P Block :Boron Group

Structure of Unit

10.0 Objectives

This chapter deals with the boron group of the periodic table. One can know the properties of boron hydride, its structure, bonding in diborane, various matalloborane, carboranes by reading this chapter.

10.1 Introduction

A boranes comprise a large group of compounds with the generic formula of B_xH_y. These compounds do not occur in nature. Many of the boranes readily oxidise on contact with air, some violently. The class is named after the parent chemical called"borane" itself, chemical formula BH_3. This compound is only known to exist as a transient intermediate since it dimerises to form diborane, B_2H_6. The larger boranes all consist of boron clusters that are polyhedral. In addition to the charge-neutral boranes, a large number of anionic boron hydrides are known. The most

important boranes are diborane B_2H_6 and two of its pyrolysis products, pentaborane B_5H_9 and decaborane $B_{10}H_{14}$.

Borane-clusters, in which metals are present are know as 'Metalloboranes'. Many metalloboranes have been prepared. In some cases metal atom is attached with the borohydride ion through hydrogen bridge. The most common and important metalloborane group is one in which direct metal boron bond is present.

A carborane is a cluster composed of boron, carbon and hydrogen atoms. Like many of the related boranes, these clusters are polyhedra and are similarly classified as closo-, nido-, arachno-, hypho-, etc. based on whether they represent a complete (closo-) polyhedron, or a polyhedron that is missing one (nido-), two (arachno-), or more vertices.Interesting examples of carboranes are the extremely stable icosahedral closo-carboranes. These boron-rich clusters exhibit unique organomimetic properties with chemical reactivity matching classical organic molecules, yet structurally similar to metal-based inorganic and organometallic species.

10.2 Boron Hydrides

Several hydrides of boron have been recognized so far, they are commonly known as boranes (analogy with the alkanes, hydrocarbons). These hydrides can be represented by two general formulae B_nH_{n+4} and BnH_{n+6}. The former are more stable than the later. According to IUPAC system of nomenclature, the number of boron atoms in the borane molecule is indicated by a Greek numerical prefix e.g. di, tri, tetra, penta, hexa etc. followed by the number which indicates the number of hydrogen atoms. For example, B_6H_{10} is called hexaborane-Iu, Here hexa indicates the number of boron atoms and 10 indicates the number of .hydrogen atoms.But for polyboranes of closed structure prefix closo is used and of non- closed structure prefix nido is used.

Classification:

On the basis of structures, molecular formula and skeletal electrons higher boranes are classified into Closo, Nido, Arachno and Hypo boranes.

1. Closo Boranes: These are closed structured (Closo, Greak, meaning cage) boranes with the molecular formula $[B_nH_n]^{2-}$ and skeletal electrons = n+1 pairs (= 2n+2 electrons). In this structure, there is one boron atom placed at each apex and there are no B-H-B bonds present in the molecule. All the member of the series from n=5 to 12 are known. $[B_5H_5]^{2-}$ is trigonal bipyramidal, $[B_6H_6]^{2-}$ is octahedral and $[B_{12}H_{12}]^{2-}$ is icosahedral. All are stable on heating and are quite inert.
2. Nido-Boranes: These boranes have nest (Nido, Latin, meaning Nest) like structure. Their general formula is B_nH_n+4 and have (n+2) pairs = 2n+4 skeletal electrons on removing one boron atom from an apex of closo structure, nido structure is obtained. Because, of the lost boron atom, these boranes have extra hydrogens for completing the valency. The polyhedra in this series have B-H-B bridge bonds in addition to B-B bonds. They are comparatively less stable than 'Closo', but more than 'Arachno' on heating.
3. Arachno-Boranes: These boranes have the general formula (B_nH_n+6) and skeletal electrons = (n+3) pairs = 2n+6 = electrons. These molecules are obtained by removing two boron atoms from two apexes of the closo structure and have spider-web like structure. They have B-H-B bridge-bonds in their structures and are very reactive and unstable on heating.