Boranes and Borohydrides

Boranes and the Bonding in boranes

Boranes are compounds consisting of boron and hydrogen. They were investigated systematically by the german scientist Alfred Stock at the beginning of the 19^{th} century. The most basic example is diborane (B_2H_6), all boranes are electron-deficient compounds. For B_2H_6 usually 14 electrons are needed to form 2c,2e-bonds, but only 12 valence electrons are present. Because of this there are two B-H-B bonds, which have three centres, but only two electrons (3c, 2e bond). This can be interpreted as a molecular orbital that is formed by combining the contributed atomic orbitals of the three atoms. In more complicated boranes not only B-H-B bonds but also B-B-B 3c, 2e-bonds occur. In such a bond the three B-atoms lie at the corners of an equilateral triangle with their sp3 hybrid orbitals overlapping at its centre. One of the common properties of boranes is, that they are flammable or react spontaneously with air. They burn with a characteristic green flame. And they are colourless, diamagnetic substances.

Nomenclature

In neutral boranes the number of boron atoms is given by a prefix and the number of Hydrogen-atoms is given in parentheses behind the name.

example: B_5H_{11} → pentaborane(11) , B_4H_{10} → tetraborane(10)

For ions primarily the number of hydrogen-atoms and than the number of boron-atoms is given, behind the name the charge is given in parentheses.

example: $[B_6H_6]^{2-}$ → hexahydrohexaborat(2-)

Wades rule, Structures of boranes

Wades rule helps to predict the general shape of a borane from its formula.

- count the number of B-H units
- every B-H unit contains 4 valence electrons, but two of them are needed to establish the bond between B and H, thus every B-H unit contributes two electrons to the skeletal electrons.
- every further H-Atom contributes a further electron to the skeletal electrons and
- charge contributes electrons
- the resulting number of electrons has to be divided by two to get the number of skeletal electron pairs within the borane. The general structure is defined by the number of skeletal electron pairs

Formula	Skeletal electron pairs	type
$[B_nH_n]^{2-}$	n+1	closo
B_nH_{n+4}	n+2	nido
B_nH_{n+6}	n+3	arachno
B_nH_{n+8}	n+4	hypho

The polyhedra are always made up of triangular faces, so they are called deltahedra. Usually there are three possible structure types:

Closo-boranes:

- closed deltahedra without B-H-B 3c,2e-bonds
- thermally stable and moderately reactive.
- example: $[B_5H_5]^{2-}$ → the ion builds up a trigonal, bipyramidal polyhedron

Nido-boranes:

- closo borane with one corner less and addition of two hydrogen-atoms instead
- B-H-B-bonds and B-B-bonds are possible.
- thermally stability lies between closo- and arachno-boranes.
- example: B_5H_9 → its structure can be assumed as the octahedral deltahedron of $[B_6H_6]^{2-}$ without one corner → tetragonal pyramide

Arachno-boranes:

- closo borane deltahedron but with two BH-units removed and two H-atoms added.
- it has to have B-H-B 3c, 2e-bonds.
- thermally unstable at room temperature and highly reactive.
- example: B_4H_{10} → the structure can be derived from $[B_6H_6]^{2-}$-deltahedron with two corners less.

There exist also other structures like the hypho-boranes, but they are less important.

Synthesis of Boranes

Diborane can be synthesized by an exchange reaction (metathesis) of a boron halide with $LiAlH_4$ or $LiBH_4$ in ether, for example:

$$3\ LiAlH_4 + 4\ BF_3 \rightleftharpoons 2\ B_2H_6 + 3\ LiAlF_4$$

The reaction has to be done under vacuum or with exclusion of air, because diborane burns in contact with air.

Higher boranes are obtained by controlled pyrolysis of Diborane in the gas phase.

example:

$$B_2H_{6(g)} \rightarrow 2BH_{3(g)}$$

$$B_2H_{6(g)} + BH_{3(g)} \rightarrow B_3H_{7(g)} + H_{2(g)}$$

$$BH_{3(g)} + B_3H_{7(g)} \rightarrow B_4H_{10(g)}$$

Sources:

D. F. Shriver, P. W. Atkins, Inorganic Chemistry Third edition, Oxford University Press, 2001