



What you already know

- Types of hybridization
- Hybridization in odd electron species
- Some molecules that change hybridization in solid states
- Resonance
- Resonating structure and resonance hybrid
- Bond order



What you will learn

- Drago's rule
- Lewis acid/base
- Coordinate bond
- Back bonding
- Factors affecting back bonding
- Consequences of back bonding



MAIN



BOARDS

Limitation of Hybridization

The exception or limitation in hybridization is given by Drago's rule.

Drago's rule

According to this rule, **hybridization does not take place for compounds of elements of 3rd period ($Z \geq 15$) and onwards, which are bonded to a less electronegative element having an electronegativity less than 2.5, like hydrogen.**

These types of compounds have bond angles near to 90° because there is no hybridization, i.e., no mixing of orbitals. So, pure p-orbitals take part in bonding.

Examples: PH_3 , H_2S , AsH_3 , etc.

Conditions for Drago's rule:

- Energy differences between the participating orbitals should be very high.
- Central atoms should have **one or more lone pairs of electrons**.
- Central atoms should belong to the **3rd period** and above.
- Side atoms should have **an electronegativity less than 2.5**.



Orbital Contraction

If a central atom forms more bonds than that of unpaired electrons present in its valence shell, then excitation of electrons from lower energy orbitals to higher energy orbitals is required. We know that the energy gap between 3s and 3p is very less, hence the excitation of electrons from 3s to 3p is possible without external factors but the excitation to 3d-orbitals is not possible without an external source (electronegative side atoms) due to large energy gap. So, for the mixing of 3s, 3p, and 3d-orbitals, we have to decrease the energy of 3d-orbital and this process of decreasing the energy is known as orbital contraction.

Examples:

- PCl_5 exists in nature but PH_5 does not exist.

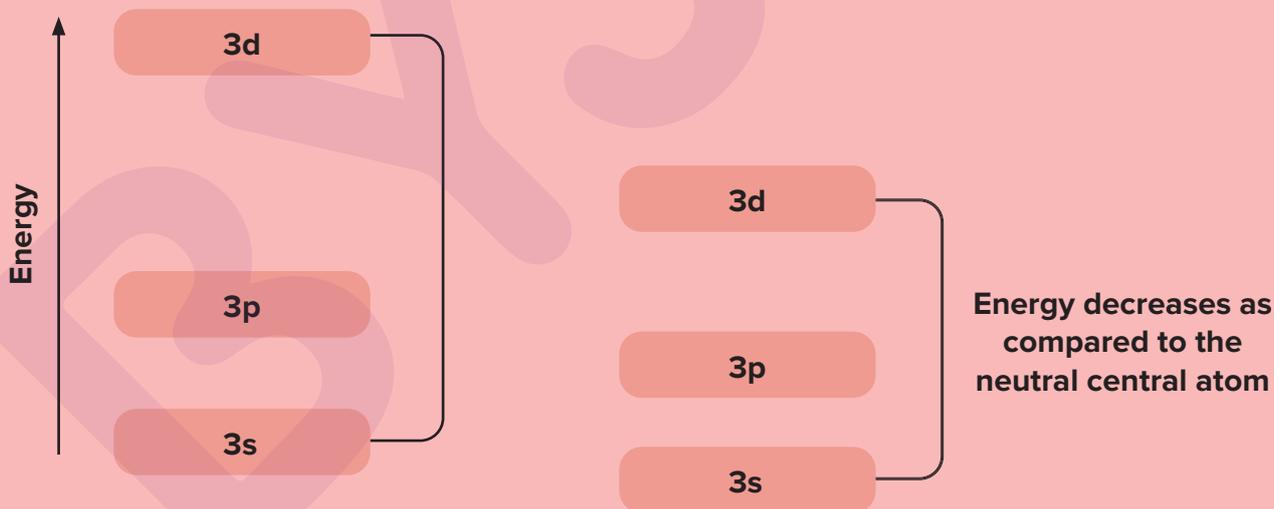
This is due to orbital contraction. The ground state electronic configuration of phosphorous can be written as follows:



Fig. 1: Ground state valence shell electronic configuration of phosphorus

In the ground state electronic configuration of phosphorus (P), there are **three unpaired electrons**, so it can form only **three sigma bonds** in its ground state. There is a need for excitation of electrons from 3s to 3d to form **five sigma bonds**.

If an **electronegative atom** is attached to the central atom, then there is a **partial positive charge** on the central atom and due to this charge, **orbital contraction** takes place, but if it is bonded with an atom having an electronegativity lower than 2.5, then orbital contraction **cannot take place**. The energies of the orbital when there is a **partial positive charge** on the central atom can be shown as:



When the central atom is neutral

When the central atom has partial positive charge

Orbital contraction

From the above figure, we can see that when **electronegative atoms** are attached to the central atom, partial positive charges are induced on the central atom. Due to this, the **energy gap** between the orbitals is **decreased**. In the orbital contraction, the **energy of 3d** decreases **maximum** because **d-orbitals are diffused** in nature and lowest for the s-orbitals. The orbitals are nearly of the same energy, hence **mixing** of **3s**, **3p**, and **3d**-orbitals takes place.

For the formation of PH_5 , H-atom cannot do excitation from the ground state of phosphorus because hydrogen has an electronegativity less than 2.5 and the central atom phosphorus belongs to the 3rd period.

So, the energy difference between orbitals is very high and due to low electronegativity, hydrogen cannot do orbital contraction.

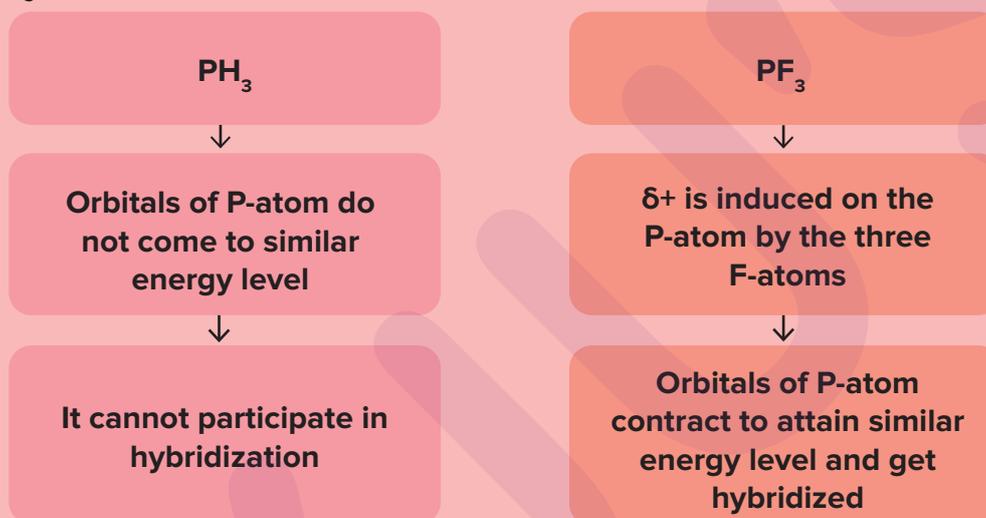
However, in PCl_5 , Cl-atom has high electronegativity and can do excitation in the ground state of phosphorus. **Hence, PCl_5 exists in nature but PH_5 does not.**

The excitation state of phosphorus is given as follows:



Fig. 2: Excited state valence shell electronic configuration of phosphorus

• PH_3 and PF_3



Application of Drago's rule

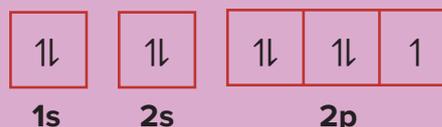
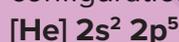
Find out the total number of molecules that **exist** among the following:



Solution

• HFO_4

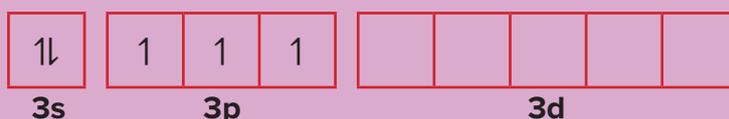
The ground state electronic configuration of fluorine is as shown:



In the ground state, fluorine can form only one bond as it has only one unpaired electron and there is no vacant orbital for excitation, i.e., valency expansion is not possible. Therefore, **HFO_4 does not exist.**

• PH_5

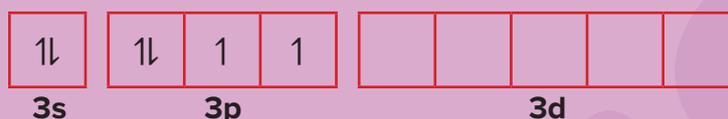
The ground state electronic configuration of phosphorus can be written as follows: $[\text{Ne}] 3s^2 3p^3$



In the ground state electronic configuration of phosphorus (P), there are only three unpaired electrons, so it can form three sigma bonds in its ground state. For five sigma bonds with phosphorus (P), a 3s electron has to be excited to an empty 3d-orbital. Since electronegativity of hydrogen is low, orbital contraction is not possible. Therefore, excitation of electrons from 3s to 3d is not possible and **PH₅ does not exist**.

- **SCI₆**

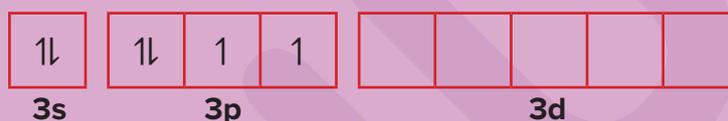
The ground state electronic configuration of sulfur can be written as follows: **[Ne] 3s² 3p⁴**



The electronegativity of chlorine is very high as compared to that of sulfur, so excitation of electrons is possible but the size of chlorine is very large, so sulfur cannot accommodate six chlorine atoms due to steric crowding. **Hence, SCI₆ does not exist**.

- **SF₆**

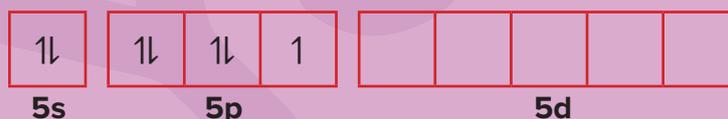
The ground state electronic configuration of sulfur can be written as follows: **[Ne] 3s² 3p⁴**



The electronegativity of fluorine is very high, so excitation of sulfur electrons is possible from 3s and 3p to 3d-orbitals. Also, fluorine has a very small size, so sulfur can accommodate six fluorine atoms. **Therefore, SF₆ exists in nature**.

- **IF₇**

The ground state electronic configuration of iodine (I) can be written as follows: **[Kr] 4d¹⁰ 5s² 5p⁵**



In the ground state of iodine, it has one unpaired electron. To form seven bonds with F-atoms, three electrons from 5s and 5p has to be excited to 5d-orbitals. Since fluorine is the most electronegative element, orbital contraction and mixing of orbitals are possible. In the excited state, iodine has seven unpaired electrons, so it can form seven sigma bonds. **Therefore, IF₇ exists in nature**.

- **XeH₄**

The ground state valence shell configuration of xenon can be written as follows: **[Kr] 4d¹⁰ 5s² 5p⁶**



To form XeH₄, two 5p electrons have to be excited to d-orbitals but due to less electronegativity of the H-atom, orbital contraction is not possible. Therefore, electron excitation is not possible and **XeH₄ does not exist**.

BOARDS

MAIN

Lewis Acids

They are the chemical species that have **empty orbitals** and are able to **accept lone pairs** to form coordinate covalent bonds. Examples: H^+ , BF_3 , etc.

Conditions for Lewis acid

- Compounds that have **incomplete octets**, i.e., have vacant orbitals, can accept the lone pairs and act as **Lewis acid**.
Examples: BF_3 , AlCl_3 , BCl_3
- Compounds that have **vacant d-orbitals** and are bonded to high **electronegativity atoms**. In such cases, a partial positive charge is induced on the central atom. Thus, they have the tendency to accept the lone pairs into **d-orbital** due to orbital contraction and act as **Lewis acid**.
Examples: SiF_4 , PCl_5 , PF_5
- Metal cations** (especially d-block metals) have low-lying **vacant orbitals**, so they can easily accept the lone pairs hence act as Lewis acid. As the magnitude of charge increases, the tendency to accept lone pairs also increases.
Examples: Mg^{2+} , Al^{3+} , Fe^{2+} , Zn^{2+}
- Compounds in which the **central atom** is attached to more **electronegative atoms multiple bonds** also have a tendency to accept the electrons. This is due to the high electronegativity of the side atoms that pull the **electron density towards themselves** and the central atom becomes electron deficient. Thus, such compounds act as **Lewis acid**.
Examples: CO_2 , SO_2

BOARDS

Lewis Base

They are the chemical species that are able to **donate** their **unshared electron pairs** to the chemical species having low-lying **vacant orbitals** via formation of a **coordinate covalent bond**.
Examples: OH^- , NH_3 , etc.

Conditions for Lewis base

- Compounds, in which the central atom has **lone pairs** in the neutral state and is surrounded by the **less electronegative atoms**, have the tendency to donate their lone pairs. Thus, they can act as **Lewis base**. **Examples:** NH_3 , H_2O , ROH , RNH_2
- Molecules or atoms having **negative charge**, i.e., anions also have a tendency to donate the electron pairs. Thus, they can act as **Lewis bases**. **Examples:** Cl^- , F^- , OH^- , NH_2^-



Note

Compounds having positive charge on the central atom cannot donate their unshared pair of electrons. **Example:** H_3O^+

BOARDS

Coordinate Bond (Dative Bond)

It is the covalent bond in which **both electrons of a shared pair** are contributed by only **one of the two bonded atoms**.

The atom that donates the electron pair is known as the donor (or Lewis base), whereas the atom that accepts the electron pair is known as the acceptor (or Lewis acid). The direction of donation of electrons is denoted by **an arrow** (\rightarrow). The arrow should be placed such that the head of the arrow points towards the **acceptor atom** and tail of the arrow is towards the **donor atom**.

Coordinate bonds can be divided into two types. They are as follows:

- **Sigma type coordinate bond**
- **Pi (π) type coordinate bond (Back bonding)**

BOARDS

Sigma Type Coordinate Bond

A covalent bond in which **both the electrons of a shared pair** are contributed by only one of the two bonded atoms **along the internuclear axis** is known as **sigma type coordinate bond**. In such bonding, **Lewis adduct formation** takes place.



Example:

Lewis acid-base adduct of NH_3 and BF_3

In case of BF_3 , there are three sigma bonds and one empty pure p-orbital. In NH_3 , sp^3 hybridized lone pair is donated to pure p-orbital of BF_3 and a dative bond is formed. So, in this acid-base adduct, BF_3 has four bonds and the geometry of BF_3 is changed from trigonal planar to tetrahedral.

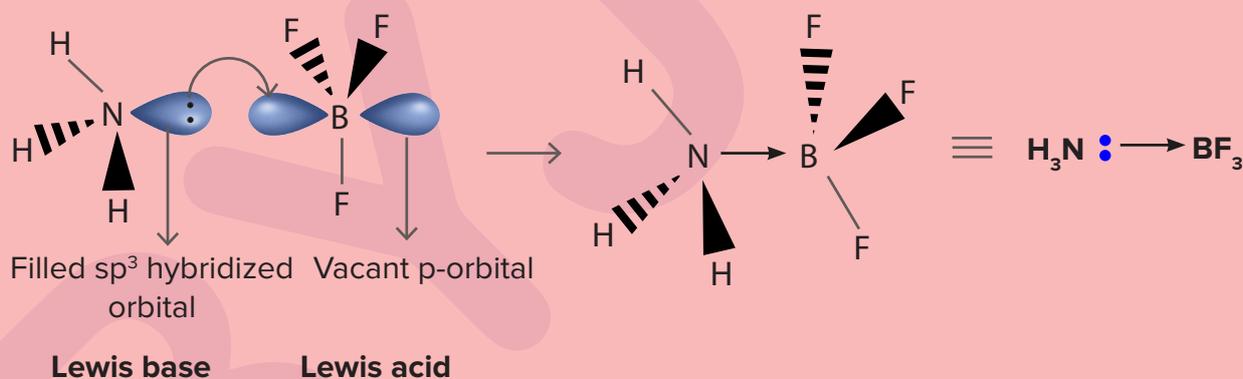


Fig. 4: Formation of Lewis acid-base adduct

BOARDS

Pi (π) Type Coordinate Bond (Back Bonding)

A covalent bond in which **both the electrons of a shared pair** are contributed by only one of the two bonded atoms **by sidewise overlapping** is known as **pi (π) type coordinate bond**. This is also known as **back bonding**.

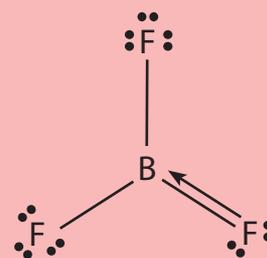


Fig. 5: Pi (π) type coordinate bond



Note

We know that there is **no difference between the sigma bond and sigma type coordinate bond**. This means that after the formation of a bond, a sigma bond has similar properties as a coordinate bond and vice versa. Similarly, there is **no difference between the pi (π) bond and pi (π) type coordinate bond (back bonding)**.



Back Bonding

Back bonding is also known as **pi (π) type coordinate bond** in which pure orbitals overlap sideways and one atom has **lone pairs**, whereas the other has **empty orbitals**.

Conditions for back bonding

- One atom should have a **non-bonded electron pair**, whereas the other should have a **vacant orbital**.
- The bond formed is **polar** because there is an **electronegativity difference** between the side atom and the central atom.
- There should be **intra-electronic repulsion** so that the donation of lone pairs happens easily.
- One of the atoms involved in **back bonding** should belong to the **2nd period**.

Example:

• Boron trifluoride (BF_3)

Boron (B) has four orbitals in its valence shell. In BF_3 , it is bonded with three fluorine atoms using three sp^2 hybridized orbitals and has one empty pure p-orbital. The pure vacant p-orbital of boron (B) and the p-orbital of fluorine (F) having lone pairs undergo sidewise overlapping. This results in the formation of the pi (π) type coordinate bond, also known as **back bonding**. All three fluorine (F) atoms have an equal tendency to donate their lone pairs and result in the resonance hybrid as shown in **Fig. 6**. Due to the back bonding, there is a partial double bond character between B and F. So, the **B-F bond in BF_3 is shorter and stronger as compared to that of the sigma B-F bond**.

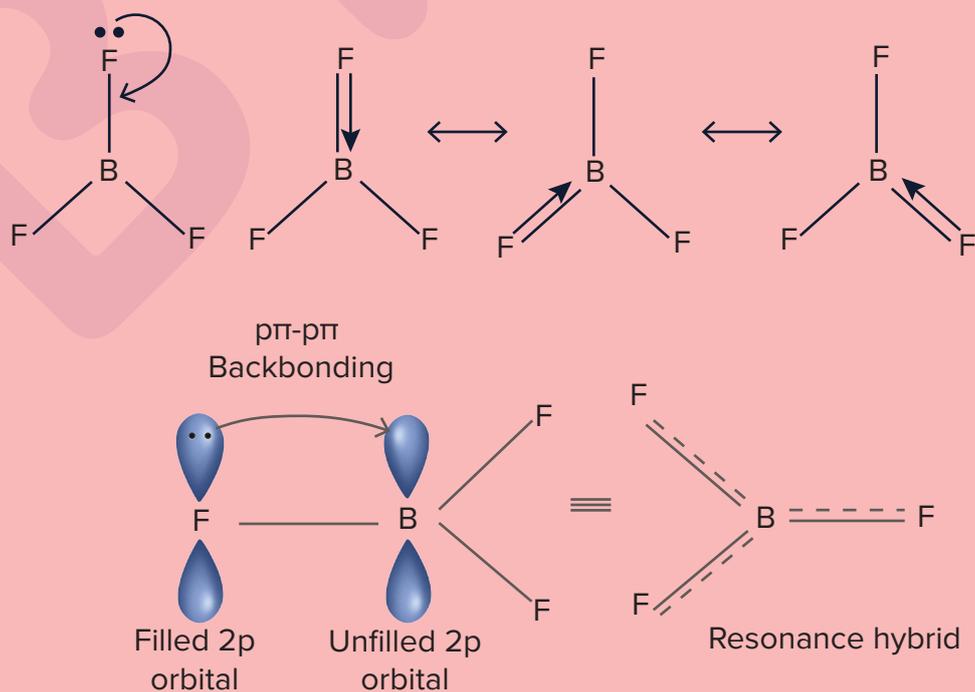


Fig. 6: Back bonding in BF_3 - Resonance hybrid

$p\pi-p\pi$ back bonding

- If both donor (which has lone pair) and acceptor atom (which has vacant orbital) use their p-orbitals to form pi (π) type coordinate bond, then it is known as **$p\pi-p\pi$ back bonding**.

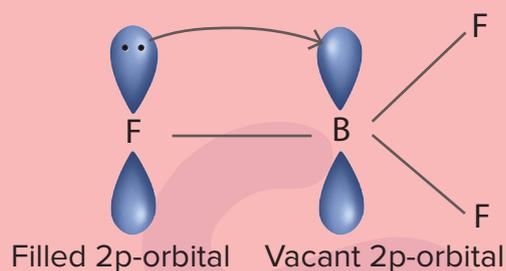


Fig. 7: $p\pi-p\pi$ back bonding

$p\pi-d\pi$ back bonding

- If the donor atom donates its lone pair from p-orbital and the acceptor atom (which has vacant orbital) accepts these electron pairs in d-orbital, then it is known as **$p\pi-d\pi$ back bonding**.

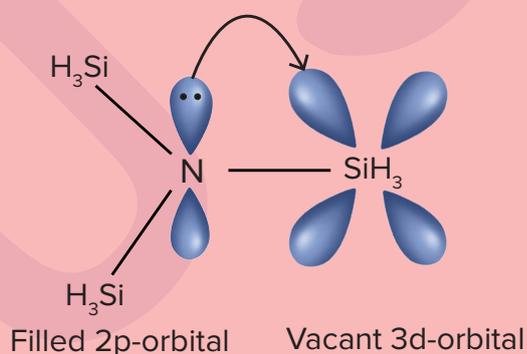


Fig. 8: $p\pi-d\pi$ back bonding



Note

In this representation, the first orbital belongs to the donor atom and the second orbital belongs to the acceptor atom.

Example: In **$p\pi-d\pi$ back bonding**, p-orbital belongs to the donor atom and d-orbital belongs to the acceptor atom.

BOARDS

MAIN

Factors Affecting the Back Bonding

- In a group**
In a group, size is the dominating factor. The extent of overlapping is inversely proportional to the size. As we move down the group, the size increases and the sidewise overlapping decreases, and as we go down in the group, the **size increases and the extent of overlapping decreases**.
 The accepting as well as donating tendency of atoms is inversely proportional to the size of participating atoms, so as the size increases, the accepting as well as donating tendency of atoms decreases.

- **In a period**

In a period, electronegativity is the dominating factor. As we move from left to right, the electronegativity value increases.

The **donating tendency of the donor atom is inversely proportional to the electronegativity**. As the electronegativity increases, the electrons are strongly attracted by the nucleus and it is very difficult to donate the lone pair of electrons.

The **accepting tendency of the acceptor atom is directly proportional to the electronegativity**, so as the electronegativity increases, the tendency to accept the electrons increases.



- **Number of lone pairs**

As the number of lone pairs on the acceptor atom **increases**, the tendency to accept the electrons **decreases** because these atoms already have a **high electron density**.

BOARDS

MAIN

Strength of Back Bonding

As the size of the **orbital increases**, the extent of the **overlapping decreases**. Hence, the strength of back bonding decreases. **Example:**



Strength of back bonding

In BF_3 , the central atom boron has pure 2p-orbitals and lone pair is also present in the 2p-orbital of fluorine, So, **$2p\pi-2p\pi$** type back bonding happens. In case of PF_3 , there is a vacant 3d-orbital in phosphorus and a lone pair is present in 2p-orbital of fluorine, so **$2p\pi-3d\pi$** type back bonding happens. As we move down the group, the extent of overlapping decreases, hence the strength of back bonding decreases. Therefore, **BF_3 has stronger back bonding than PF_3 .**



Based on back bonding

Which of the following represents the **correct order** of extent of back bonding?

- (a) $\text{PF}_3 < \text{SiF}_4$ (b) $\text{PF}_3 > \text{SiF}_4$ (c) $\text{PF}_5 < \text{SiF}_4$ (d) $\text{PF}_5 > \text{SiF}_4$

Solution

- **Comparison in PF_3 and SiF_4**

In case of PF_3 , both phosphorus (P) and fluorine (F) have lone pairs. Also, phosphorus (P) has a

vacant orbital, so the back bonding happens from F to P. On the other hand, in SiF_4 , only fluorine (F) has lone pairs, whereas silicon (Si) has a vacant d-orbital, so the back bonding happens from F to Si.

We know that as the number of lone pairs increases on the acceptor atom, the tendency to accept the electrons decreases. So, in PF_3 , **due to the presence of lone pairs on phosphorus atom, it has lesser tendency to accept the electron pairs via back bonding and has less extent of back bonding as compared to SiF_4 .**

So, option (a) is correct and option (b) is incorrect.

• Comparison in PF_5 and SiF_4

In case of PF_5 , fluorine (F) has lone pairs, whereas phosphorus (P) has vacant d-orbitals, so back bonding happens from F to P. Similarly, in SiF_4 , fluorine (F) has lone pairs and vacant orbitals are present in silicon (Si), so back bonding takes place from F to Si.

In both the compounds, i.e., SiF_4 and PF_5 , 2p-3d orbitals are involved in back bonding. Also, the central atom does not have any lone pair. So, the charge on the central atom is the dominating factor. In case of PF_5 , there are five fluorine atoms bonded with P, whereas SiF_4 has only four atoms attached to Si. So, **due to the high charge on P, there is more orbital contraction as compared to Si. Therefore, PF_5 has greater extent of the back bonding as compared to SiF_4 .** Hence, (a) and (d) are the correct options.



Order of Accepting Tendency

- **As the number of lone pairs increases on the acceptor atom, the accepting tendency decreases.** As we move from Si to Cl, the number of lone pairs continuously increases and the tendency to accept the electrons decreases. The order of accepting tendency is:

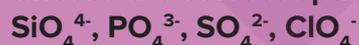


- **When lone pairs are absent on the central atom, the accepting tendency of the central atom increases as we move from left to right in the periodic table.** As we move from Si to Cl, the charge on the central atom increases and as the charge increases, the tendency to accept the electrons increases. The order of accepting tendency can be written as follows:



Application of back bonding

Choose the **correct option(s)** regarding the following molecules:

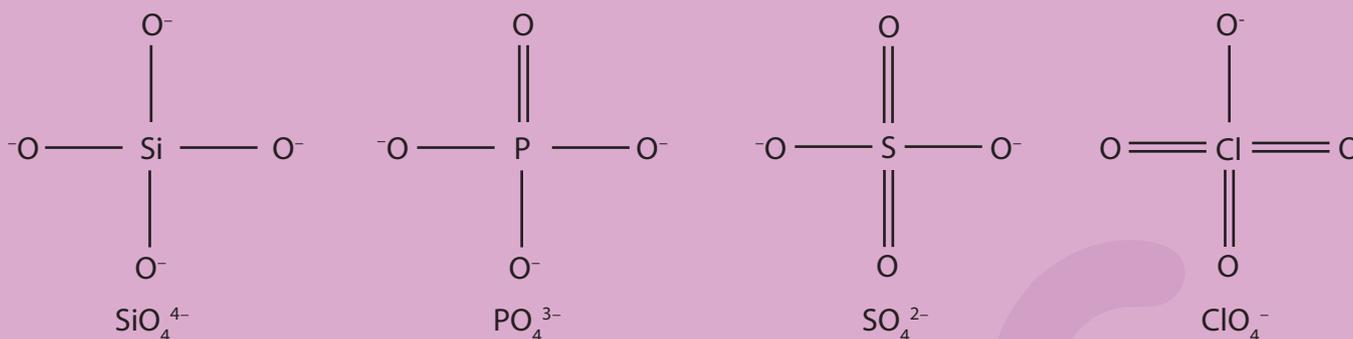


- $\text{SiO}_4^{4-} < \text{PO}_4^{3-} < \text{SO}_4^{2-} < \text{ClO}_4^-$ (Extent of back bonding)
- $\text{SiO}_4^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{ClO}_4^-$ (Extent of back bonding)
- $\text{SiO}_4^{4-} < \text{PO}_4^{3-} < \text{SO}_4^{2-} < \text{ClO}_4^-$ (Polymerization tendency)
- $\text{SiO}_4^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{ClO}_4^-$ (Polymerization tendency)

Solution

Finding the extent of back bonding:

The Lewis structure of the compound can be written as:



In all the compounds, oxygen has lone pairs and the central atom has vacant orbitals. Therefore, the back bonding takes place from oxygen to central atom. Also, all the atoms have maximum covalency, i.e., have zero lone pairs. As the number of bonds on the central atom increases, the partial positive charge also increases. This leads to a decrease in the size of the atom, i.e., orbital contraction. Among the given compounds, **Cl has the maximum bonds and maximum orbital contraction, whereas Si has the least contraction. Hence, as we move from SiO_4^{4-} to ClO_4^- , the extent of back bonding increases.**

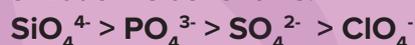
Therefore, (a) is the correct option.

Finding extent of polymerization:

As the tendency to form pi bonds with the central atom increases, the tendency to form bonds with the other molecules decreases or tendency of polymerization decreases.

In other words, we can say that the tendency **to polymerize is inversely proportional to the back bonding**. As the extent of back bonding increases, the polymerization tendency decreases.

Hence, the correct order of polymerization is as follows:



Therefore, (d) is the correct option.

Hence, options (a) and (d) are the correct answer.

BOARDS

MAIN

Consequences of Back Bonding

ADVANCED

Consequences of back bonding

Lewis acidic strength

Lewis basic strength

Bond length

Bond angle

Hybridization

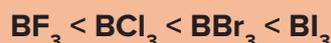
• Lewis acidic strength

Lewis acidic strength is inversely proportional to the back bonding. As the extent of the back bonding increases, the Lewis acidic strength decreases. This is because if the back bonding increases, then the electron density on the atom which has vacant orbital increases and the tendency to accept electrons from Lewis base decreases.

Example: Lewis acid strength of boron halides, i.e., BF_3 , BCl_3 , BBr_3 , BI_3

As we move down in the group, i.e., F to I, the size increases due to the increase in number of subshells. We know that the extent of back bonding is inversely proportional to the size of participating atoms. Therefore, as we move down in the group, the back bonding decreases and the Lewis acidic strength increases.

So, the correct order of Lewis acidic strength can be written as follows:

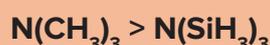


- **Lewis basic strength**

Lewis basic strength is inversely proportional to the back bonding. As the extent of the back bonding increases, the Lewis basic strength decreases. This is because if the **extent of back bonding increases, then the electron density of the donor atom is shared via back bonding.** Therefore, electrons are not available for donation to other molecules and Lewis basic strength decreases.

Example: Basic strength of $\text{N}(\text{CH}_3)_3$ is greater than $\text{N}(\text{SiH}_3)_3$.

In $\text{N}(\text{CH}_3)_3$, nitrogen (N) has one lone pair but there is no vacant orbital on carbon (C) in CH_3 , so back bonding is not possible in $\text{N}(\text{CH}_3)_3$. On the other hand, in $\text{N}(\text{SiH}_3)_3$, silicon has vacant d-orbitals in which the lone pairs of nitrogen can be easily donated via back bonding. So, lone pairs are not available for donation to the other molecules as they were present in $\text{N}(\text{CH}_3)_3$. Therefore, order of basic strength can be written as follows:

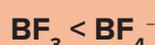


- **Bond length**

Bond length is inversely proportional to the back bonding. As the extent of back bonding increases, the bond length decreases. This is because as the back bonding increases, the pi bond character increases. Therefore, the bond order increases and the bond length decreases.

Example: Bond length of BF_3 is less than BF_4^- .

In case of BF_3 , there is a vacant orbital in B (Boron) and F has lone pairs. So, in BF_3 , back bonding takes place but in case of BF_4^- , there is no vacant orbital in boron, so no back bonding takes place. Bond length is inversely proportional to the back bonding, hence BF_4^- has higher bond length than BF_3 . The correct order of bond length is given as follows:



- **Bond angle**

Back bonding may or may not affect the bond angle. When the lone pair of side atoms participates in back bonding, it is known as **side atom to central atom back bonding and there is no effect on hybridization** due to back bonding. However, if the lone pair of the central atom is participating in the back bonding, then it is known as the **central atom to side atom back bonding and in such case, there is a decrease in steric number and an increase in bond angle.**

Example: Bond angle of $\text{O}(\text{CH}_3)_2$ is less than $\text{O}(\text{SiH}_3)_2$.

In $\text{O}(\text{CH}_3)_2$, oxygen has lone pair of electrons, whereas carbon (C) does not have vacant orbitals, so no back bonding takes place. On the other hand, in $\text{O}(\text{SiH}_3)_2$, oxygen (O) has lone pairs and silicon (Si) has vacant d-orbitals, so back bonding takes place and it happens from the central atom to the side atom. Therefore, hybridization of the central atom changes from sp^3 to sp^2 and the bond angle increases. Hence, the correct order of the bond angle is given as follows:



- **Hybridization**

Back bonding may or may not affect the hybridization. We know that the lone pair of the side atom has no effect on hybridization, whereas if the lone pair of the **central atom** is participating in the **back bonding**, then this lone pair **has no participation in steric number**. Hence, there is a decrease in steric number and change in hybridization.

Example: Hybridization of N in $\text{CH}_3\text{-N=C=O}$ & $\text{SiH}_3\text{-N=C=O}$ is sp^2 & sp respectively.

There is no back bonding in $\text{CH}_3\text{-N=C=O}$ because carbon (C) does not have any vacant orbital, whereas in $\text{SiH}_3\text{-N=C=O}$, silicon (Si) has vacant d-orbitals which can accept lone pairs from nitrogen (N), so back bonding takes place. When the back bonding happens from central atom to side atom, a change in hybridization takes place. The hybridization is given as follows:

$\text{CH}_3\text{-N=C=O}$ (No back bonding)

Number of lone pairs on N = 1

Number of sigma bonds = 2

Steric number = $1 + 2 = 3$

Hybridization = sp^2

$\text{SiH}_3\text{-N=C=O}$ (Back bonding)

Number of lone pairs on N = 0

Number of sigma bonds = 2

Steric number = $0 + 2 = 2$

Hybridization = sp



Back Bonding in NCl_3

In NCl_3 , both nitrogen (N) and chlorine (Cl) have lone pairs but the vacant orbital is present only in Cl. So, the back bonding happens from the central atom to the side atom (N to Cl). In NCl_3 , the lone pair of N participates in back bonding.

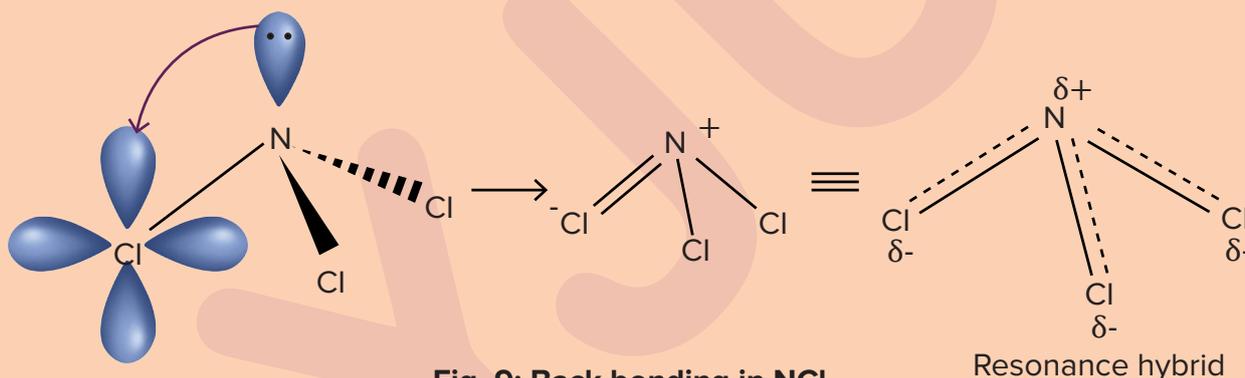


Fig. 9: Back bonding in NCl_3



Application of back bonding

$\text{N}(\text{CH}_3)_3$ is pyramidal but $\text{N}(\text{SiH}_3)_3$ is planar. **Why?**

Solution

Step 1: Finding hybridization in $\text{N}(\text{CH}_3)_3$

In $\text{N}(\text{CH}_3)_3$, nitrogen (N) has one lone pair but there is **no vacant orbital on carbon (C)**, so back bonding is not possible. Hybridization can be deduced as follows:

Number of lone pairs on N = 1

Number of sigma bonds = 3

Steric number = $1 + 3 = 4$

Hybridization = sp^3

Due to **sp^3 hybridization** with one lone pair, $\text{N}(\text{CH}_3)_3$ has a **trigonal pyramidal shape**.

Step 2: Finding hybridization in $N(\text{SiH}_3)_3$

In $N(\text{SiH}_3)_3$, nitrogen (N) has one lone pair and silicon (Si) has vacant d-orbitals. So, due to the presence of both lone pairs and vacant d-orbital, back bonding is possible. The **transfer of electrons happens from the central atom (N) to the side atom (Si)**. Hence, hybridization changes due to reduction in steric number by one. Hybridization of $N(\text{SiH}_3)_3$ can be deduced as follows:

Number of lone pairs on N = 0

Number of sigma bonds = 3

Steric number = 0 + 3 = 3

Hybridization = sp^2

Due to **sp^2 hybridization** with zero lone pairs, $N(\text{SiH}_3)_3$ has a **trigonal planar shape**.

**Application of back bonding**

$N(\text{SiH}_3)_3$ is planar while $P(\text{SiH}_3)_3$ is pyramidal. **Why?**

Solution**Step 1: Finding hybridization in $N(\text{SiH}_3)_3$**

In $N(\text{SiH}_3)_3$, nitrogen (N) has one lone pair and silicon (Si) has vacant d-orbitals. So, due to the presence of both lone pairs and vacant d-orbitals, back bonding is possible. The transfer of electrons happens from the central atom (N) to the side atom (Si). Hence, hybridization changes due to reduction in steric number by a unit. Hybridization of $N(\text{SiH}_3)_3$ can be deduced as follows:

Number of lone pairs on N = 0

Number of sigma bonds = 3

Steric number = 0 + 3 = 3

Hybridization = sp^2

Due to **sp^2 hybridization** with zero lone pairs, $N(\text{SiH}_3)_3$ has a **trigonal planar shape**.

Step 2: Finding hybridization in $P(\text{SiH}_3)_3$

In $P(\text{SiH}_3)_3$, phosphorus (P) has one lone pair and silicon (Si) has vacant d-orbitals, so back bonding is possible in $P(\text{SiH}_3)_3$. When we move down the group, the size increases and due to the increase in size, the extent of back bonding decreases. P belongs to the 3rd period, so it has a larger size than N. So, **in $P(\text{SiH}_3)_3$, $3p\pi-3d\pi$ type back bonding happens which is very poor**. Hence, in $P(\text{SiH}_3)_3$, the extent of back bonding is negligible and due to this, hybridization does not change. Hybridization of $P(\text{SiH}_3)_3$ can be deduced as follows:

Number of lone pairs on P = 1

Number of sigma bonds = 3

Steric number = 1 + 3 = 4

Hybridization = sp^3

Due to **sp^3 hybridization** with one lone pair, $P(\text{SiH}_3)_3$ has a **trigonal pyramidal shape**.

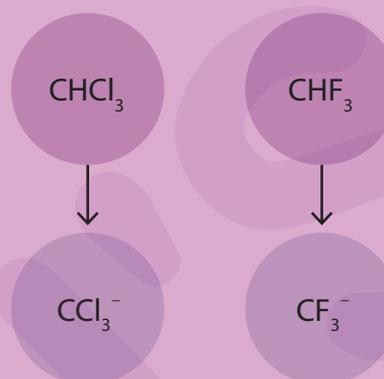


Application of back bonding

Why is CHCl_3 **more acidic** than CHF_3 ?

Solution

Acidity is the tendency to lose the proton easily. It depends on the stability of the anion which is formed after losing the proton. Loss of proton in the given compounds can be shown as:



In CCl_3^- and CF_3^- , carbon (C) atom has negative charge. In CCl_3^- , vacant d-orbitals are present on chlorine (Cl). Thus, **$2p\pi-3d\pi$ type** back bonding is possible from **carbon to chlorine**. **Due to this reason**, the negative charge on carbon is stabilized. On the other hand, in CF_3^- , **fluorine (F)** does not have **vacant orbitals**, so **back bonding is not possible in this case**. Therefore, the negative charge on carbon is **not stabilized** to a greater extent as done by back bonding in CCl_3^- and the acidity is dependent upon the stability of the anion. **Therefore, CHCl_3 is more acidic than CHF_3 .**



Summary

1. Drago's rule

According to this rule, hybridization does not take place for compounds of elements of 3rd period ($Z \geq 15$) and onwards, which are bonded to a less electronegative element, having an electronegativity less than 2.5, like hydrogen.

Example: PH_3 , H_2S , AsH_3 , etc.

2. Conditions for Drago's compound

- Energy differences between the participating orbitals should be very high.
- Central atoms should have one or more than one lone pair.
- Central atoms should belong to the 3rd period and above.
- Side atoms should have an electronegativity less than 2.5.

3. Lewis acid

They are the chemical species that have empty orbitals and are able to accept the lone pairs to form coordinate covalent bonds.

Examples: H^+ , BF_3 , etc.

4. Lewis base

They are the chemical species that are able to donate their unshared electron pairs to a chemical species having low-lying vacant orbitals via formation of a coordinate covalent bond.

Examples: OH^- , NH_3 , etc.

5. Coordinate bond

A covalent bond in which both the electrons of a shared pair are contributed by only one of the two bonded atoms is known as coordinate bond. Coordinate bonds can be divided into two types. They are as follows:

- **Sigma type coordinate bond**
- **Pi (π) type coordinate bond (Back bonding)**

6. Sigma type coordinate bond

A covalent bond in which both the electrons of a shared pair are contributed by only one of the two bonded atoms along the internuclear axis is known as sigma type coordinate bond. In such bonding, Lewis adduct formation takes place.

7. Pi (π) type coordinate bond (Back Bonding)

Back bonding is also known as Pi (π) type coordinate bond in which pure orbitals overlap sideways and one atom has lone pairs, whereas the other has empty orbitals.

8. Conditions for back bonding

- One atom should have a non-bonded electron pair, whereas the other should have a vacant orbital.
- The bond formed is polar because there is an electronegativity difference between the side atom and the central atom.
- There should be intra-electronic repulsion so that the donation of lone pairs happens easily.
- One of the atoms involved in back bonding should belong to the 2nd period.

9. $p\pi$ - $p\pi$ back bonding

If both donor (which has lone pair) and acceptor atom (which has vacant orbital) use their p-orbitals to form pi (π) type coordinate bond, then it is known as $p\pi$ - $p\pi$ back bonding.

10. $p\pi$ - $d\pi$ back bonding

If the donor atom donates its lone pair from p-orbital and the acceptor atom (which has vacant orbital) accepts these electron pairs in d-orbital, then it is known as $p\pi$ - $d\pi$ back bonding.

11. Consequences of back bonding

- Lewis acidic strength decreases
- Lewis basic strength decreases
- Bond length decreases
- Bond angle may change
- Hybridization may change