

Bonding in Metal Carbonyls

CO is considered to be a good σ -donor as well as a π -acceptor ligand. This property of CO and the other π -acceptor ligands such as CN^- , NO, C_2H_4 etc. can be explained by the MO diagram of CO (Figure. 2.1). When energy difference between $2s$ and $2p$ -orbitals is small there will be mixing of s and p_x orbitals. Since the energy difference between $2s$ and $2p$ -orbitals for carbon is small, therefore, the $2s$ and $2p_x$ orbitals on carbon mix to produce two sp_x mixed atomic orbitals. The higher energy sp_x orbital on carbon is closer in energy to its pure $2p_x$ orbital and, therefore, has major contribution from it whereas the lower energy sp_x orbital of carbon is closer to its pure $2s$ orbital and, therefore, has major contribution from it.

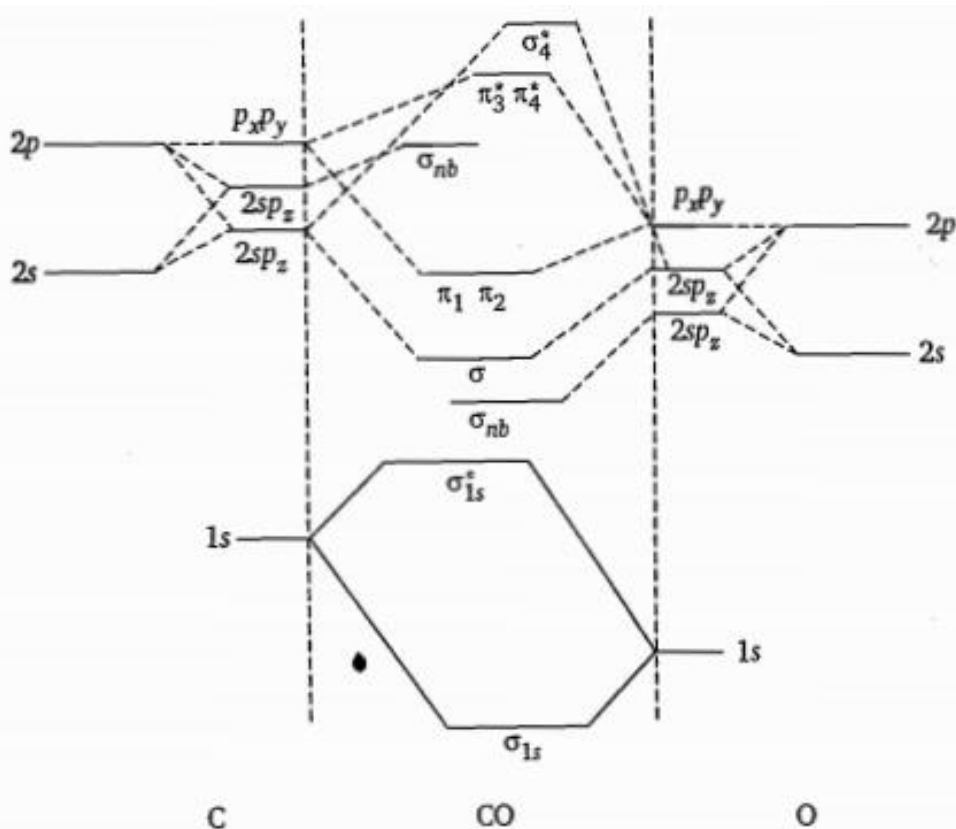


Fig. 2.1 Molecular orbital diagram of CO

The lower energy atomic orbitals of oxygen contribute more to the bonding molecular orbital and the higher energy atomic orbital of carbon contribute more to antibonding molecular orbitals (Figure. 2.1). Therefore, in CO the bonding molecular orbitals will have the character of orbitals of oxygen and the antibonding molecular orbitals have the character of orbitals of less electronegative carbon. This is due to the conservation of orbitals.



Fig. 2.2 : (a) One π -bonding MO (b) One π -antibonding MO

Singly filled sp_x and p_x orbitals on each atom form a σ and a π -bond respectively. This leaves the p_y orbital empty on carbon and the doubly filled p_y orbital on oxygen (Fig. 2.3). The p_y orbital on oxygen donates its pair of electrons to the empty p_y orbital of carbon to form a dative bond or coordinate

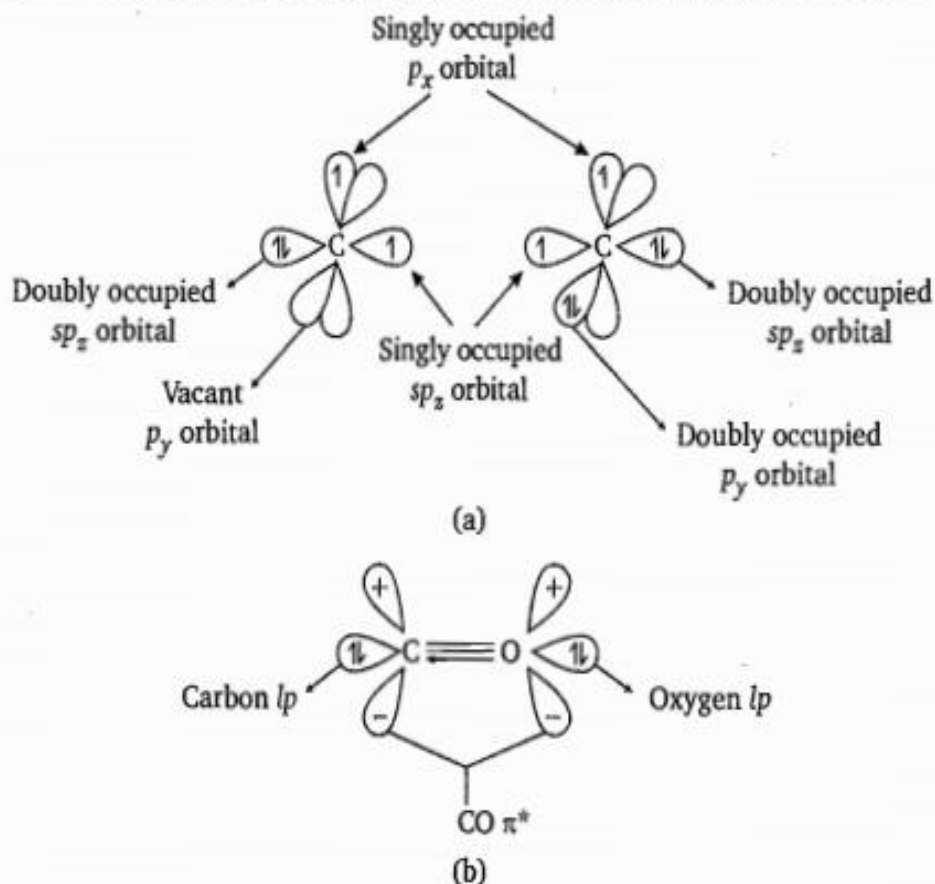


Fig. 2.3

bond [Fig. 2.3(b)]. This dative bond is also a π -bond. This dative bond leads to a $\bar{C}-O^+$ polarization in CO molecule which is almost exactly cancelled by an opposite polarization $^+C-O^-$ caused by the higher electronegativity of oxygen. Due to high electronegativity of oxygen the π -bonding electrons are localized on oxygen and cause $C^+ - O^-$ polarization.

The molecular orbitals energy level diagram (Figure. 2.1) shows that the HOMO has a σ symmetry and the HOMO is localized on carbon, not on oxygen because the effective nuclear charge or electronegativity of carbon is less than that of oxygen. The HOMO of CO ligand donates its lone pair of electrons to the empty orbital of suitable symmetry on the metal (e.g., an $sp_x d_{z^2}$ hybrid orbital) to form a M—CO σ -bond (Figure. 2.4).

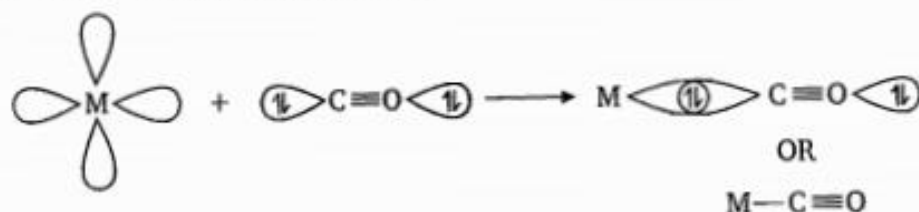


Fig. 2.4

Carbon monoxide has two LUMO π^* orbitals which are also localized on carbon. These orbitals have correct symmetry to overlap with non-bonding metal d -orbitals that have π symmetry such as the t_{2g} (d_{xy} , d_{yz} or d_{zx}) orbitals in octahedral complex. A metal atom having electrons in a d -orbital of suitable symmetry can donate electron density to the LUMO π^* of CO (Fig. 2.5). The π interaction leads to the delocalization of electrons from filled d -orbitals of suitable symmetry on the metal atom into the empty π^* orbitals on the CO ligands. Because the electron density is flowing from the metal d -orbitals to the π^* orbitals on ligands, this donation is known as π back donation or back bonding and the CO ligand is said to be a strong π -acceptor (or π -acid). The σ -donor and π -acceptor interaction are shown in Figure. 2.5.

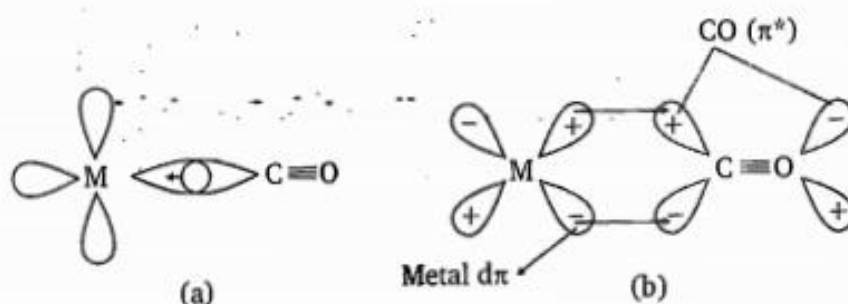


Fig. 2.5 : (a) σ -bonding, (b) π Back-bonding.

On the basis of foregoing discussion, the CO ligand is said to be a σ -donor and a π -acceptor and the metal is a σ -acceptor and a π donor. Some other π -acceptor ligands are CN^- , NO^+ , CNR , N_2 etc.

Both the σ - and π -bonding reinforce (*i.e.*, strengthen) each other. The formation of σ -bond results in the increase in electron density on metal and tends to make the CO ligand positive. Both the increase in electron density on the metal, and the positive charge on CO increase the π -accepting ability of CO. The greater electron density on the metal and greater partial positive charge on CO ligand make the effective return of electron density from metal d -orbital to the π^* orbital of CO ligand. As the electron density delocalized from metal d -orbital onto π^* orbitals of CO increases, further electron flow from CO to metal d -orbital results. The result of this two way electron flow is that the metal-ligand bond is stronger than the sum of isolated ligand to metal σ -bonding and metal to ligand π -bonding effects. This kind of mutual strengthening of σ - and π -bonding is called **synergism** and this effect is called **synergistic effect**.

The metal to ligand π back bonding results in the increase in M—C bond strength as the bond order tends to increase. Since the π -back bonding results in occupation of π^* on CO ligand, the bond order of CO ligand itself decreases and, therefore, the C—O bond becomes longer and weaker. Alternatively, increased M—C double bonding leads to decrease C—O multiple bonding as shown by the resonance structures (Fig. 2.6).

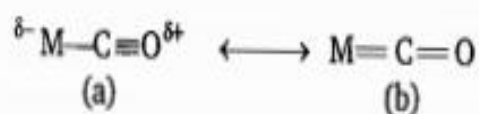
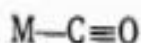


Fig. 2.6

If a metal is in high oxidation state, then there will be poor π -back bonding and the bond order of M—C is close to 1 and that of C—O is close to 3.



If the metal is in low oxidation state (*i.e.*, electron rich), then there will be strong π bonding between metal and CO and the bond order of both M—C and C—O is close to 2.

