

TDC Part I
Paper I, Group B
Inorganic Chemistry



Department of Chemistry

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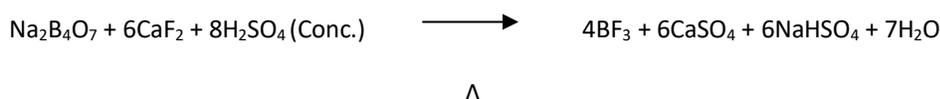
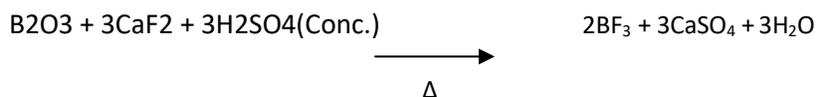
Dr. Priyanka

TOPIC: - p-block group 13

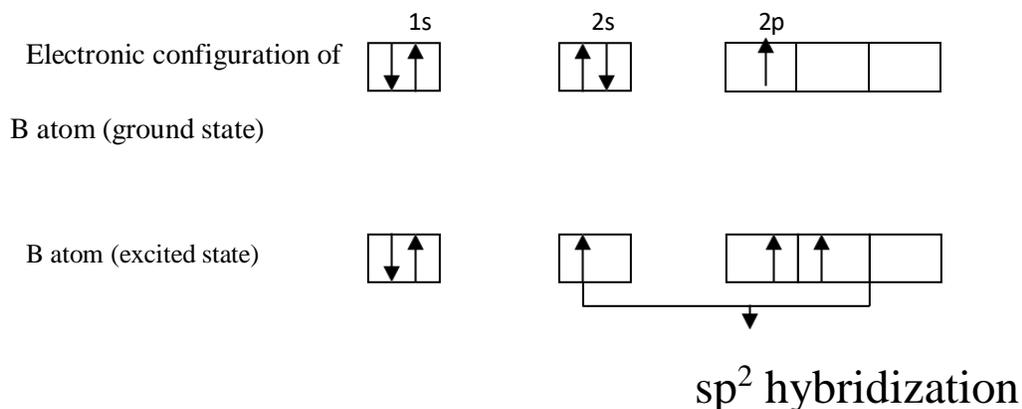
Halides

Halides

Tri-halides (MX_3) are known for all elements except TlI_3 . Due to inert pair effect Tl(I) is stable and Tl(III) is oxidizing in nature. It oxidizes iodide to iodine. Thallium (III) chloride and bromide are also unstable. The halides of boron are covalent. BF_3 is the most important halide and is prepared by the following reaction:



BF_3 is an electron deficient compound and boron has a sextet of electrons around itself (instead of an octet) VSEPR theory predicts a planar triangle structure with bond angle of 120°



The B-F bond lengths (130 pm) are shorter than the sum of covalent radii of B (80 pm) and F (72pm). The bond energy is also higher than that of a single bond. This implies development

of double bond character in the B-F bond. The vacant 2p orbital on B overlaps with one of the filled 2p orbital of fluorine to form a dative π bond ($p\pi - p\pi$ bond) fig 9.

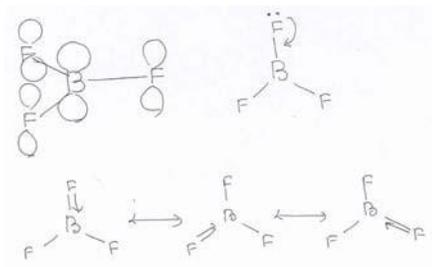
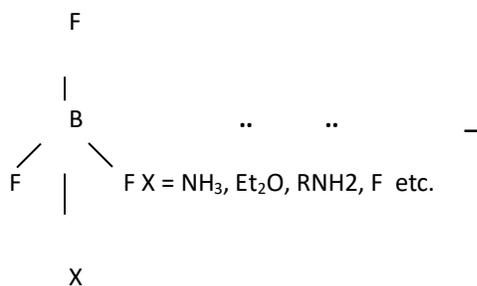


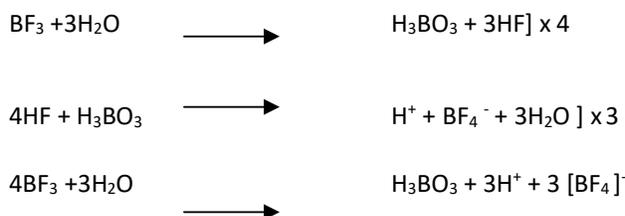
Fig. 9: Structure of BF_3

As a result of this π bond formation, the boron atom attains an octet of electrons and remedies the electron deficiency. All bond lengths are identical indicating resonance between three forms (fig 9). As may be expected from their electron deficient nature, the tri-halides of boron act as Lewis acids and accept electron pairs from Lewis bases like ammonia, amines and ethers. The electrons are donated to the vacant 2p orbital and the resultant adducts have tetrahedral structure.

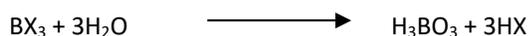


In these compounds the B-F bond length is longer than that in BF_3 as there is no vacant 2p orbital on B and the dative bond

cannot be formed. Fluorine is the most electro-negative halogen and the order of acid strength of BX_3 is expected to be $BF_3 > BCl_3 > BBr_3 > BI_3$ but the reverse is true. These compounds act as Lewis acids because of their electron deficiency. We have seen that an internal compensation of electron deficiency is achieved by dative bond formation. In order to form a strong dative bond, it is essential that the orbitals of the combining atoms be matched in size so as to allow effective overlap. The 2p orbital of fluorine is matched in size with the 2p orbital of boron resulting in a strong bond and reduction of electron deficiency on boron. As the size of the halogen increases, the orbitals become larger and more diffuse to allow effective overlap with the 2p orbital of boron. Thus the electron deficiency on boron increases and the relative acid strength follows the order: $BF_3 < BCl_3 < BBr_3 < BI_3$. The boron halides undergo hydrolysis; the hydrolysis of BF_3 is partial and the hydrolysis products, boric acid and hydrogen fluoride, combine to give fluoborate ion



The other tri-halides are hydrolyzed completely to give boric acid and the corresponding hydrogen halide.



It exists in non-eclipsed and planar conformations with free rotation about the B-B bond (fig10) Gallium and indium form di-halides, GaCl_2 and InCl_2 they are better represented as $\text{M}^+ [\text{MCl}_4]^-$, i.e. they contain M(I) and M(III).

Boron forms some monohalides which are polymeric and are represented as $(\text{BX})_n$, Chlorides with $n=4, 8, 9, 10, 11$ and 12 are reported, B_4Cl_4 , B_8Cl_8 are crystalline solids having closed cage of boron atoms (fig 10)

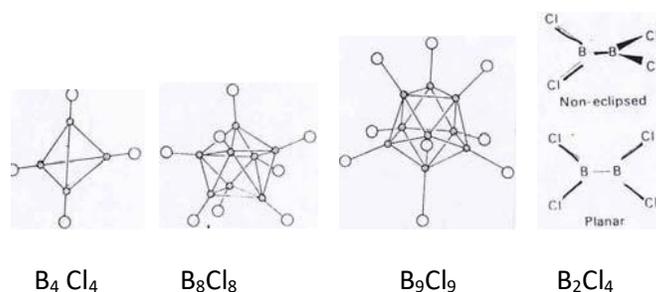


Fig. 10: Structures of $(\text{BCl})_n$

Each boron atom is bonded to three other boron atoms and one chlorine atom by multi-centred bonding.