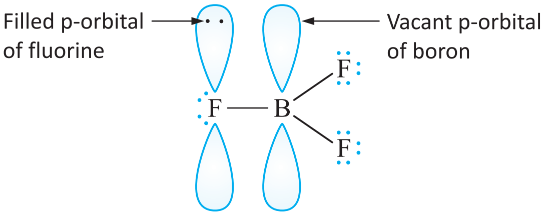
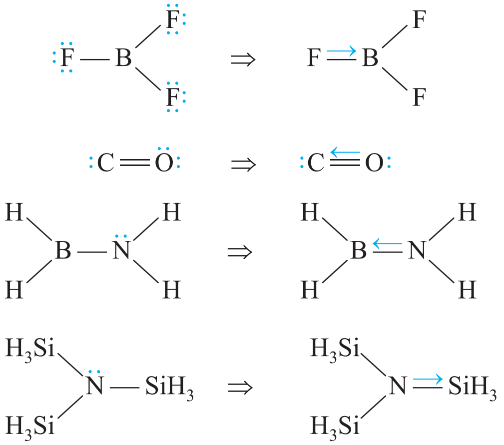
Chemical Bonding - II

Till now we have learnt about the various aspects of chemical bonding. In this part of the chapter we will try to summarize the method to find shapes and hybridisation of molecules and will also learn about Molecular Orbital Theory.

BACK BONDING Section - 1

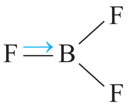
Back (π) bond is a co-ordinate bond formed between electron rich atom (donor) and neighbouring electron deficient atom or atom having vacant orbital (acceptor) of a molecular species. For example in BF_3 back bonding is due to by donation of an electron pair from filled orbital of fluorine atom to vacant p-orbital of boron.



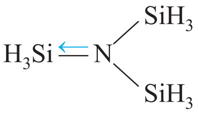


This back (π) bonding may results in change in hybridization state, molecular geometry, bond angle, bond strength and Lewis basic strength. For example in $N(SiH_3)_3$ hybridization state of nitrogen atom is sp^2 and it is not a Lewis base.

Further this back (π) bonding can be Pπ-Pπ and Pπ-dπ type depending upon type of filled orbital and vacant orbital. For example:



Pπ-Pπ Back bonding



Pπ-dπ Back bonding

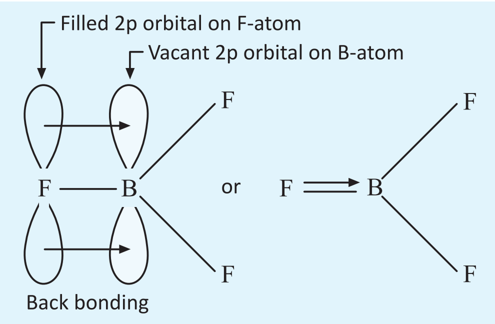
Illustration - 1 *Account for the fact that Lewis acid character of BF_3, BCl_3 and BBr_3 increases as $BF_3 < BCl_3 < BBr_3$.*

SOLUTION :

The increasing order of Lewis acid strength (or character) ($BF_3 < BCl_3 < BBr_3$) can be explained on the basis of the concept of ($p\pi$-$p\pi$) back bonding that takes place in given halides.

We know that in each of the given trihalide molecules B-atom is sp^2 hybridised and has one unused vacant $2p$ orbital. Each of the three halogen atoms in each BX_3 molecule (X : F, Cl, Br) has three pairs of electrons which are present in s and p-orbitals respectively ($F = 2s^2\ 2p^2\ 2p^2\ 2p^1$; $Cl = 3s^2\ 3p^2\ 3p^1$; $Br = 4s^2\ 4p^2\ 4p^2\ 4p^1$). p-orbital having unpaired electron is used up in forming B – X bond in BX_3 molecule by overlapping with singly-filled sp^2 hybrid orbital of B-atom.

In BF_3 molecule, vacant $2p$ orbital on B-atom and fully-filled $2p$ orbital of F-atom overlap sidewise to form (F →B) π-bond which is called dative or ($p\pi$-$p\pi$) bonding. It is due to ($p\pi$-$p\pi$) back bonding that B – F bond acquires some double bond character.



Formation of $p\pi$-$p\pi$ back bonding in one of the three B – F bonds in BF_3.

Back bonding in BF_3 molecule is supported by the fact that the observed B – F bond length in BF_3 which is equal to 1.30 Å is significantly shorter than the sum of the covalent radii of B and F atoms (B = 0.80 Å, F = 0.72 Å, Sum = 0.80 + 0.72 = 1.52 Å).

The formation of ($p\pi$-$p\pi$) bond results in that the electron pair is transfered from F-atom to the electron deficient B-atom and hence electron density on B-atom in BF_3 molecule is increased or the tendency of B-atom to accept the electron pair is decreased, i.e. the Lewis acid strength of BF_3 molecule, according to lewis concept, is also decreased.

We have seen above that ($p\pi$-$p\pi$) back bonding in BF_3 molecule result from [$2p^2$(F) – $2p^0$ (B)] sidewise overlap, but the same in BCl_3 and BBr_3 molecules is obtained by [$3p^2$(Cl) – $2p^0$ (B)] and [$4p^2$ (Br) – $2p^0$ (B)] sidewise overlaps respectively.

Now since the energy and shape of two $2p$ orbitals (one $2p$ orbital on B-atom and one $2p$ orbtal on F-atom) involved in [$2p^2$ (F) – $2p^0$ (B)] overlap to from ($p\pi$ -$p\pi$) bonding in BF_3 molecule is the same, this overlap is symmetrical and hence is the most effective. Consequently the transfer of electron pair from $2p$ orbtial of F-atom to the vacant $2p$ orbital of B-atom takes place to the maximum extent and hence maximum electron density developed on B-atom in BF_3 molecule. Due to maximum electron density developed on B-atom in BF_3 molecule, this molecule shows minimum tendency to accept electron pair donated by a Lewis base (electron pair donor species) and hence is the weakest Lewis acid. On the other hand, since the energy and shape of 4p orbital of Br atom and $2p$ orbital of B-atom involved in [$4p^2$ (Br) – $2p^0$ (B)] overlap in BBr_3 molecule is largely different, this overlap is unsymmetrical and hence is the least effective. Conseqnently the transfer of electron pair from $4p$ orbtal of Br-atom to the vacant $2p$ orbital of B-atom takes place to the minimum extent and hence minimum electron density is developed on B-atom in BBr_3 molecule. Due to minimum electron density developed on B-atom, BBr_3 molecule shows maximum tendency to accept electron pair donated by a Lewis base and hence is the strongest Lewis acid.

Above discussion shows that the tendency to form ($p\pi$ – $p\pi$) back bonding decreases rapidly as we move from BF_3 to BBr_3 and hence the tendency of BF_3, BCl_3 and BBr_3 molecules to accept electron pair from Lewis bases increases in the same direction, i.e. Lewis acid strength (or character) increases as $BF_3 < BCl_3 < BBr_3$.

Illustration - 2 *($p\pi - p\pi$) back bonding occurs in the halides of boron but not in those of aluminium. Explain.*

SOLUTION :

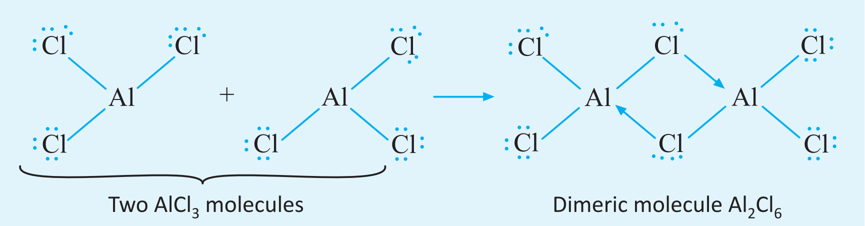
The tendency of the central atom (A) in AX_3 molecules (A = B or Al, X = halogen) to from ($p\pi$-$p\pi$) back bonding depends on the size of the central atom (A) . Smaller is the size of the central atom, greater is its tendency to form ($p\pi$-$p\pi$) back bonding. Since B-atom is smaller in size than Al-atom, BX_3 molecules have ($p\pi$-$p\pi$) back bonding while AlX_3 molecules do not have this type of back bonding.

Illustration - 3 *Explain why $AlCl_3$ exists as a dimer, $(AlCl_3)_2$ or Al_2Cl_6 while BCl_3 exits as a monomer.*

OR Explain the formation of dimeric structure of $AlCl_3$ in benzene (inert solvent) and in the vapour state.

OR Explain why all Al – Cl bonds in Al_2Cl_6 are not equivalent.

SOLUTION :



In $AlCl_3$ molecule, Al-atom is surrounded by six electrons which are less by two electrons from an octet. In dimeric structure (Al_2Cl_6), Al-atom of both $AlCl_3$ molecules completes its octet by accepting an electron pair from Cl-atom of the other $AlCl_3$ molecule as shown. Thus we see that in Al_2Cl_6 dimer each Al-atom is holding four large-sized Cl-atoms around it.

Since B-atom is very small in size, this atom is not capable of holding four large-sized Cl-atoms around it in B_2Cl_6 molecule and hence BCl_3 molecule cannot dimerise to form dimeric molecule, $(BCl_3)_2$ or B_2Cl_6.

The formation of dimeric molecule, Al_2Cl_6 can be explained on the basic of hydridisation concept as follows. We know that in $AlCl_3$ molecule Al-atom (Al = $3s^1$ $3p^1$ $3p^1$ $3p^0$) is sp^2 hydridised and one $3p$ orbtal remains vacant and unhydridised. In $AlCl_3$ molecule Al has coordination number equal to 3. In the formation of Al_2Cl_6, the vacant and unhybridised $3p$ orbital on Al-atom of one $AlCl_3$ molecule receives a lone pair of electrons from $3p$ orbital of Cl-atom (Cl = $3s^2$ $3p^2$ $3p^2$ $3p^1$) of the other $AlCl_3$ molecule and thus forms a [$3p^2$ (Cl) $\longrightarrow$ $3p^0$ (Al)] coordinate bond. In this way each Al-atom completes its octet and coordination number of Al-atom is increased from 3 (in $AlCl_3$) to 4 (Al_2Cl_6). Thus we see that two bridges are formed by two Cl-atoms between two Al-atoms.

The structure of Al_2Cl_6 has six Al – Cl covalent bonds and two Cl $\longrightarrow$ Al coordinate bonds, these bonds donot have equal length, i.e. all Al – Cl bonds in Al_2Cl_6 are not equivalent.