_{11} are B_4H_{10} and B_2H_6 (100°C, 10 min).

The equilibrium constants of this reversible reaction were measured in the range 100–140°C and the entropy and enthalpy of the process were determined [173]. On heating B_5H_{11} in the presence of hydrogen [8], in addition to B_2H_6, B_4H_{10}, and higher boron hydrides, B_5H_9 and B_6H_{10} are also formed in small amounts; when a mixture of B_5H_{11} and B_2H_6 (8 and 92% respectively) is heated the main products of the reaction are B_4H_{10}, B_5H_9, B_6H_{10}, and higher boron hydrides.

4. Reaction of B_5H_{11} with Lewis Bases

Stock and Poland [174] studied the reaction of B_5H_{11} with NH_3 at temperatures between -130° and +20°C and found that pentaborane(11) forms an addition compound with ammonia. The structure of the compounds obtained and the course of the reaction were not found. On heating, the addition product was changed into borazole.

Burg and Boone showed, in a series of papers, the ability of B_5H_{11} to be changed into other boron hydrides under the influence of Lewis bases and controlled conditions. This is an interesting property of B_5H_{11}, which once again shows its instability. Under the action of water at low temperature (the reagents were heated from -78° to 0°C until the ice started to melt) and a short time of contact (1 min) pentaborane(11) is partly hydrolysed, with formation of tetraborane(10) in 96% yield[56,57]:

$$B_5H_{11} + 3H_2O \rightarrow B_4H_{10} + B(OH)_3 + 2H_2.$$

The conversions of B_5H_{11} into B_6H_{10} [175,176] (on passing B_5H_{11} over a large surface of diglyme [bis-(2-methoxyethyl) ether] at temperatures from -78° to -20°C the yield of B_6H_{10} is up to 65%) and into B_9H_{15} [176] (with hexamethylenetetramine at 0°C, yield of B_9H_{15} up to 13%) have been proposed as convenient laboratory methods for these boron hydrides which previously were practically inaccessible. These are the main new methods for the conversion of some boron hydrides into others with chemical reagents, and not by thermal decomposition of the molecule.

Detachment of a BH_3 group from the B_5H_{11} molecule and subsequent disproportionation of the fragments occurs under the influence of Lewis bases — $(CH_3)_3N$, $[(CH_3)_2N]_2BH$, $(CH_2)_6(NH_2)_4$, $(CH_3)_2O$, $CH_3OCH_2CH_2OCH_2CH_2OCH_3$ — and in this both boron hydrides with less boron (B_2H_6, B_4H_{10} [56,175]) and also higher boron hydrides [175,176] are formed (B_6H_{10}, B_9H_{15}, $B_{10}H_{14}$); part of the pentaborane(11) is always converted into stable pentaborane(9). $(CH_3)_2O$ and B_5H_{11} at -78°C form an addition product with the empirical formula $B_5H_{11}.1.5(CH_3)_2O$.[176] It is assumed that the ether is coordinated to two type B_{II} boron atoms. The bonding of the ether to these boron atoms weakens the bond with the bridge hydrogens and facilitates the conversion of the B_5H_{11} molecule into other boron hydrides. A similar explanation is given for the conversion of B_5H_{11} into B_4H_{10} under the influence of water: the detachment of a B–H fragment, obtained from a B_{II} atom coordinated with oxygen and the formation of a B_4H_{10} molecule with minimal and localised rearrangement of the structure. The reaction of pentaborane(11) with amines also probably starts with electron-donor attack of the atom at these B_{II} atoms (specially bound) and with the formation of corresponding addition compounds.

In the reaction of $(CH_3)_3N$ with B_5H_{11},[175] as well as boron hydrides, trimethylamine-borane $(CH_3)_3N.BH_3$ is formed, the yield of which rises as the ratio $(CH_3)_3N : B_5H_{11}$ is raised to 2 : 1. Much less boron hydrides are then formed. It was also found[176] that $(CH_3)_3N.BH_3$ is a catalyst for the conversion of B_5H_{11} into other boron hydrides, which shows the greater acceptor ability of B_5H_{11} in comparison with BH_3. It has been shown that the strength of the Lewis base affects the composition of reaction products in the disproportionation of B_5H_{11}: addition products of B_5H_{11} with weak Lewis bases are readily decomposed with liberation of BH_3. Then high yields of B_2H_6 and B_4H_{10} are obtained; too strong Lewis bases form stable complexes with BH_3 group scission from the B_5H_{11}, continually removing it from the reaction zone, leading to a decrease in the yield of higher boron hydrides, particularly B_6H_{10}. The best yield of B_6H_{10} is obtained when Lewis bases of medium strength are employed, for example, diglyme.

When carbon monoxide acts on B_5H_{11} under mild conditions (20–25°C, CO pressure 7–20 atm) scission of the molecule (typical for B_5H_{11}) into BH_3 and B_4H_8 and formation of B_4H_8CO occur[77]. A detailed description of the preparation of B_4H_8CO and of its physical and chemical properties has appeared[78].

The course of the reaction of B_5H_{11} with CO is expressed by the equations:

$$B_5H_{11} \rightarrow B_4H_8 + BH_3,$$
$$B_4H_8 + CO \rightarrow B_4H_8CO,$$
$$BH_3 + CO \rightarrow BH_3CO.$$

The method of obtaining B_4H_8CO from B_5H_{11} is simpler and faster than that from B_4H_{10}, but completely pure pentaborane(11) is necessary for it, and this is not readily available. Therefore at present the preparation of B_4H_8CO from B_4H_{10} is more rational.

PF_3 reacts with B_5H_{11} like CO [78] with the formation of $B_4H_8.PF_3$ and $BH_3.PF_3$ under mild conditions (at ~ 30°C for 2 h). $B_4H_8.PF_3$ is quantitatively and reversibly converted into B_4H_8CO with CO (1 h at 18°C):

$$B_4H_8 \cdot PF_3 + CO \rightleftarrows B_4H_8 \cdot CO + PF_3.$$

5. Alkyl Derivatives of Pentaborane(11)

Various alkylating agents have been used to alkylate B_5H_{11}, these reactions also showing the lability of the pentaborane(11) molecule and its tendency to split into B_4H_8 and BH_3 groups. The alkyl derivatives of B_5H_{11} are unstable compounds.

Lutz and Ritter[74] obtained methyl derivatives of pentaborane(11) by its reactions with $CH_3B_2H_5$ under mild conditions (at 35°C for 30 min) or by reaction of B_4H_{10} with 1,2-dimethyldiborane at 100° for 15 min:

$$B_5H_{11} + B_2H_5CH_3 \rightleftarrows B_5H_{10}CH_3 + B_2H_6,$$
$$B_4H_{10} + {}^1/_2(BH_2CH_3)_2 \rightleftarrows B_5H_{10}CH_3 + H_2.$$

Methylpentaborane(11) $B_5H_{10}CH_3$ rather rapidly disproportionates at room temperature (16% after 30 min) with formation of B_5H_{11} and $B_5H_9(CH_3)_2$; on heating (90°C), the substance partly decomposes with liberation of B_5H_{11}, B_2H_6, $B_2H_5CH_3$, $B_5H_8CH_3$, traces of B_5H_9, solid boron hydrides, and $B_5H_9(CH_3)_2$. During the reaction of methylpentaborane(11) with diborane there is an exchange reaction with formation of $B_2H_5CH_3$ and B_5H_{11}: 72% of the $B_5H_{10}CH_3$ reacts after 30 min at 25°C. At a low temperature (from -78° to 0°C) diethyl ether decomposes $B_5H_{10}CH_3$ with release of B_5H_9, B_5H_{11}, and a little $B_5H_9(CH_3)_2$. $B_5H_{10}CH_3$ and $B_5H_9(CH_3)_2$ were identified and characterised with the help of infrared, NMR, and mass spectra. In the mass spectrum of $B_5H_{10}CH_3$ the most intense peaks correspond to the ions $B_5H_6CH_3^+$, $B_5H_8CH_3^+$, and $B_5H_4CH_3^+$; in the mass spectrum of $B_5H_9(CH_3)_2$ the most intense peaks are those of the ions $B_5H_5(CH_3)_2^+$, $B_5H_7(CH_3)_2^+$, and $B_5H_3(CH_3)_2^+$; that is, in methylpentaborane(11) and in dimethylpentaborane(11) the B–H bonds are split more easily than the B–C bond; furthermore, the tendency to the loss of hydrogen atoms in pairs is kept.

$B_5H_9(CH_3)_2$ is partly disproportionated at room temperature; the mass spectrum of a specimen of $B_5H_9(CH_3)_2$ which has been kept standing at 20–25°C contains peaks corresponding to $B_5H_8(CH_3)_3$.

The ^1H-NMR spectra of $B_5H_{10}CH_3$ and B_5H_{11} show that: (1) the CH_3 group is localised at B_{III} atoms; (2) geometrical isomerism exists in the $B_5H_{10}CH_3$ molecule; (3) an inductive effect may appear in a delocalised polyhedral

system. The infrared spectra of $B_5H_{10}CH_3$ and $B_5H_9(CH_3)_2$ confirm these conclusions.

Maguire and coworkers [177] studied the reaction of ethylene with pentaborane(11). After 30 min at 25°C and a pressure of 500 mmHg $C_2H_5B_5H_{10}$ is formed in 96% yield at 18% conversion of the B_5H_{11}; furthermore, small quantities of B_4H_{10}, H_2, $C_2H_5B_2H_5$, $C_2H_4B_4H_8$, and traces of $(C_2H_5)_2B_5H_9$ are formed. The formation of dimethylenetetraborane identical with the reaction product of B_4H_{10} and C_2H_4 was unexpected. The authors showed that $B_4H_8C_2H_4$ is not a decomposition product of $B_5H_{10}C_2H_5$ but is formed independently, together with $C_2H_5B_5H_{10}$:

$$B_5H_{11} \rightleftarrows B_4H_8 + BH_3,$$

$$C_2H_4 + B_4H_8 \rightarrow C_2H_4B_4H_8,$$

$$C_2H_4 + BH_3 \rightarrow C_2H_5BH_2,$$

$$C_2H_5BH_2 + B_4H_8 \rightarrow C_2H_5B_5H_{10}.$$

The decomposition of $C_2H_5B_5H_{10}$ in the liquid and gas phase in the presence of other boron hydrides has been studied to try to establish the mechanism of the reaction. A very complex mixture of products is obtained here, and the authors could not draw any definite conclusions.

The same authors studied the exchange reaction of $C_2H_5B_2H_5$ with B_5H_{11} [178] under mild conditions (30 min, 0°C) and found that there are then competing reactions of exchange of H at the C_2H_5 group and symmetrisation of $C_2H_5B_2H_5$:

$$C_2H_5B_2H_5 \xrightarrow{} {}^1/_2\,B_2H_6 + {}^1/_2(C_2H_5)_2B_2H_4$$

$$C_2H_5B_2H_5 \xrightarrow{B_5H_{11}} B_2H_6 + C_2H_5B_5H_{10}$$

Pentaborane(11) also undergoes an exchange reaction with symmetrical $(C_2H_5)_2B_2H_4$ to give $(C_2H_5)_2B_5H_9$ with C_2H_5 groups at different boron atoms. Other boron hydrides (B_4H_{10}, B_5H_9, $B_{10}H_{14}$) which have been studied under these conditions do not react with $C_2H_5B_2H_5$ and $(C_2H_5)_2B_2H_4$. These reactions are yet another proof of the lability of the H and B atoms in the B_5H_{11} molecule, and probably proceed with scission of the reacting molecules:

$$B_5H_{11} \rightleftarrows BH_3 + B_4H_8; \quad RB_2H_5 \rightleftarrows RBH_2 + BH_3.$$

The exchange reaction between $C_2H_5B_2H_5$ and B_5H_{11} reaches an equilibrium.

There are several patents on methods of alkylating B_5H_{11}. The reaction of an alkyl halide (C_2H_5Br, n-C_3H_7Cl, n-C_4H_9Cl) with a mixture of pentaboranes (70–90% B_5H_{11} and 10–30% B_5H_9) in the presence of $AlCl_3$ under mild conditions (20°C, 560 mmHg) for 1 h gives a mixture of alkylated pentaboranes [179] which was separated by fractionation. Liquid products were obtained in the reaction of B_5H_{11} with conjugated dienes [180] at 20–40°C but their composition is not given.

VII. HEXABORANE(10)

1. Structure of Hexaborane(10)

The molecular structure of hexaborane(10), B_6H_{10}, was established by X-ray analysis and NMR-spectroscopy. Lipscomb and coworkers [181,182] showed that the boron atoms in B_6H_{10} form a pentagonal pyramid (Fig. 11), which is a fragment of an icosahedron, and they determined the interatomic distances by an X-ray diffraction method.

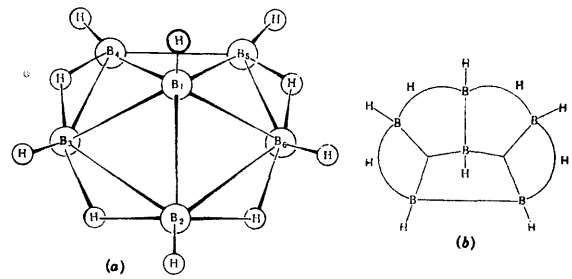


Fig. 11.

They give [182] the following data: $B_{(1)}-B_{(4)} = B_{(1)}-B_{(5)} = 1.795 \pm 0.01$ Å; $B_{(1)}-B_{(3)} = B_{(1)}-B_{(6)} = 1.753 \pm 0.009$ Å; $B_{(1)}-B_{(2)} = 1.740 \pm 0.014$ Å; $B_{(4)}-B_{(5)} = 1.596 \pm 0.012$ Å; $B_{(4)}-B_{(3)} = B_{(5)}-B_{(6)} = 1.737 \pm 0.001$ Å; $B_{(3)}-B_{(2)} = B_{(6)}-B_{(2)} = 1.79 \pm 0.009$ Å; $B-H_{terminal} = 1.21 \pm 0.07$ Å; $B_{(4)}-H_{bridge} = 1.35$ Å; $B_{(8)}-H_{bridge} = 1.31$ Å; $B_{(3)}-H_{bridge} = 1.48$ Å; $B_{(4)}-H_{bridge} = 1.32$ Å.

For the six boron atoms which form a pentagonal pyramid, two types of distributions of the bonds have been proposed [183]. After detailed study and calculations for the B_6H_{10} molecule Lipscomb and coworkers [10,182] proposed a structure which does not contain BH_2 groups, has four B–H–B bridge bonds, and a planar symmetry. Each of the five boron atoms which form the base of the pyramid are connected to a terminal hydrogen atom; in the base there are four B–H–B three-centre bonds and one B–B two-centre bond, connecting the atoms $B_{(4)}$ and $B_{(5)}$. The last atoms use one orbital and half an electron for a bond with the apical boron atom; the atoms $B_{(3)}$, $B_{(2)}$, and $B_{(6)}$ use for this purpose one sp^3-orbital and one electron. The apical boron atom is connected with one terminal hydrogen, the remaining three orbitals and two electrons being used for bonds with the basal boron atoms: one two-centre bond $B_{(1)}-B_{(2)}$ and two central three-centre bonds between the atoms $B_{(4)}-B_{(1)}-B_{(3)}$ and $B_{(5)}-B_{(1)}-B_{(6)}$ are formed on both sides of the plane of symmetry. The authors explain the unusually short distance between atoms $B_{(4)}$ and $B_{(5)}$ (1.596 Å) by all the bonds formed by these atoms (the $B_{(4)}-B_{(1)}-B_{(3)}$ and $B_{(4)}-H-B_{(3)}$ three-centre bonds and the B–H and $B_{(4)}-B_{(5)}$ two-centre bonds) exhibiting quite marked departures of the valence angle from the tetrahedral configuration and a corresponding bond shortening. This situation is comparable with that in the cyclopropane ring, where the strong strain in the ring leads to unusually short interatomic distances. Starting from the assumed structure for B_6H_{10}, the charges of the boron atoms were calculated [182]: $-\frac{1}{3}$, $-\frac{1}{6}$, $+\frac{1}{3}$, and 0 for the atoms $B_{(1)}$, $B_{(4)}$, $B_{(3)}$, and $B_{(2)}$†. The NMR spectral data [184] agree with this structure of hexaborane in the main. The ^{11}B-NMR spectrum contains two doublets with relatively intense peaks 5 : 5 : 1 : 1, corresponding to the B–H groups of the base and the B–H group at the apex of the pyramid. The basal boron atoms in the B_6H_{10} molecule are more electropositive [184] than the corresponding boron atoms in B_5H_9. However, the conclusion can be drawn from the ^{11}B-NMR spectrum of B_6H_{10} that all the boron atoms lying in the base of the pentagonal pyramid are identical; that is, the third type of boron atom, indicated by

† The original reference lists these charges in the order $B_{(1)}$, $B_{(2)}$, $B_{(3)}$, $B_{(4)}$ (Ed. of Translation).

Lipscomb's results, is not observed. The identity of these boron atoms is explained[185] by a tautomeric conversion of the two isomers of B_6H_{10}, which differ from one another in the type of bonds. The second isomer of B_6H_{10}, which is less stable, also has a structure of a pentagonal pyramid, but in it the basal boron atoms form three B–H–B three-centre bonds and the $B_{(4)}$ atom is bound to two terminal hydrogens, that is, there is a BH_2 group in the base.

The energies of the bonds in B_6H_{10} have been calculated from the lengths of the B–B and B–H bonds. The calculations show that some of the data on interatomic distances need to be determined more accurately.

2. Preparation and Properties of Hexaborane(10)

Hexaborane(10) was first obtained by Stock[41,94] in very small quantities by the hydrolysis of metal borides with acids; it was mixed with other boron hydrides and was practically inaccessible. Later Lipscomb and coworkers[181], and then Kotlensky and Schaeffer[186] obtained B_6H_{10} by the action of a silent electric discharge (15 kV) on diborane, followed by low-temperature fractionation of the mixture. The yield of B_6H_{10} was small (~ 1%), the main reaction products being B_4H_{10}, B_5H_9, and B_5H_{11} (yields of 40, 20, and 30% respectively); in addition, small amounts of B_9H_{15} and $B_{10}H_{14}$ are formed.

Hexaborane(10) became available after Boone and Burg[57,175,176,187] developed a method of making it from B_5H_{11} by the action of basic reagents. On passing B_5H_{11} vapour over a large surface of diglyme at a low pressure pure B_6H_{10} was obtained in 65% yield[176]. This method of obtaining hexaborane(10) is most convenient. A proposal has been made[188] to obtain B_6H_{10} by the hydrolysis of Mg_3B_2 under somewhat modified conditions compared with those of Stock. The total yield of boron hydrides does not exceed 12%, B_6H_{10} being obtained in a yield from 2 to 6%.

The physical properties of B_6H_{10} have been determined: m.p. -62.3°C [176] or -63.2° ± 0.1°C;[189] b.p. 108°C [176] or 82.2°C (calculated)[189]; the temperature dependence of vapour pressure is described by the equation $\log P_{mmHg} = 5.2124 - (1566.3/T) + 0.005841T$.[189] The heat of vaporisation of B_6H_{10} and its Trouton constant (= 25.7) have also been found[189], the latter showing that the B_6H_{10} molecule is not associated in the liquid state. The mass spectrum of pure B_6H_{10} [189] (differing somewhat from the mass spectrum recorded earlier for insufficiently pure B_6H_{10} [186]) shows that the most stable ion is $B_6H_8^+$; the general tendency for all boron hydrides to lose hydrogen atoms in pairs is observed. The infrared spectrum of B_6H_{10} contains bands corresponding to $B–H_{terminal}$ and $B–H_{bridge}$ bonds; bands of the BH_2 groups are absent[189]. B_6H_{10} slowly decomposes above 0°C,[189] although it is more stable than B_5H_{11} (a method has been proposed for purifying B_6H_{10} from B_5H_{11}, based on the lower stability of B_5H_{11} at -80°C and at +100°C in the presence of hydrogen). B_6H_{10} is thermally a little more stable than B_4H_{10}.[94]

A preliminary study of the deuterium exchange of B_6H_{10} with B_2D_6 showed[189] that the terminal hydrogen atoms of B_6H_{10} react more rapidly than the bridge hydrogens.

The chemical reactions of B_6H_{10} have been little studied. B_6H_{10} reacts slowly with water in the cold[94], and on heating the reaction:

$$B_6H_{10} + 18H_2O \rightarrow 6H_3BO_3 + 14H_2,$$

occurs. The hydrolysis is faster in acid than in alkali.

VIII. HEXABORANE(12)

1. Structure of Hexaborane(12)

The structure of hexaborane(12) has not been determined experimentally, but Lipscomb has proposed[185] for it the structure of a pentagonal pyramid by analogy with the structure of B_6H_{10} and on the basis of the principles of boron hydride topology. The proposed structure contains two BH_2 groups, four B–H–B bridge bonds, two B–B–B central three-centre bonds, and one B–B two-centre bond; the B_6H_{12} molecule has eight terminal hydrogen atoms and four bridging hydrogen atoms. The other possible structure for B_6H_{12} is apparently less stable, has three BH_2 groups, three B–H–B bridge bonds, and an apical boron atom, connected by three B–B–B three-centre bonds with boron atoms lying in the base of the pyramid. Gaines and Schaeffer[190] on the basis of the topology of the molecule (4212), the ^{11}B-NMR spectra, and the method of preparation from B_3H_7, proposed for B_6H_{12} a structure of an open type unusual for boron hydrides, and which is not a fragment of an icosahedron. Lutz and coworkers[191] consider that the structure of B_6H_{12} is similar to the structure of B_5H_{11} and gives a structure obtained from the B_5H_{11} molecule by replacing one B–H–B bond by a BH_2 group. This structure also agrees with the topology of the molecule, and in the main, with the ^{11}B-NMR spectrum. The absence of X-ray diffraction data does not at present permit a choice to be made between these structures.

2. Preparation and Properties of Hexaborane(12)

Gibbins and Shapiro[192] first isolated B_6H_{12} from the mixture of boron hydrides obtained by the action of an electric discharge on B_2H_6 [186] and identified it by mass spectroscopy. The authors showed that B_6H_{12} is much less stable than B_6H_{10}; it decomposes at room temperature. Gaines and Schaeffer[190,193] obtained B_6H_{12} in ~ 4% yield by the reaction of $(CH_3)_4NB_3H_8$ with polyphosphoric acid and isolated it by high-vacuum distillation. B_6H_{12} slowly decomposes at ~ 20°C with liberation of hydrogen and boron hydrides; the decomposition is accelerated in the presence of water or $(CH_3)_2O$. NMR spectra of B_6H_{12} and its vapour pressure (17 mmHg at 0°C) have been given. Lutz and coworkers[191] isolated and identified B_6H_{12}, which they obtained in low yields (~ 1%) in the decomposition of B_4H_{10} and B_5H_{11} under different conditions. Hexaborane(12) has been purified by gas–liquid chromatography. Its physical properties are: m.p. -82.3°C, vapour pressure 17.1 mmHg at 0°C, 3.8 mmHg at 23.6°C.[191] Study of the decomposition of hexaborane(12) at 25°C (pure and in the presence of B_2H_6) showed that the chemical stability of B_6H_{12} increases with increase in the purity of the compound[191]; the infrared and mass spectra of B_6H_{12} have been recorded. The chemical properties of B_6H_{12} have hardly been studied at all. With water or $(CH_3)_2O$, hexaborane(12) decomposes rapidly according to the equations[191]:

$$B_6H_{12} + 6H_2O \rightarrow B_4H_{10} + 2B(OH)_3 + 4H_2,$$

$$2B_6H_{12} \xrightarrow{(CH_3)_2O} 2B_5H_9 + B_2H_6.$$

IX. HEPTABORANES

Heptaboranes have not been obtained pure, although in several papers[8,186,192,194] it has been shown that they are present in mixtures of boron hydrides. Lipscomb[185] considers possible the existence of three B_7 boron hydrides:

B_7H_{11}, B_7H_{13}, and B_7H_{15}, and proposes for each of them a structure with a less compact arrangement of the boron atoms than for the other boron hydrides, which explains the extremely low stability of these compounds. Schaeffer and coworkers [195] in a mass spectrometric examination of tetraborane obtained from B_2H_6 observed in individual specimens peaks of a previously unknown boron hydride, to which the authors ascribed the formula B_7H_{13}. In the same work there is a statement on the existence of B_7H_{15}. Fehlner and Koski [8] showed that, in the distillation and mass spectrometric analysis of the products of the pyrolysis of B_2H_6, two heptaboranes B_7H_{11} and B_7H_{13} are probably formed (although they did not exclude the possibility of the formation of another pair of heptaboranes: B_7H_{13} and B_7H_{15}). Heptaboranes have not been isolated from mixtures of boron hydrides.

Ditter and coworkers [196] have doubted the existence of heptaboranes on the basis of the mass spectra of specimens of the "heptaborane" fraction after its purification on a chromatograph. The authors consider that ethylpentaboranes, triethoxyboranes, and other impurities, formed from traces of ethane and diethyl ether usually present in boron hydrides, have been erroneously taken for heptaboranes.

X. OCTABORANE(12) B_8H_{12}

The first indication of the formation of octaborane(12) in the pyrolysis of B_5H_{11}, based on measurements of the vapour pressure of the compound obtained, was in a study by Burg and Schlesinger [47], but it was found later [176] that B_9H_{15} is formed in this. Shapiro and coworkers [197,198] recorded the mass spectrum of octaborane(12) present in a mixture with other boron hydrides, and on the basis of this the compound was given the formula B_8H_{12}. Lipscomb and coworkers [199] succeeded in obtaining, isolating in the pure form, and finding the structure of octaborane(12). B_8H_{12} was obtained by the action of an electric discharge on a mixture of B_2H_6 and B_5H_9 (molar ratio 2 : 1), and rapid separation of the reaction products by vacuum low-temperature fractionation with simultaneous mass spectrometric analysis of the fraction. X-Ray analysis of the compound showed that the B_8H_{12} molecule has a plane of symmetry and is a fragment of an icosahedron. Fig. 12 shows the structure of B_8H_{12}.

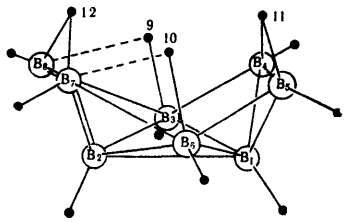


Fig. 12.

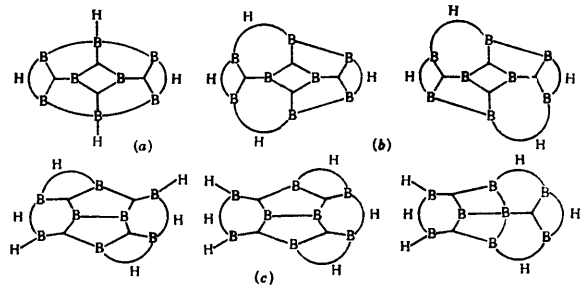


Fig. 13.

The following interatomic distances have been determined: $B_{(1)}-B_{(3)} = B_{(2)}-B_{(3)} = B_{(3)}-B_{(4)} = B_{(5)}-B_{(6)} = B_{(6)}-B_{(7)} = B_{(2)}-B_{(6)} = 1.790 \pm 0.007$ Å; $B_{(1)}-B_{(4)} = B_{(1)}-B_{(5)} = 1.690 \pm 0.006$ Å; $B_{(2)}-B_{(7)} = B_{(2)}-B_{(8)} = 1.720 \pm 0.002$ Å; $B_{(1)}-B_{(2)} = 1.803$ Å; $B_{(3)}-B_{(8)} = 1.800$ Å; $B_{(4)}-B_{(5)} = 1.672$ Å; $B_{(7)}-B_{(8)} = 1.706$ Å; $B-H_{terminal} = 1.10 \pm 0.03$ Å; $B_{(3)}-H_{(9)} = B_{(6)}-H_{(10)} = 1.28 \pm 0.02$ Å; $B_{(8)}-H_{(9)} = B_{(7)}-H_{(10)} = 1.47 \pm 0.01$ Å. Each boron atom in the B_8H_{12} molecule has one terminal hydrogen atom; furthermore, there are two symmetrical hydrogen bridges $B_{(4)}-H_{(11)}-B_{(5)}$ and $B_{(7)}-H_{(12)}-B_{(8)}$ and two unsymmetrical bridges $B_{(3)}-H_{(9)}-B_{(8)}$ and $B_{(6)}-H_{(10)}-B_{(7)}$, in which the hydrogen atom is situated close to the $B_{(3)}$ and $B_{(6)}$ atoms. The character of the bonds between the boron atoms was not analysed in this work; however, previously Lipscomb [1], on the basis of the topology of B_8H_{12} (4420) had proposed a structure (Fig. 13) in which the molecule contains four central B–B–B three-centre bonds and two B–B two-centre bonds, in addition to bonds with hydrogen atoms. B_8H_{12} is an extremely unstable compound; therefore the study of its structure is done at a low temperature (below -20°C).

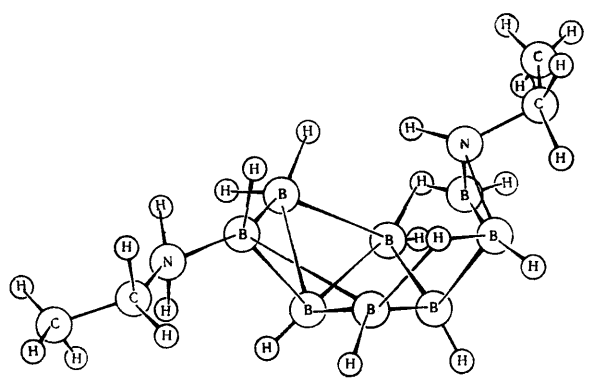


Fig. 14.

In addition to B_8H_{12}, a derivative of octaborane of the composition $C_2H_5NH_2B_8H_{11}NHC_2H_5$ has been obtained [200] by the action of $C_2H_5NH_2$ on a nonaborane complex, $B_9H_{13}S.(C_2H_5)_2$; it was isolated in the pure state and studied by X-ray diffraction [200,201]. It was shown that there is a B–N–B bridge bond in this compound, like the bond in aminodiborane, formally replacing one B–H–B bond. This type of bond was first observed in the higher boron hydrides in this example. It is assumed that this compound is a derivative of the hypothetical ion $B_8H_{13}^-$; its structure is shown in Fig. 14.

The geometry of the molecule shows that the lattice of boron atoms is a fragment of an icosahedron. All the interatomic distances were determined and the precise positions

of all the boron, nitrogen, and carbon atoms were found, and of all the hydrogen except one hydrogen atom in the NH_2 group and three hydrogens in one CH_3 group. The compound is rather stable thermally and chemically, probably owing to stabilisation by the ethylamine molecules. If the bridge nitrogen atom is formally replaced by hydrogen, then (by analogy with $B_2H_5NR_2$ and B_2H_6) $B_8H_{12}.L$ (where L denotes ligand) is obtained, from which it is possible to obtain the hypothetical $B_8H_{13}^-$ ion, which is a derivative of B_8H_{14}. The authors suggested the instability of this octaborane is due to steric hindrance.

Hence the octaboranes are also extremely unstable representatives of the boron hydrides and at present have been very little studied.

XI. NONABORANE(15)

Nonaborane(15), B_9H_{15}, is yet another boron hydride which has been obtained comparatively recently. Mention of some nonaborane among the decomposition products of pentaborane(11) when the latter is kept for a long period is made by Norton [172]. B_9H_{15} was first obtained by Kotlensky and Schaeffer [186] as a by-product produced in extremely small amounts in a mixture with B_6H_{10} and $B_{10}H_{14}$ (total amount of the three boron hydrides ~ 1%) by the action of a silent electric discharge on diborane. Its formula and structure were established by X-ray analysis and mass spectrometrically [202,203], in which extremely small quantities of material were used and were of insufficient purity. In 1962, Burg and Kratzer [176] developed a method for obtaining B_9H_{15} by the catalytic decomposition of B_5H_{11} in the presence of hexamethylenetetramine at 0°C, yield of B_9H_{15} ~ 13%. The constants obtained for pure nonaborane (m.p. +2.8°C, vapour pressure 0.8 mmHg at 28°C) differ considerably from those of the specimen used earlier by Lipscomb [202,204] for establishing the structure of B_9H_{15} (m.p. -18° to -20°C); however, Burg and Kratzer showed with the aid of ^{11}B-NMR, infrared, and mass spectra that the specimens were identical in chemical structure, and the difference in constants is explained by the presence of other boron hydrides as impurities. Ditter and coworkers [196] obtained nonaborane(15) from B_5H_{11} and B_2H_6 (excess of diborane, pressure 27 atm) and recorded the mass spectrum of pure B_9H_{15}.

Nonaborane(15) has the structure shown in Fig. 15.

The interatomic distances [202] are (in Å): $B_{(1)}-B_{(3)} = B_{(1)}-B_{(8)} = 1.76$; $B_{(3)}-B_{(8)} = 1.80$; $B_{(3)}-B_{(9)} = B_{(8)}-B_{(9)} = 1.86$; $B_{(3)}-B_{(4)} = B_{(7)}-B_{(8)} = 1.95$; $B_{(1)}-B_{(4)} = B_{(1)}-B_{(7)} = 1.75$; $B_{(1)}-B_{(2)} = 1.77$; $B_{(2)}-B_{(4)} = B_{(2)}-B_{(7)} = 1.82$; $B_{(2)}-B_{(5)} = B_{(2)}-B_{(6)} = 1.76$; $B_{(5)}-B_{(6)} = 1.78$; $B_{(4)}-B_{(5)} = B_{(6)}-B_{(7)} = 1.84$; $B-H_{terminal} = 1.15 \pm 0.32$; $B-H_{bridge} = 1.36 \pm 0.32$; accuracy of B-B distances 0.07 Å.

The boron atoms in the B_9H_{15} molecule are disposed in the form of a fragment of an icosahedron, but there is some deformation of the boron framework owing to an increase in the distances $B_{(3)}-B_{(4)}$ and $B_{(7)}-B_{(8)}$. Each boron atom is connected to a terminal hydrogen atom, the direction of these bonds approximately coinciding with the lines leading from the centre of the icosahedron to the boron atom concerned. The atom $B_{(9)}$ has two terminal hydrogen atoms so that these atoms are directed perpendicular to the plane formed by the atoms $B_{(8)}B_{(9)}B_{(3)}$, and are situated on opposite sides of this plane. In the B_9H_{15} molecule there are five B-H-B bridge bonds and six types

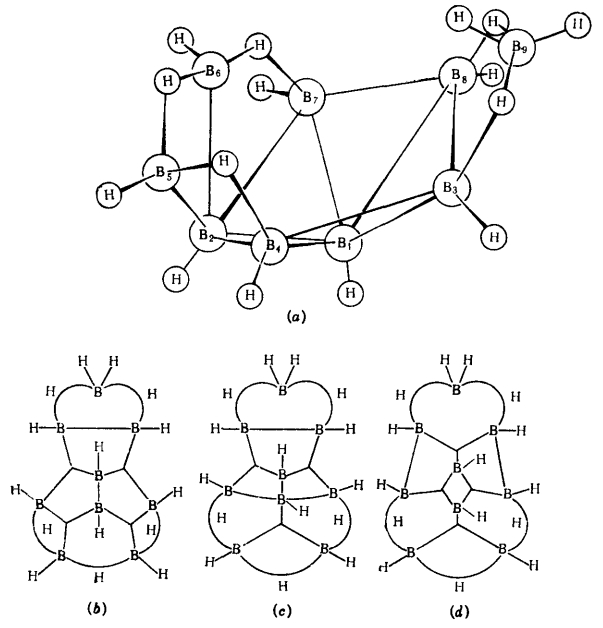


Fig. 15.

of boron atoms. The structure of the valence bonds in the molecule around the atoms $B_{(2)}-B_{(4)}-B_{(5)}-B_{(6)}-B_{(7)}$ is reminiscent of the structure of the B_5H_{11} molecule; just as in this compound, three B-H-B bridge bonds are directed inwards towards the centre of the icosahedron. On the other hand (near the BH_2 group) the bonding of the molecule is reminiscent of B_4H_{10}. In the molecule of B_9H_{15} the boron atoms are bound to one another (apart from the five B-H-B bridge bonds) by another two two-centre and four three-centre bonds. A topological calculation has shown [183] that such a structure is the best for B_9H_{15}. There are three possible ways of arranging the three-centre bonds between the boron atoms in a B_9H_{15} molecule which is a fragment of an icosahedron, when a plane of symmetry is present (Figs. 15*b*–15*d*). All these structures can be converted into one another by a small change in atomic orbitals. The LCAO-MO method was used to calculate the charge distribution between the boron atoms, the bond energies, and the ionisation potentials [38] for the ideal B_9H_{15} molecule. The ^{11}B-NMR spectrum of B_9H_{15} [176] contains two triplets in the low and high potential regions; the interpretation of this spectrum is complex but it evidently agrees with the structure of B_9H_{15} obtained by the X-ray analysis of the compound. The infrared spectrum is also very complex; it contains lines corresponding to three types of B-H-B bond, five types of terminal B-H bond, and also several types of B-B bond.

2. Properties of B_9H_{15}

Some information has been obtained on the stability of B_9H_{15}: [176] the compound is unchanged after 1 h at 0°C; on holding for 40 s at 74.9°C and 3.89 mmHg (to determine the molecular weight), the melting point of the compound is lowered to 0.6–0°C and a little hydrogen is released (0.016 moles hydrogen per mole B_9H_{15}), that is, there is slight decomposition of the B_9H_{15}. However, the stability of B_9H_{15} surpasses that of B_8H_{12} and the B_7 hydrides and is

comparable with that of B_5H_{11}. The kinetics of the decomposition of nonaborane(15) into B_8H_{12} and B_6H_{10} have been studied with the mass spectrograph [196].

Nonaborane derivatives of the type $B_9H_{13}.L$ (where L is a ligand) are derivatives of the hypothetical anion $B_9H_{14}^-$ and were first obtained and characterised by Graybill and coworkers [205,206] by the action of diethylamine on decaborane(14) followed by treatment with aqueous HCl, when the following reactions take place:

$$B_{10}H_{14} + (C_2H_5)_2NH \xrightleftharpoons{\text{rapid}} (C_2H_5)_2\overset{+}{N}H_2B_{10}H_{13}^- \xrightarrow[\text{slow}]{(C_2H_5)_2NH}$$

$$\rightarrow (C_2H_5)\overset{+}{N}H_2B_{10}H_{13}^- \cdot [(C_2H_5)_2NH],$$

$$B_{10}H_{13}^- \cdot [(C_2H_5)_2NH] + H_3\overset{+}{O} + 2H_2O \rightarrow 2H_2 + B(OH)_3 + B_9H_{13} \cdot [(C_2H_5)_2NH].$$

The same compounds are obtained by alcoholysis of $B_{10}H_{12}L_2$ ($L = CH_3CN$ or Et_2S):

$$B_{10}H_{12}L_2 + ROH \rightarrow B_{10}H_{13}L \cdot (ROH) + L,$$

$$B_{10}H_{12}L \cdot (ROH) + 2ROH \rightarrow B_9H_{13}L + B(OR)_3 + H_2.$$

The authors showed that in the compound $B_9H_{13}S(C_2H_5)_2$ the ligand undergoes substitutions with CH_3CN, $P(C_5H_5)_3$, pyridine and its derivatives, $(C_2H_5)_2NH$, or $(C_2H_5)_3N$. When this compound is treated with an excess of diethylamine there is partial degradation of the anion and formation of a derivative of octaborane, $C_2H_5NH_2B_8H_{11}NHC_2H_5$. [200] When $B_9H_{13}S(C_2H_5)_2$ is treated with strong bases L is replaced and a derivative of a new anion, $B_9H_{12}^-$, is formed [205]:

$$B_9H_{13}S(C_2H_5)_2 + (CH_3)_4NOH \rightarrow (CH_3)_4N^+ + B_9H_{12}^- + H_2O + S(C_2H_5)_2.$$

The compounds $B_9H_{13}.L$ can give derivatives of $B_9H_{12}^-$ also on reaction with pyridine. The anion $B_9H_{12}^-$ is much less stable than $B_9H_{14}^-$; its structure has not been established. Methanolysis of $B_9H_{12}N(CH_3)_4$ leads to decomposition of the anion $B_9H_{12}^-$ and the relatively stable anion $B_3H_8^-$, which is a method of obtaining the latter [18].

The structure of $B_9H_{13}CNCH_3$ was found by X-ray diffraction [207,208], and is shown in Fig. 16.

The boron atoms form a fragment of an icosahedron and are arranged like nine of the boron atoms in the $B_{10}H_{12}(CNCH_3)_2$ molecule, from which $B_9H_{13}CNCH_3$ is obtained; two of the boron atoms have two terminal hydrogens, the rest each have one hydrogen atom; in addition, there are two B–H–B bridge bonds in the molecule. The character of the bonds between the boron atoms in the $B_9H_{13}CNCH_3$ molecule is somewhat different from that of the B_9H_{15} molecule; the authors attribute this difference to tautomerism of the hydrogen atoms in the boron hydride

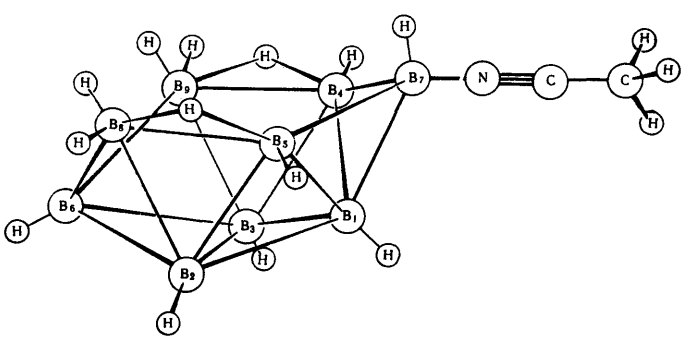


Fig. 16.

as a result of which yet another BH_2 group and a negative ion (or its derivative) are formed. Graybill and coworkers [205] suggest that the boron atom connected to the ligand molecule has sp^2-hybridisation (analogous to the atoms $B_{(6)}$ and $B_{(9)}$ in $B_{10}H_{12}.L_2$). The authors found that in the excited state in $B_9H_{13}.L$ (where L is pyridine itself or a pyridine substituted in the ring) there is an interaction between the π-electron orbital of the pyridine ring and the open three-centre bond B–B–B (p-orbitals) of the B_9H_{13} molecule: the excitation energy depends linearly on the Hammett constant (σ) in the pyridine series. A compound of the $B_9H_{13}.L$ type (where L is a neutral molecule, a donor of electrons) form a unique class of complex compound united by the properties of compounds with infra- and inter-molecular exchange of charges.

Muetterties and Aftandilian [209] obtained a compound of yet another type of nonaborane derivative, $B_9H_{14}P(C_6H_5)_2$ (however, the problem of the composition of the fragment has not been settled conclusively) by the alkaline hydrolysis of $B_{10}H_{13}P(C_6H_5)_2$ in alcoholic medium:

$$B_{10}H_{13}P(C_6H_5)_2 + 3H_2O \rightarrow B_9H_{14}P(C_6H_5)_2 + B(OH)_3 + H_2O.$$

A few salts of the anion $B_9H_{14}^-$ – with the cations Cs^+, $(CH_3)_4N^+$, and $(CH_3)_3\overset{+}{N}H$ – have been obtained [210] in the hydrolysis of $B_{10}H_{14}$ by aqueous bases; the salts were isolated and the anion characterised. Several reciprocal conversions of the compounds $B_9H_{13}.L$ and $X^+B_9H_{14}^-$ have been made, which confirm the structural similarity of these types of molecule.

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The boron hydrides are extremely reactive compounds, capable of various types of chemical reaction depending on the types of bond in them. Boron hydride chemistry is now developing very intensively both as regards the study of compounds already known and also in the preparation and study of new representatives of this class. The theory of the chemical structure of the boron hydrides still requires greater precision as the geometry of some boron hydrides and their NMR spectra have not been completely explained.

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NOTE ADDED IN PROOF

After submission of this paper for publication several review articles and collections of papers were published: Adams [211] dealt with the chemistry of the boron hydrides, Schaeffer [212] with the NMR spectra, Campbell [213] with structure, and Levinskass [214] with the toxicity of boron hydrides; new boron hydrides were also obtained: the anion $B_6H_6^{2-}$, octaborane(18) B_8H_{18}, [216] and iso-nonaborane iso-B_9H_{15}. [217] Furthermore, articles have appeared on individual questions of boron hydride chemistry: on triborane [218], tetraborane [218-224], pentaboranes [225-229], hexaboranes [215,230-232], octaboranes [196,230,231,233], and nonaboranes [196,227,234].

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COVALENT ORGANODIELEMENTARY COMPOUNDS

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I. INTRODUCTION

Among organodielementary compounds we include compounds containing, apart from the usual elements (C, H, O, N, Cl, etc.), two inorganic elements. When the latter are metals, the compounds will be termed organodimetallic compounds.

In organodielementary compounds the inorganic elements may be separated by hydrocarbon groups or may be adjacent to one another. In the latter case the bond between them may be either ionic or covalent. Razuvaev and his coworkers are playing an active part in developing methods for the synthesis of organodielementary compounds having a covalent bond between the inorganic elements and also in examining their reactivity. The present paper reviews work in this field and is based on the literature up to May 1965. Investigations on organodielementary compounds having an ionic bond between the inorganic elements have been discussed several times in reviews and monographs [1-5].

II. METHODS OF PREPARATION

Organodielementary compounds containing an M–M' bond (here and below M and M' denote the inorganic elements) are usually prepared by reaction of R_3SiLi and analogous compounds with inorganic or organoelementary halides (method A), e.g.

$$(C_6H_5)_3SiK + (C_6H_5)_3SnCl \longrightarrow KCl + (C_6H_5)_3SiSn(C_6H_5)_3, \quad (1)$$

$$3(C_6H_5)_3GeNa + SiHCl_3 \longrightarrow [(C_6H_5)_3Ge]_3SiH + 3NaCl. \quad (2)$$

The yield of triphenyltriphenylsilyltin from reaction (1) is 76%;[6] tristriphenylgermylsilane is formed in quantitative yield in conformity with Eqn. (2).[7]

Method A has been used to synthesise several compounds containing Si–Ge,[6,8-12] Si–Sn,[7,13-16] Ge–Sn[17,18], Ge–Pb[18], and Sn–Pb[18] groups. Covalent organotrielementary compounds have been obtained in a similar manner[1]:

$$[(C_6H_5)_3Ge]_3SiLi + ClSn(C_6H_5)_3 \longrightarrow [(C_6H_5)_3Ge]_3SiSn(C_6H_5)_3 + LiCl.$$

In 1964 this method was used to synthesise a series of organodimetallic compounds having a neopentane configuration of metal atoms[18-21]:

$$4(C_6H_5)_3MLi + M'Cl_4 \longrightarrow [(C_6H_5)_3M]_4M' + 4LiCl,$$

$$4(C_6H_5)_3MLi + 2PbCl_2 \longrightarrow [(C_6H_5)_3M]_4Pb + Pb + 4LiCl,$$

where M = Pb, Sn and M' = Sn, Ge.

The attempt to obtain tetrakistriphenylgermyltin from triphenylgermyl-lithium and tin tetrachloride was unsuccessful[18], since in this case metal–halogen exchange predominates, with the formation of hexaphenyldigermane:

$$(C_6H_5)_3GeLi + SnCl_4 \longrightarrow (C_6H_5)_3GeCl + [LiSnCl_3],$$

$$(C_6H_5)_3GeCl + (C_6H_5)_3GeLi \longrightarrow LiCl + (C_6H_5)_6Ge_2.$$

This work showed that, in the synthesis of compounds of the type $[(C_6H_5)_3M]_4M'$ the tendency for metal–halogen exchange to occur diminishes in the sequence

$$(C_6H_5)_3GeLi > (C_6H_5)_3SnLi > (C_6H_5)_3PbLi.$$

The occurrence of this secondary process, which often leads to the formation of difficultly separable mixtures of products[8,17], is a substantial disadvantage of method A. Thus the interaction of $(C_6H_5)_3GeK$ with $(C_6H_5)_3SiCl$, for example, yields a difficultly separable mixture containing $(C_6H_5)_6Ge_2$, $(C_6H_5)_6Si_2$, and $(C_6H_5)_3GeSi(C_6H_5)_3$.[8,17] The attempt to prepare $(C_6H_5)_3SnSi(CH_3)_3$ from $(CH_3)_3SiCl$ and $(C_6H_5)_3SnLi$ failed, since in this system metal–halogen exchange and its accompanying processes occur preferentially[14]:

$$(C_6H_5)_3SnLi + (CH_3)_3SiCl \longrightarrow (C_6H_5)_3SnCl + (CH_3)_3SiLi,$$

$$(C_6H_5)_2SnCl + (C_6H_5)_3SnLi \longrightarrow LiCl + (C_6H_5)_6Sn_2 \text{ (yield 69\%)},$$

$$(CH_3)_3SiLi + (CH_3)_3SiCl \longrightarrow LiCl + (CH_3)_6Si_2.$$

Blake et al. have made the interesting observation that the interaction of $(CH_3)_3SiCl$ with $(C_4H_9)_3SnLi$ is preceded by dissociation of the latter compound[22]:

$$(C_4H_9)_3SnLi \rightleftarrows (C_4H_9)_2Sn + C_4H_9Li,$$

$$C_4H_9Li + (CH_3)_3SiCl \longrightarrow LiCl + (CH_3)_3SiC_4H_9,$$

the yield of butyltrimethylsilane being 54%. Such a process is not characteristic of the reaction of triphenylstannyl-lithium with triphenylchlorosilane[14].

Method A has been employed also for the synthesis of organodielementary compounds containing Si–Hg bonds. Attempts to use the reaction of triphenylsilyl-lithium with mercury halides, phenylmercuric chloride, or diphenylmercury were unsuccessful[23]. It was therefore supposed