7.2 RE-DOX REACTIONS

The reaction in which the transfer of an electron from one atom to the other occurs and hence the oxidation state of some atoms change is called 'Redox reaction'.

These reactions of transition metal complexes are divided into two classes on the basis of their mechanism :

1. Electron – exchange Process : In which the electron transfer results in no net chemical change. For example change of $[Fe(CN)_6]^{3-}$into $[Fe (CN)_6]^{4-}$ or that of $[Co(en)_3]^{3+}$ into $[Co (en)_3]^{2+}$.

   These reactions have outer sphere electron-transfer mechanism and are followed only indirectly, e.g. by isotopic lebelling or by nmr.

2. Those reactions which involve net chemical change as a result of electron transfer e.g. change of $[Cr (NH_3)_5 X]^{2+}$ into $[Cr (H_2O)_6]^{2+}$ or that of $[Cr (H_2O)_5Cl]^{2+}$ into $[Cr (H_2O)_6]^{2+}$.

   These reactions follow inner sphere or bridge mechanism and can be traced using standard chemical and physical methods.

7.2.1 Mechanism of one Electron Transfer Reactions :

Most of these reactions are believed to follow the following two mechanism :

(a) Electron transfer or outer – sphere mechanism, and

(b) Bridge or inner – sphere mechanism.

7.2.2 Outer Sphere Mechanism

In these reactions neither the bonds are formed nor broken up. Hence there is no change in the coordination sphere of metal ions, except their oxidation states are changed.

These reactions occur by direct electron transfer and the electron effectively hops from one species to the other and the ligands act as electron-conduction media. It involves movement of an electron from the outside of a ligand in one co-ordination sphere over the outside of a second sphere. This mechanism is appropriate with large conjugated ligands like phenonthroline and bipyridine.

For example : Transfer of an electron from $[\mathrm{Fe^{II}(CN)_4}]^{4-}$ to $[\mathrm{Fe^{III}(CN)_6}]^{3-}$. Which can be studied by labelling of the complexes with a radioactive isotope of Fe or ^{14}C.

$$[^*\mathrm{Fe^{2+}(CN)_6}]^{4-} + [\mathrm{Fe^{3+}(CN)_6}]^{3-} \rightarrow [^*\mathrm{Fe^{3+}\,(CN)_6}]^{3-} + [\mathrm{Fe^{2+}\,(CN)_6}]^{4-}$$

Ferrocyanide ion Low spin and inert	Ferricyanide ion Low spin and inert	Fe-C bonds longer	Fe-C bonds shorter

In this reaction only charges of complex species are changed. Fe(II) in ferrocyanide ion is oxidised to Fe(III), while Fe(III) in ferricyanide ion is reduced to Fe(II) state. These reactions may be considered analogues to collision – model.

The reaction is fast with second order constant 10^5 at 25^oC and there is no heat change in the reaction and gives same products after the electron transfer both the axions are inert.

During this reaction none of the elements Fe, C, or N moves. The Fe-C bond in $[\mathrm{Fe\,(CN)_6}]^{3-}$ is likely shorter than that in $[\mathrm{Fe\,(CN)_6}]^{4-}$. Thus if an electron is to be transferred between the axions in their ground state equilibrium configurations by the Frank condon principle, the product $[\mathrm{Fe\,(CN)_6}]^{3-}$ would be expanded and the $[\mathrm{Fe\,(CN)_6}]^{4-}$ would be compressed.

The reaction rates for outer sphere redox reactions, where the complex retains its full coordination sphere, and the electron must pass through both the coordination shells (a tunneling mechanism), vary from (second order rate k_2) 10^{-4} for $[Co\ (C_2O_4)_3]^{3-}$ - $[Co(C_2O_4)_3]^{4-}$ through 10^3 for MnO_4^- – MnO_4^{2-} to more than 10^6 for $[Fe\ (dipy)_3]^{3+}$ - $[Fe\ (dipy)_3]^{2+}$ and $[W(CN)_8]^{3-}$ - $[W\ (CN)_8]^{4-}$ complexes.

Electron transfer processes where no change in the chemical species takes place (e.g., the couples written above), can be followed by the isotopic tracers or magnetic resonance methods. In one novel method, the rate of loss of optical activity on mixing solutions of a D-complex of one oxication state and the L-complex of another oxidation state (both complexes being kinetically inert) gives the rate of electron transfer by the reaction.

$$D\text{–}[Os\ (dipy)_3]^{2+} + L\text{–}[Os\ (diply)_3]^{3+} \leftrightarrows L\text{-}[Os(dipy)_3]^{2+} + D\text{–}[Os\ (dipy)_3]^{3+}$$

Where both reactants are non-labile, e.g. in the case of $[Fe\ (CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$, a close approach of the metal atoms is impossible, and the electron transfer must take place by a tunnelling or outer sphere mechanism. Although for an isotopic change the equilibrium constant is nearly unity and ΔG^o is nearly zero, activation energy is required to overcome the electrostatic repulsion between ions of like charge, to distort the coordination of both species and to modify the solvent structure around both species.

The $[Fe\ (CN)_6]^{4-}$ - $[Fe\ (CN)_6]^{3-}$ exchange reaction is catalysed by alkali metal ions, the effect being greatest for caesium and smallest for lithium. The very large cation Ph_4As^+ has little effect, however. These results suggest that a partly desolvated cation accelerates exchange by helping to overcome electrostatic repulsion by formation of a transition state such as

$[Fe(CN)_6]^{4-}$ ..... M+ $[Fe(CN)_6]^{3-}$

A small cation holds its hydration sheath too strongly, whilst a very large one does not bring the anions into close proximity. It is interesting to note that the MnO_4^{2-} - MnO_4^- exchange reaction is also subject to alkali metal ion catalysis, the order of effectiveness being the same as for the $[Fe(CN)_6]^{4-}$ - $[Fe(CN)_6]^{3-}$ reaction.

Outer-sphere reactions between complexes of different metals (e.g. the $[Os(dipy)_3]^{2+}$ - $[Mo(CN)_8]^{3-}$ - reaction mentioned earlier) are usually faster than outer sphere exchange reactions between different oxidation states of the same element. For such reactions the decrease in energy when excited states of products are converted into ground states can appear as the free energy of the reaction (ΔG^o must be negative, or the reaction would not take place). This is tantamount to saying that for such reactions the structure of the transition state is more like that of the reactants; hence the activation energy is lowered and the rate is increased.

The outer sphere electron transfer may be represented as follows :

If oxidant = 0 and reductant = R, then

$$O + R \rightarrow [O \ldots R]$$
$$[O \ldots R] \rightarrow [O \ldots R]^*$$
$$[O \ldots R]^* \rightarrow [O \ldots R^+]$$
$$[O^- \ldots R^+] \rightarrow O^- + R^+$$

First the oxidising agent (O) and the reducing agent (R) come closer to form precursor complex. During activation of the precursor complex there is reorganisation of solvent molecules and the bond lengths of metal ligand bonds are changed. However this takes place before the electron transfer. In the last step ion – pairs are transformed in to product ions.

For the outer sphere redox reactions, the following characteristics are observed.

(1) Electron transfer is expected to be fast when no change in the molecular dimensions takes place.

(2) Fast electron transfer takes place when the electrons are able to reach the surface of the complex through conjugation (in the ligands attached) or through monatomic ligands.

(3) The ligand exchange is slower than the electron exchange process.

(4) The rate constant depends upon the cation present in the solution; ion pair formation decreases the activation energy by reducing the electrostatic repulsion energy.

(5) Reactions involving large size differences proceed slowly.