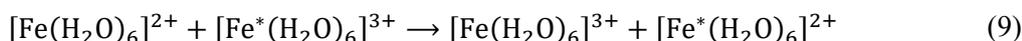


❖ Mechanism of Electron Transfer Reactions – Types; Outer Sphere Electron Transfer Mechanism and Inner Sphere Electron Transfer Mechanism

The process of electron transfer from one species to another species leads to the oxidation of the donor and the reduction of the acceptor. The electron donor acts as the reducing agent and called as reductant while the electron acceptor acts as the oxidizing agent and called as the oxidant. We have already studied the redox reaction of simple species like:



However, the ligand displacement reactions, we have studied so far, do not involve any change in the oxidation state of the metal center but the substitution reactions involving the electron transfer between complex species do exist. The oxidation-reduction reaction may or may not occur through the net chemical change. A simple example of electron transfer between complex species can be given as:



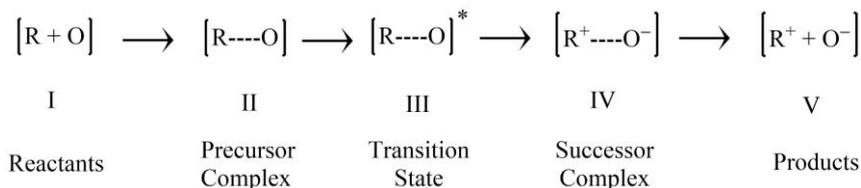
The mechanism by which the electron transfer occurs in transition metal complexes can be classified into two types as given below.

➤ *Outer Sphere Electron Transfer Mechanism*

In this mechanism, there is a direct transfer of electrons from the reductant to oxidant and the coordination sphere remains intact. The ligands in both the reactants remain as such and the bond making or bond-breaking does not take place. In other words, the complexes do not undergo ligand substitution and no new bonds are formed or broken. Consider the following example.



If R is the reductant and O is the oxidant, the outer sphere electron transfer can be shown as:



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It has been observed that the formation of precursor complex and the dissociation of the successor complex is very fast but the electron transfer is quite slow. The course of the complete reaction is shown below.

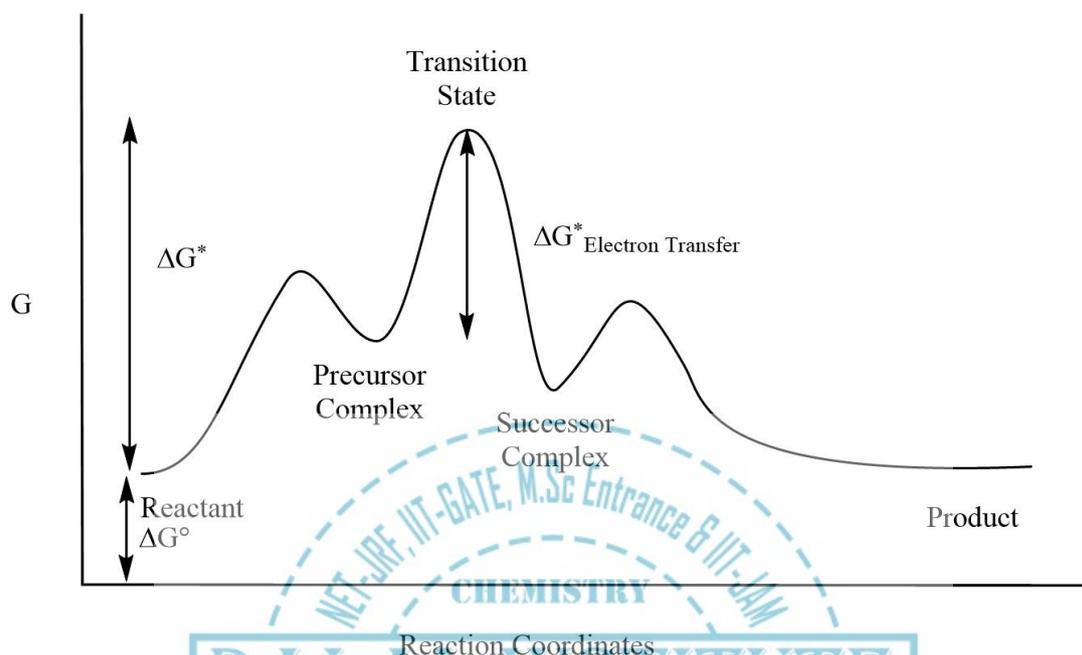


Figure 15. The general reaction coordinate diagram for the mechanism involved outer-sphere electron transfer reactions.

In the transition state of the complex, the electrons have equal probability to be present on either of the metal center. In order to proceed further, we need to recall the concept of inert and labile complexes first.

Inert Complexes



Labile Complexes



It is worth remembering that low-spin complexes are generally formed by the strong field ligands like CO, PR_3 , CN^- or by the transition metal ions from 2nd and 3rd transition series. Co(III) complexes are also generally low spin in nature. On the other hand, high-spin complexes are generally formed by the weak field ligands like H_2O , NH_3 , Cl^- or by the transition metal ions of 1st transition series. Co(II) complexes are also generally high-spin in nature.

The overall activation energy and hence the rate dependence of outer-sphere electron transfer reactions can be given as:

$$\Delta G^* = \Delta G_t^* + \Delta G_o^* + \Delta G_i^* \quad (11)$$

Where

- i) ΔG_i^* is the energy required to bring the reactant molecules closer to each other against the Coulombic repulsion.
- ii) ΔG_o^* is the energy required to reorganize the solvent molecules. As the solvent interactions like H-bonding with the complex molecules increase, the rate of the reaction decreases. On the other hand, solvents with less or no interaction will increase the reaction rate.

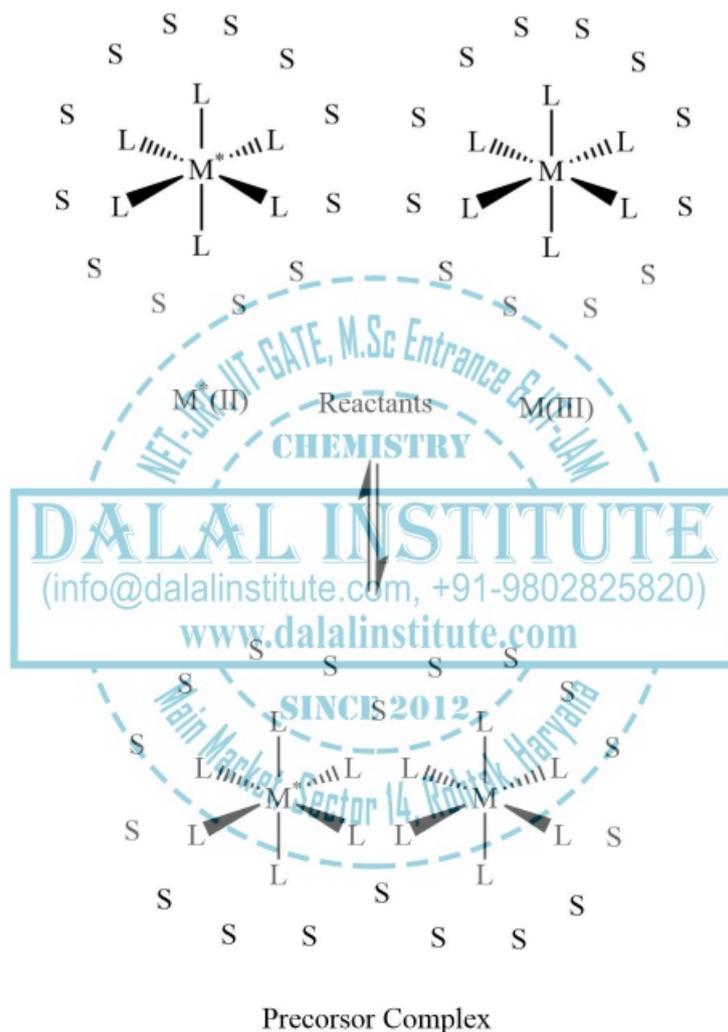
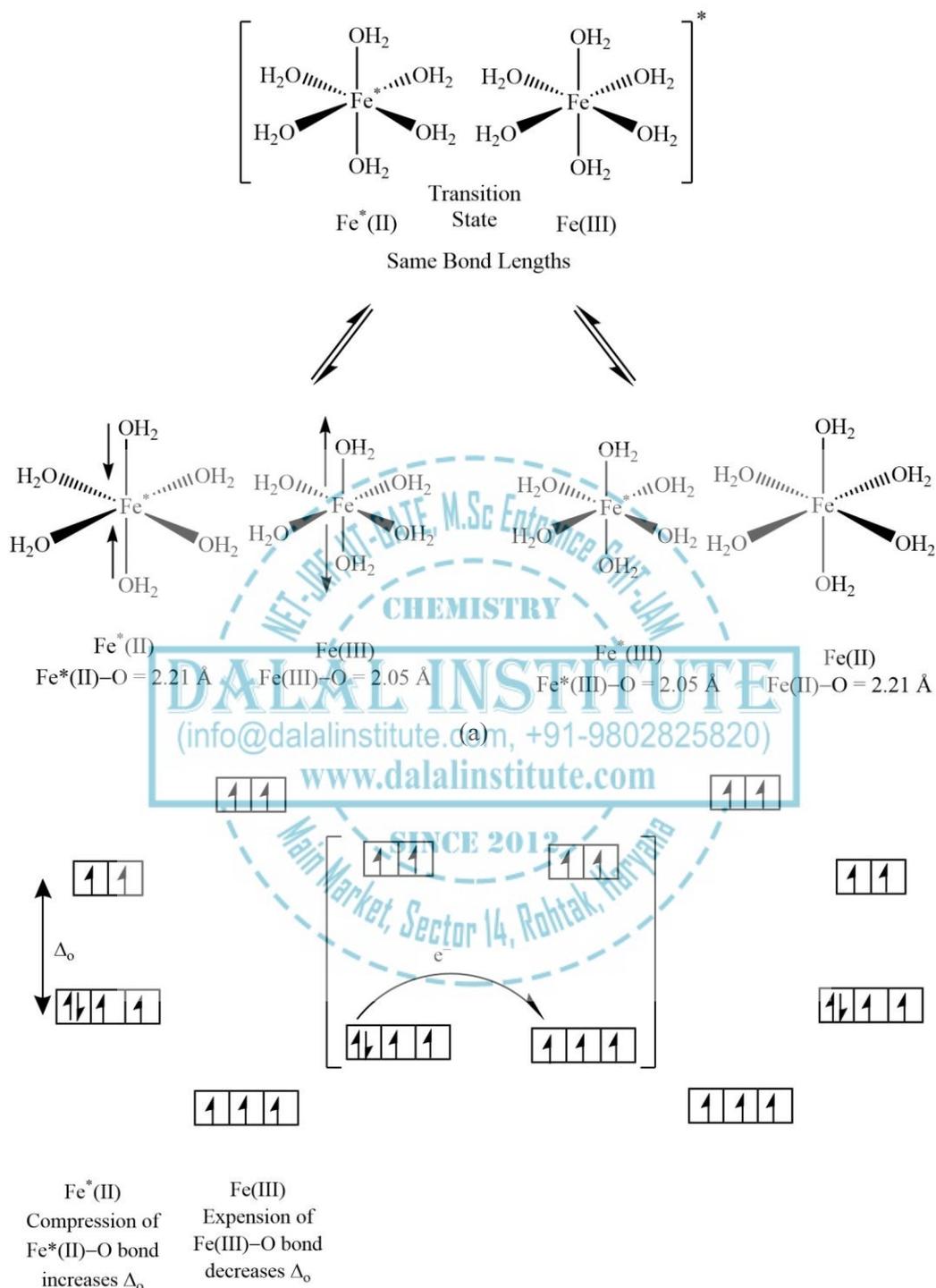


Figure 16. The solvent reorganization during the formation of the precursor complex.

iii) ΔG_i^* is energy required for the reorganization of various bond lengths to make the interacting orbitals of the approximately same energy. This can be explained in terms of the Frank-Condon principle which states that the electronic transitions occur at a much faster rate than the nuclei can respond. Now as we know that the metal-ligand bond lengths are highly dependent on the oxidation state of the metal center, it is pretty obvious that complexes must adjust their bond lengths for the electron transfer to occur.



(b)

Figure 17. Formation of (a) internal reorganization and (b) corresponding ligand field splitting.

The main factors affecting the outer sphere electron transfer are:

1. Orbital Symmetry: Electron transfer outer-sphere mechanism requires orbital overlap and occurs between orbitals of the same symmetry.

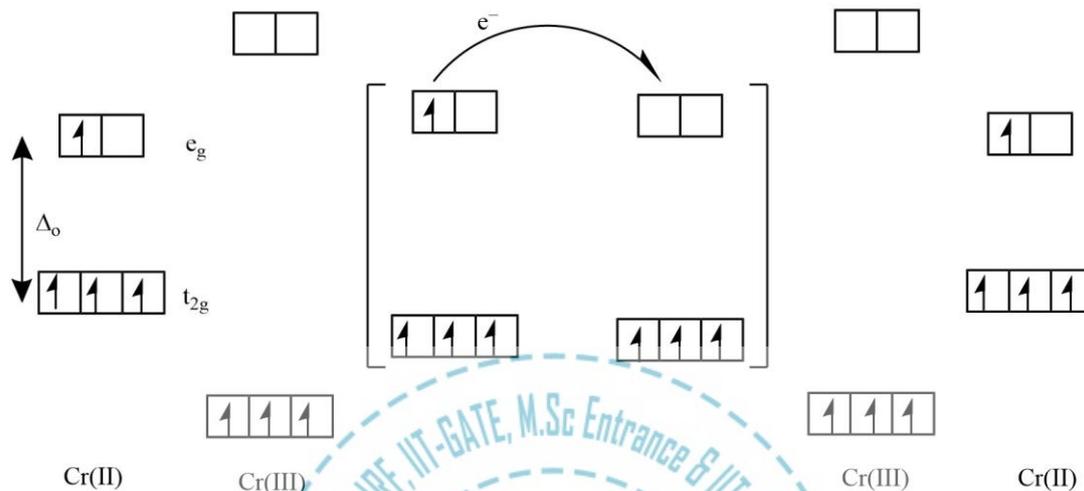


Figure 18. The electron transfer in $e_g \rightarrow e_g$ ($\sigma^* \rightarrow \sigma^*$) transition.

In the octahedral fields, $e_g \rightarrow e_g$ ($\sigma^* \rightarrow \sigma^*$) transition requires a large change in bond lengths and orbital overlap is also very small due to the ligand steric. This results in an electron transfer at a very slow rate. On the other side, $t_{2g} \rightarrow t_{2g}$ ($\pi/\pi^* \rightarrow \pi/\pi^*$) transition involves a small change in bond lengths and the orbital overlap is also very good which depends upon the nature of the ligands. This results in an electron transfer at a very fast rate.

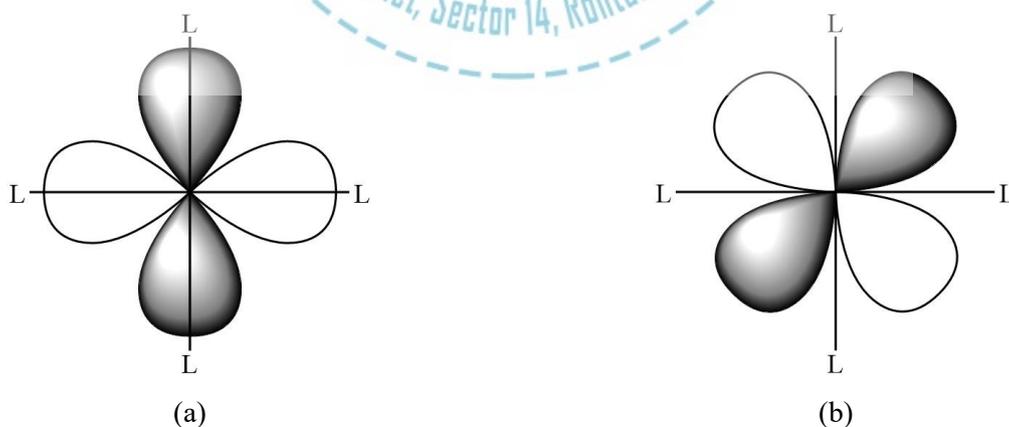


Figure 19. The electron transfer in (a) $e_g \rightarrow e_g$ ($\sigma^* \rightarrow \sigma^*$) transitions is having poor overlap; while (b) the $t_{2g} \rightarrow t_{2g}$ ($\pi/\pi^* \rightarrow \pi/\pi^*$) transitions involve better overlap.

2. Orbital Overlap: It has been observed that outer-sphere electron transfer is generally faster for 2nd and 3rd transition series metal ion than that 1st which can be explained in terms of better overlap of 4d and 5d orbitals as compared to the 3d one. Moreover, the stronger crystal field also results in less bond length distortion. Ligands with extended π -system also speed up the transfer rate.



Figure 20. Ligands with extended π -conjugation supporting orbital overlap (a) 1,10-phenanthroline (b) 2,2'-bipyridine.

3. Electronic Configuration: If the electron transfer occurs through a change in electronic configuration (high-spin to low-spin or low-spin to high-spin), the activation energy barrier will be very high and a slow electron transfer is expected. In another view, electron reorganization induces a large change in bond lengths and hence slows down the rate of electron transfer.

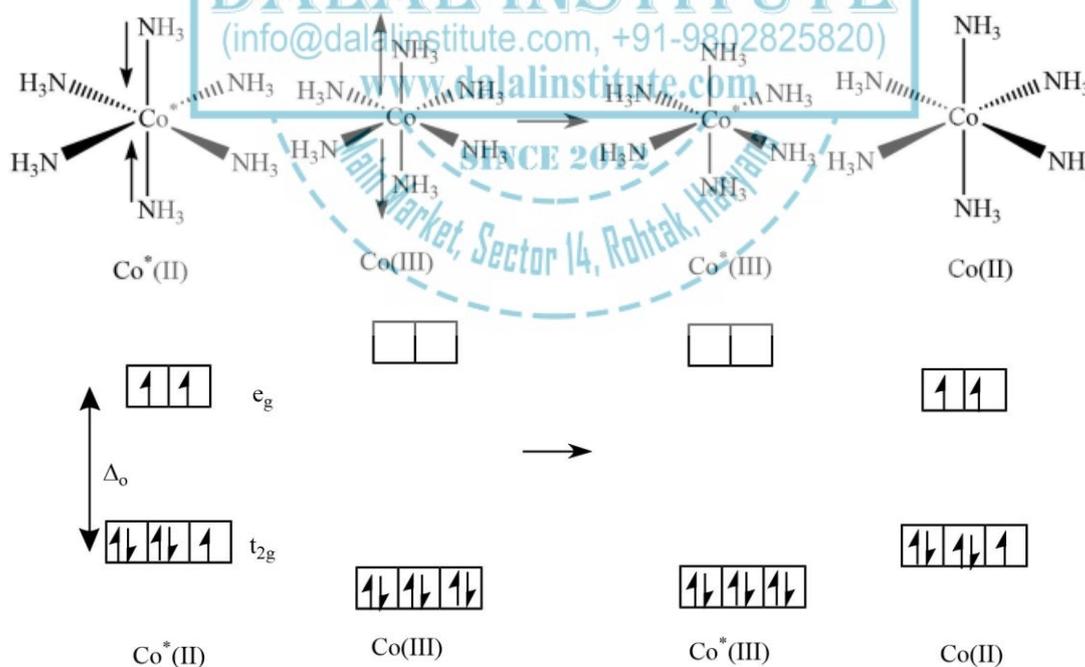
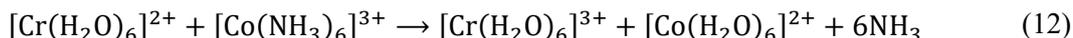


Figure 21. The electron transfer phenomena in transitions involving a reorganisation of electronic configuration.

➤ **Inner Sphere Electron Transfer Mechanism**

In this mechanism, the electron is transferred from the reductant to oxidant through a bridge activated complex. The bridging ligand shared in the precursor, successor and activated complex may or may not be transferred during the course of the reaction. The octahedral complexes require the dissociation of one ligand so that the bridging ligand can play its role in creating an intimate contact between the reductant and oxidant so that electron transfer can occur. Inner sphere reactions generally have one labile and one inert reactant. Consider the following example.



The electron transfer reaction shown by equation (12) is extremely slow with a rate constant of $10^{-3} \text{ M}^{-1}\text{s}^{-1}$ and can easily be explained in terms of outer-sphere mechanism. However, the electron transfer results in the formation of $[\text{Co}(\text{NH}_3)_6]^{2+}$ which is labile in nature (d^7 high-spin) and immediately hydrolyzed to $[\text{Co}(\text{NH}_3)_5]^{2+}$ yielding six NH_3 .



On the other side, the value of the rate constant for electron transfer shown by equation (13) is $6 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ which is too high to be explained via outer-sphere mechanism. Moreover, if we use $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ at the start and add Cl^- afterward, Cl^- is not found in the final product. It suggests that the electron transfer has occurred via a bridge activated complex.

The course of the complete reaction is shown below.

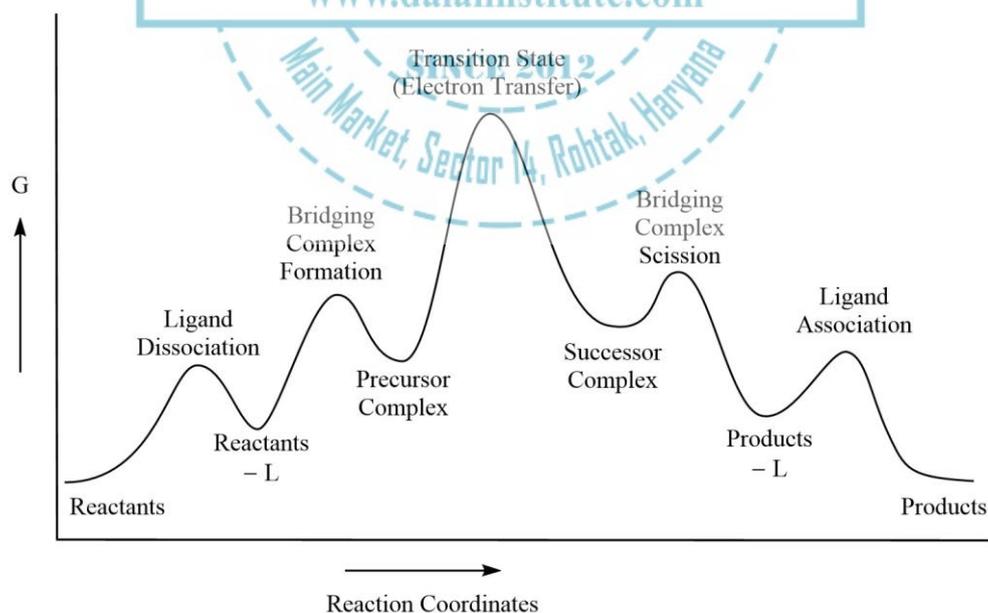


Figure 22. The reaction coordinate diagram for inner sphere electron transfer mechanism.

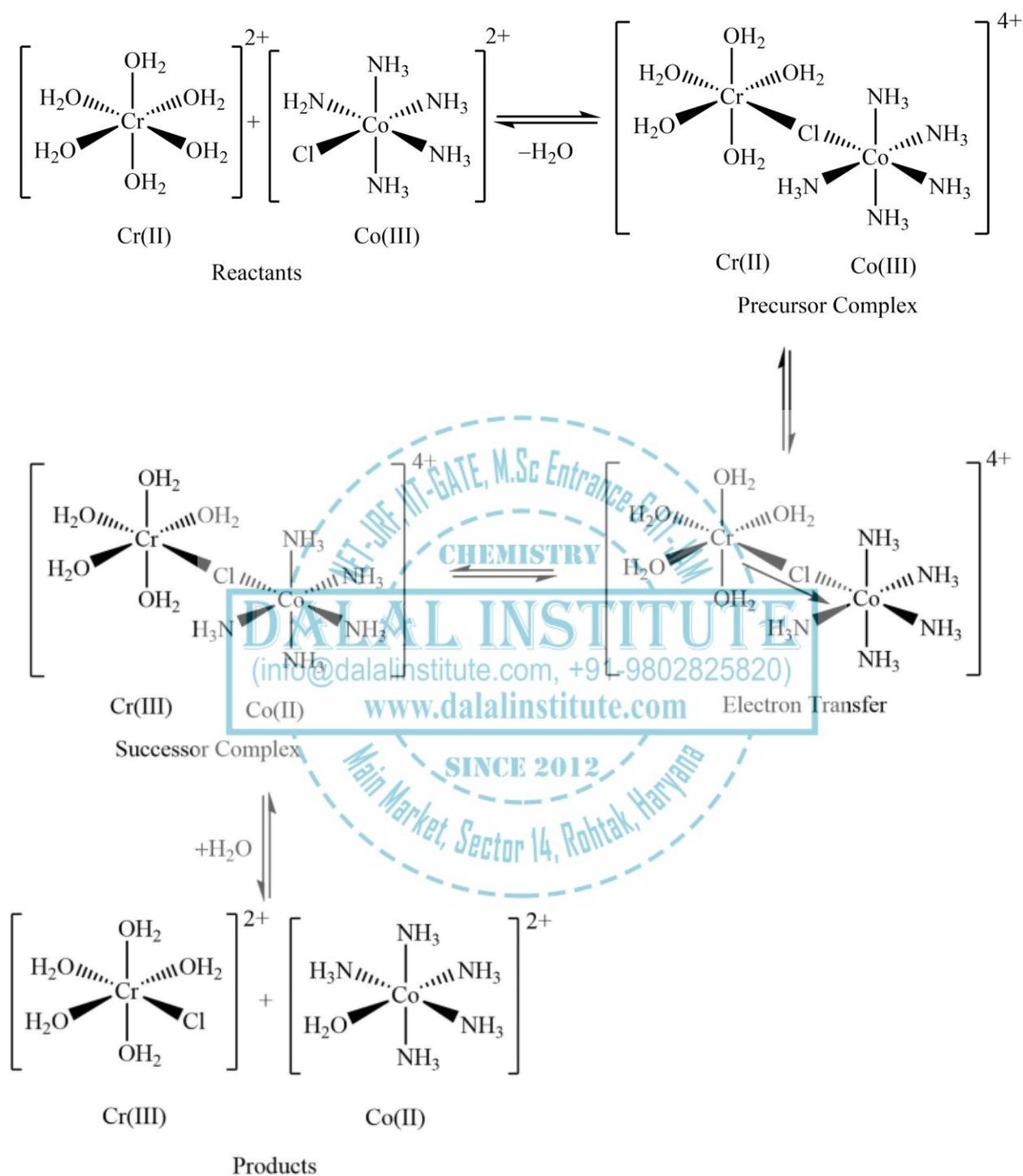


Figure 23. The formation of precursor complex, successor complex and the state of electron transfer in inner-sphere electron transfer mechanism.

The electron transfer results in the formation of $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ which is labile in nature (d^7 high-spin) and immediately hydrolyzed to $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ releasing five NH_3 . The main factors affecting the inner sphere electron transfer are:

1. Bridging Complex: It has been observed that instead of the electron transfer step, the formation of the bridging complex can also be the rate-determining step, sometimes. This will primarily be dependent on how labile or inert the complexes are. Furthermore, it is also possible that the scission of the bridging complex is actually playing as the rate-limiting step.

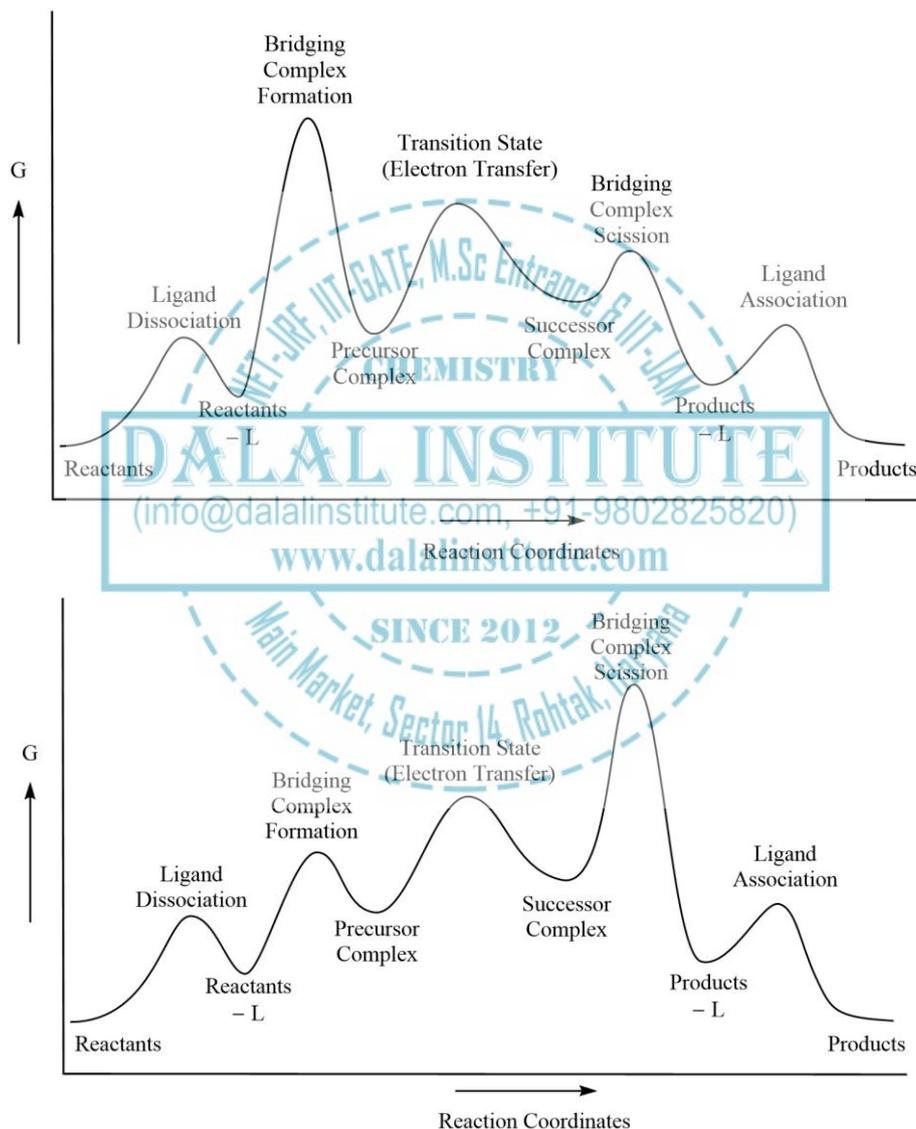


Figure 24. The reaction coordinate diagram for inner-sphere electron transfer mechanism with bridging complex formation and scission as the rate-determining step.

2. Electronic Configuration: The interaction between e_g orbitals and the bridging ligand is greater than their t_{2g} counterparts which can be attributed to the orientation of the lobes along the bonding axis. Hence, an acceleration in rates is observed as we go from outer to inner sphere mechanism due to the facilitation of electron transfer via bridging ligands and orbital symmetries.

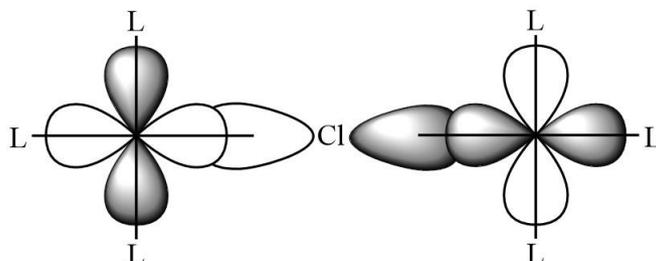
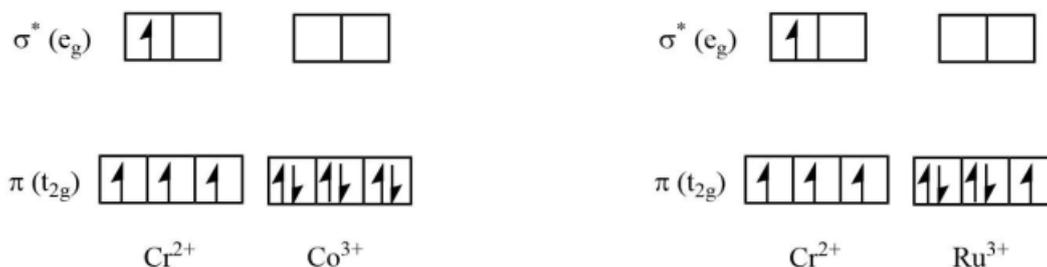


Figure 25. The interaction between e_g orbitals through the bridging ligand in the inner-sphere electron transfer mechanism.

Table 1. The correlation between the frontier molecular orbitals (FMOs) and the acceleration in going from outer-sphere to inner-sphere mechanism.

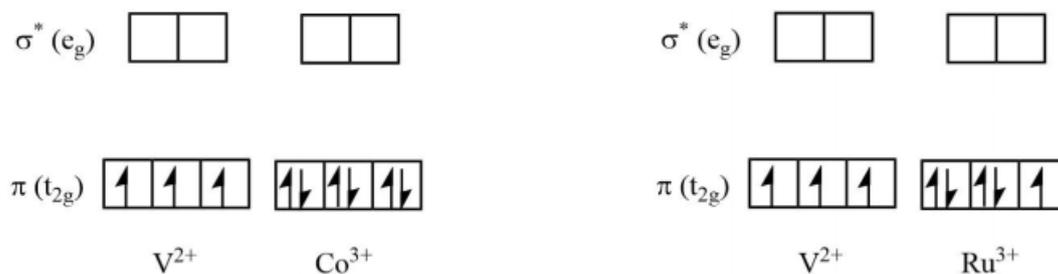
Reaction	HOMO	LUMO	Acceleration in going from outer-sphere to inner-sphere
$\text{Cr}^{2+} \rightarrow \text{Co}^{3+}$	σ^*	σ^*	$\sim 10^{10}$
$\text{Cr}^{2+} \rightarrow \text{Ru}^{3+}$	π^*	π^*/π	$\sim 10^2$
$\text{V}^{2+} \rightarrow \text{Co}^{3+}$	π^*	σ^*	$\sim 10^4$
$\text{V}^{2+} \rightarrow \text{Ru}^{3+}$	π	π	All outer-sphere



Large reorganization for Co^{3+} outer-sphere. Inner-sphere is much faster.

Reorganisation of Ru^{3+} less than Co^{3+}

Figure 26. Continued on the next page...

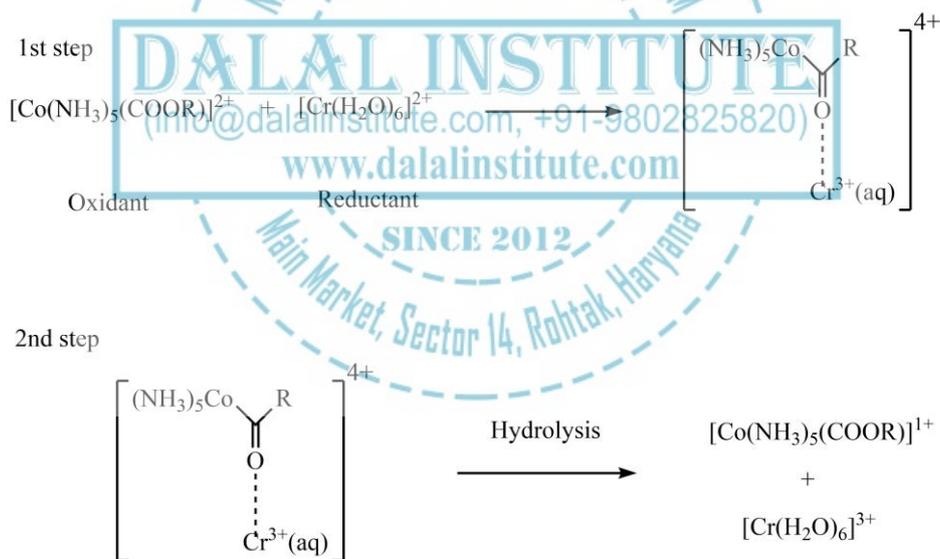


Large reorganization for Co^{3+} outer-sphere. Inner-sphere is much faster.

No reorganization is involved. Allowed in outer-sphere.

Figure 26. The solvent reorganization various redox pairs.

3. Nature of the bridging ligand: The rate of inner-sphere electron transfer is mechanism is highly sensitive to the nature of the bridging ligand. The rate of the reaction generally increases with the increase in the nucleophilic character of the bridging ligand. Furthermore, the substitution on the bridging ligand can also affect the rate significantly. Consider the following example.



When

R =	H	Me	Ph	^t Bu
k (M ⁻¹ s ⁻¹)	7.2	0.35	0.15	9.6 × 10 ⁻³

Hence, as the bulkiness of the R group increases, the binding capacity of the bridging decreases which in turn slows down the overall rate of the electron transfer.

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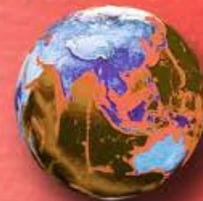
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