# COMPOUNDS OF BORON

## Boron Halides ($BX_3$)

## Halides, Alums and Other Metal Salts

Boron trihalides are strictly monomeric, trigonal planar molecules. This difference from aluminum is attributed to back-donation from "nonbonding" electrons on halogen atoms into the "empty" $P_{az}$ orbital of boron which lends some double bond character to B–X bonding (manifested by bond shortening) and stabilizes the monomer.

Preparation:

(i) Boron can be obtained through the reaction: $2B + 3Cl_2 \rightarrow 2BCl_3$.

(ii) Alternatively, Boron trifluoride (BF3) can be synthesized from Boron trioxide ($B_2O_3$) through the reaction: $B_2O_3 + 3CaF_2 + 3H_2SO_4 \rightarrow 2BF_3 + 3CaSO_4 + 3H_2O$.

Properties:

(i) Boron halides undergo swift hydrolysis when in contact with water:

$$BCl_3 + H_2O \rightarrow H_3BO_3 + 3HCl$$

$$2BF_3 + H_2O \rightarrow H_3BO_3 + 2HF + HBF_4.$$

(ii) Boron forms adducts with Lewis bases like $H_2N$ and $H_2S$:

$$H_3N{+}BF_3 \rightarrow H_3N{\cdot}BF_3.$$

(iii) Boron halides exhibit Lewis's acid behavior, with acid strength following the order:

$$BF_3 < BCl_3 < BBr_3 < BI_3.$$

This trend is attributed to the weakening of pπ - pπ back bonding as one moves down the group.

## Boron Trioxide ($B_2O_3$)

Preparation:

$$\underset{\text{Boric acid}}{H_3BO_3} \xrightarrow{100\ ^oC} HBO_2 \xrightarrow{160\ ^oC} H_2B_4O_7 \xrightarrow{\text{red hot}} B_2O_3$$

Properties:

It is an acidic oxide and is anhydride of boric acid and it reacts with alkali's or bases to form borates.

$$3Na_2O + B_2O_3 \longrightarrow 2Na_3BO_3 \text{ (sodium orthoborate).}$$

It reacts with water slowly to form orthoboric acid.

$$H_2O + B_2O_3 \longrightarrow 2HBO_2 \quad ; \quad HBO_2 + H_2O \longrightarrow H_3BO_3$$

When heated with transition metal salts, it forms coloured compounds.

$$3B_2O_3 + Cr_2(SO_4)_3 \xrightarrow{\Delta} 3SO_3 + 2Cr(BO_2)_3 \text{ (green)}$$

$$2B_2O_3 + 2Cu(NO_3)_2 \xrightarrow{\Delta} 4NO_2 + O_2 + 2Cu(BO_2)_2 \text{ (blue)}$$

It also shows weakly basic properties according to the following reaction.

$$B_2O_3 + P_2O_5 \rightleftharpoons 2BPO_4$$

It reacts with hydrogen fluoride in presence of $H_2SO_4$ forming $BF_3$.

$$B_2O_3 + 6HF + 3H_2SO_4 \longrightarrow 2BF_3 + 3H_2SO_4.H_2O.$$

## Boric Acid ($H_3BO_3$)

Preparation:

(i) It is precipitated by treating a concentrated solution of borax with sulphuric acid.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3^-$$

(ii) From Colemanite: Powdered colemanite is suspended in water and excess $SO_2$ is passed through it. On filtering and cooling the filtrate, white crystals of $H_3BO_3$ are obtained.

$$Ca_2B_6O_{11} + 4SO_2 + 11H_2O \longrightarrow 2Ca(HSO_3)_2 + 6H_3BO_3$$

Properties:

It is a weak monobasic acid, soluble in water and in aqueous solution the boron atom completes its octet by accepting $OH^-$ from water molecules:

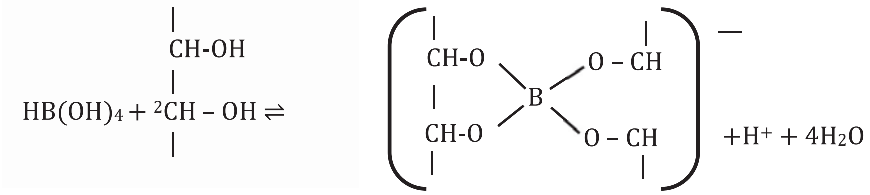
$$B(OH)_3(aq) + 2H_2O(l) \rightleftharpoons [B(OH)_4]^-(aq) + H_3O^+(aq). \quad pK = 9.25.$$

It, therefore, functions as a Lewis acid and not as a proton donor like most acids.

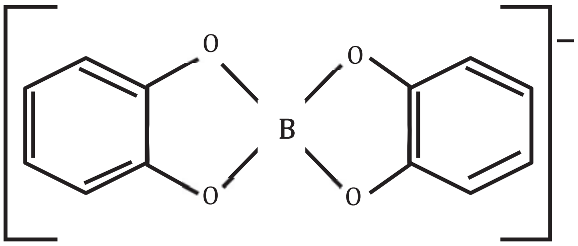
Since $B(OH)_3$ only partially reacts with water to form $H_3O^+$ and $[B(OH)_4]^-$, it behaves as a weak acid. Thus, $H_3BO_3$ cannot be titrated satisfactorily with NaOH as a sharp end point is not obtained. If certain organic polyhydroxy compounds such as glycerol, mannitol or sugars are added to the titration mixture, then $B(OH)_3$ behaves as a strong monobasic acid and it can be now titrated with NaOH and the end point is detected using phenolphthalein as indicator (pH = 8.3 - 10.0).

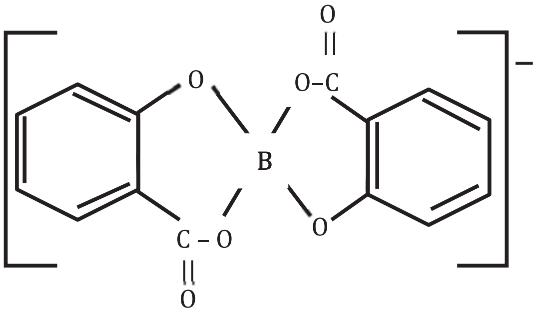
The added compound must be a cis-diol, to enhance the acid properties. The cis-diol forms very stable complex with the $[B(OH)_4]^-$, thus removing it from solution. The reaction is reversible and thus removal of one of the products shifts the equilibrium in the forward direction and thus all the $B(OH)_3$ reacts with NaOH; in effect it acts as a strong acid in the presence of the cis-diol.

$$2B(OH)_3 + 2NaOH \longrightarrow Na[B(OH)_4] + NaBO_2 + 2H_2O$$



Ethanol does not form similar complex but catechol, salicylic acids, mannitol form similar complexes.





When heated it first forms meta boric acid ($HBO_2$) and then boron trioxide.

$$\underset{\text{Boric acid}}{H_3BO_3} \xrightarrow{100^{o}C} HBO_2 \xrightarrow{160^{o}C} H_2B_4O_7 \xrightarrow{\text{red hot}} B_2O_3$$

Orthoboric acid is greasy to touch less soluble in cold water but more soluble in hot water. In the solid state, the $B(OH)_3$ units are hydrogen bonded together in to two dimensional sheets with almost hexagonal symmetry. The layered are quite a large distance apart (3.18 Å) and thus the crystal breaks quite easily into very fine particles.

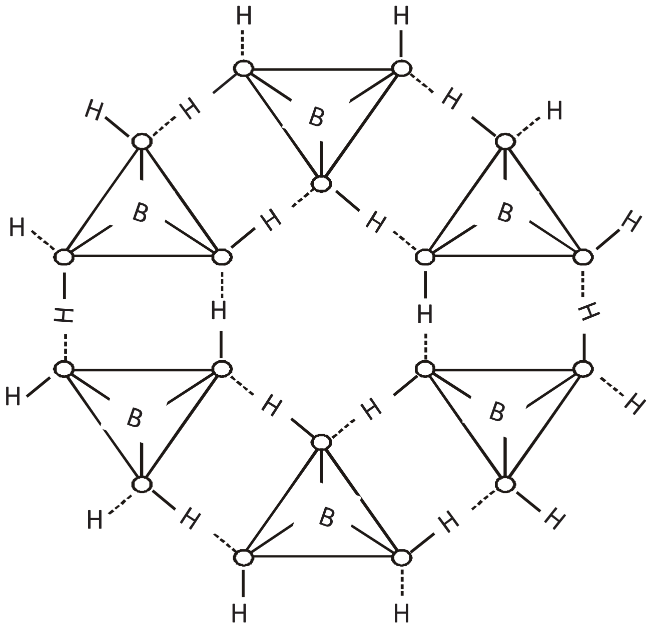
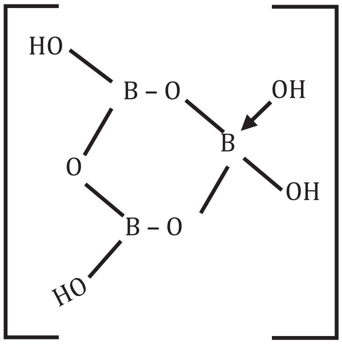


Figure: 1

- Polymeric metaborate species are formed at higher concentration, for example,

$$3B(OH)_3 \rightleftharpoons H_3O^+ + [B_3O_3(OH)_4]^- + H_2O, \quad pK = 6.84$$



- Boric acid dissolves in aqueous HF forming $HBF_4$ (fluoroboric acid).

$$B(OH)_3 + 4HF \rightleftharpoons H_3O^+ + BF_{4-}^- + 2H_2O$$

## Test for Borate Radical

When boric acid is heated with ethyl alcohol, the evolved gas is burned forming a green edged flame.

$$H_3BO_3 + 3C_2H_5OH \longrightarrow \underset{\text{ethyl borate (volatile)}}{B(OC_2H_5)_3} + 3H_2O$$

Uses:

(i) It is an antiseptic and its water solution is used as an eyewash.

(ii) It is also used in glass, enamel and pottery industry.

## Borax Or Sodium Tetraborate

## Borax ($Na_2B_4O_7.10H_2O$)

Preparation:

It is found in nature but can also be prepared by the following methods.

(i) From Colemanite.

When colemanite powder is heated with $Na_2CO_3$ solution, the following reaction occurs with the precipitation of $CaCO_3$.

$$Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow 2CaCO_3{}^{-} + Na_2B_4O_7 + 2NaBO_2$$

The filtrate is cooled when white crystals of borax are precipitated. The mother liquor on treatment with $CO_2$ converts $NaBO_2$ to $Na_2B_4O_7$ which precipitates out on crystallization.

$$4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3$$

(ii) From orthoboric acid.

Borax is obtained by the action of $Na_2CO_3$ on orthoboric acid.

$$4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2$$

Properties:

(i) Borax is a white powder, less soluble in cold water, more soluble in hot water.

(ii) Its aqueous solution is alkaline because of its hydrolysis to weak acid $H_3BO_3$ and strong alkali NaOH.

$$Na_2B_4O_7 + 7H_2O \longrightarrow 4H_3BO_3 + 2NaOH$$

(iii) Action of heat.

When borax powder is heated, it first swells due to loss of water in the form of steam but at 740°C it becomes converted into colourless transparent borax bead.

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10\ H_2O$$

$$Na_2B_4O_7 \xrightarrow{740^{\circ}C} 2NaBO_2 + B_2O_3 \text{ (borax bead)}$$

(iv) Oxidation of boric acid or sodium metaborate with $H_2O_2$.

$$Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + 2H_2O_2 + 6H_2O \longrightarrow Na_2\,[(OH)_2B\,(O—O)_2B(OH)_2].6H_2O$$

Sodium per oxo borate is used as a brightener in washing powder. In very hot water (over 80ºC) the peroxide linkages —O—O— break down to give $H_2O_2$.

(v) It is a useful primary standard for titrating against acids. One mole of it reacts with two moles of acid. This is because when borax is dissolved in water both $B(OH)_3$ and $[B(OH)_4]^-$ are formed, but only the $[B(OH)_4]^-$ reacts with HCl.

$$[B_4O_5(OH)_4]^{2-} + 5H_2O \rightleftharpoons 2B(OH)_3 \text{ (weak acid)} + 2[B(OH)_4]^- \text{ (salt)}$$

$$2[B(OH)_4]^{2-} + 2H_3O^+ \longrightarrow 2B(OH)_3 + 4H_2O$$

On cooling, the white flakes of boric acid are obtained Borax is also used as a buffer since its aqueous solution contain equal amounts of weak acid and its salt.

(vi) $Na_2[B_4O_5(OH)_4] + 12HF \xrightarrow{-H_2O} [Na_2O(BF_3)_4] \xrightarrow{+H_2SO_4} 4BF_3 + 2NaHSO_4 + H_2O$

Correct formula of borax is $Na_2[B_4O_5(OH)_4]$. $8H_2O$. It contains boron in both planar $BO_3$ and tetrahedral $BO_4$ units. It contains five B—O—B linkages.

## Borax-Bead Test

Borax reacts with certain metal salts such as, $Ni^{2+}$, $Co^{2+}$, $Cr^{3+}$, $Cu^{2+}$, $Mn^{2+}$ etc. to form coloured metaborates. The colour of the metaborates can be used to identify the metallic ions (cations) in salts.

$$Na_2B_4O_7.10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \xrightarrow{740^{\circ}C} \underbrace{2NaBO_2 + B_2O_3}_{\text{glassymass}};CuO + B_2O_3 \rightarrow Cu(BO_2)_2$$

(blue bead)

Uses :

(i) In borax bead test.
(ii) In purifying gold.
(iii) As flux during welding of metals.
(iv) In production of glass.

## Hydrides Boranes

Binary compounds of B with H are called boron hydrides or boranes. These compounds form following two types of series:

$B_nH_{n+4}$ - $B_2H_6, B_5H_9, B_6H_{10}, B_{10}H_{14}$
$B_nH_{n+6}$ - $B_4H_{10}, B_5H_{11}, B_6H_{12}, B_9H_{15}$

The chemistry of diborane has aroused considerable interest because of its usefulness in many synthetic reactions and also because the elucidation of its structure helped to clarify the basic concepts about the structure of electron deficient compounds.

## Diborane ($B_2H_6$)

Preparation

(i) $4BF_3 + 3LiAlH_4 \xrightarrow{\text{ether}} 2B_2H_6 + 3Li[AlF_4]$
(ii) $2BCl_3 + 6H_2 \text{ (excess)} \xrightarrow[\text{discharge}]{\text{silent electric}} B_2H_6 + 6HCl$
(iii) $8BF_3 + 6LiH \xrightarrow{\text{ether}} B_2H_6 + 6LiBF_4$
(iv) $2NaBH_4 + I_2 \xrightarrow{\text{ether}} B_2H_6 + 2NaI + H_2$
(v) $3NaBH_4 + 4BF_3 \xrightarrow[450K]{\text{ether}} 3NaBF_4 + 2B_2H_6$
(vi) It can also be prepared by treating $NaBH_4$ with concentrated $H_2SO_4$ or $H_3PO_4$.
$2NaBH_4 + H_2SO_4 \longrightarrow B_2H_6 + 2H_2 + Na_2SO_4$ ; $2NaBH_4 + 2H_3PO_4 \longrightarrow B_2H_6 + 2H_2 + 2NaH_2PO_4$
(vii) $2BF_3 + 6NaH \xrightarrow{453\text{ K}} B_2H_6 + 6NaF$ (Industrial method)
(viii) $B_2O_3 + 3H_2 + 2Al \xrightarrow[150°C]{750\text{ atm}} B_2H_6 + Al_2O_3$
(ix) $Mg_3B_2 + H_3PO_4 \longrightarrow$ mixture of boranes mainly, $B_4H_{10} \xrightarrow{\Delta} B_2H_6$.

Properties

(i) $B_2H_6$ is colourless gas and highly reactive (boiling point 183 K).
(ii) Controlled pyrolysis of diborane leads to most of the higher boranes.
It catches fire spontaneously in air and explodes with $O_2$. Reaction with oxygen is extremely exothermic.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O \qquad DH = -2160 \text{ kJ mol}^{-1}$$

➢ Mixtures of diborane with air or oxygen inflame spontaneously producing large amount of heat. Diborane has a higher heat of combustion per unit weight of fuel than most other fuels. It is therefore used as a rocket fuel.
➢ At red-heat the boranes decompose to boron and hydrogen.

(iii) Reaction with water is instantaneous.

$$B_2H_6 + 6H_2O \longrightarrow 2B(OH)_3 + 6H_2$$

Diborane is also hydrolyses by weaker acids (e.g., alcohols) or aqueous alkali.

$$B_2H_6 + 6ROH \longrightarrow 2B(OR)_3 + 6H_2$$
$$B_2H_6 + 2KOH + 2H_2O \longrightarrow 2KBO_2 + 6H_2$$

(iv) Reaction with HCl replaces a terminal H with Cl.

$$B_2H_6 + HCl \longrightarrow B_2H_5Cl + H_2$$

(v) Reaction with chlorine gives the trichloride.

$$B_2H_6 + 6Cl_2 \longrightarrow 2BCl_3 + 6HCl$$

(vi) The electron deficient 3c-2e BHB bridges are sites of nucleophilic attack.
Small amines such as $NH_3$, $CH_3NH_2$ and $(CH_3)_2NH$ give unsymmetrical cleavage of diborane.

$$B_2H_6 + 2NH_3 \longrightarrow [H_2B\,(NH_3)_2]^+ + [BH_4]^-$$

➢ Large amines such as $(CH_3)_3N$ and pyridine give symmetrical cleavage of diborane.

$$2(CH_3)_3N + B_2H_6 \longrightarrow 2H_3B \longleftarrow N(CH_3)_3$$

$$B_2H_6 + 2Me_3P \longrightarrow 2Me_3PBH_3$$

➢ $B_2H_6 + 2CO \xrightarrow{200^\circ C, 20atm} 2BH_3CO$ (borane carbonyl)

➢ The bromonium ion products $[H_2BL_2]^+$, are tetrahedral and can undergo substitution by other bases

$$[H_2B(NH_3)_2]^+ + 2PR_3 \longrightarrow [H_2B(PR_3)_2]^+ + 2NH_3$$

➢ The reaction with ammonia depends on conditions.

$$B_2H_6 + NH_3 \xrightarrow[\text{low temperature}]{\text{Excess } NH_3} B_2H_6.2NH_3 \text{ or } [H_2B(NH_3)_2]^+ [BH_4]^-$$

(ionic compound).

$$\xrightarrow[\text{higher temperature } (> 200^\circ C)]{\text{Excess } NH_3} (BN)_x \text{ boron nitride.}$$

$$\xrightarrow[\text{higher temperature } (200^\circ C)]{\text{Ratio } 2NH_3 : 1\, B_2H_6} B_3N_3H_6 \text{ borazine.}$$

Borazine is much more reactive than benzene. Borazine readily undergoes addition reactions which do not occur with benzene. Borazine also decomposes slowly and may be hydrolyses to $NH_3$ and boric acid at elevated temperature. If heated with water, $B_3N_3H_6$ hydrolyses slowly.

$$B_3N_3H_6 + 9H_2O \longrightarrow 3NH_3 + 3H_3BO_3 + 3H_2O$$

(vii) Reduction of diborane can be accomplished with sodium or with sodium borohydride.

$$2B_2H_6 + 2Na \longrightarrow NaBH_4 + NaB_3H_8$$

$$B_2H_6 + NaBH_4 \longrightarrow NaB_3H_8 + H_2.$$

➢ Reductions of diborane with $NaBH_4$ can also lead to higher borane anions.

$$2NaBH_4 + 5B_2H_6 \longrightarrow Na_2B_{12}H_{12}$$

(viii) $B_2H_6 + 2LiH \longrightarrow 2LiBH_4$