BORON SUBHALIDES AND RELATED COMPOUNDS WITH BORON-BORON BONDS

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I. INTRODUCTION

The boron subhalides are those halides in which the halogen to boron ratio is less than three. This review is mainly concerned with the chemistry of the diboron tetrahalides B_2X_4 and compounds derived from them. Most of these compounds contain two or more directly linked boron atoms; such linkages are found also in the higher boron hydrides, but consideration of these latter compounds is excluded from this review except insofar as their properties correlate with the simpler boron–boron compounds.

There is at present no accepted system of nomenclature for compounds containing boron–boron bonds, other than the name "hypoboric acid" for $B_2(OH)_4$, recommended by IUPAC (45). It is unfortunate that the word "borine" is still used for derivatives of BH_3 as well as the more recent "borane" since such usage makes the use of "diborine" (a suggested name for the hypothetical hydride B_2H_4 (103)) ambiguous. We shall use here the simple designation "——diboron" for compounds containing one B–B unit, except for the tetrahalides B_2X_4 where the now commonly accepted names will be used.

The first boron subhalide to be identified was diboron tetrachloride; it was obtained in an impure state and very low yield by passage of an electric discharge between zinc electrodes immersed in liquid boron trichloride (89). Perhaps because of the difficulties of the preparation, and the instability of the tetrachloride, few studies were made at the time (1925). Nor were many other studies reported until about twenty years later, when Schlesinger and his co-workers at Chicago re-investigated the preparation to examine the possibility of using the tetrachloride to obtain the hydride B_2H_4 (103). It may be noted that in 1925 the chemistry of the boron hydrides already had received much investigation, but the idea that these compounds were analogous to the silanes in structure (88), *i.e.*, having only simple B–H and B–B bonds, influenced the direction of work until after World War II. Thus Stock stated that "diboron tetrachloride and its products of hydrolysis, together with the boron hydrides, illustrate the chain linkage of boron atoms" (88). Had it been recognized earlier that diboron tetrachloride, and not diborane, contains a simple B–B bond, investigations might have been stimulated.

Lack of progress in boron subhalide studies may also be explained by the fact that they rarely are formed by any chemical reduction of the boron trihalides. Thus reduction of the trichloride (60) or the tribromide (54) by passage of halide/hydrogen mixtures over heated metal filaments yielded mainly elementary boron, with hydrogen chloride and diborane when the trichloride was used. Reduction of boron trichloride by hydrogen at 200–500° in the presence of various metals also yields diborane (44). Reduction of boron trihalides by alkali metals has also been investigated; sodium vapor with boron trichloride gives sodium chloride and boron (73), and alkali metals dissolved in various ether-type solvents give no subhalides, side reactions producing alkanes and alkyl halides (22, 67, 83). Mixtures of sodium/potassium alloy and boron tribromide detonated violently on slight shock (83). Liquid zinc reduced the trichloride to boron (24). Boron trichloride or a mixture of the trichloride and trifluoride remained unchanged in a silent electric discharge (13, 67, 78); in the presence of mercury, boron trichloride formed boron and mercurous chloride in a 35 kv. silent discharge (67). Mixtures of boron trichloride and carbon monoxide did not yield diboron tetrachloride in an 11 kv. silent discharge, although reaction to give polymeric products $(BCl_3 \cdot 2CO)_x$ occurred (79). The trifluoride and carbon monoxide reacted similarly. No reaction has been detected between nickel carbonyl and boron trichloride (71).

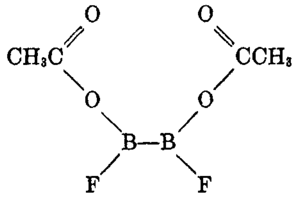
In the now classical preparation of diborane by passage of an electric discharge through mixtures of boron trihalide and hydrogen (80, 81, 92), it was found possible to isolate small quantities of diboron tetrachloride from the exit gases if a high trichloride/hydrogen ratio (1.5:1) was used (90). This was the basis of the discharge methods later developed by Schlesinger and others to give the first effective means of preparing diboron tetrachloride; these methods are described in Section IIA.

It is appropriate now to refer to other approaches to the problem of forming boron–boron bonds. The reaction of chlorodialkoxyboranes with sodium amalgam was reported (106) to yield tetra-alkoxydiborons, $B_2(OR)_4$; attempts to repeat this work have been unsuccessful, but the similar reaction of chloro- or bromobis-(dimethylamino)-borane with highly dispersed alkali metals gives excellent yields of tetra-(dimethylamino)-diboron (15, 71). Quantities of the order of hundreds of grams can be prepared in each experiment, contrasting sharply with the yields of ~1 g. of diboron tetrachloride obtainable by arc discharge methods. The general properties of the amino- and alkoxydiborons are discussed later (Sections II-C-2, II-C-3), but it may be noted here that their conversion to boron monoxide, and treatment of the latter with boron trichloride, gives good yields of diboron tetrachloride, thus establishing the first synthesis of the latter in quantity by a method not involving an electric arc.

Another possibility of obtaining boron–boron bonds is by formation of diborates $M^I_2[B_2X_6]$. The colored compounds obtained when alkali metals react with triaryl boranes, *e.g.*, $NaB(C_6H_5)_3$, are diamagnetic under certain conditions (18) and may be dimerized, *i.e.*, $Na_2B_2(C_6H_5)_6$; there is, however, no direct evidence for such structures. The reaction of sodium in liquid ammonia with tetramethyldiborane gives the compound Na_2BHMe_2 and this can add on one mole of boron trimethyl to give $Na_2B_2Me_5H$ which is considered to contain a direct boron–boron bond (16). Thermal decomposition of triallylborane yields diallyl and a compound which corresponds in analysis and molecular weight to tetra-allyl diboron (107)

$$2(C_3H_5)_3B \rightarrow (C_3H_5)_2 + (C_3H_5)_4B_2$$

The reaction of acetyl chloride with dihydroxyfluoroboric acid yields an acetoxyboron fluoride for which the formula $(CH_3CO{\cdot}OBF)_2$ is suggested (52); a possible structure for this compound involves boron–boron bonds, *viz.*



II. DIBORON TETRACHLORIDE

A. METHODS OF PREPARATION

As previously mentioned (Section I) the initial preparation of diboron tetrachloride by the reduction of liquid boron trichloride using an arc between zinc electrodes gave a very poor yield (89). When the reduction was carried out in the vapor phase by passing boron trichloride at 1–2 mm. pressure through a mercury arc maintained at 15–24 ma., the yield of diboron tetrachloride increased considerably; mercury vapor was considered to be responsible for the reduction (83)

$$2BCl_3 + 2Hg \rightarrow B_2Cl_4 + Hg_2Cl_2$$

The boron trichloride was transferred through the arc by sublimation under high vacuum from a trap held at −78° into a second trap at −196° on the far side of the arc.

Several refinements in the arc production of diboron tetrachloride have resulted in higher yields. By mounting two discharge cells in series to the gas flow, 19.7 g. of the pure tetrachloride was isolated over a period of six months (2). By using higher currents of about 500 ma. one mmole (0.16 g.) of diboron tetrachloride could be produced per hour; using a d.c. arc it was possible to establish a linear relationship between arc current and yield of tetrachloride (37, 67). The use of either a relay-operated mercury pump (97) or a three-jet single stage mercury diffusion pump (38) gives a more efficient transfer of boron trichloride through the arc. The formation of diboron tetrachloride by arc-reduction of boron trichloride is always accompanied by the formation of other monochlorides $(BCl)_n$ (Section III); it appears to be inhibited by traces of hydrogen chloride.

The microwave excitation of boron trichloride at 1–2 mm. pressure results in the formation of diboron tetrachloride, the reaction being (28)

$$2BCl_3 \rightarrow B_2Cl_4 + Cl_2$$

No boron monochlorides were apparent in these experiments, but the spectrum of the glow discharge induced in the boron trichloride by the microwave energy contained only lines which could be attributed to BCl radicals. With the reservations that BCl_2 radicals may be too unstable for their spectrum to be obtained (or that their spectrum was in a region not examined) it was suggested (43) that the BCl radical might be an intermediate in the formation of diboron tetrachloride. The appearance of tetraboron tetrachloride B_4Cl_4 and $(BCl)_n$ in the arc preparations supports this postulate.

Three promising methods of preparing the tetrachloride which do not employ discharges have been described. The reduction of boron trichloride at 900–1000° gives small yields of diboron tetrachloride (71), and the reaction of boron trichloride with tetra-(dimethylamino)-diboron (Section II-C-2) also is reported to give the tetrachloride (71). A high yield of diboron tetrachloride is obtained by passage of boron trichloride over boron monoxide, using a short time of contact at 200–300° (86); the possibility of obtaining the monoxide without the necessity of making a diboron compound first (Section VIII) makes this method one of great potential value.

B. PHYSICAL PROPERTIES AND STRUCTURE

Diboron tetrachloride is a colorless liquid which decomposes at temperatures above 0° (103); its physical characteristics must therefore be observed at low temperatures. The vapor pressure–temperature curve is given by (97)

$$\log p_{\mathrm{mm}} = 8.057 - (1753/T)$$

corresponding to a boiling point of 65.5° and giving the heat of evaporation as 8029 cal./mole and the Trouton constant 23.7. By careful handling and using rapid transfers, a sample of purity 98.5% has been prepared (56) and used to obtain thermodynamic data; this specimen gave a melting range −99 to −93°, the estimated m.p. of pure diboron tetrachloride being −92.95°. The average heat of fusion is 2579 ± 4 cal./mole and the heat capacity measured over the range 20–220°K. shows no abnormalities.

Measurements of the heat of chlorination of diboron tetrachloride give ΔH^0 for the reaction

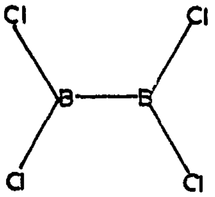
$$B_2Cl_4(l) + Cl_2(g) \rightarrow 2BCl_3(g)$$

as −68 ± 2 kcal./mole and a standard heat of formation of −126.2 kcal./mole for the liquid. Assuming the thermochemical bond energy for the B–Cl bonds is equal to that in boron trichloride, then E(B–B) is calculated as 79 kcal., to be compared with the dissociation energy of B_2 of 69 kcal. (30).

The structure of solid diboron tetrachloride has been examined by X-ray diffraction (11) and an electron diffraction study has been made on the vapor (34). The bond lengths (in Å.) and the bond angles observed are shown in Table I. The good agreement for the bond lengths and Cl–B–Cl angle is in contrast to the different symmetry assignments; a planar structure I is indicated in the solid state while the structure II in the vapor has the two BCl_2 planes at right angles. Examination of the infrared and Raman spectra (55, 62) has confirmed the nonplanar structure II in the liquid and vapor states.

TABLE 1

B–Cl	B–B	Cl–B–Cl	Symmetry	Reference
1.728 ± 0.020	1.75 ± 0.05	120.5 ± 1.3°	V_h	11
1.73 ± 0.02	1.73 – 1.76	120°	V_d	34



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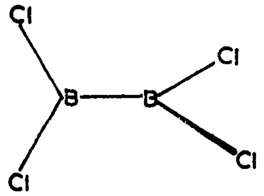


II

Calculation of the energy barrier to rotation about the B–B bond, assuming only ordinary van der Waals repulsions between nonbonded atoms, gives a lower result than that obtained from calorimetric data, 1.7 ± 0.6 kcal./mole (64).

The B–Cl bonds in diboron tetrachloride differ only slightly in length from those in boron trichloride (1.75 Å.) and the quadrupole coupling constants for Cl^{35} (38.65 and 40.38 Mc. for solid diboron tetrachloride) are close to the value 43.2 Mc. for boron trichloride (57). The B–B bond length is somewhat greater than that expected (1.60 Å.) for a "normal" B–B bond (33), but the boron radius can vary with different environmental factors and the calculated stretching frequency and force constant (34) do not suggest that the B–B bond is abnormal.

In solid diboron tetrachloride, the intermolecular distances are as expected, and the crystal is essentially molecular; there is some slight evidence of weak intermolecular π-interaction between the chlorine atom on one tetrachloride molecule and the B–B region of an adjacent molecule (11).

The structural evidence suggests that the boron atoms in diboron tetrachloride each form three coplanar σ-bonds by using sp^2 hybrid orbitals as in boron trichloride. The similar B–Cl bond lengths in diboron tetrachloride and boron trichloride suggest that some π-donation from the chlorine to the boron atoms occurs also in the tetrachloride. The structures of tetraboron tetrachloride and octaboron octachloride (Sections III-A, III-B) require that π electrons from the chlorine atoms participate in the B_4 and B_8 ring systems and are not confined to the B–Cl bonds only. In liquid or vapor form, donation of π electrons from the chlorine atoms of diboron tetrachloride to both boron atoms may impose the observed configuration; in the solid, π donation from the chlorine atom of one molecule to the B–B system of an adjacent molecule may permit the planar structure. The foregoing physical data do not suggest that the B–B bond in diboron tetrachloride is particularly weak; the instability of the compound and its high reactivity (to be discussed in following sections) must therefore arise because of the direct bonding of two acceptor atoms with formally vacant p-orbitals—a unique situation so far as first row elements of the Periodic Table are concerned. If this view is correct, then in any compound $X_2B\text{-}BX_2$ the ability of X to fill the vacant boron orbitals by π donation $X \rightarrow B$ may determine the stability. In support of this view, compounds where X does not contain any lone pairs of electrons have not been isolated; diboron tetrafluoride (Section IV) is more stable than the tetrachloride and rather less reactive; and compounds of the type $B_2(NR_2)_4$ and $B_2(OR)_4$ are more stable than any of the tetrahalides.

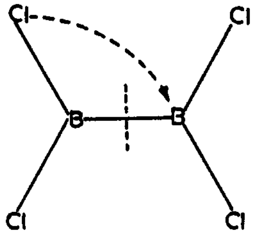
C. CHEMICAL PROPERTIES

1. Thermal Decomposition and Chloride Substitution Reactions

The properties to be discussed in this Section are those where donation of a reacting species does not appear to be an essential precursor of reaction.

Reference has been made (Section II-B) to the decomposition of diboron tetrachloride above 0° and to the difficulty of obtaining a pure specimen. Additionally, the inflammability and ease of hydrolysis necessitate handling in a high vacuum out of contact with grease and other contaminants which react readily. The rate of decomposition at 0° is much influenced by other substances; many accelerate decomposition, but some haloethylenes have a stabilizing effect, possibly by loose compound formation (17, 25), and these might be used as solvents; however, most reactions so far reported have been studied in the absence of solvent. The low stability and reactivity of diboron tetrachloride often preclude the attainment of whole-number stoichiometry in the reactions studied.

Diboron tetrachloride decomposes to give boron trichloride and a less volatile residue of over-all composition $(BCl_n)_x$ where $n \rightarrow 1$ (97). This residue contains the moderately volatile pale yellow tetraboron tetrachloride (Section IIIA), the red octaboron octachloride (Section IIIB) and a white nonvolatile solid $(BCl_{0.6})_y$. The decomposition to give boron trichloride and $(BCl_n)_x$ is often accelerated initially when a donor molecule D (*e.g.*, pyridine) is added, since this removes boron trichloride as the adduct $D \rightarrow BCl_3$; the donor also undergoes coördination with unchanged diboron tetrachloride to give an adduct which is usually stable, and further decomposition therefore ceases. The unsymmetrical mode of decomposition and the initial destabilization by a donor suggest that decomposition may be a unimolecular process involving internal coördination (III) and rupture of the weakened B–B bond, rather than by direct B–B bond fission or by a bimolecular mechanism; the function of the destabilizing donor may be to assist the process III by initially coördinating at one boron atom.



III

Diboron tetrachloride does not react with iodine, sulfur, or white phosphorus at ordinary temperatures, but reacts readily with chlorine and bromine below 0° (3)

$$Cl_2 + B_2Cl_4 \rightarrow 2BCl_3$$

$$3Br_2 + 3B_2Cl_4 \rightarrow 2BBr_3 + 4BCl_3$$

Reaction with antimony trifluoride yields diboron tetrafluoride (Section IV) and boron tribromide gives diboron tetrabromide (Section V). Hydrogen reacts readily at ordinary temperatures or below (97); liquid diboron tetrachloride gives a variety of products including boron trichloride, diborane and unidentified solids, and viscous liquids. With diboron tetrachloride vapor, the predominant reaction is

$$3B_2Cl_4 + 3H_2 \rightarrow 4BCl_3 + B_2H_6$$

Monochlorodiborane is also produced. This reaction probably proceeds by direct addition of the hydrogen to give $B_2Cl_4H_2$ which then disproportionates to give the observed products.

Diboron tetrachloride does not react with lithium aluminum hydride in the presence or absence of ether, but both lithium and aluminum borohydride react readily at low temperatures giving diborane and higher boron hydrides (97); the initial reaction appears to be

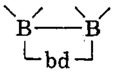
$$B_2Cl_4 + 4LiBH_4 \rightarrow B_4H_{10} + B_2H_6 + 4LiCl$$

the other boranes then being formed by decomposition or reaction of the unstable tetraborane. Treatment of diboron tetrachloride with diborane in the absence of solvent gives a complex mixture of products, but in the presence of ether at −23° a 1:1 addition reaction occurs, the product decomposing on removal of ether to give a colorless product formulated as $(B_2Cl_4\cdot BH_3)2(C_2H_5)_2O$ (97).

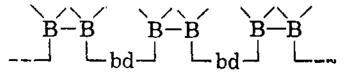
Attempts to replace the chlorine atoms of diboron tetrachloride by methyl groups (*e.g.*, by reaction with dimethylzinc) have been unsuccessful, the products being trimethylborane and unidentified black solids (97). (The reaction of dimethylchloroborane with sodium also failed to produce tetramethyldiboron (106).)

2. Addition Reactions with Nitrogen-containing Donor Molecules

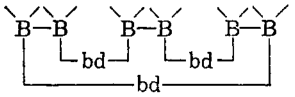
The presence of two boron atoms each with a vacant orbital in diboron tetrachloride suggests that one or both may act as acceptors as does the boron atom in boron trichloride. However, it seems in general that the stability of the adduct formed by a donor molecule D and the tetrachloride is greater for $2D,B_2Cl_4$ than for D,B_2Cl_4, for with the latter elimination of the adduct D,BCl_3 may lead to rapid decomposition in the absence of excess of D (Section II-C-1). As with boron trichloride, elimination of hydrogen chloride from an adduct where the donor has reactive hydrogen atoms can be expected to follow donation. The presence of two adjacent, directly bonded boron atoms in the diboron compounds leads to specific acceptor properties toward π-bonded molecules, such as those considered in Section II-C-4; it also permits, in theory, 1:1 donation by bidentate donor molecules in two possible ways, either to a single molecule (IV) or by chain or ring formation (V, VI) (bd for bidentate donor).



IV



V



VI

It is convenient to deal first with those nitrogen-donor molecules where elimination of hydrogen chloride does not occur. Trimethylamine forms with diboron tetrachloride the white stable adduct $2Me_3N,B_2Cl_4$ by direct reaction at low temperatures (97). The adduct retains B–B bonding, reacting with alkali to give hydrogen, and possesses high thermal stability, showing no decomposition below the m.p. at ~228°. These properties and the low reactivity (*e.g.*, no hydrogen chloride formed by reaction with an alcohol) suggest the structure $Me_3\overset{+}{N}\cdot\overset{-}{B}Cl_2\cdot\overset{-}{B}Cl_2\cdot\overset{+}{N}Me_3$. However a specimen recrystallized from benzene and purified by fractional sublimation had a molecular weight in benzene corresponding to the tetramer $[(Me_3N)_2B_2Cl_4]_4$ and unpurified samples may contain more highly polymerized material (36). Diboron tetrachloride is not displaced from the adduct by boron trichloride or boron trifluoride; methylation could not be effected by dimethylcadmium and the attempted reduction by lithium aluminum hydride or borohydride gave a complex mixture of products (97). The adduct can take up other molecules; addition of 2 moles of hydrogen chloride without loss of any volatile product occurs (36), and 2:1 addition of hydrogen cyanide or methyl cyanide (36) and of ethyl alcohol (97) is also observed; in all these cases the B–B bond is retained. These facts suggest formation of a diborate $[Me_3NR]_2[B_2Cl_4X_2]$ where R = Me, Et, H; X = OH, Cl, CN, analogous to the formation of a tetrachloroborate containing the anion BCl_4^- from adducts of boron trichloride. Support for this view has been obtained where X = Cl by conductometric titration of diboron tetrachloride in anhydrous hydrogen chloride as solvent with tetramethylammonium chloride; the end-point corresponds to the reaction

$$B_2Cl_4 + 2Me_4NCl \rightarrow (Me_4N)_2B_2Cl_6$$

and the solid quaternary diborate is precipitated as a white solid (42).

Pyridine forms a white solid adduct with diboron tetrachloride $(C_5H_5N)_2,B_2Cl_4$ and this is thermally stable. Hydrolysis indicates some loss of B–B bonding in the adduct, and the uptake of hydrogen chloride does not approach the 2:1 ratio achieved for the trimethylamine adduct (36); this may be due to a rearrangement of the structure (*cf.* the boron trichloride–pyridine adduct for which $[(C_5H_5N)_2BCl][BCl_4]$ is a possible structure (29)).

Hydrogen cyanide and methyl cyanide both form 2:1 adducts with diboron tetrachloride. The methyl cyanide adduct shows some dissociation at 130°; reaction with trimethylamine displaces some methyl cyanide but addition to form the diborate $[(Me_4N)_2][B_2Cl_4(CN)_2]$ also occurs (36). The bidentate donor molecule of N,N′-tetramethylethylenediamine undergoes 1:1 addition with diboron tetrachloride, indicating donation by both nitrogen atoms; the product retains B–B bonding but reacts very slowly with hydrogen chloride and is insoluble in organic solvents, suggesting a chain structure (V) rather than (IV). None of the adducts just discussed reacts with simple olefins as does the uncoördinated diboron tetrachloride.

Donor molecules which can eliminate hydrogen chloride as the hydrochloride of the donor base react with diboron tetrachloride:

Ammonia (97)

$$xB_2Cl_4 + 6xNH_3 \rightarrow 4xNH_4Cl + [B_2(NH)_2]_x$$

Dimethylamine (36, 97)

$$B_2Cl_4 + 8NHMe_2 \rightarrow 4NH_2Me_2Cl + B_2(NMe_2)_4$$

Hydrazine (36)

$$xB_2Cl_4 + 5xN_2H_4 \rightarrow 4xN_2H_5Cl + (B_2N_2)_x$$

N,N-Dimethylhydrazine (36)

$$xB_2Cl_4 + 3xMe_2N\cdot NH_2 \rightarrow 2xMe_2N\cdot NH_3Cl + (Cl_2BNMe_2BN)_x$$

Ethylenediamine (36)

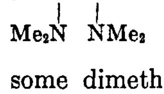
$$xB_2Cl_4 + 5x(CH_2NH_2)_2 \rightarrow 4x[(CH_2NH_2)_2HCl] + [B_2(NCH_2)_2]_x$$

Except with dimethylamine, the products are in each case involatile white solids, in which B–B bonding is substantially retained; the nature of the products suggests that they are polymeric. Dimethylamine, however, gives a mixture of tetra-(dimethylamino)-diboron (as indicated by the equation above) and also some tri-(dimethylamino)-borane, with a nonvolatile residue presumably containing $(BNMe_2)_x$ (36). As already stated (Section I), tetra-(dimethylamino)-diboron has been prepared by a method not involving prior formation of a diboron compound. This compound is monomeric in benzene and yields 1 mole of hydrogen with alkali, indicating B–B bonding. In contrast to the diboron tetrahalides it is stable in dry air up to 200° and does not react with oxygen at 100°. Other amino-diborons $B_2(NHR)_4$ (*e.g.*, R = Me, $(CH_2)_5CH_3$, C_6H_5) are prepared from it readily by trans-amination. Reaction with an alcohol in presence of hydrogen chloride yields tetra-alkoxydiborons (Section II-C-3); acid hydrolysis gives hypoboric acid (Section VIII) (15). The reaction of tetra-(dimethylamino)-diboron with boron trichloride gives some diboron tetrachloride as well as the compound $B_2(NMe_2)_2Cl_2$ (71).

The retention of some B–B bonding in the reaction product $(B_2N_2)_x$ obtained when hydrazine and diboron tetrachloride were allowed to react indicates that this product is not identical with boron nitride (36). The reactions with N,N-dimethylhydrazine and ethylenediamine gave solid products possessing some thermal stability (36).

It is now appropriate to refer to some reactions of nitrogen donors with diboron tetrachloride where simple donation by the nitrogen atom either does not occur or is accompanied by some other mode of addition. With tetramethylaminoborane $Me_2N{:}BMe_2$, the predominant reaction of diboron tetrachloride is acceptance of 2 moles of the borane through the nitrogen atoms and then elimination of dimethylchloroborane and formation of the compound (VII).

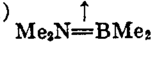
(VII)



$$\begin{array}{c}Cl\!-\!B\!-\!B\!-\!Cl\\ \quad|\qquad|\\ Me_2N\ \ NMe_2\end{array}$$

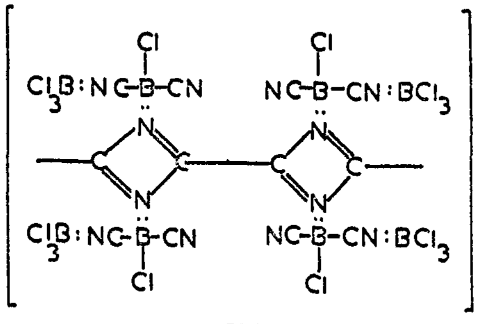
However, formation of some dimethylaminodichloroborane and polymeric $(BCl)_x$ suggests that π-donation might occur (41)

(VIII)



$$\begin{array}{c}Cl_2B\!-\!BCl_2\\ \uparrow\\ Me_2N\!=\!BMe_2\end{array} \rightarrow Me_2NBCl_2 + Me_2BCl + BCl$$

The reaction of cyanogen with diboron tetrachloride gives the solid addition compound B_2Cl_4, 1.5 $(CN)_2$ (4). This adduct readily adds on 2 moles of trimethylamine at low temperatures, contains no B–B bonding, and yields 1 mole of boron trichloride on thermal decomposition; the structure (IX) has been suggested on the basis of these properties. However, these same properties are shown by diboron tetrachloride-olefin adducts, where a carbon chain bridges two BCl_2 groups rather than BCl and BCl_3 (Section II-C-4); the structural unit $Cl_2B(CN)_xBCl_2$ may also therefore occur in the cyanogen adduct.



(IX)

Addition of excess nitric oxide to diboron tetrachloride at low temperatures produces a green solid adduct NO, B_2Cl_4 stable at −78° and unaffected by oxygen or ethylene at this temperature; further addition of nitric oxide does not occur (40). The adduct decomposes above −40° to give 1 mole of boron trichloride and a glassy white solid; this decomposition is assisted by addition of trimethylamine. The white solid slowly loses more boron trichloride on standing; if heated to 90 ± 5° the solid erupts violently in the reaction vessel and becomes incandescent, with rapid loss of boron trichloride but little other decomposition. This thermal change is notably similar to that shown by certain forms of boron monoxide (Section VIII). Complete removal of all the chlorine as boron trichloride is difficult but is assisted by addition of trimethylamine. The residual solid has the empirical formula $B_2(NO)_3$ and possesses considerable thermal stability; hydrolysis yields some ammonia but no nitrate or nitrite. The structure of "$B_2(NO)_3$" is not known, but the evolution of ammonia on hydrolysis suggests nitride formation, and intercalation of boron trichloride in boron nitride is possible. The observed composition $B_2N_3O_3$ clearly does not permit a complete explanation in terms of a mixed BO–BN structure.

The coördination of cyanogen, tetramethylaminoborane, and nitric oxide to diboron tetrachloride seems to imply some kind of π-coördination involving donation from the double bond to the B–B bond; it is worth noting that nitric oxide forms only a very unstable 1:1 adduct with boron trifluoride (27) and hence is not a good donor in the usual sense. Some better examples of

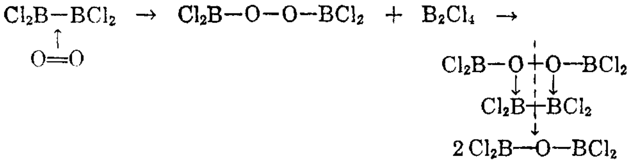
π-coördination occur with olefins and the matter is therefore considered further in Section II-C-4.

3. *Addition Reactions with Oxygen-, Sulfur-, and Phosphorus-containing Donor Molecules*

Oxygen.—Diboron tetrachloride reacts very rapidly with dry oxygen at −78° or below to give boron trichloride and boric oxide (3)

$$6B_2Cl_4 + 3O_2 \rightarrow 8BCl_3 + 2B_2O_3$$

At room temperature violent ignition takes place and free chlorine can be identified among the products. This oxidation has been postulated to proceed initially by π-donation from the oxygen molecule to the B–B bond of the tetrachloride and then rearrangement to give a B–O–O–B linkage; the oxygen atoms here then donate to the boron atoms of a second molecule of the tetrachloride, and the resulting complex breaks down as shown (40)



(X)

$$Cl_2B{-}O{-}BCl_2 \rightarrow BCl_3 + BOCl$$

$$3BOCl \rightarrow BCl_3 + B_2O_3$$

Water.—Stock originally noted (89) that diboron tetrachloride evolved hydrogen on hydrolysis. At 0° very little hydrogen is evolved when distilled water is used, and hypoboric acid is formed (100)

$$B_2Cl_4 + 4H_2O \rightarrow B_2(OH)_4 + 4HCl$$

This reaction probably proceeds by initial coördination of two water molecules to the tetrachloride. Increasing the temperature of hydrolysis produces progressively more hydrogen as the boron–boron bond is attacked, but the reaction is not quantitative until a temperature of 100° is attained (1)

$$B_2(OH)_4 + 2H_2O \rightarrow 2B(OH)_3 + H_2$$

In the presence of concentrated alkali the above hydrolysis is quantitatively complete in 3 hours at 70° (103). This reaction has wide application to compounds containing boron-to-boron linkages, as both a diagnostic test for their presence and as a means of determining quantitatively the extent of B–B bonding.

At 90° *in vacuo*, hypoboric acid begins to lose water but the final traces are only lost after 4 hours at 220° (100); the product is boron monoxide

$$xB_2(OH)_4 \rightarrow 2xH_2O + (B_2O_2)_x$$

Further properties of hypoboric acid and boron monoxide are given in Section VIII.

Hydrogen Sulfide.—At 78° diboron tetrachloride reacts with hydrogen sulfide to form the adducts, H_2S,B_2Cl_4 and $2H_2S,B_2Cl_4$ (101). At room temperature or above cleavage of the B–B bond occurs to give hydrogen, boron sulfide, boron trichloride, and the compounds $B_3Cl_3S_3$ and BCl_2SH

$$3B_2Cl_4 + 3H_2S \rightarrow 4BCl_3 + B_2S_3 + 3H_2$$

$$B_2S_3 + 3H_2S \xrightarrow{90^\circ} 2B(SH)_3$$

$$2B(SH)_3 + 4BCl_3 \xrightarrow{90^\circ} 6BCl_2{\cdot}SH$$

$$B_2S_3 + BCl_3 \rightarrow B_3S_3Cl_3$$

Alcohols.—Rapid and almost quantitative conversion of diboron tetrachloride to the corresponding tetra-alkoxydiboron is achieved readily by addition of methyl or ethyl alcohol (97)

$$B_2Cl_4 + 4ROH \rightarrow 4HCl + B_2(OR)_4$$

The preparation of alkoxydiborons by reaction of an alkali metal and dialkoxychloroboranes has been reported (106); more recently they have been prepared in good yield from the corresponding tetra-alkylaminodiborons, by the reaction (14)

$$B_2(NR_2)_4 + 4ROH + 4HCl \xrightarrow[\text{ether}]{-78^\circ} B_2(OR)_4 + 4NR_2H_2Cl$$

$$(R = Me, Et, CHMe_2, C_6H_5)$$

The tetra-alkoxydiborons are volatile liquids, hydrolyzed by water to give hypoboric acid and by alkali to yield 1 mole of hydrogen. Tetramethoxydiboron is stable up to 110° *in vacuo;* the ethoxy compound decomposes at ~90°, and decomposition gives solids of formula $(BOR)_x$ (86). The alkoxydiborons react only slowly with oxygen; at 25° the ethoxy compound gives ethyl borate and a solid $(EtOBO)_x$ (14).

Ethers.—With excess of diethyl ether, diboron tetrachloride forms a crystalline dietherate $2Et_2O,B_2Cl_4$. At room temperature *in vacuo* the dietherate slowly loses a mole of ether to give the liquid mono-etherate Et_2O,B_2Cl_4, which is unstable and decomposes with elimination of ethyl chloride (97).

Diboron tetrachloride reacts with 4 moles of ethylene oxide to give the liquid tetra-(2-chloroethoxy)-diboron at −78° (68).

$$B_2Cl_4 + 4(CH_2)_2O \rightarrow B_2(OCH_2{\cdot}CH_2Cl)_4$$

Hydrolysis of the product at 0° gives 2-chloroethanol and hypoboric acid; with alkali at 90° hydrogen is produced

$$B_2(OCH_2CH_2Cl)_4 + 4H_2O \xrightarrow{0^\circ} B_2(OH)_4 + 4ClCH_2CH_2OH$$

$$B_2(OCH_2CH_2Cl)_4 + 6H_2O \xrightarrow{90^\circ} H_2 + B(OH)_3 + 4ClCH_2CH_2OH$$

Oxygen is slowly absorbed by tetra-(2-chloroethoxy)-diboron, giving finally boric oxide and tri-(2-chloroethoxy)-borane

$$6B_2(OCH_2CH_2Cl)_4 + 3O_2 \rightarrow 2B_2O_3 + 8B(OCH_2CH_2Cl)_3$$

Reaction with trimethylamine is slow and the uptake achieved is less than that required for donation to both boron atoms. These reactions suggest that tetra-(2-chloroethoxy)-diboron is intermediate in behavior between diboron tetrachloride and tetra-(ethoxy)-diboron, the chlorine atoms of the chloroethoxy groups reducing π-donation to the boron atoms sufficiently to permit weak acceptor behavior to ordinary donors (*e.g.*, trimethylamine) and to π-donors (*e.g.*, oxygen).

Thermal decomposition of tetra-(2-chloroethoxy)-diboron leads to slow loss of B–B bonding at 135°; at 240°, decomposition is rapid giving ethylene, dioxane, ethyl chloride, and 1,2-dichloroethane. The low temperature decomposition is again similar to that observed for other B_2X_4 type compounds, yielding tri-(2-chloroethoxy)-borane (68)

$$nB_2(OCH_2CH_2Cl)_4 \rightarrow nB(OCH_2CH_2Cl)_3 + (ClCH_2CH_2OB)_n$$

Acetone.—Diboron tetrachloride forms a white solid adduct $2Me_2CO,B_2Cl_4$ with acetone at −23°. At higher temperatures, acetone is lost together with hydrogen chloride. Using excess of diboron tetrachloride, reaction ratios approaching the 1:1 value expected for the adduct Me_2CO,B_2Cl_4 can be obtained (66). Heating the adducts to 100° causes rapid evolution of hydrogen chloride and polymerization of the organic residue; the $HCl:B_2Cl_4$ ratio is close to 2:1. At 150°, some hydrogen chloride is lost by attack on the organic residue. Unlike the corresponding reaction between acetone and boron trichloride, alkyl chlorides, *viz.*, 2-chloropropane and *tert*-butyl chloride, are found as products.

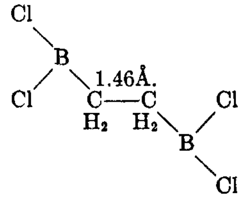
Dimethyl Sulfide.—Dependent on the reaction conditions, diboron tetrachloride and dimethyl sulfide give one of the adducts $2Me_2S,B_2Cl_4$ or Me_2S,B_2Cl_4 (101). Unlike the diethyl ether analog, the bis-(dimethyl sulfide) adduct possesses no dissociation pressure and is stable *in vacuo* at room temperature.

Phosphine.—Diboron tetrachloride and phosphine react at room temperature to give the stable adduct $2PH_3,B_2Cl_4$ (101); conductometric titration of the tetrachloride in anhydrous hydrogen chloride as solvent with phosphorus pentachloride gives evidence for the formation of the unstable hexachlorodiborate $[PCl_4]_2[B_2Cl_6]$ (42).

4. Addition Reactions with Olefins and Other π-Bonded Molecules

Many olefins in the presence of the boron trihalides undergo polymerization. However, acetylene and boron trichloride give 2-chlorovinyl compounds, $(ClCH{=}CH)_nBCl_{3-n}$ (n = 1, 2, or 3), when passed over heated catalysts (5), and addition of some cyclic olefins to boron trichloride has been reported recently (47); it was noted that the olefins which reacted were those which form strong π-bonds with transition metals.

These few examples of boron trihalide–olefin interaction contrast with the many examples of interaction of olefins with diborane in which π-donation may occur (6). More remarkable is the contrast with the boron subhalides where ready interaction with simple olefins is an outstanding and characteristic property. The first reaction studied was that of diboron tetrachloride with ethylene (96); 1:1 addition proceeded readily at −78° to give a colorless liquid adduct which did not yield any hydrogen on hydrolysis and had a vapor density corresponding to $B_2Cl_4 \cdot C_2H_4$. The structure Cl_2B-$CH_2CH_2BCl_2$ was assigned to the compound and confirmed later by structural analysis (10) which showed the molecule to be planar (excluding hydrogens) with the BCl_2– groups in the *trans* position (to the carbon–carbon bond) and trigonal bonds to the boron atoms XI. Therefore it may be named 1,2-bis-(dichloroboryl)-ethane



(XI)

1,2-Bis-(dichloroboryl)-ethane melts at −28.5°; the liquid fumes in moist air but is not spontaneously inflammable unless the air is dry. The boiling point (extrapolated) is 142°, with the vapor pressure-temperature relation

$$\log p_{mm} = 8.230 - (2220/T)$$

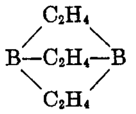
The heat of evaporation is 10.140 kcal./mole and the Trouton constant 24.4 (96). The compound does not react with trimethylborane, but reacts with dimethylzinc, using either trimethylborane or n-pentane as solvent, thus

$$Cl_2BCH_2CH_2BCl_2 + 2ZnMe_2 \rightarrow Me_2BC_2H_4BMe_2 + 2ZnCl_2$$

The product is not very stable, losing trimethylborane slowly at ordinary temperature and more rapidly at 100°, the main reaction being

$$3Me_2BC_2H_4BMe_2 \rightarrow 4BMe_3 + B_2(C_2H_4)_3$$

Structures such as (XII) have been suggested for $B_2(C_2H_4)_3$ (96).



(XII)

Hydrogenation of 1,2-bis-(dichloroboryl)-ethane has been partially achieved using diborane or lithium borohydride, but the products were unstable and were not identified (96).

The two boron atoms in 1,2-bis-(dichloroboryl)-ethane are both formally trivalent and therefore should possess acceptor properties. Hence two moles of trimethylamine are absorbed readily to give a white solid adduct (38) which is stable in contact with air, water, methyl alcohol, and hydrogen chloride at room temperature; on slight heating, the adduct absorbs two moles of hydrogen chloride, the diborate $[NMe_3H]_2^{++}$-$[B_2Cl_6.C_2H_4]^{--}$ probably being formed (*cf.* formation of the hexachlorodiborate anion, Section II-C-2).

With ammonia, monomethylamine and dimethylamine the initial addition of amine is followed by secondary reactions in which hydrogen chloride is eliminated and this reacts further with excess amine to form the hydrochlorides (38)

$$xB_2Cl_4C_2H_4 + 6xNH_3 \rightarrow 4xNH_4Cl + [B_2(NH)_2C_2H_4]_x$$

$$xB_2Cl_4C_2H_4 + 6xNH_2Me \rightarrow 4xNH_3MeCl + [B_2(NMe)_2C_2H_4]_x$$

$$B_2Cl_4C_2H_4 + 8NHMe_2 \rightarrow 4NMe_2H_2Cl + B_2(NMe_2)_4C_2H_4$$

The hydrolysis of 1,2-bis-(dichloroboryl)-ethane with distilled water produces four moles of hydrogen chloride and the acid $B_2(OH)_4C_2H_4$, an air-stable white solid which loses two moles of water reversibly *in vacuo* at 120° (38)

$$B_2Cl_4C_2H_4 + 4H_2O \rightarrow 4HCl + B_2(OH)_4C_2H_4$$

$$B_2(OH)_4C_2H_4 \rightleftarrows 2H_2O + B_2O_2C_2H_4$$

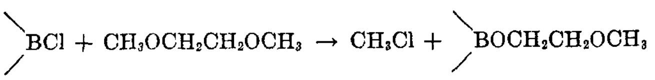
Addition of mannitol to the aqueous acid gives enhanced monobasic acid behavior (*cf.* mannitol and hypoboric acid, Section VIII).

In a remarkable reaction, 1,2-bis-(dichloroboryl)-ethane and dry oxygen produce ethylene in yields as high as 50%. At room temperature the mixture ignites with a vivid green flask producing carbon monoxide, carbon dioxide, and hydrogen chloride. Below −3° no ignition occurs and one mole of oxygen is absorbed to give ethylene, boron trichloride, and hydrogen chloride. The yield of ethylene is markedly dependent on temperature, falling from 45–50% at 22° to almost zero at −78° (38).

Methanolysis produces 1,2-bis-(dimethoxyboryl)-ethane in high yield (96)

$$B_2Cl_4C_2H_4 + 4CH_3OH \rightarrow B_2(OCH_3)_4C_2H_4 + 4HCl$$

On prolonged heating in sealed tubes at 150°, 1,2-bis-(dichloroboryl)-ethane and propionic acid produce almost quantitative yields of ethane; traces of ethylene, methane, and hydrogen also are formed (20, 65). In the presence of ethylene glycol dimethyl ether as solvent, much methyl chloride is evolved because of an ether-splitting reaction between the solvent and the 1,2-bis-(dichloroboryl)-ethane:



$$\gt BCl + CH_3OCH_2CH_2OCH_3 \rightarrow CH_3Cl + \gt BOCH_2CH_2OCH_3$$

1,2-Bis-(dichloroboryl)-ethane is very stable thermally; after four days at 200° only 50% decomposition occurs. At 500° charring is rapid, to give methane, hydrogen, ethane, boron trichloride, methyl boron dichloride, and, possibly, dichloroborane BCl_2H. The ratio $BCl_3/B_2Cl_4C_2H_4$ is *ca.* 1.1:1, showing that all the chloride is not evolved as boron trichloride (39)

$$3B_2Cl_4C_2H_4 \rightarrow 4BCl_3 + B_2(C_2H_4)_3$$

No carbon–chloride compounds are detected but traces of yellow boron monochloride $(BCl)_x$ are observed.

Acetylene and cyclopropane react with diboron tetrachloride much as does ethylene (96), in a 1:1 ratio; a more extended study of the reaction of diboron tetrachloride with other olefins and di-olefins also has been made (17). Although the 1:1 acetylene adduct still contains C=C bonds, no further addition of diboron tetrachloride occurs, nor does addition to form a stable adduct occur between diboron tetrachloride and vinyl halides or other halo-ethylenes. The effect of BCl_2-groups adjacent to double bonds is therefore similar to halogen atoms in decreasing the reactivity of the double bonds. If, however, chlorine or BCl_2-groups are attached to carbon atoms not involved in double-bonding, then their inhibiting effect is much less evident. Thus allyl chloride and 4-chlorobutene-1 form 1:1 addition compounds with diboron tetrachloride, although the allyl chloride adduct decomposes easily. Allyl fluoride gives the reaction

$$4C_3H_5F + B_2Cl_4 \rightarrow 4C_3H_5Cl + B_2F_4$$

With butadiene, addition of either 1 or 2 moles of diboron tetrachloride can be achieved. Although haloethylenes do not form 1:1 adducts, they have been observed (17) to stabilize diboron tetrachloride, decomposition of the latter not occurring in some cases until temperatures as high as 100° have been achieved. Stabilization is also observed with trichloroethylene (25) and here n.m.r. studies of the mixture with diboron tetrachloride indicate some degree of adduct formation, although no adduct has been isolated. The formation of a π-complex, retaining the olefinic double bond, could prevent decomposition of the diboron tetrachloride.

Isobutene is polymerized rapidly by diboron tetrachloride, and no adduct has been isolated (25). Addition of butene-2 to diboron tetrachloride occurs to give a 1:1 adduct, with m.p. reported as −44.8° (17). A further study of this reaction using either *cis*- or *trans*-butene-2 gives 1:1 adducts which, though chemically identical and all having the same vapor pressure–temperature curves as previously reported show wide variations in melting point; for different samples, the melting range is not correlated with the particular butene-2 isomer used (25). An investigation of the n.m.r. spectra of these samples suggests that the melting point variations are due to mixtures of rotational isomers, the amounts of each varying in each preparation, and the energy barriers separating the isomers being too high to permit interconversion below 60°. There is no evidence for double bonding in these compounds, and hindered rotation of the CH_3 groups about the C–C bond must be due to steric interference by the BCl_2 groups. The butene-2 adduct is therefore formulated as 1,2-bis-(dichloroboryl)-*n*-butane $Cl_2B \cdot CHMeCHMe$-

BCl_2. The reactions of this compound are comparable with those of the corresponding ethane; thus, addition of 2 moles of trimethylamine occurs readily to give a stable adduct; this can further add on 2 moles of hydrogen chloride to give a compound $[Me_3NH]_2^+$ $[Cl_3BCHMeCHMeBCl_3]^-$.

The bis-borylbutane reacts with 6 moles of ammonia to give a compound $[B_2(NH)_4C_4H_8]_n$. Hydrolysis yields the acid $(HO)_2BCHMeCHMeB(OH)_2$, acidity again being enhanced by mannitol addition. However, the reaction of oxygen with the bis-borylbutane is much less vigorous than with the ethane, and no butene is formed; the chief products are hydrogen chloride and a nonvolatile solid, with a small amount of 2-chlorobutane (25). Methylation with zinc dimethyl gives 1,2-bis-(dimethylboryl)-*n*-butane, b.p. 127° (17).

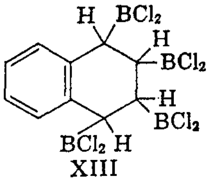
The reaction of diboron tetrachloride and benzene at room temperature gives, after many days, a high yield of phenyldichloroborane (102); but all the benzene and diboron tetrachloride disappear earlier in the reaction period, with evolution of 1 mole of boron trichloride; the suggested reaction scheme is

$$2B_2Cl_4 + C_6H_6 \xrightarrow{\text{slow}} C_6H_6\cdot 2B_2Cl_4$$

$$C_6H_6\cdot 2B_2Cl_4 \xrightarrow{\text{fast}} C_6H_6\cdot 2BCl + 2BCl_3$$

$$C_6H_6\cdot 2BCl \xrightarrow{\text{slow}} C_6H_5BCl_2 + \text{other products}$$

When naphthalene and diboron tetrachloride are mixed at room temperature, an immediate yellow coloration is observed, but the reactants are still separable. After two weeks, the diboron tetrachloride has disappeared and a yellow liquid $C_{10}H_8\cdot 2B_2Cl_4$ is formed. This loses all the chlorine as chloride on hydrolysis, gives no hydrogen on hydrolysis with alkali, and the n.m.r. spectrum gives peaks for protons in both a benzene- and a saturated-type ring; on the basis of this evidence the structure (XIII) has been suggested (102). This compound decomposes on heating to 140°, giving boron trichloride and a yellow solid. It absorbs only 3 moles of trimethylamine; coördination of a fourth molecule probably is prevented by steric limitations.



XIII

The physical properties of diboron tetrachloride addition compounds with some unsaturated organic compounds are given in Table 2. The constants *A* and *B* refer to the vapor pressure–temperature equation, $\log p_{mm} = A - B/T$; H = heat of vaporization (cal./mole).

TABLE 2

Compound	M.p., °C.	B.p., °C.	*A*	*B*	*H*	Trouton constant	Ref.
B_2Cl_4, C_2H_4	−28.5	142	8.230	2220	10,140	24.4	17
B_2Cl_4, CH_3CHCH_2	−130	165	7.701	2105	9,600	22.1	17
B_2Cl_4, $(CH_3CH)_2$	Variable	171	8.147	2339	10,700	24.1	17, 25
B_2Cl_4, $(CH_2)_3$	−69.2	152	7.873	2123	9,880	22.8	17
B_2Cl_4, C_2H_2	−129 to −130	144	7.666	1995	9,100	21.8	17

It is of interest to note that several compounds containing B–C–C–B units have been prepared by methods not involving the boron sub-halides. Thus, 1,2-bis-(dialkylboryl)-acetylene has been prepared by the reaction of a dialkyl boron iodide on the Grignard reagent BrMgC≡CMgBr (32)

$$2R_2BI + Br_2Mg_2C_2 \rightarrow 2MgIBr + R_2BC{\equiv}CBR_2$$

The product is soluble in benzene, diethyl ether, carbon tetrachloride and chloroform but insoluble in petroleum ether. With water, free acetylene is produced (*cf.* 1,2-bis-(dichloroboryl)-ethane which produced no alkane on hydrolysis at 100°)

$$R_2BC{\equiv}CBR_2 + 2H_2O \rightarrow 2R_2BOH + C_2H_2$$

Two moles of oxygen are absorbed to produce 1,2-bis-(dialkoxyboryl)-acetylene

$$R_2BC{\equiv}CBR_2 + 2O_2 \rightarrow (RO)_2BC{\equiv}CB(OR)_2$$

$$(RO)_2BC{\equiv}CB(OR)_2 + 6H_2O \rightarrow C_2H_2 + 4ROH + 2B(OH)_3$$

Other workers have been unable to repeat this type of preparation (19, 63).

Tetraborane, B_4H_{10}, and ethylene lose hydrogen in a hot/cold reactor to produce dimethylene tetraborane, $B_4H_8C_2H_4$, which on alcoholysis gives 1,2-bis-(dialkoxyboryl)-ethane (13), *indicating the presence* of the $>BCH_2CH_2B<$ unit.

Dichloroborane, $HBCl_2$, has been found to react with alkenes to give the corresponding alkyl boron dichloride (87); *e.g.*

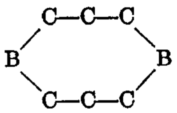
$$HBCl_2 + C_2H_4 \rightarrow Cl_2BC_2H_5$$

With acetylene, a compound analyzing as B_2Cl_4,C_2H_4 apparently was formed (61)

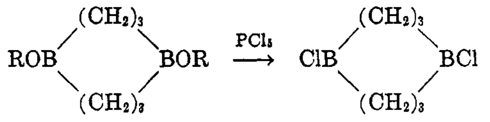
$$2HBCl_2 + C_2H_2 \rightarrow Cl_2BCH_2CH_2BCl_2$$

but later work indicates that only ethyl boron dichloride is produced (104).

Compounds containing links have been isolated by heating tri-allylborane with tri-iso-butylborane at 130–140°; butene was evolved. On boiling the resulting polymer with alcohol, 1,5-



dialkoxy-1,5-diborocane is formed; on treatment with phosphorus pentachloride this gives 1,5-dichloro-, 5-diborocane (69)



All the diborocane derivatives are spontaneously inflammable.

III. BORON MONOCHLORIDES

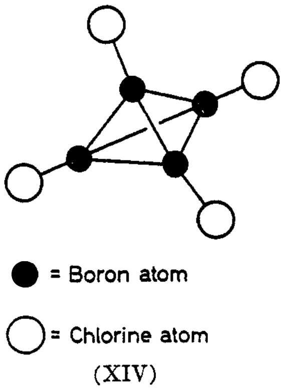
A. TETRABORON TETRACHLORIDE, B_4Cl_4

In the preparation of diboron tetrachloride, a pale yellow, crystalline solid forms in the discharge tube and is trapped out in adjacent parts of the apparatus with diboron tetrachloride. Decomposition of diboron tetrachloride at 0° produces a similar material. The yellow solid is slightly volatile at room temperature and molecular weight determination and analysis showed it to be B_4Cl_4 (98). The vapor pressure–temperature relation is:

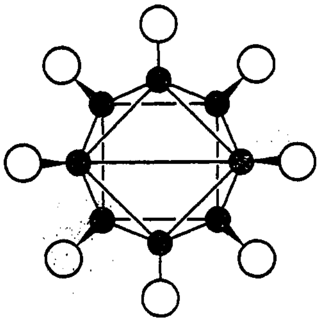
$$\log p_{mm} = 9.464 - (2719/T)$$

Tetraboron tetrachloride inflames in air more vigorously than diboron tetrachloride, but is not decomposed at 70° *in vacuo*. There is little or no reaction on heating with hydrogen, and trimethylboron does not react at temperatures up to −10°. However, there is evidence for some degree of methylation using trimethylaluminum; a colorless volatile liquid and solid materials are formed. With methyl alcohol, each mole of tetraboron tetrachloride yields six equivalents of hydrogen with methyl chloride, methyl borate, and a white solid—hence all B–B bonding is destroyed in this reaction.

The structure of tetraboron tetrachloride (7, 8) shows that the four boron atoms form a tetrahedron with a chlorine bonded to each boron (XIV)



(XIV)



(XV)

Since each boron atom is bonded to one chlorine atom and to three other boron atoms, the structure is formally electron-deficient. Explanations of the structure in terms of molecular orbitals have been given (23, 58). Four electrons (one from each boron) are assigned to the normal B–Cl bonds, using the 3pσ orbital of each chlorine atom. The remaining eight electrons of the boron atoms are assigned to four bonding molecular orbitals of the tetrahedron; there remain two more permissible molecular orbitals. These have the same symmetry as two combinations of the 3pπ orbitals of the chlorine atoms and hence there is "back donation" by the chlorine atoms into the tetrahedron.

B. OCTABORON OCTACHLORIDE, B_8Cl_8

Besides the yellow tetraboron tetrachloride, decomposition of diboron tetrachloride yields a red solid originally formulated as $(BCl_{0.9})_x$; this can be separated from less well-defined and nonvolatile BCl polymers by sublimation (67). It is soluble in organic solvents and in boron trichloride; two crystalline forms can be obtained from the latter solvent (9). The density determined by measurement of crystal size and weight is 1.75 g. cm.$^{-3}$, corresponding to B_8Cl_8.

The structure of this compound has been shown (10, 46) to be similar to that of tetraboron tetrachloride, with a polyhedron of boron atoms, each bonded to a chlorine atom (XV).

An explanation of the structure similar to that for B_4Cl_4, involving back coördination of the π-electrons of the Cl atoms into the bonding orbitals of the polyhedron, has been given (46).

C. OTHER COMPOUNDS $(BCl)_n$

This bright yellow solid is formed during the arc-preparation of diboron tetrachloride as a deposit on the apparatus walls near the exit of the discharge cell. Its formation is the first visible indication that reduction of the boron trichloride is proceeding correctly since deposits of $(BCl)_n$ have never been noted without the simultaneous formation of diboron tetrachloride (and *vice versa*). This has been considered as further evidence for the participation of BCl radicals in the preparation of diboron tetrachloride (67)

$$BCl_3 + 2Hg \rightarrow Hg_2Cl_2 + BCl$$
$$nBCl \rightarrow (BCl)_n$$
$$BCl + BCl_3 \rightarrow B_2Cl_4$$

In the silent electric discharge diboron tetrachloride gives a quantitative yield of the yellow monochloride (78)

$$nB_2Cl_4 \rightarrow nBCl_3 + nBCl \rightarrow (BCl)_n$$

Little work has been carried out on the compound. It has been stated (99) to be a two-dimensional polymer but no evidence was quoted. Hydrogen is liberated on hydrolysis showing the presence of boron–boron bonds but the evolution is slow and obviously not quantitative since the solution formed retained strong reducing properties, *e.g.*, toward silver nitrate (78).

IV. DIBORON TETRAFLUORIDE

Boron trifluoride is unaffected by the action of a mercury discharge of the type used to prepare diboron tetrachloride (26). A convenient method for the formation of diboron tetrafluoride is the action of antimony trifluoride on diboron tetrachloride at either −45 or −78°; after treatment with two separate amounts of antimony trifluoride the yield of diboron tetrafluoride is *ca.* 80% (26). The reaction of diboron tetrachloride with allyl fluoride produced a 40% yield of diboron tetrafluoride (17)

$$4C_3H_5F + B_2Cl_4 \rightarrow B_2F_4 + 4C_3H_5Cl$$

Diboron tetrafluoride is considerably more volatile and more stable than the tetrachloride. At 100° the decomposition, to give boron trifluoride, is very slow and even at 200° only 40% decomposition occurred after several hours to give a yellow involatile residue which has not been further studied: since boron trifluoride is the volatile product it is reasonable to assume the residue contains $(BF)_x$-type polymers as are found in the decomposition of all the other tetrahalides.

The melting point of pure diboron tetrafluoride is −56.0°; the vapor pressures of the solid and liquid are reproduced by the equations (p in mm.)

$$\log p_{\text{solid}} = 10.82 - (1856/T)$$

$$\log p_{\text{liquid}} = 9.009 - (1466/T)$$

which lead to the values of −34° for the normal boiling point, 6700 cal./mole for the heat of evaporation, and 28 for Trouton's constant (26). X-Ray diffraction studies of the solid indicate (95) a planar, centrosymmetric molecule with two molecules in the monoclinic unit cell; the calculated density is 1.92 g./cc. The angle F–B–F is 120° with the B–F distance of 1.32 ± 0.04 Å. (*cf.* BF_3, 1.29 Å.); the boron–boron bond is considerably shorter at 1.67 ± 0.04 Å. than in diboron tetrachloride (1.75 ± 0.05 Å.), which is consistent with a greater degree of delocalization of the π electrons of the halogen atoms over the whole molecule in B_2F_4.

Diboron tetrafluoride is reported to react explosively with oxygen (95). With excess of diethyl ether at room temperature a dietherate $B_2F_4 \cdot 2Et_2O$ is formed; on pumping at 0° this gradually loses one mole of ether to give a crystalline monoetherate $B_2F_4 \cdot Et_2O$ (compare the monoetherate $B_2Cl_4 \cdot Et_2O$ which is liquid). The monoetherate loses ethyl fluoride on standing (26).

Trimethylamine and diboron tetrafluoride react on being warmed slowly from −78° to room temperature to form a slightly volatile white solid of composition $[B_2F_4 \cdot 2NMe_3]_4$ (26). The vapor pressures of this solid are given by

$$\log p_{\text{mm.}} = 9.915 - (3400/T)$$

(vapor pressure at −78° is still 2 mm.) giving the heat of sublimation as 15,550 cal.

Diboron tetrafluoride reacts with unsaturated hydrocarbons more slowly than does the tetrachloride, although the products are more stable; compounds of the type $F_2B{-}R{-}BF_2$, where R is derived from C_2H_4, $(CH_3CH)_2$, C_3H_5Cl, C_3H_5Cl, C_3H_5F, C_4H_7Cl, and C_2H_2, have been prepared in this manner (17). In the case of $F_2BC_4H_7ClBF_2$ (derived from 4-chlorobutene-1) and $F_2BCH{=}CHBF_2$ the products also could be formed by fluorination of the appropriate chloro-derivative using antimony trifluoride. Table 3 summarizes the physical properties of the F_2BRBF_2-type compounds (17).

TABLE 3

log p (mm.) $A-(B/T)$; H = heat of vaporization in cal./mole.

Compound	M.p., °C.	B.p., °C.	A	B	H	Trouton constant
$B_2F_4 \cdot C_2H_4$	−31.4	35	8.259	1656	7,550	24.4
$B_2F_4 \cdot (CH_3CH)_2$	—	68	7.770	1667	7,600	22.3
$B_2F_4 \cdot C_2H_2$	−81.7 to −82.6	15	8.565	1635	7,450	25

The chemical properties of these substituted alkanes have not been studied in any detail: 1,2-bis-(difluoroboryl)-ethane decomposes very slowly at 270° to give boron trifluoride, diboron tetrafluoride, and ethyl difluoroborane, $C_2H_5BF_2$.

V. BORON SUB-BROMIDES

Very tentative evidence for a boron sub-bromide was obtained during the decomposition of the adduct $BBr_3 \cdot AgCN$ at 150° (72). Diboron tetrabromide is formed in small yield by passing argon/boron tribromide mixtures through a discharge between mercury or nickel electrodes (21); but a high yield of the tetrabromide results from the reaction (97)

$$3B_2Cl_4 + 4BBr_3 \xrightarrow[\text{temp.}]{\text{room}} 3B_2Br_4 + 4BCl_3$$

Diboron tetrabromide is a thermally unstable liquid of melting point 0.5 to 1.5°; hydrogen is produced quantitatively on hydrolysis with 10% caustic soda at 70°. The only recorded vapor pressure determination gave 5.5 mm. at 22.5° (97).

Boron monobromide $(BBr)_x$, a red solid, is formed during the arc-preparation of the tetrabromide. It is insoluble in dioxane, benzene, or toluene and has no melting point; sublimation takes place on warming with the free flame. Alkaline hydrolysis is incomplete, giving a little hydrogen, boric acid, and a boron hydride. However, ammonia does not cause evolution of hydrogen, but forms the compound $(B_2NH)_x$ (21).

The action of a silent electric discharge on boron tribromide was stated to give the monobromide (21)

$$xBBr_3 \rightarrow (BBr)_x + xBr_2$$

but other workers have failed to repeat this reaction (78). Amorphous solids of composition $BBr_{0.2-0.4}$ also were isolated during the arc-formation of the tetrabromide (21).

VI. BORON SUBIODIDES

Diboron tetraiodide is formed in about 15% yield by passing boron tri-iodide at low pressure through a radio-frequency discharge (84). It is a pale yellow crystalline solid which can be sublimed at 1 μ at 60–70°. Decomposition occurs at room temperature or above

$$xB_2I_4 \rightarrow yBI_3 + (BI)_{2x-y} + (x - y)I_2$$

At room temperature only a trace of iodine is formed and the decomposition becomes

$$xB_2I_4 \rightarrow xBI_3 + (BI)_x$$

Water causes vigorous hydrolysis to give a reducing solution; alkaline hydrolysis produces hydrogen. The mono-iodide, $(BI)_x$, can be made by pyrolysis of boron tri-iodide at 250° or by heating the tri-iodide with silver at 185°; it also results from the decomposition of diboron tetra-iodide.

A black solid of composition B_xI_y also was isolated during the action of a radio-frequency discharge on boron tri-iodide.

VII. MISCELLANEOUS COMPOUNDS $(BX)_n$

Several compounds of the general formula $(BX)_n$ (X = H, alkyl or aryl, *etc.*) have been described in the literature; these may be considered as derivatives of $(BCl)_n$. The preparation and properties of these compounds are discussed briefly below.

$(BH)_n$.—Polymeric solids of the approximate composition $(BH)_n$ arise from the decomposition of the volatile boron hydrides either at moderate temperatures (82, 88) or in the silent electric discharge (51, 91). A convenient method of forming the solid $(BH)_n$ in bulk is to heat the boron trialkyls at 200° in the presence of hydrogen, any carbon being removed by further treatment with hydrogen (50).

When a mixture of diborane and decaborane, $B_{10}H_{14}$, is heated at 100°, approximately four moles of hydrogen are eliminated (85)

$$B_{10}H_{14} + B_2H_6 \rightarrow 4H_2 + (BH)_{12}$$

The yellow solid $(BH)_{12}$ is unstable at temperatures employed, hydrogen being evolved as polymerization takes place; however, it has been stated that low temperature reactions may enable $B_{12}H_{12}$ to be isolated as a stable compound even though it has been predicted on a molecular orbital basis, that the B_{12} unit is an unstable configuration (59). The infrared spectrum of the solid fails to show any B–H–B bridges.

These solid boron hydrides have not been studied in any detail. Chlorination above 50° gives boron trichloride and hydrogen chloride (35). Above 300°, 80–95% of the boron is recovered as boron trichloride, the reaction being postulated to take place in two steps

$$(BH)_n + Cl_2 \xrightarrow{1} HCl + \text{Chlorinated solids}$$

$$\text{Chlorinated solids} \xrightarrow{2} \text{Boron trichloride}$$

$(BC_6H_5)_n$.—The yellow powder of formula $(BC_6H_5)_{9-10}$ formed in the reduction of phenyl boron dichloride with sodium in toluene (53) is oxidized rapidly by air and is soluble in benzene, toluene, and dioxane. Hydrolysis in neutral solutions gave only 10% of the hydrogen required by the equation

$$(C_6H_5B)_n + 2H_2O \rightarrow nC_6H_5B(OH)_2 + nH_2$$

although the yellow hydrolysis product still possessed reducing properties toward potassium permanganate and silver nitrate (*cf.* the incomplete hydrolysis of the $(BCl)_n$ polymers (Section III-C)). Ammonolysis produced the stable solid $(C_6H_5BNH_3)_x$.

$(BC_6H_{13})_n$.—This polymer, together with hydrogen, *trans*-3-hexene, and the heterocycle $(CH_2)_5BC_6H_{13}$, are formed when tri-*n*-hexylboron decomposes under reflux conditions. Its properties have not been described (107).

$(BC_4H_9)_n$ and $B(C_4H_9)_2$.—Dibutyl boron chloride and liquid sodium-potassium alloy in ether give dibutyl boron, $(C_4H_9)_2B$, which was soluble in ether and considered to be a polymer of unknown complexity (12). When excess of the alloy was used, the ion $(C_4H_9)_2B^-$ was produced

$$Bu_2BCl + 2M \rightarrow MBu_2B + MCl$$

Dibutylboron decomposed on removal of the ether solvent to give tributylboron and $(C_4H_9B)_n$; hydrolysis caused the evolution of hydrogen as did the reaction with hydrogen chloride

$$Bu_2B + HCl \rightarrow Bu_2BCl + {}^1/_2H_2$$

Other reactions studied which involved the production of boron monobutyl were

$$MBu_2B + Bu_2BCl \rightarrow MCl + Bu_3B + BBu$$

$$2MBu_2B + 2HCl \rightarrow Bu_3B + 2MCl + H_2 + BBu$$

$$2MBu_2B + 2Et_3NHCl \rightarrow Bu_3B + 2MCl + H_2 + 2Et_3N + BBu$$

It is probable that the dibutylboron formed in these reactions was diboron tetrabutyl, $B_2(C_4H_9)_4$, and was stabilized in ether solvent by the formation of the dietherate $B_2(C_4H_9)_4 \cdot 2Et_2O$ in the same way that trimethylamine increases the stability of diboron tetrachloride.

Other compounds of type $(BX)_n$ are $(BOR)_n$ (Section II-C-3), $(BNR_2)_n$ (Section II-C-2), and $(BOCH_2\text{-}CHCl)_n$ (Section II-C-3).

VIII. BORON MONOXIDE AND HYPOBORIC ACID

Since it has proved possible to prepare diboron tetrachloride from boron monoxide (Section I), it is of interest to discuss the various methods used to isolate the oxide in a pure state.

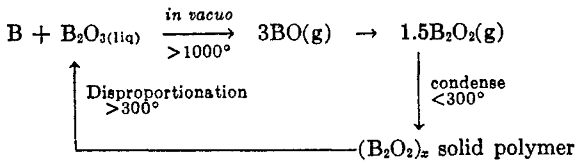
Hydrolysis of B_2X_4, X = Cl (100), NR_2 (15), or OR

(14, 106) with water at low temperature produces hypoboric acid, $H_4B_2O_4$, which on dehydration gives the monoxide (100). When the temperature of dehydration is about 220° the oxide is white and soluble in water and methanol; however, at 650° a brown form of oxide is produced which is hard, brittle, and inert. Traces of water cause the oxide to undergo a violent eruption when heated to 400° during which the solid is heated to incandescence and is changed to the inert form. Boron monoxide has been prepared from magnesium boride, Mg_3B_2, by several different procedures which vary only in the treatment of boride. The action of water on the boride gives an acid, α-$H_6B_2O_2$, which on evaporation and ignition produces boron monoxide (94). Potassium hydroxide gives α-$K_2H_2B_2(OH)_2$, β-$K_2H_4B_2O_2$, β-$K_2H_2B_2O_2$, or β-$K_4H_2B_2O_2$ depending on the concentration of the alkali; acidification of these salts gives the free acid from which boron monoxide is formed by heating (74, 75). The residues obtained by prolonged and repeated extraction of the magnesium boride with water produce, on treatment with concentrated ammonia, two salts which on heating give two boron sub-oxides, B_2O_2 and B_4O_5 (77)

$$(NH_4)_2B_2H_2O_2 \rightarrow B_2O_2 + 2H_2 + 2NH_3$$
$$(NH_4)_2B_4O_6 \rightarrow B_4O_5 + H_2O + 2NH_3$$

The sub-boric acids and their derivatives have been reviewed previously (76, 93, 94, 105).

Zirconium dioxide is reduced by boron at 1800° in vacuum to give a condensate of boron monoxide on a cold finger (108). Reduction of boric oxide with boron at *ca.* 1350° results in a 60–70% yield of boron monoxide which at the low pressures used in the experiments (10^{-4} mm.) collects as yellow or red sublimate on the cooler parts of the apparatus (48, 49). The carbon-boric oxide reaction proved unsuccessful because of the copious evolution of carbon monoxide and/or dioxide which prevented the attainment of high vacuum and hence the sublimation of the boron monoxide; mixtures of tantalum powder and boric oxide gave very low yields of monoxide. This mechanism of the boron–boric oxide reaction is suggested (48)



The solid boron monoxide formed by this method was assumed to be polymeric because it had neither melting nor boiling point and was amorphous as shown by X-Ray diffraction; its density as determined by the flotation method is 1.765 ± 0.001.

The properties of this type of boron monoxide show it to be much more reactive than samples prepared by dehydration of hypoboric acid (100). Some of the sublimates formed in the preparation are found to be pyrophoric on exposure to dry air; decomposition to boron and boric oxide begins at temperatures between 300 and 400° and is complete within a few minutes at 700° (*cf.* p. 309); no solvent has been found for B_2O_2 which does not attack it—thus it is insoluble and unreactive toward concentrated sulfuric acid, $SOCl_2$, CH_3COCl, glacial acetic acid, pyridine, acetone, benzene, or diethyl ether. With ethyl or methyl alcohols, hydrogen, trialkyl borates, and hypoboric acid, $H_4B_2O_4$, are formed, the series of reactions postulated being

$$B_2O_2 + 4MeOH \rightarrow B_2(OMe)_4 + 2H_2O$$
$$B_2O_2 + 6MeOH \rightarrow 2(MeO)_3B + 2H_2O + H_2$$
$$B_2(OMe)_4 + 4H_2O \rightarrow B_2(OH)_4 + 4MeOH$$
$$3B_2(OH)_4 \rightarrow 4B(OH)_3 + 2B$$

The latter reaction is of interest since it is the only instance so far discovered of a compound containing a boron–boron bond disproportionating to give free boron as one product. Previous examples (89, 106) have been shown to be incorrect (14).

Polymeric boron monoxide reacts vigorously with water, evolving considerable amounts of hydrogen; on evaporation the solution yields boric acid (30% of B_2O_2 added) and hypoboric acid. At 0° the oxide has no action on 10 *M* sodium hydroxide, but at room temperature it dissolves slowly with the evolution of hydrogen.

Hypoboric acid is a white crystalline solid, very soluble in water or alcohols. Its acid strength is comparable to that of boric acid and like the latter $H_4B_2O_4$ liberates one titratable hydrogen when complexed with mannitol in aqueous solution. An outstanding property of hypoboric acid is its reducing ability, a fact which contributes seriously to the difficulties of studying its chemical behavior in solution; MnO_4^-, Ce^{3+}, I^2, Ag^+, and O_2 are reduced readily. In alkaline solution the reaction

$$2H_4B_2O_4 + 2H_2O + O_2 \rightarrow 4H_3BO_3$$

is complete in only a few minutes. Attempts to form and crystallize salts of hypoboric acid have been unsuccessful.

A. ANALYSIS OF HYPOBORIC ACID

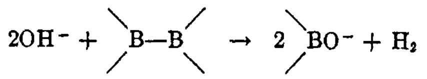
It is appropriate to discuss briefly analysis of hypoboric acid since hydrolysis of diboron compounds leads ultimately to this acid.

1. Hydrogen Evolution Method

This is the most generally used method for the determination of diboron compounds. In the absence of oxygen this reaction is quantitative

$$2OH^- + B_2O_4^{4-} \rightarrow 2BO_3^{3-} + H_2$$

or more generally



Hence 1 mole of hydrogen $\equiv$ 1 mole of hypoboric acid $\equiv$ 1 equiv. of boron–boron bonds.

2. Mannitol–NaOH Titration Method

It has been mentioned previously (p. 311) that hypoboric acid acts as a titratable monoprotic acid when complexed with mannitol and on oxidation liberates two moles of boric acid. This allows mixtures of ortho- and hypo-boric acids to be determined in the same solution. The difference between two titration results of similar aliquots, one before oxidation and one after, will measure the quantity of hypoboric acid in the original samples; the oxidation of $H_4B_2O_4$ is effected virtually instantaneously by the addition of excess 1:1 nitric acid to the solution. Thus if "a" ml. of NaOH is used before oxidation and "b" ml. after oxidation, then $(b - a)$ ml. $\times N(\text{NaOH}) \times 10^{-3} \equiv$ moles of $H_4B_2O_4$ per aliquot taken.

3. Silver Nitrate Oxidation Method

Hypoboric acid quantitatively reduces silver according to the equation

$$2Ag^+ + H_4B_2O_4 + 2H_2O \rightarrow 2Ag + 2H_3BO_3 + 2H^+$$

For the determination, excess of silver nitrate is added to the aliquot of $H_4B_2O_4$ solution maintained below pH 5 with acetic acid and the resultant silver precipitate collected and weighed in the usual way; the method is independent of excess silver nitrate or boric acid.

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