CHAPTER 4

Reaction Mechanism of Transition Metal Complexes – II:

❖ Mechanism of Ligand Displacement Reactions in Square Planar Complexes

The ligand displacement in square-planar complexes is much more favorable via the associative pathway than that of the dissociative one which can be explained in terms of low steric crowding due to the lesser coordination number. In order to understand this claim, consider the general ligand displacement in square planar complexes:

$$\mathrm{MA_3L + E \ \longrightarrow \ MA_3E + L} \qquad (1)$$

Now, if the concentration of the entering ligand E is very large, the observed pseudo first-order rate law for the above reaction can be given by:

$$\mathrm{Rate} = k_1[\mathrm{MA_3L}] + k_2[\mathrm{MA_3L}][\mathrm{E}] \qquad (2)$$

On rearrangement

$$\mathrm{Rate} = (k_1 + k_2[\mathrm{E}])\ [\mathrm{MA_3L}] \qquad (3)$$

or

$$\mathrm{Rate} = k_o[\mathrm{MA_3L}] \qquad (4)$$

Where k_o is the observed rate constant and is equal to

$$k_o = k_1 + k_2[\mathrm{E}] \qquad (5)$$

The value of k_1 and k_2 can be calculated from the intercept and slope of the plot of the observed rate constant vs concentration of the entering group E. It has been observed that, for all type of entering ligands, the values of both k_1 and k_2 are nonzero which suggests a possibility of dissociative pathway too.

➢ ***Solvent Assisted SN_2 Pathway***

The non-zero value of k_1 can also be interpreted in some other form of the associative pathway in which the solvent molecules also act as the nucleophile and compete with E to form MA_3S. The following process is responsible for the first term in equation (2).

$$\mathrm{MA_3L + S} \ \underset{-\mathrm{L}}{\overset{k_1}{\longrightarrow}} \ \mathrm{MA_3S} \ \underset{-\mathrm{S}}{\overset{+\mathrm{E}}{\longrightarrow}} \ \mathrm{MA_3E} \qquad (6)$$

Now, as the concentration of the solvent is practically constant, the rate of the reaction depends upon the concentration of MA_3L only and becomes of first-order kinetics.

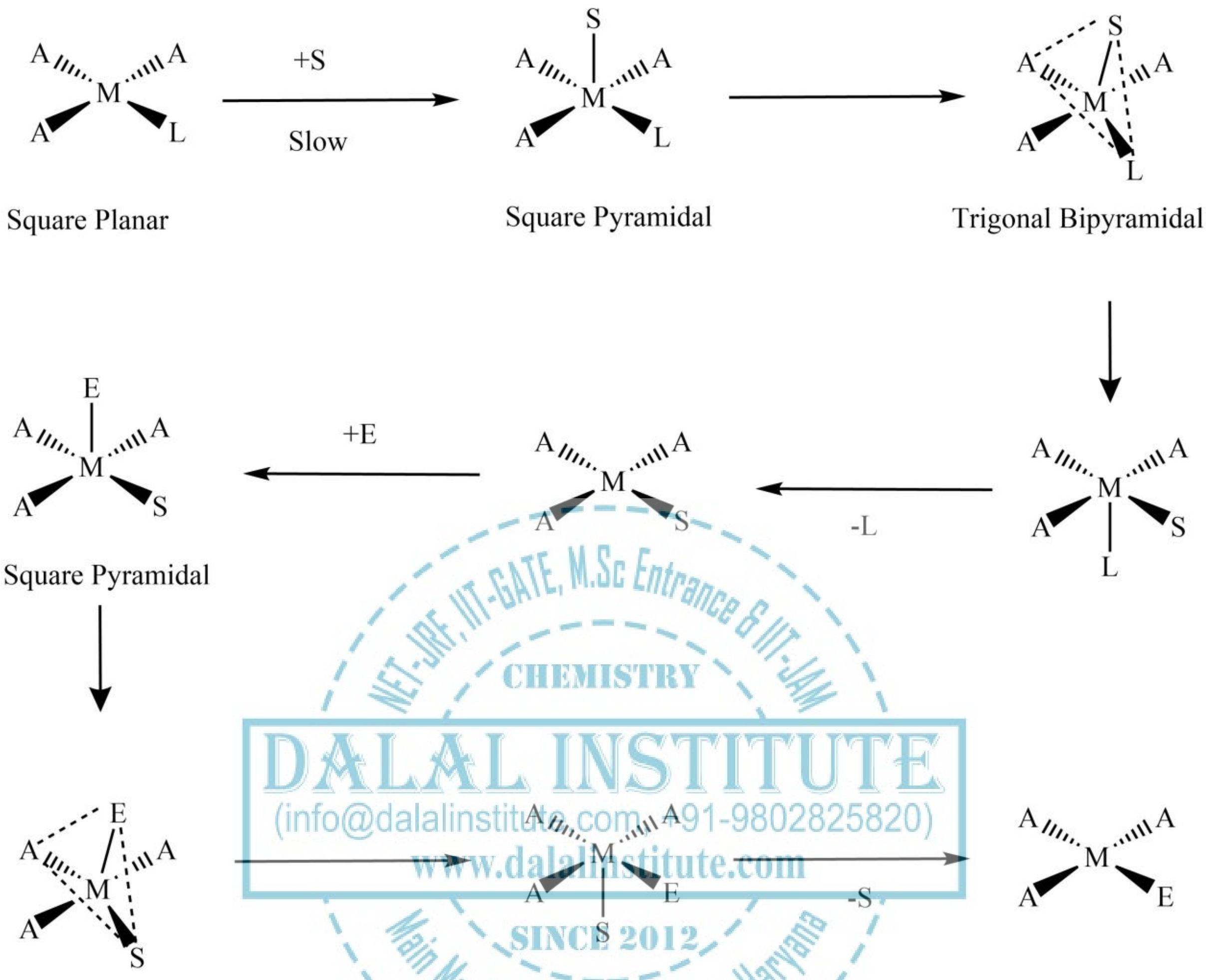


Figure 1. The systematic mechanism of solvent-assisted ligand displacement reactions in square planar complexes.

➢ *Normal SN₂ Pathway*

The non-zero value of k_2 can be explained in terms of the normal associative route in which the entering ligand replaces the leaving group via a five-membered transition state. The reaction scheme can be shown as:

$$\mathrm{MA_3L + E} \underset{-\mathrm{L}}{\overset{k_2}{\longrightarrow}} \mathrm{MA_3E} \tag{7}$$

It has also been observed that the rate of the direct associative route is generally higher than the rate via solvent assistance. Moreover, the rate has also been found dependent on the nucleophilicity of the solvent suggesting a key role of the solvent attack in ligand displacement.

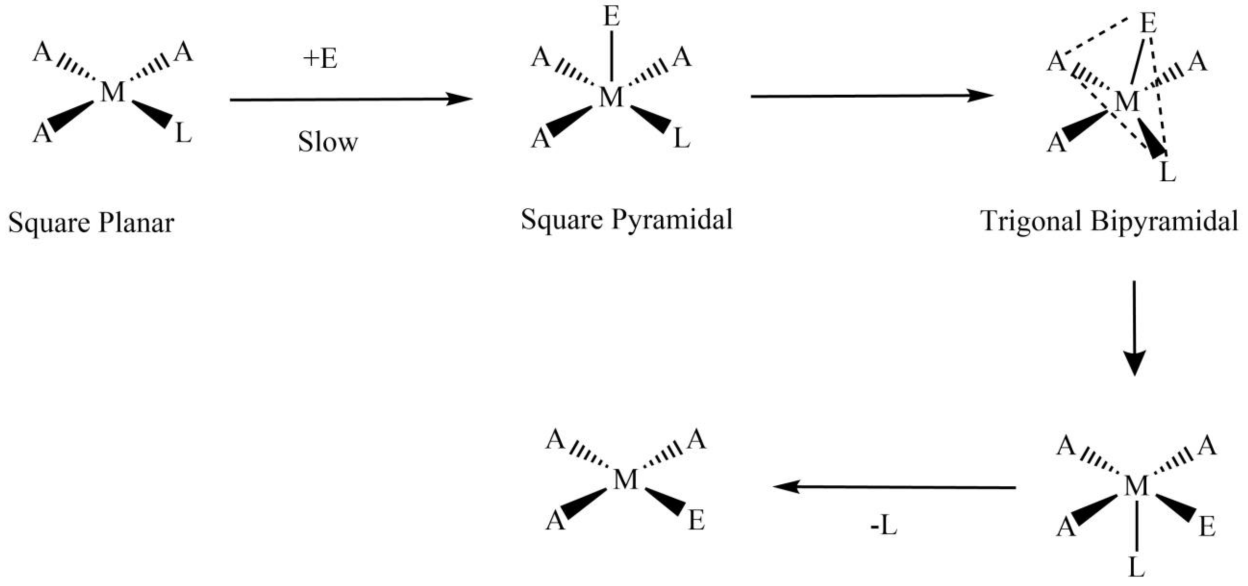


Figure 2. Mechanism of ligand displacement in square planar complexes via normal associative pathway.

❖ The Trans Effect

The tendency of an already attached group to direct the incoming ligand to its trans position in ligand displacement reactions in square-planar complexes is called as the trans effect and such groups are labeled as the trans-directing ligands.

It is worthy to mention that various ligands have different trans directing effects and when these ligands are arranged in increasing order of their trans effect, the order is termed as the trans-effect series which is given below.

$CN^- > C_2H_4 > CO > NO > SCN^- > I^- > Br^- > Cl^- > Py > NH_3 > OH^- > H_2O$

In other words, the trans-effect may also be defined as the labilization (the easier displacement) of the ligands trans to other trans-directing ligands. Moreover, the trans-directing ligands are also called as the spectator ligands as they are neither the entering nor the leaving group yet affect the rate of the ligand substitution considerably. Most of the people are actually quite confused about the nature of the trans-effect, weather is it kinetic or thermodynamic. The trans-effect may be classified into two types.

➢ *Kinetic Trans Effect or Trans Effect*

The kinetic trans-effect or trans-effect proper in square-planar complexes is the phenomenon in which certain ligands increase the rate of displacement of the ligands positioned trans to them. Now as this effect deals with the rate only, it must not be confused with trans-influence which involves a weakening of the trans bond and hence is thermodynamic in nature. If E is the entering ligand, T_1 and T_2 as the trans-directing groups, k_1 and k_2 as the rate constants and L is the leaving group; the process can be depicted as:

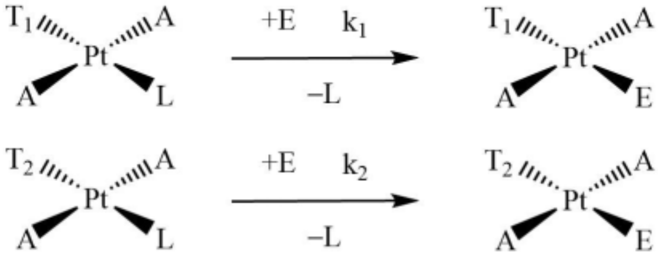


Figure 3. Kinetic trans-effect in action with $k_2 >> k_1$ showing that T_2 ligand is having greater trans-effect strength than T_1.

- ***Thermodynamic Trans Effect or Trans Influence***

The thermodynamic trans-effect or trans influence may be defined as the impact of a ligand on the length of the bond trans to it in the ground state of a square-planar complex. Like trans-effect, trans-influence is also independent of metal ion but depends primarily upon the geometry of the metal center.

Figure 4. Thermodynamic trans-effect in action showing that T_2 ligand is having greater trans-influence strength than T_1.

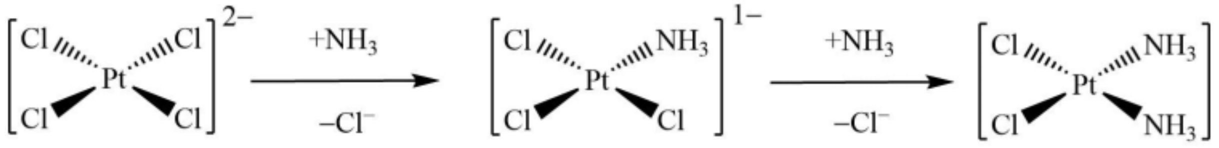
It can be seen very clearly that elongation of trans-bond-length is done more profoundly by T_2 than T_1; which infer that the thermodynamic trans-effect of T_2 ligand is higher than T_1.

- ***Applications of the trans effect***

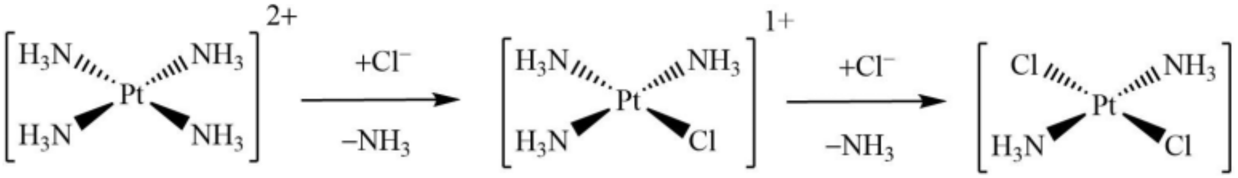
1. Synthesis of the cis and trans platin: $[PtCl_2(NH_3)_2]$ exists in two isomeric forms as given below.

Figure 5. (a) cis-$[PtCl_2(NH_3)_2]$ (b) trans-$[PtCl_2(NH_3)_2]$

These two isomers can be synthesized via a number of number chemical routes by exploiting the trans effect. However, the most common are given below.



(a)



(b)

Figure 6. The general synthesis route for the preparation of cis-$[PtCl_2(NH_3)_2]$ or cis-platin and Trans-$[PtCl_2(NH_3)_2]$ or trans-platin complexes.

The initial raw materials for the synthesis of isomeric forms are different as the Cl^- has a higher trans effect than NH_3. Hence, the trans effect plays a major role in product formation. It is worth noting that the cis-platin is having very important therapeutic uses in the treatment of cancer.

2. Synthesis of the isomers of [Pt(Cl)(NH₃)(Br)(Py)]: The [Pt(Cl)(NH₃)(Br)(Py)] complex can exist in three different isomeric forms which can successfully be synthesized by using the trans-effect order of the participating ligands.

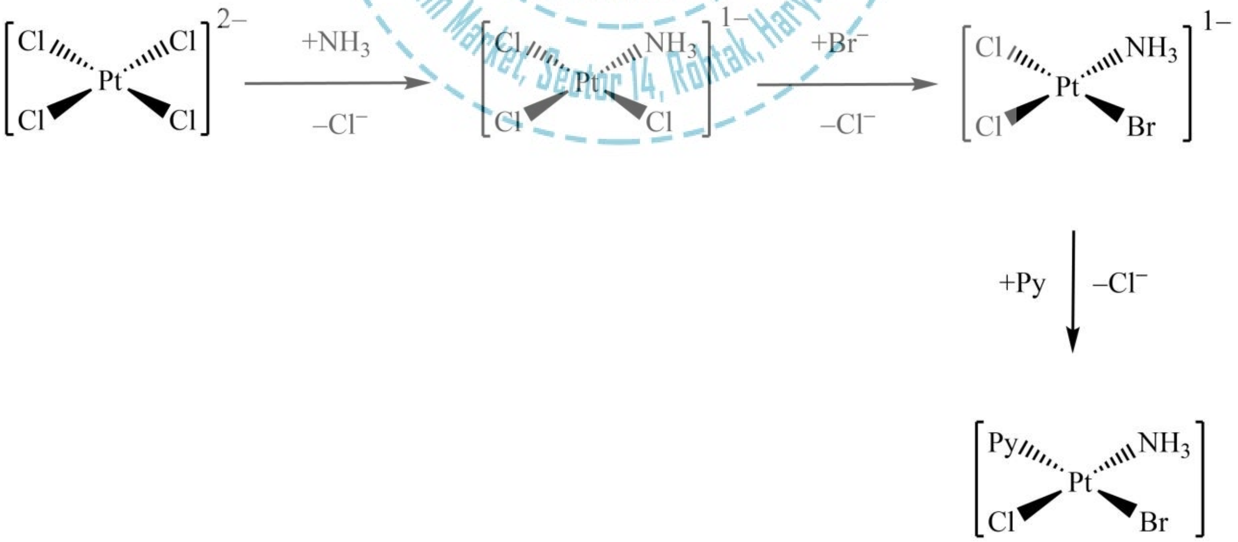


Figure 7. Continued on the next page…

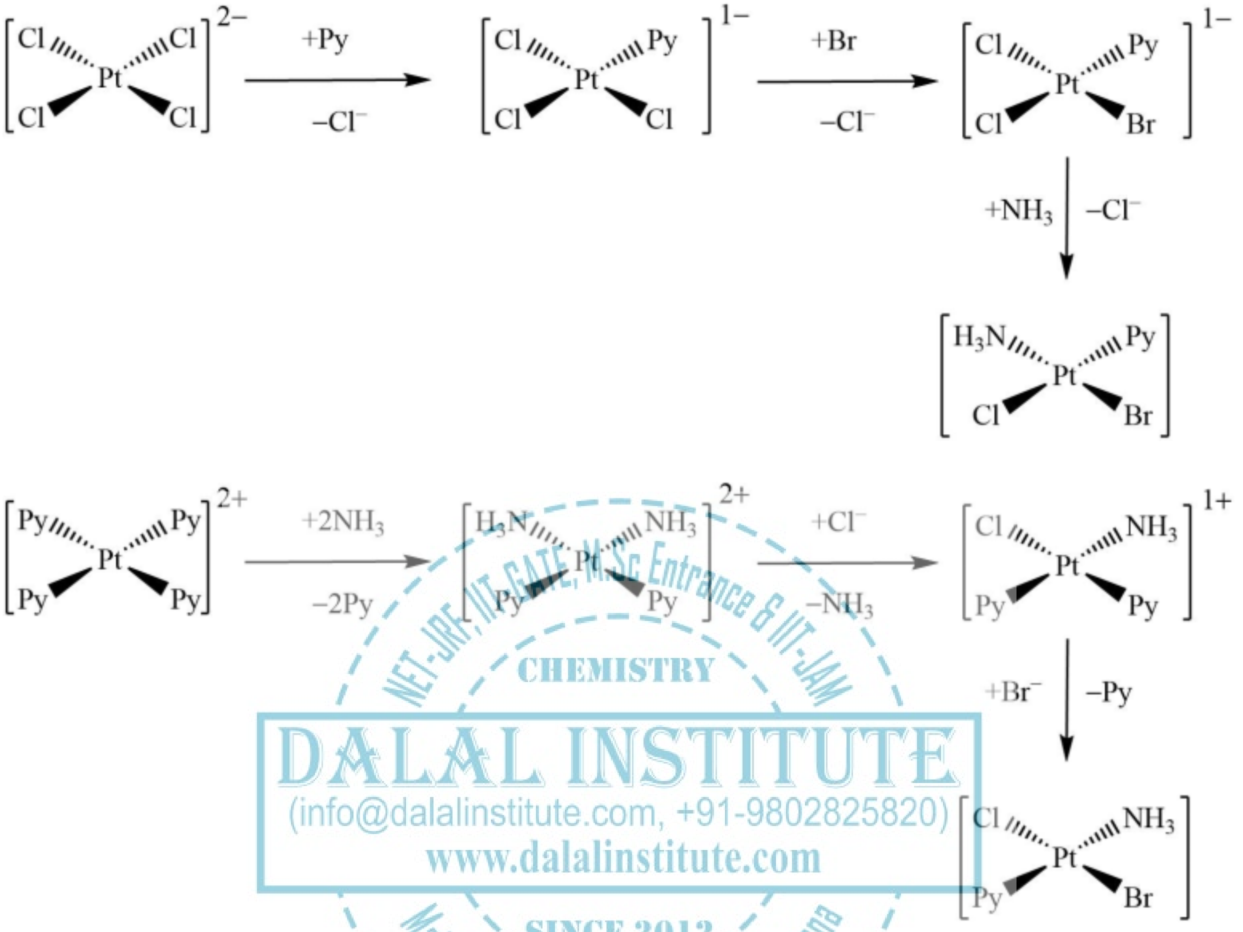
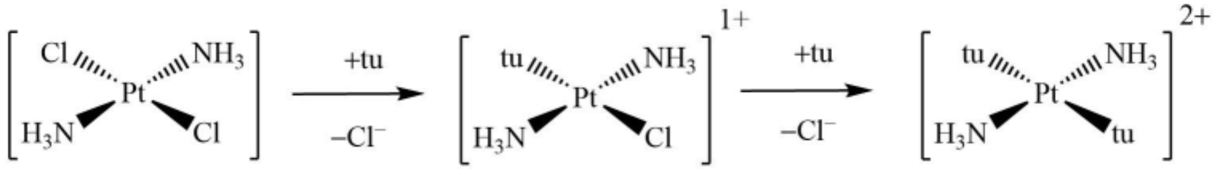


Figure 7. Synthesis route for [Pt(Cl)(NH$_3$)(Br)(Py)] complexes.

3. Differentiating between cis and trans isomers of [PtCl$_2$(NH$_3$)$_2$]: A Russian scientist Kurnakov has used the trans effect to distinguish between the cis and trans platin. The experimental route he invented is named after him as the Kurnakov test in which thiourea is used as a primary component. The trans effect of thiourea is greater than chloride and amine ligands. The addition of thiourea to the trans platin results in the replacement of trans chloride ions and the reaction stops. However, when the thiourea is added to the cis isomer, all the four ligands are displaced and [Pt(tu)$_4$]$^{2+}$ is formed.



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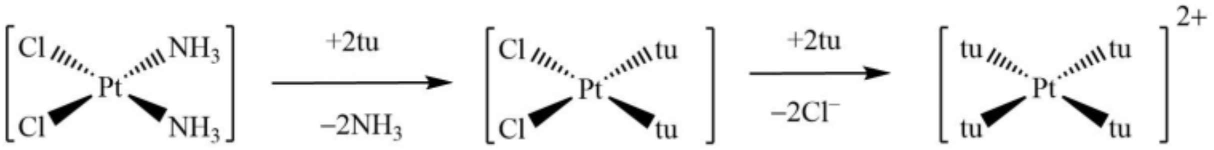
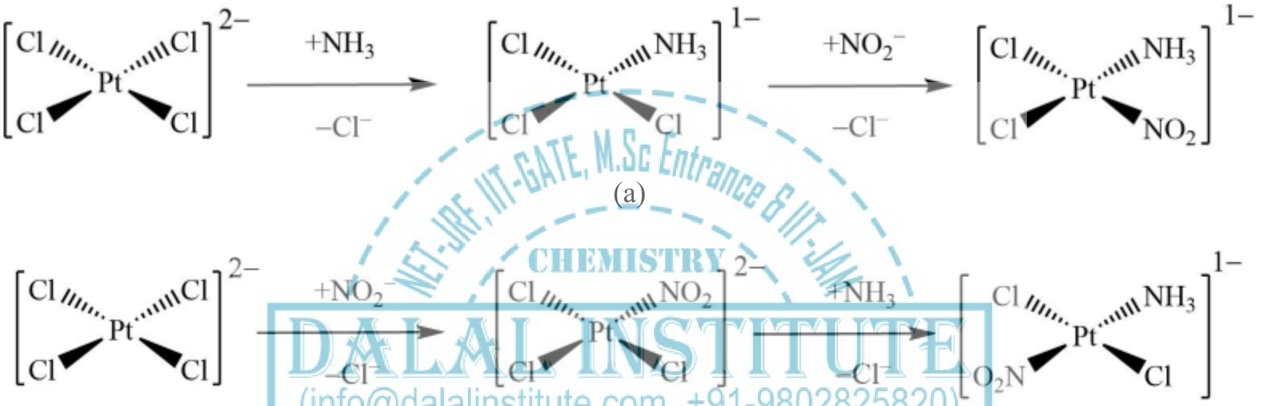


Figure 8. Differentiating route for cis and trans-platin complexes.

4. Synthesis of the isomers of $[Pt(NH_3)(NO_2)Cl_2]^{1-}$: The trans-effect order of the three groups in $[Pt(NH_3)(NO_2)Cl_2]^{1-}$ complex is $NO_2^- > Cl^- > NH_3$.



(a)

(b)

Figure 9. Synthesis route for (a) cis-$[Pt(NH_3)(NO_2)Cl_2]^{1-}$ and trans-$[Pt(NH_3)(NO_2)Cl_2]^{1-}$ complexes.

5. Synthesis of the isomers of $[Pt(C_2H_4)(NH_3)Cl_2]$: The trans-effect order of the three groups in $[Pt(C_2H_4)(NH_3)Cl_2]^{1-}$ complex is $C_2H_4 > Cl^- > NH_3$.

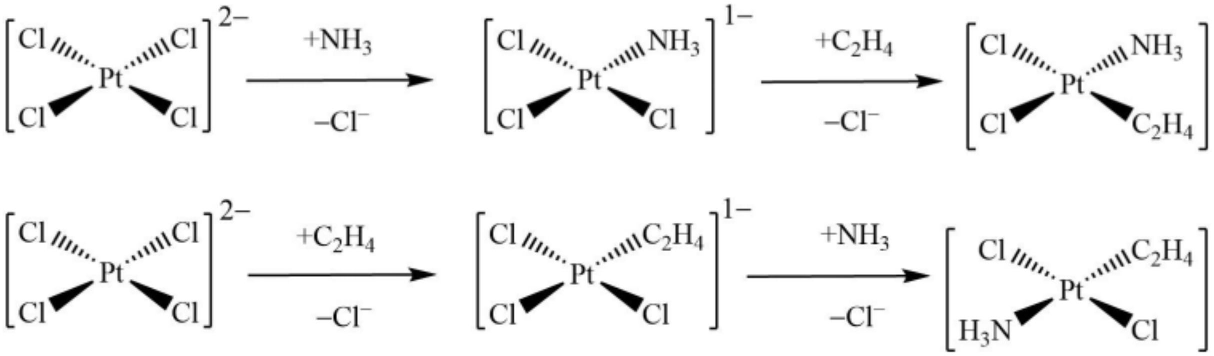


Figure 10. Synthesis route for (a) cis-$[Pt(C_2H_4)(NH_3)Cl_2]^{1-}$ and trans-$[Pt(C_2H_4)(NH_3)Cl_2]^{1-}$ complexes.

6. Synthesis of the isomers of [Pt(PR_3)$_2$$Cl_2$]: The trans-effect order of the two groups in [Pt(PR_3)$_2$$Cl_2$] complex is $PR_3 > Cl^-$.

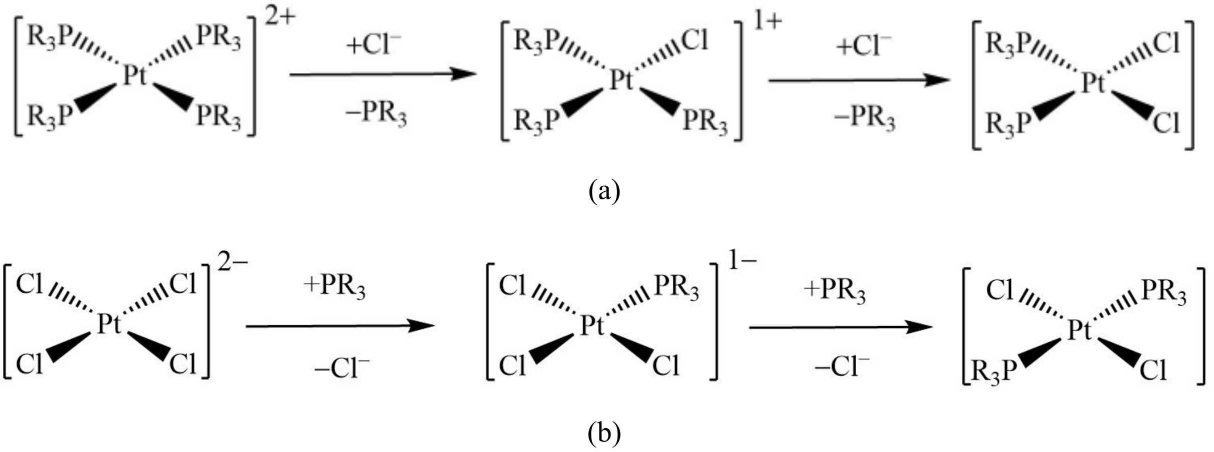


Figure 11. Synthesis route for (a) cis-[Pt(PR_3)$_2$$Cl_2$] and trans-[Pt($PR_3$)$_2$$Cl_2$] complexes.

❖ Theories of Trans Effect

Owing to the kinetic nature of the trans-effect, it is quite sensible to think of activation energy in terms of the ground state (the complex before substitution) as well as activated complex. Hence, all the factors which can affect the energy of the ground state or activated complex are expected to have a profound effect on the activation energy of the ligand displacement reaction and thus expected to govern the trans effect of the attached groups. The two theories which are sought for the explanation of trans-effect are given below.

➢ *The Polarization Theory*

This theory mainly deals with the ground state of the complex and proposes that the metal center has a tendency to induce a dipole moment in the surrounding ligands by polarizing them according to Fajans' rule. In the case of MA_4 type complexes, metal ion induces an equal dipole moment in all the four surrounding ligands which are, in turn, cancel out each other due to square-planar geometry. However, in the case of MA_3B type complexes, the situation is quite different as the polarizability of all the four ligands is not anymore, the same. If the polarizability of B type ligand is higher than that of A-type then the primary charge of the metal ion will polarize the electronic cloud of A more effectively and thus will induce a strong dipole moment in A-type ligand. Furthermore, this dipole moment is also bound to induce an alternate dipole in the metal center also. The orientation of this dipole is such that it repels the negative charge on the ligand, A-type, situated trans to B. This results in the weakening and consequently lengthening of the metal-ligand bond trans to the B-type group. Therefore, according to this concept, the trans effect is directly proportional to the polarizability of the ligand. It is also worth noting that the trans-effect is more prominent with a large and more polarizable metal center. The general order can be given as Pt(II) > Pd(II) > Ni(II).

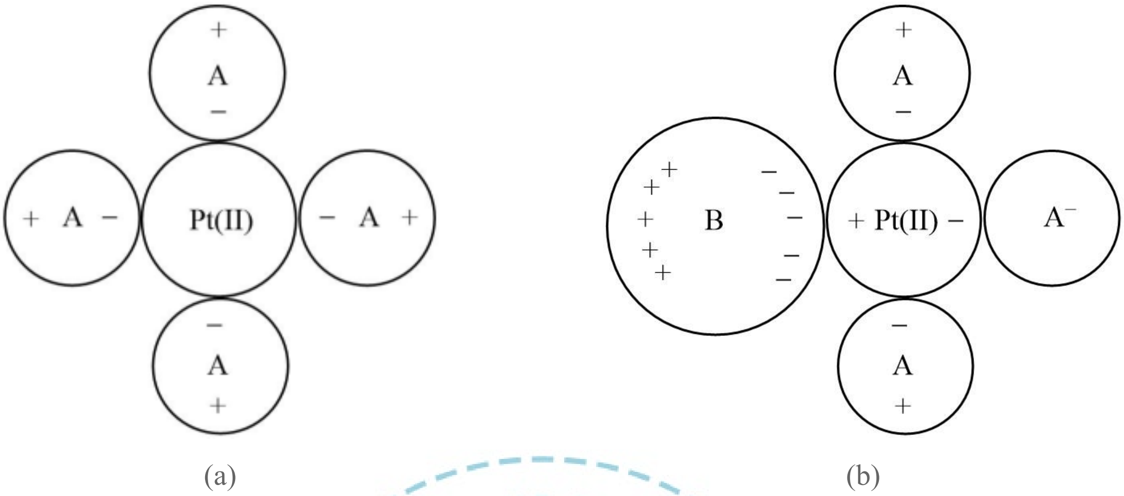


Figure 12. The effect of polarization in (a) MA_4 and (b) MA_3B complexes.

- ***The π-Bonding Theory***

The nature of the trans-effect is electronic instead of steric which clearly means that the electronic profile of the ligand is primarily governing trans-effect strength of various groups. Considering the trans-effect order of halide ions, $I^- > Br^- > Cl^- > F^-$, it seems that the increasing electronegativity makes them poor σ-donor or σ-base which in turn also decreases their trans-effect strength. However, the exceptionally high trans-effect of the ligands like CO, C_2H_4 or PR_3 cannot be explained by σ-donation ability as they are not very good σ-donor but π-acceptor in nature. Therefore, we can conclude that a stronger trans-effect is the combination of both, either it should be a strong σ-base or it should show a good π-acid character.

Now, in order to understand the whole process by which the trans-directing groups speed-up the ligand displacement in square-planar complexes, we will have to recall the mechanism of ligand substitution. Let T be the trans-directing group, L as the leaving group and E as the entering group. The entering ligand binds to 16-electron Pt(II) complex to form 18-electron complex which in turn again converted into a new 16-electron complex as:

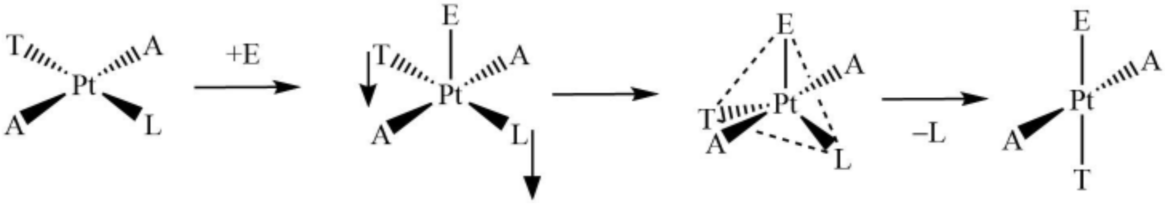


Figure 13. The mechanism of associative ligand substitution of Pt(II) complexes.

The characteristic features of this mechanism are:

i) The entering ligand always sits at the equatorial position of the activated complex which is trigonal-bipyramidal in nature.

ii) The trans-directing group and the leaving group are pushed down to create the equatorial plane of the activated complex.

iii) As the entering group E attacks at the equatorial site, the leaving must also be from the equatorial plane; which is followed directly from the principle of microscopic reversibility.

The rate-determining step is when the entering ligand "E" pushes down the trans-director T and the leaving group L. Now as the equatorial sites of the trigonal-bipyramidal intermediate are richer in electron density than the axial ones, ligands with greater π-acidity like to be pushed down to get this privilege of stronger back-bonding. This forces the leaving group "L" to no other choice but to detach from the activated complex.

The transition state is stabilized by the overlap of empty π* orbital of "T" and the filled d_{xz} orbital of the metal center. This results in a decrease in the electron density in metal-leaving group bond which makes the displacement of L by E much easier.

Figure 14. The transition state of Pt(II) complexes is stabilized by the overlap between empty π* orbital of the trans-directing group and filled d_{xz} orbital of Pt(II) metal center.

Thus, the stronger trans-effect of π-acid ligands is explained in terms of the stabilization of the activated complex (which in turn decreases the activation energy). However, it has also been observed that the bond length between metal ion the leaving group is generally larger than the expected values when ligands with strong trans-effects are there. This suggests that these π-acid ligands affect the ground state as well and a combination on both contributes to the over trans-effect strength.

In addition to the polarization theory, the trans-effect strength of σ-donor ligands can also be explained in the activated complex framework. It can be assumed that trans-directing group T and leaving group L are in direct competition for the σ-donation to the same metallic d-orbital. Thus, the greater σ-donation ability of the trans-director weakens the opposite bond. Though the effect is thermodynamic in nature (trans-influence), the destabilization of the ground state decreases the value of activation required for the ligand substitution making it a kinetic phenomenon too. In other words, the strong σ-donors will decrease the height of the activation barrier and consequently increase the rate of ligand displacement reactions in transition metal complexes with square-planar geometry.

❖ 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:

$$\mathrm{Na} + \mathrm{Cl} \longrightarrow \mathrm{Na}^{+} + \mathrm{Cl}^{-} \tag{8}$$

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:

$$[\mathrm{Fe(H_2O)_6}]^{2+} + [\mathrm{Fe^{*}(H_2O)_6}]^{3+} \longrightarrow [\mathrm{Fe(H_2O)_6}]^{3+} + [\mathrm{Fe^{*}(H_2O)_6}]^{2+} \tag{9}$$

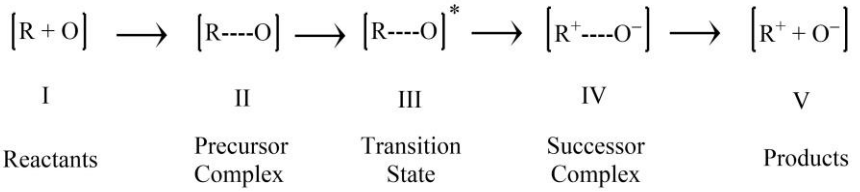
The mechanism by which the electron transfer occurs in transition metal complexes can be classified into two types as given below.

➢ ***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.

$$[\mathrm{Cr(H_2O)_6}]^{2+} + [\mathrm{Co(H_2O)_6}]^{3+} \longrightarrow [\mathrm{Cr(H_2O)_6}]^{3+} + [\mathrm{Co(H_2O)_6}]^{2+} \tag{10}$$

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



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.

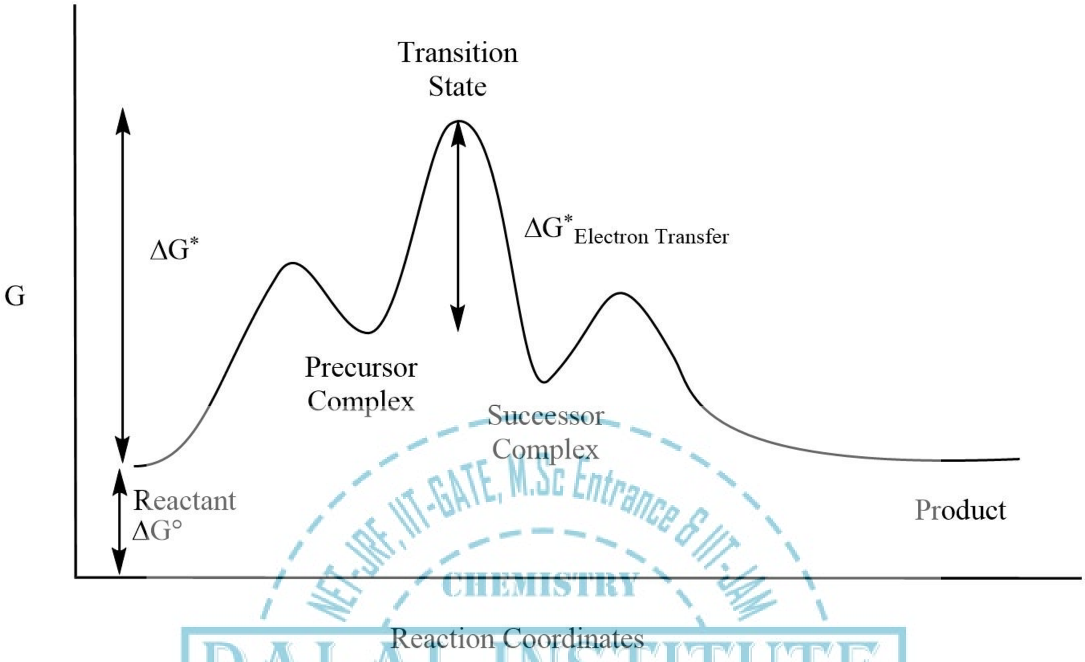


Figure 15. The general reaction coordinate diagram for the mechanism involved outer-sphere electron transfer reactions.

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
d^3, d^4 LS, d^5 LS, d^6 LS, d^8	d^0, d^1, d^2, d^4 HS, d^5 HS, d^7, d^6 HS, d^9, d^{10}

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:

$$\Delta G^* = \Delta G_t^* + \Delta G_O^* + \Delta G_i^* \tag{11}$$

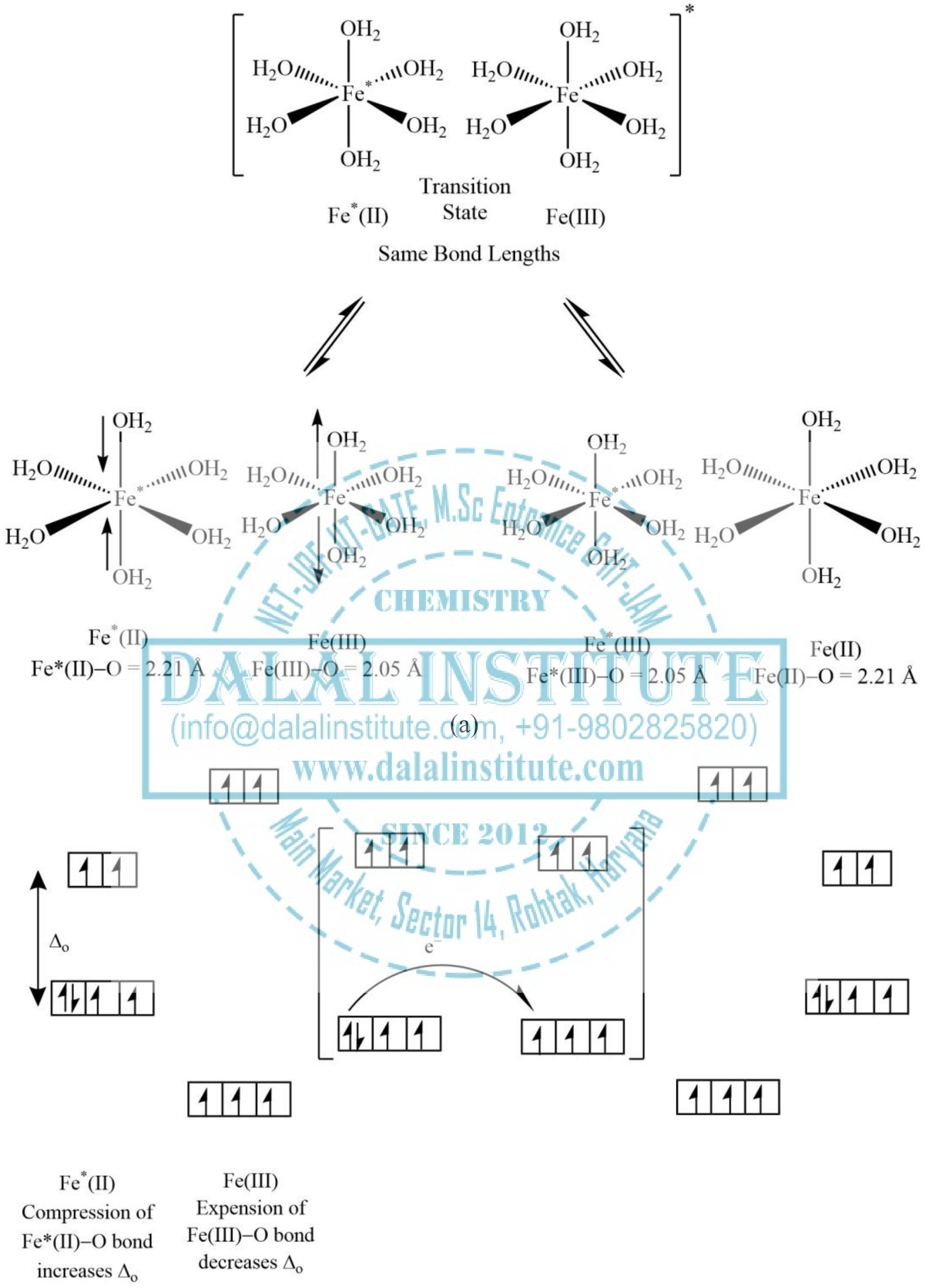
Where

i) ΔG_t^* 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.



(a)

(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.

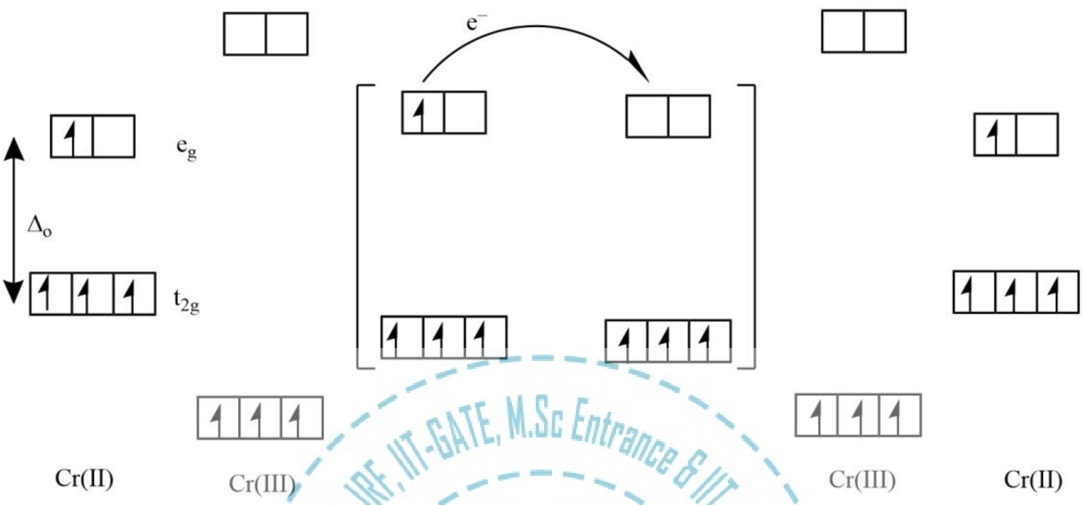
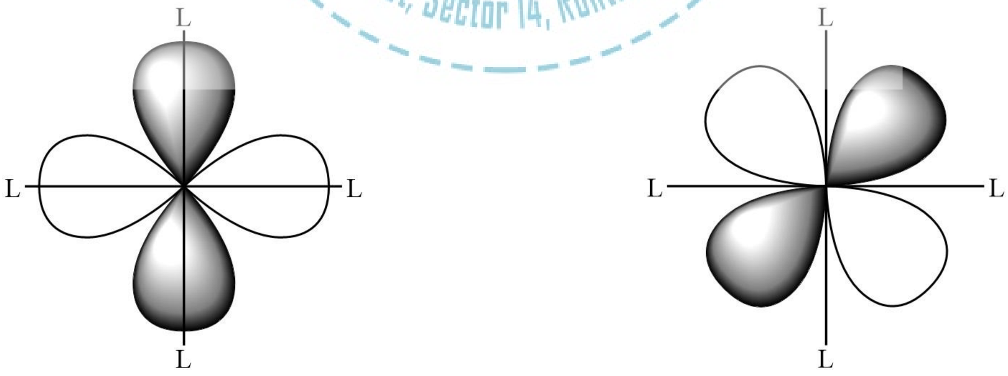


Figure 18. The electron transfer in $e_g \longrightarrow e_g$ ($\sigma^* \longrightarrow \sigma^*$) transition.

In the octahedral fields, $e_g \longrightarrow e_g$ ($\sigma^* \longrightarrow \sigma^*$) 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, $t_{2g} \longrightarrow t_{2g}$ ($\pi/\pi^* \longrightarrow \pi/\pi^*$) 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.



(a) (b)

Figure 19. The electron transfer in (a) $e_g \longrightarrow e_g$ ($\sigma^* \longrightarrow \sigma^*$) transitions is having poor overlap; while (b) the $t_{2g} \longrightarrow t_{2g}$ ($\pi/\pi^* \longrightarrow \pi/\pi^*$) transitions involve batter 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 batter overlap of 4*d* and 5*d* orbitals as compared to the 3*d* one. Moreover, the stronger crystal field also results in less bond length distortion. Ligands with extended π-system also speed up the transfer rate.

(a) (b)

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.

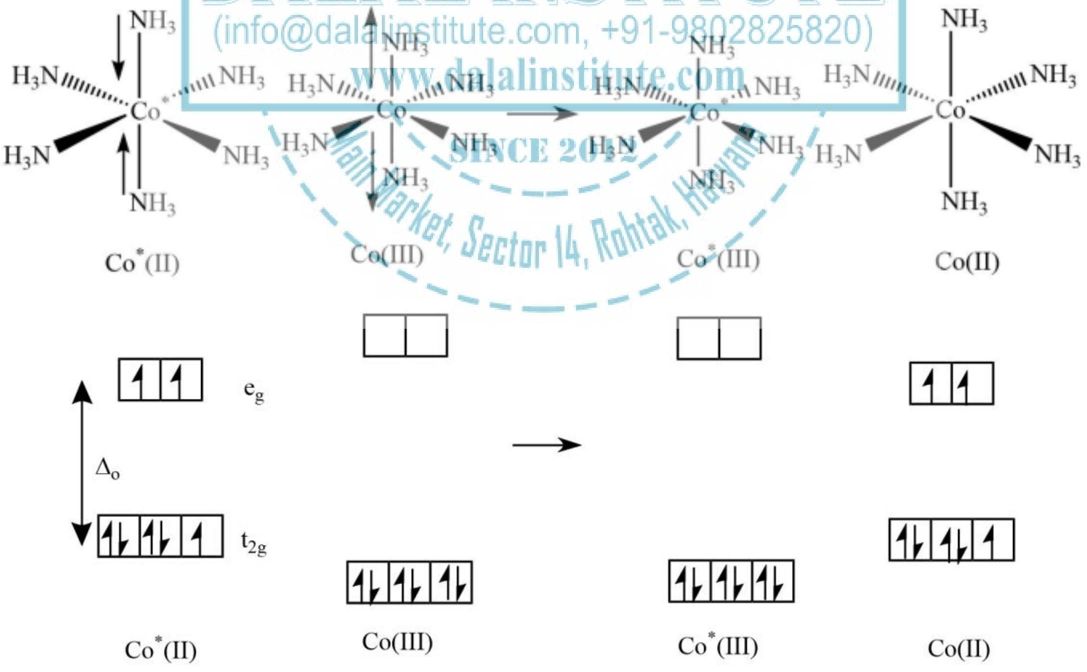


Figure 21. The electron transfer phenomena in transitions involving a reorganisation of electronic configuration.

➢ ***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.

$$[\mathrm{Cr(H_2O)_6}]^{2+} + [\mathrm{Co(NH_3)_6}]^{3+} \longrightarrow [\mathrm{Cr(H_2O)_6}]^{3+} + [\mathrm{Co(H_2O)_6}]^{2+} + 6\mathrm{NH_3} \qquad (12)$$

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

$$[\mathrm{Cr(H_2O)_6}]^{2+} + [\mathrm{Co(NH_3)_5Cl}]^{2+} \longrightarrow [\mathrm{Cr(H_2O)_5Cl}]^{2+} + [\mathrm{Co(H_2O)_6}]^{2+} + 5\mathrm{NH_3} \qquad (13)$$

On the other side, the value of the rate constant for electron transfer shown by equation (13) is 6×10^5 $M^{-1}s^{-1}$ which is too high to be explained via outer-sphere mechanism. Moreover, if we use $[Co(NH_3)_5Cl]^{2+}$ 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.

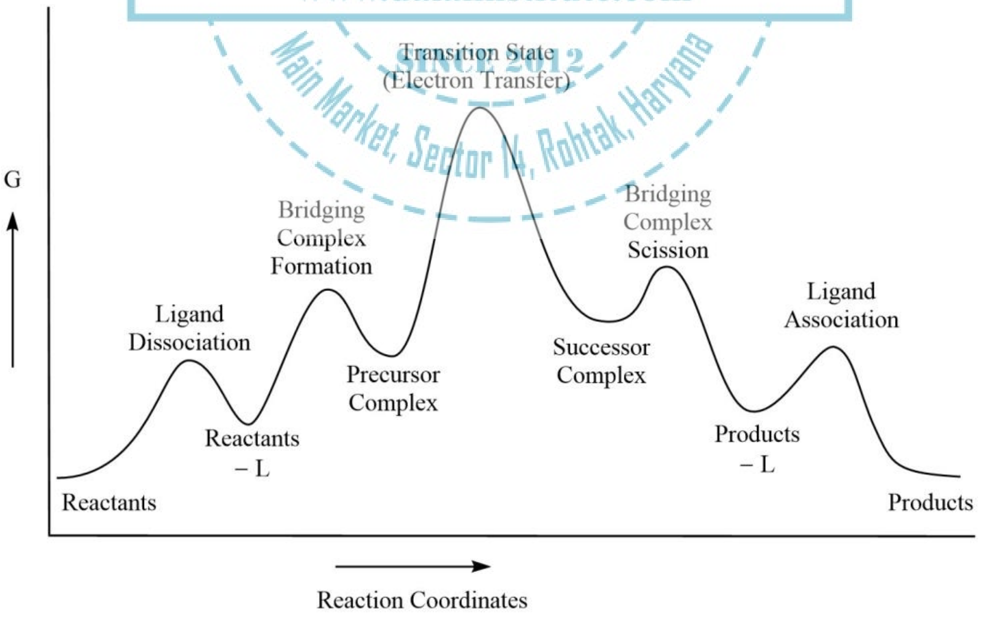


Figure 22. The reaction coordinate diagram for inner sphere electron transfer mechanism.

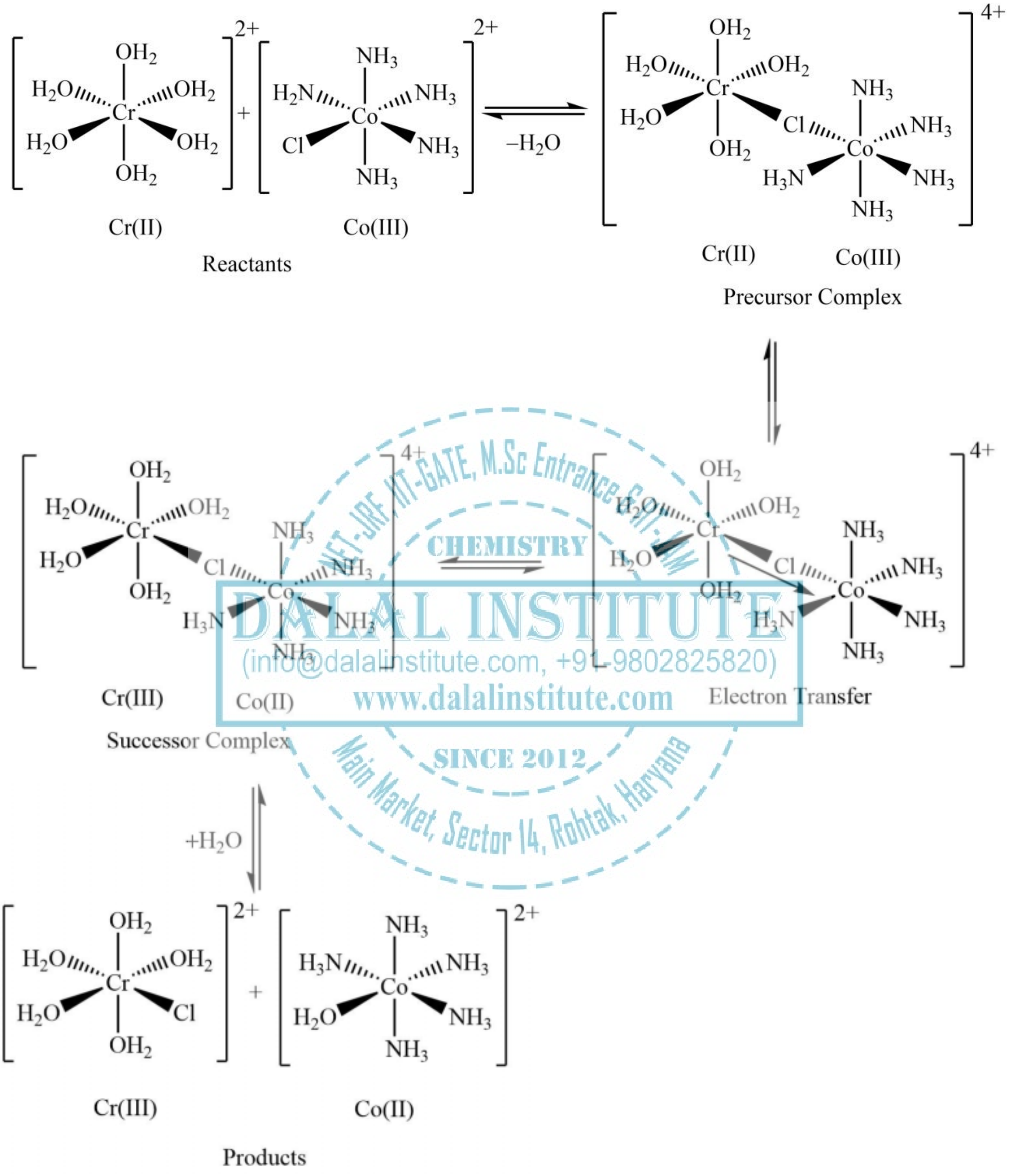


Figure 23. The formation of precursor complex, successor complex and the state of electron transfer in inner-sphere electron transfer mechanism.

The electron transfer results in the formation of $[Co(NH_3)_5(H_2O)]^{2+}$ which is labile in nature (d^7 high-spin) and immediately hydrolyzed to $[Co(H_2O)_6]^{2+}$ 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.

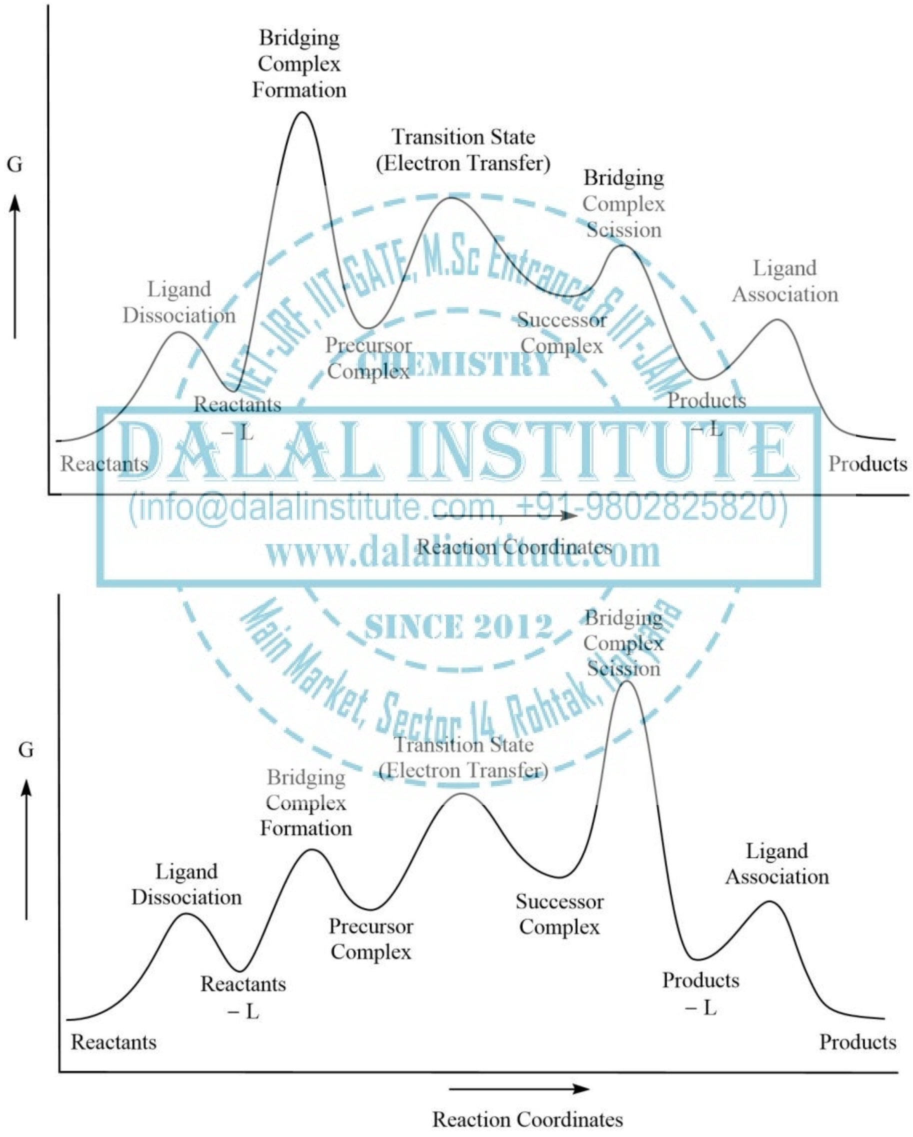


Figure 24. The reaction coordinate diagram for inner-sphere electron transfer mechanism with bridging complex formation and scission as the rate-determining step.

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.

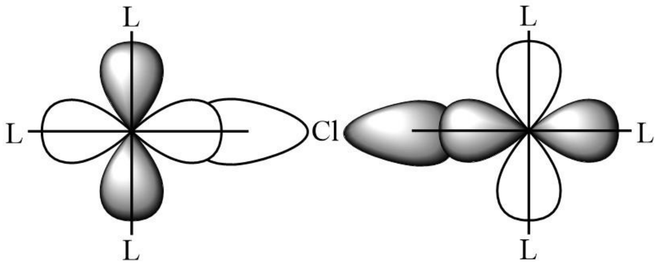
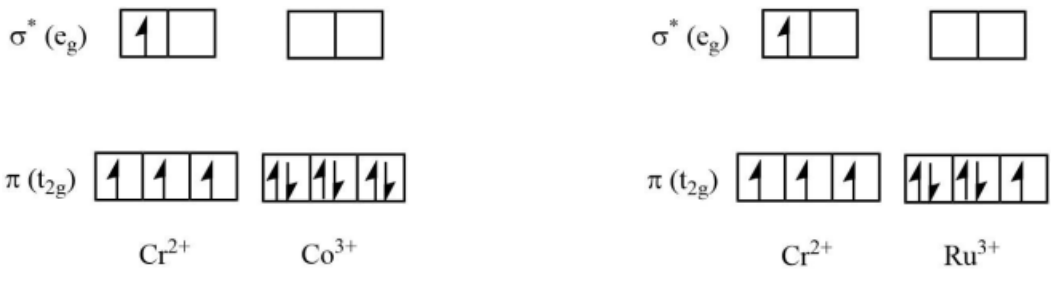


Figure 25. The interaction between e_g orbitals through the bridging ligand in the inner-sphere electron transfer mechanism.

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

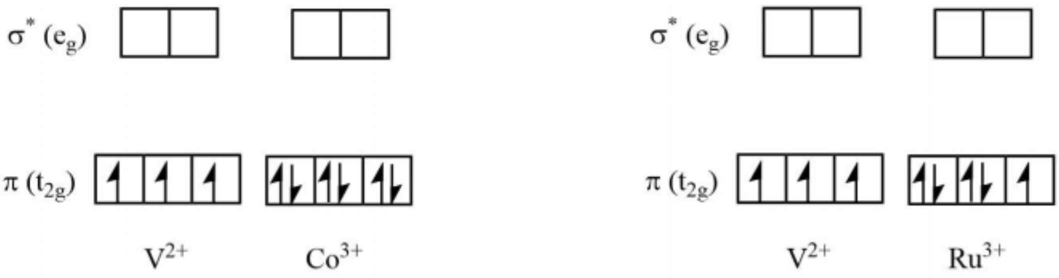
Reaction	HOMO	LUMO	Acceleration in going from outer-sphere to inner-sphere
$Cr^{2+} \longrightarrow Co^{3+}$	σ^*	σ^*	$\sim 10^{10}$
$Cr^{2+} \longrightarrow Ru^{3+}$	σ^*	π^*/π	$\sim 10^{2}$
$V^{2+} \longrightarrow Co^{3+}$	π^*	σ^*	$\sim 10^{4}$
$V^{2+} \longrightarrow Ru^{3+}$	π	π	All outer-sphere



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…

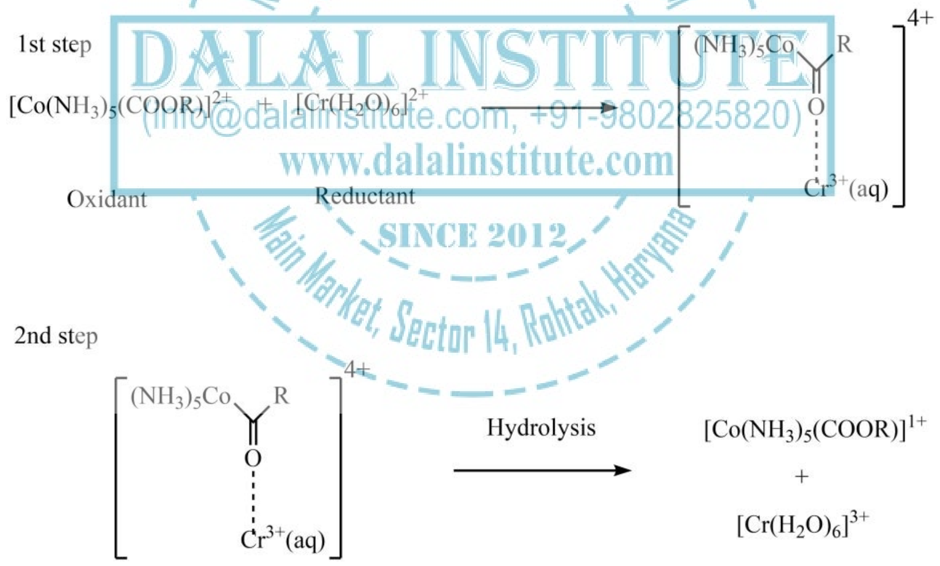


Large reorganization for Co^{3+} outer-sphere. Inner-sphere is much faster.

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.

❖ Electron Exchange

On the basis of the mechanism involved, the redox reactions of transition metal complexes have been divided into two types; outer-sphere and inner-sphere. We have already studied the same in the previous section. However, these electron-transfer reactions can also be classified on the basis of the metal centers involved as given below.

i) The electron transfer between two different oxidation states of the same metal ion. These reactions are generally called as self-exchange reactions.

ii) The electron transfer between two completely different metal complexes. These reactions are called as the cross-reactions.

The *electron exchange or self-exchange reactions may simply be defined as the redox reactions involving the transfer of electrons between two complexes having the same ligands and metal ions but with different oxidation states.*

In other words, the reactants in electron-exchange reactions are indistinguishable from the products. These reactions result in no net chemical change and can be studied only by special experimental techniques.

$$[\mathrm{Fe(H_2O)_6}]^{2+} + [\mathrm{Fe^*(H_2O)_6}]^{3+} \longrightarrow [\mathrm{Fe(H_2O)_6}]^{3+} + [\mathrm{Fe^*(H_2O)_6}]^{2+} \qquad (14)$$

$$[\mathrm{Co(NH_3)_6}]^{2+} + [\mathrm{Co^*(NH_3)_6}]^{3+} \longrightarrow [\mathrm{Co(NH_3)_6}]^{3+} + [\mathrm{Co^*(NH_3)_6}]^{2+} \qquad (15)$$

$$[\mathrm{Mn(CN)_6}]^{4-} + [\mathrm{Mn^*(CN)_6}]^{3-} \longrightarrow [\mathrm{Mn(CN)_6}]^{3-} + [\mathrm{Mn^*(CN)_6}]^{4-} \qquad (16)$$

All of the above are electron-exchange reactions proceeding via the outer-sphere electron transfer mechanism. The rate measurement of these reactions is quite difficult to record as the reactants are chemically equivalent to the products. Out of various techniques such as isotopic tracer, optical activity and EPR-NMR spectroscopy; isotopic labeling is the most convenient and widely accepted method to study the process of self-exchange. After mixing the reactants, the rate at which the radioactivity disappears in M^*(III) complex is the rate of electron exchange in the two complexes. Similarly, the rate at which the radioactivity appears in the M^*(II) complexes can also be used to estimate the rate of electron exchange.

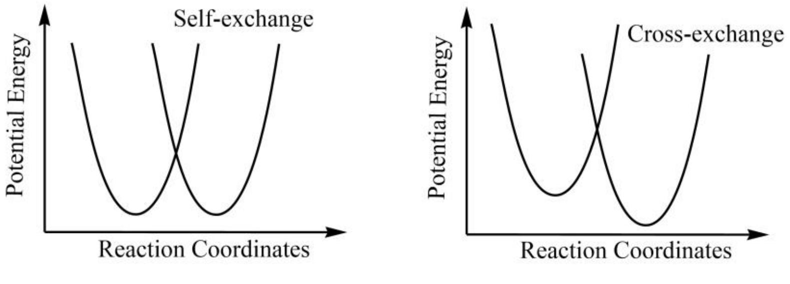


Figure 27. The comparison of potential energy curves of self-exchange and cross-exchange.

Table 2. The values of rate constants for some electron-exchange processes of type $[ML_6]^{2+} + [M^*L_6]^{3+} \longrightarrow [ML_6]^{3+} + [M^*L_6]^{2+}$.

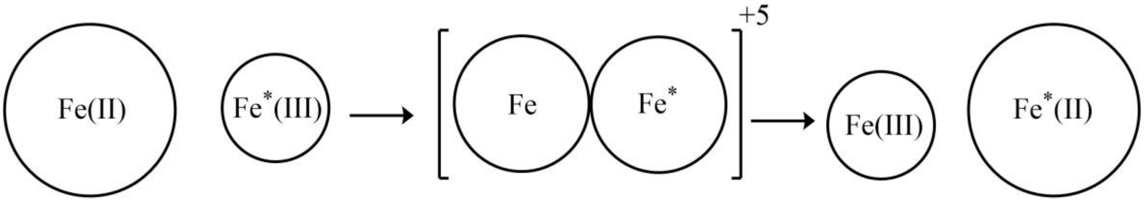
Complex	Electronic configuration M(II) ⟶ M*(III)		k ($M^{-1}s^{-1}$)	T(°C)
$Cr(H_2O)_6$	$t_{2g}^3\ e_g^1$	$t_{2g}^3\ e_g^0$	2×10^{-5}	25
$Fe(H_2O)_6$	$t_{2g}^4\ e_g^2$	$t_{2g}^3\ e_g^2$	4.2	25
$Co(H_2O)_6$	$t_{2g}^5\ e_g^2$	$t_{2g}^4\ e_g^2$	5	25
$Co(en)_3$	$t_{2g}^5\ e_g^2$	$t_{2g}^6\ e_g^0$	7.7×10^{-5}	25
$Fe(phen)_3$	$t_{2g}^6\ e_g^0$	$t_{2g}^5\ e_g^0$	1.3×10^7	3
$Co(phen)_3$	$t_{2g}^6\ e_g^1$	$t_{2g}^6\ e_g^0$	12	25

Now, as the electron-exchange reactions are the simplest type of outer-sphere mechanism; factors like transition-type, orbital overlap, and reorganization of electronic configuration can be used to explain the large differences in the electron-exchange rates listed in Table 2.

In order to get a wider view of the mechanism involved in electron-exchange, we need to recall the Frank-Condon principle which says the electronic rearrangements are so rapid that the nuclei can be considered as stationary. Moreover, the electron transfer from one complex to another is expected only when it has the same energy in both of the sites. Hence, the activation energy to achieve this goal is mainly governed by nuclear rearmaments. Consider the following reaction:

$$[Fe(H_2O)_6]^{2+} + [Fe^*(H_2O)_6]^{3+} \longrightarrow [Fe(H_2O)_6]^{3+} + [Fe^*(H_2O)_6]^{2+} \qquad (17)$$

The potential energy curves for the reactants and products should be parabolic because the metal–ligand deformations are almost harmonic in nature. The activated complex is present at the intersection point of the two curves.



(a)

Figure 28. Continued on the next page…

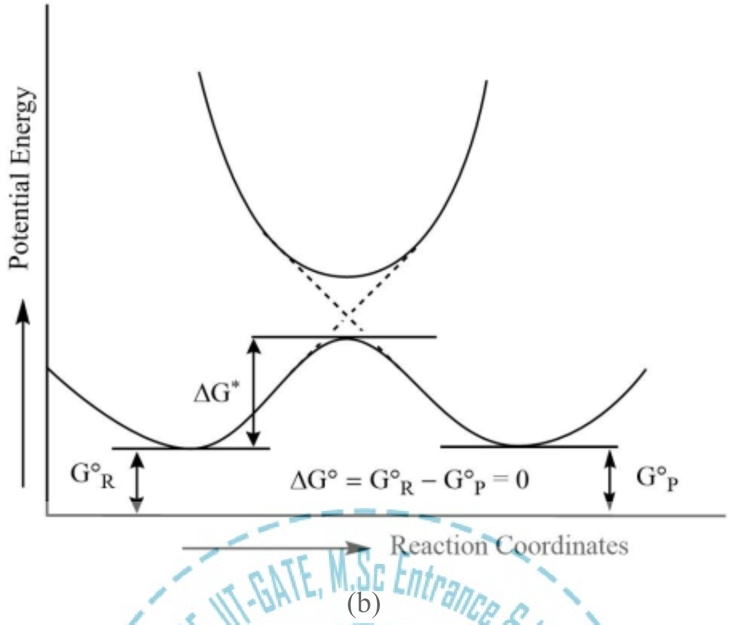


Figure 28. The (a) reaction course and (b) potential energy curve for electron-exchange reactions.

During the formation of activated complex, the Fe(II) bonds shorten while the Fe*(III) bonds lengthen which facilitates the transfer of electron. It is worth noting that the Gibbs free energy change for self-exchange reactions is zero but free energy of activation is still a non-zero term.

Rudolph A. Marcus derived an equation using the first principle to predict the overall rate constant for outer-sphere electron transfer reactions from the self-exchange rate constants of each of the redox couples involved and overall equilibrium constant. The equation can be given as:

$$k = [k_1 k_2 \mathrm{K} f]^{1/2} \tag{18}$$

Where k_1 and k_2 are rate contents for two electron-exchange reactions and K is the equilibrium constant for the overall reaction. The factor *f is* a complex parameter composed of the rate constants and has been incorporated to correct the free energy differences of the two reactants. Consider the example,

$$[\mathrm{Fe(CN)_6}]^{4-} + [\mathrm{Fe^*(CN)_6}]^{3-} \longrightarrow [\mathrm{Fe(CN)_6}]^{3-} + [\mathrm{Fe^*(CN)_6}]^{4-} \tag{19}$$

$k_1 = 7.4 \times 10^2\ \mathrm{M^{-1}s^{-1}}$

$$[\mathrm{Mo(CN)_6}]^{4-} + [\mathrm{Mo^*(CN)_6}]^{3-} \longrightarrow [\mathrm{Mo(CN)_6}]^{3-} + [\mathrm{Mo^*(CN)_6}]^{4-} \tag{20}$$

$k_2 = 3 \times 10^4\ \mathrm{M^{-1}s^{-1}}$

$$[\mathrm{Fe(CN)_6}]^{4-} + [\mathrm{Mo^*(CN)_6}]^{3-} \longrightarrow [\mathrm{Fe(CN)_6}]^{3-} + [\mathrm{Mo^*(CN)_6}]^{4-} \tag{21}$$

$\mathrm{K} = 1.0 \times 10^2$

Now, putting the values of k_1, k_2 and K from equation (19), (20) and (21) in equation (18); the value of rate constant for the overall reaction is found to be 4×10^4 $M^{-1}s^{-1}$; and it is obviously pretty much comparable to the experimental value of 3×10^4 $M^{-1}s^{-1}$.

In 1992, R. A. Marcus received the Nobel Prize in the field of Chemistry for his work on the theory of electron transfer reactions occurring in chemical systems. His theory is also named after him, the Marcus theory, and it provides a kinetic and thermodynamic framework for describing outer-sphere electron transfer reactions involving one electron.

❖ Problems

Q 1. Explain the mechanism of ligand displacement reactions in square-planar complexes.

Q 2. Write a short note on trans-effect and also explain the synthesis route of trans-platin.

Q 3. How would you explain the exceptionally high trans-effect of strong π-acceptor ligands like CN^{-1}, CO or ethylenediamine?

Q 4. Discuss the π-bonding theory of trans effect in detail.

Q 5. What do you understand from the outer-sphere electron transfer reactions? Also, discuss the factors affecting in detail.

Q 6. Discuss the nature of the inner-sphere electron transfer mechanism with special reference of electronic configuration.

Q 7. Define electron-exchange reactions. How can the Marcus equation be used to study cross-reaction?

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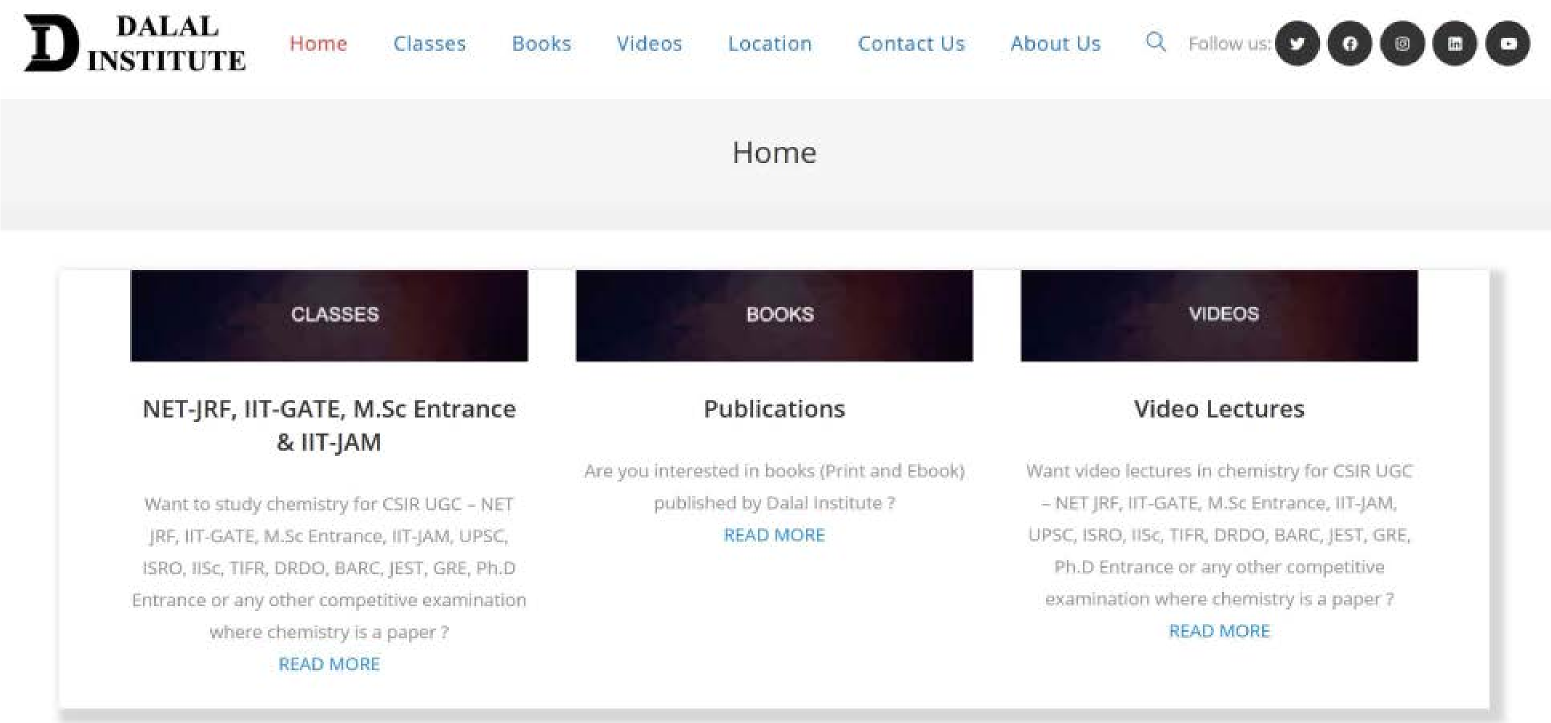

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