Borates

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Introduction

- Borates are the name for a large number of boron-containing oxyanions. The term "borates" may also refer to tetrahedral boron anions, or more loosely to chemical compounds which contain borate anions.
- joined together via shared oxygen atoms and may be cyclic or linear in structure.
Importance:

- stimulate plant growth
- inhibit bacteria and fungi
- increase crop yields
- to remove stains
- increase its resistance to heat and chemicals
- to personal care products to prevent bacterial growth
- as flame retardants
### Classification

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Orthoborate

- The simplest borate anion
- $\text{BO}_3^{-3}$ is known in the solid state, example in $\text{Ca}_3(\text{BO}_3)_3$
- trigonal planar structure
- Isoelectronic to $\text{CO}_3^{-2}$
Metaborate anion

- Tetrahedral form
- When it is heated, boric acid loses water to form various condensed boric acids, such as cyclic metaboric acid
Triborate anion

- The triborate anion is a six-member BO ring (referred to as a boroxylic ring).
- Triborate B3O5−7, found in CaAlB3O7 (johachidolite).
The tetraborate anion is a bridged eight-member B-O ring.

The tetraborate anion (tetramer) includes two tetrahedral and two trigonal boron atoms symmetrically assembled in cyclic structure.

Sodium tetraborate, Na$_2$[B$_4$O$_5$(OH)$_4$]·8H$_2$O, which is commonly called borax, formula is often written as Na$_2$B$_4$O$_7$·10H$_2$O.
Pentaborate anion

- consists of two six-member B-O rings sharing a common boron atom.
Hexaborate anion

- consists of three B-O rings that share three boron atoms and one oxygen atom.
Boric acid:

- Boric acid is a weak proton donor (pKa ~ 9) in the sense of Brønsted acid, but is a Lewis acid, i.e., it can accept an electron pair.
- Boric acid does not dissociate in aqueous solution, but is acidic due to its interaction with water molecules, forming tetrahydroxyborate.
- Acidic, its reaction with OH– from water, forming the tetrahydroxyborate complex (B(OH)\(^-\)\(^4\)), proton left by the water autoprotolysis.

\[
\text{B(OH)}_3 + 2\text{H}_2\text{O} \rightleftharpoons \text{B(OH)}^-\text{H}^+ + \text{H}_3\text{O}^+ \quad (\text{pKa} = 8.98)
\]
Polymeric ions:

- Under acid conditions boric acid undergoes condensation reactions to form polymeric oxyanions:

\[ 4B(OH)_4^- + 2H^+ \rightleftharpoons B_4O_5(OH)_4^{2-} + 7H_2O \]
Borate esters:

- organic compounds of the type B(OR)₃ where R is alkyl or aryl
- prepared by condensation reaction of boric acid and the alcohol:
  \[ \text{B(OH)}_3 + 3 \text{ROH} \rightarrow \text{B(OR)}_3 + 3 \text{H}_2\text{O} \]
- Borate esters are volatile and can be purified by distillation
- alkyl borates burn with a characteristic green flame
- Trimethyl borate B(OCH₃)₃ is a popular borate ester used in organic synthesis
- Borate esters are prepared from alkylation of trimethyl borate:
  \[ \text{ArMgBr} + \text{B(OCH₃)}₃ \rightarrow \text{MgBrOCH}_₃ + \text{ArB(OCH₃)}₂ \]
  \[ \text{ArB(OCH₃)}₂ + 2 \text{H₂O} \rightarrow \text{ArB(OH)}₂ + 2 \text{HOCH₃} \]
- These esters hydrolyze to boronic acids, which are used in Suzuki couplings
Suzuki couplings

The Suzuki reaction is an organic reaction, classified as a coupling reaction, where the coupling partners are a boronic acid and an organohalide catalyzed by a palladium complex.
Natural Occurrence:
Ulexite:

- \((\text{NaCaB}_5\text{O}_6\text{(OH)}_4\cdot8\text{H}_2\text{O})\) (hydrated sodium calcium borate hydroxide)
- sometimes known as TV rock
- is usually found as evaporite deposits along with borax
- occurs in the form of white, rounded crystalline masses or as closely packed fibrous crystals
- The isolated borate poly anion \([\text{B}_5\text{O}_9]^{-3}\) has five boron atoms, therefore placing ulexite in the pentaborate group.
- Widely used on basis of optical properties.
Colemanite

- \((\text{CaB}_3\text{O}_4\text{(OH)}_3\cdot\text{H}_2\text{O})\) secondary mineral that forms by alteration of borax and ulexite
- It has many industrial uses, like the manufacturing of heat resistant glass.
- Deposits in parts of Turkey, the United States (particularly Death Valley, Argentina, and Kazakhstan), as well as other parts of the globe