

## **KINETICS AND MECHANISM OF REACTIONS IN METAL COMPLEXES**

The kinetics and mechanisms of the reactions of transition metal complexes has not been fully understood by chemists. This can be attributed to the inherent difficulties involved in systematising the reactions of a no. of elements, in contrast to organic chemistry. Even attempts to predict from one element to another in the same group are not always successful. However, different types of reactions have been classified for metal complexes.

### **THERMODYNAMIC AND KINETIC STABILITY**

The kinetics and mechanisms of metal complexes can be better understood by making a distinction between the thermodynamic terms stable and unstable and the kinetic terms labile and inert. For example, consider the cyano complexes,  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $[\text{Mn}(\text{CN})_6]^{3-}$  and  $[\text{Cr}(\text{CN})_6]^{3-}$ . Though these complexes are stable from thermodynamic point of view, kinetically they are different. Rates of exchange of radiocarbon labeled cyanide (for cyanide exchange reaction) vary much.  $[\text{Ni}(\text{CN})_4]^{2-}$  exchanges cyanide ions rapidly ( $t_{1/2} \approx 30$  s),  $[\text{Mn}(\text{CN})_6]^{3-}$  exchanges moderately ( $t_{1/2} \approx 1$  h) and  $[\text{Cr}(\text{CN})_6]^{3-}$  is somewhat inert ( $t_{1/2} \approx 24$  days).

Generally, complexes that react completely within one minute at 25°C can be considered labile and those that take longer are considered inert.  $[\text{Ni}(\text{CN})_4]^{2-}$  is a good example of a thermodynamically stable complex that is kinetically labile. The lability of four coordinate  $\text{Ni}^{2+}$  complexes can be associated with the ready ability of  $\text{Ni}^{2+}$  to form five- or six- coordinate complexes. The additional bond energy of the fifth or sixth bond in part compensates for the loss of ligand field stabilization energy. Example for a kinetically inert complex that is thermodynamically unstable is the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  cation in acid solution. Several days are required at room temperature for degradation of the complex despite the favourable thermodynamics. The inertness of the complex is considered to be from the absence of a suitable low energy pathway for the acidolysis reaction. The reaction for  $[\text{Co}(\text{NH}_3)_6]^{3+}$  must involve either an unstable seven coordinate species or five coordinate species with concomitant loss of energy and LFSE.

### **Valence Bond Theory**

Several explanations have been put forward for the explanation of lability and inertness of complexes. According to Valence Bond Theory, the octahedral complexes are of two types; 1) outer orbital complexes which use  $sp^3d^2$  hybridisation and 2) inner orbital complexes which use  $d^2sp^3$  hybridisation. Outer orbital complexes are generally labile. This weakness is correlated to the weakness of the bonds of  $sp^3d^2$  as compared to  $d^2sp^3$  bonds. In the case of inner orbital complexes, if all the three  $t_{2g}$  levels are filled either singly or doubly, then they are inert kinetically. If an inner orbital complex contains one or two electrons in the  $t_{2g}$  set, then atleast one level will be vacant. For example, in  $[\text{V}(\text{H}_2\text{O})]^{3+}$ , two of the three  $t_{2g}$  levels are singly occupied. Hence the third level can be used to accept the electron pair donated by the incoming ligand to form a 7-coordinated intermediate which is less stable. To get itself stabilised, one of the original six ligands is expelled leading to a substitution product and hence  $[\text{V}(\text{H}_2\text{O})]^{3+}$  is labile. But in  $[\text{Cr}(\text{H}_2\text{O})]^{3+}$ , there is no d level vacant to accept the electron pair donated by the incoming ligand, hence this complex is inert.

**Taube's Explanation**

According to Taube, the degree of lability or inertness of a transition metal complex can be correlated with the d electronic configuration of the metal ion. If a complex contains electrons in the antibonding  $e_g^*$  orbitals, the electrons are expected to be weakly bound and easily displaced; it is labile. If the metal contains an empty  $t_{2g}$  orbital, the four lobes of that orbital correspond to directions from which an incoming ligand can approach the complex with relatively little electrostatic repulsion. Therefore it can be concluded that a complex with one or more  $e_g^*$  electrons or with fewer than three d electrons should be relatively labile and that a complex with any other electronic configuration should be relatively inert.

**Crystal Field Theory**

In Crystal Field Theory, Crystal Field Activation Energy is defined as the change in the Crystal Field Stabilisation Energy when the reacting complex is transformed into the transition state.

$$\text{CFAE} = \text{CFSE of intermediate} - \text{CFSE of reacting complex}$$

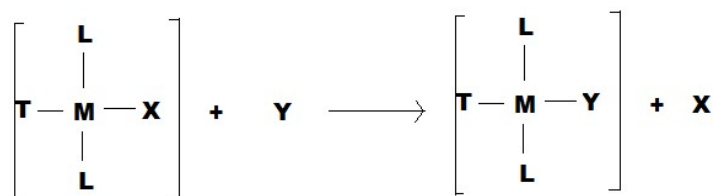
Thus it infers that octahedral complexes having negative or zero CFAEs would therefore be labile whereas those having positive CFAEs would be slow to react.

Octahedral complexes with metal ion configurations of  $d^3$  and spin paired  $d^5$  and  $d^6$  and to some extent  $d^4$  would be slow to react by  $S_N1$  and  $S_N2$  mechanism (strong field causes pairing of electron spins). Similarly, octahedral complexes with metal ion configuration of  $d^8$  would be slow to react whatever be the strength of the ligand field and whatever be the mechanism of substitution reaction.

Octahedral complexes with metal ion configurations of  $d^0$ ,  $d^1$ ,  $d^2$  spin free  $d^4$ ,  $d^5$ ,  $d^6$ ,  $d^7$ ,  $d^9$  and  $d^{10}$  configurations have negative or zero CFAEs and would therefore be labile.

**NUCLEOPHILIC SUBSTITUTION REACTIONS IN SQUARE PLANAR COMPLEXES**

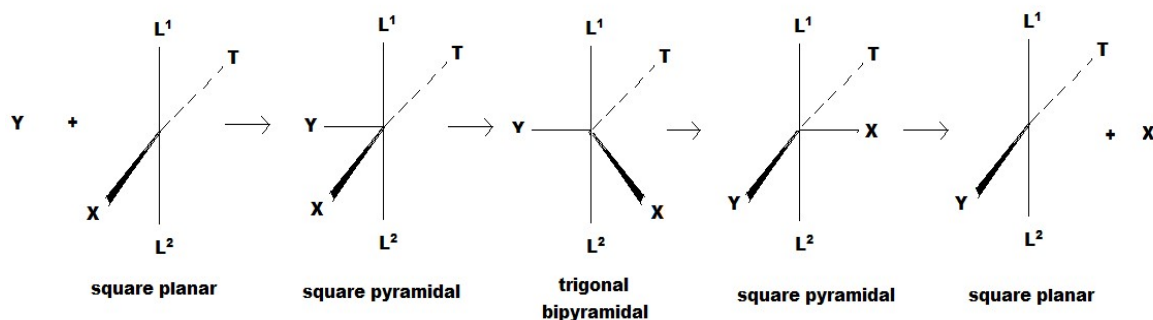
Square planar complexes with  $d^8$  configurations undergo substitution reactions of the type,



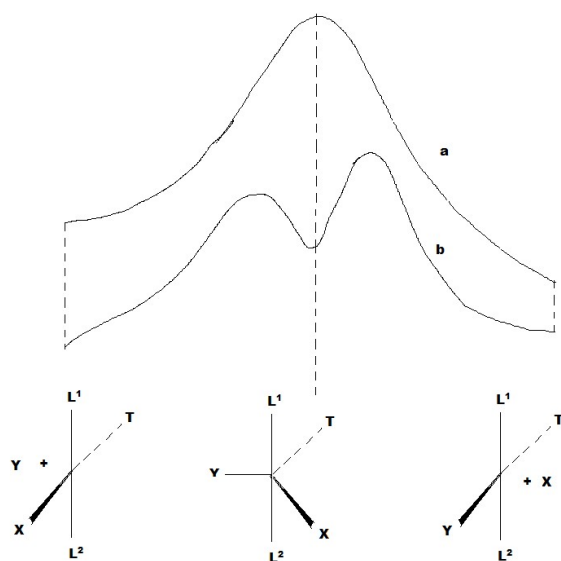
in which Y is the entering nucleophilic ligand, X is the leaving ligand and T is the ligand trans to X.

## MECHANISM

Pt(II) complexes are widely used for studying the mechanism and kinetics since the substitutions are comparatively slow and hence easier to study. From kinetic studies scientists have arrived at an associative  $S_N2$  mechanism for substitution reactions in square planar complexes. Consider a nucleophile Y attacking a  $d^8$  complex from either side of the plane. In addition to being attracted to the electron deficient metal centre, the ligand experiences repulsion from the filled metal d orbitals and from the bonding electrons. However, it coordinates to the metal through an empty  $p_z$  orbital to form a square pyramidal species, though electronic repulsions as well as steric factors slow the attack. Once formed, the square pyramidal species will undergo a transformation to a trigonal bipyramidal structure. It will have three ligands (Y, T and X) in its equatorial plane and two of the groups that were trans to each other in the original complex will occupy the axial positions. As X departs from the trigonal plane, the T-M-Y angle opens up and the geometry will pass through a square pyramid on its way to the square planar product.



The trigonal bipyramidal species that forms during the reaction may exist either as an activated complex or as a true intermediate. The distinction between the two depends on the lifetime of the species. The term activated complex refers to the configuration of the reactants and products at a peak in the reaction profile energy curve. i.e at the transition state. The term intermediate implies that a species has a detectable lifetime (though short) and that it is at least somewhat more stable than any activated complexes.



Reaction coordinate/energy profile for a square planar substitution reaction having a) trigonal bipyramidal activated complex and b) a trigonal bipyramidal intermediate.

### Evidences for the mechanism

The mechanism of substitution reactions of square planar complexes appears to be associative  $S_N2$  rather than dissociative  $S_N1$ . The evidences for this are,

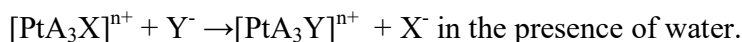
1. In the case of square planar complexes of Ni(II), Pd(II) and Pt(II), five empty orbitals of comparable energy can be made available for bonding of which four are used up for bonding with ligands. The fifth orbital can easily accommodate electrons from the attacking ligand forming a five coordinate intermediate. i.e an associative  $S_N2$  mechanism.
2. There exists a parallelism between the reactivity of the square planar complexes of Ni(II), Pd(II) and Pt(II) complexes (Ni(II) > Pd(II) > Pt(II)) and their ease with which these expand their coordination no: which indicates the formation of an intermediate with a higher coordination no:.
3. The rates of aquation reactions of  $[PtCl_4]^{2-}$ ,  $[PtCl_3NH_3]$ , cis  $[Pt(NH_3)_2Cl_2]$  and  $[Pt(NH_3)_3Cl]^+$  changes only by a factor of 2 whereas the charge of the complex changes from -2 to +1. This suggests that both bond breaking and bond making are important, which is characteristic of an associative  $S_N2$  mechanism.
4. Nature of the entering ligand greatly affects the rate of substitution in square planar complexes indicating that the entering ligand takes part in the rate determining step. This is another evidence for  $S_N2$  mechanism.
5. The nature of the departing group, does not affect much the rate constants of these reactions indicating that the dissociative  $S_N1$  mechanism in which the departing ligand has a greater role is not operative.
6. It has been observed that substitution in Pt(II) square planar complexes occurs with retention of configuration. i.e cis  $\rightarrow$  cis and trans  $\rightarrow$  trans. This is in agreement with a

trigonal bipyramidal intermediate. With a 3 coordinate intermediate (dissociative mechanism), the entering group can lead to both cis and trans isomers.

- As the bulkiness of the ligands other than the entering and departing ligands increases, the reaction rate decreases, indicating an associative mechanism.

## KINETICS

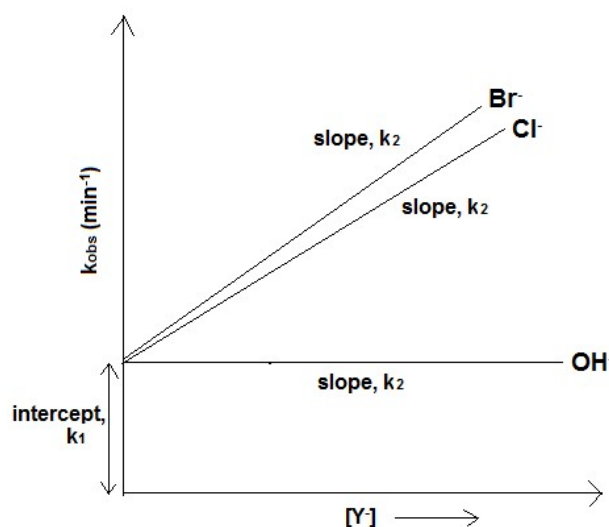
The kinetics of the reaction can be illustrated by the reaction,



For this reaction, a two term rate law was found out.

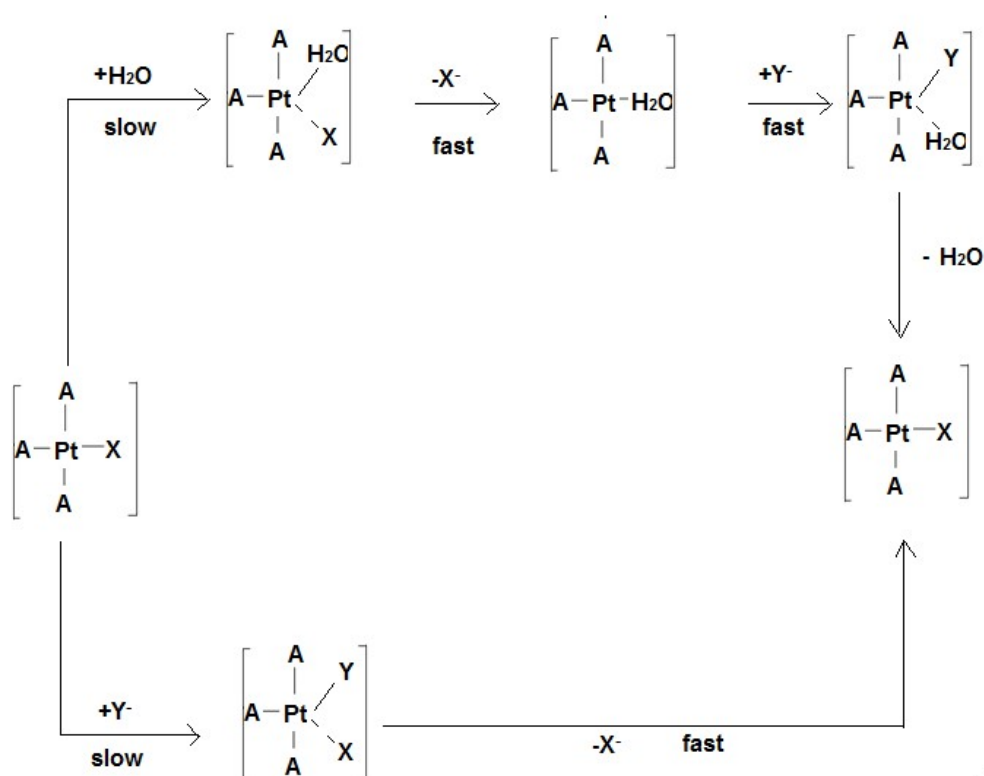
$$\text{Rate} = k_1[\text{PtA}_3\text{X}^{n+}] + k_2[\text{PtA}_3\text{X}^{n+}] [\text{Y}^-]$$

where  $k_1$  = first order rate constant for solvent controlled reaction and  $k_2$  = second order rate constant for reaction with  $\text{Y}^-$ . The analysis of the rate constants is made by conducting the reactions with a large excess of nucleophile,  $\text{Y}^-$ . Then the observed rate constant,  $k_{\text{obs}}$  is pseudo first order and is related to  $k_1$  and  $k_2$  as  $k_{\text{obs}} = k_1 + k_2[\text{Y}^-]$ . Thus for the same complex, linear plots of  $k_{\text{obs}}$  against different nucleophile concentration,  $[\text{Y}^-]$  should be obtained, having the same intercepts  $k_1$  and different slopes,  $k_2$ .



Plots of  $k_{\text{obs}}$  for the reaction:  $[\text{Pt}(\text{dien})\text{Cl}]^+ + \text{Y}^- \rightarrow [\text{Pt}(\text{dien})\text{Y}]^+ + \text{Cl}^-$  against concentration of nucleophile,  $[\text{Y}^-]$

The obtained rate law indicates that the reaction of  $[\text{PtA}_3\text{X}]^{n+}$  with  $\text{Y}^-$  to yield  $[\text{PtA}_3\text{Y}]^{n+}$  is occurring by a two path mechanism, of which only one involves  $\text{Y}^-$  in the rate determining step.



The upper path is the solvent path (also called  $Y^-$  independent path) and the lower path is the direct path (reagent path). In the solvent path, the solvent  $H_2O$  replaces  $X^-$  in a slow step. It is subsequently replaced by  $Y^-$  in a rapid step. Experiments show that  $Y^-$  independent path is not an  $S_N1$  process, but is a direct  $S_N2$  displacement of leaving group by nucleophile in probably second order path while the solvent path gives pseudo first order kinetics.

The rate constant  $k_1$  is due to solvent path, while  $k_2$  is due to the direct displacement of the leaving group by nucleophile. Hence solvent path  $k_1$  can be designated as  $k_s$  and the direct displacement path  $k_2$  as  $k_Y$  so that

$$k_{obs} = k_s + k_Y[Y^-]$$

### Factors affecting the rates of substitution reactions in square planar complexes

1. Trans Effect
2. Effect of leaving group

For the reaction,  $[Pt(dien)X]^+ + py \rightarrow [Pt(dien)py]^{2+} + X^-$ , the rates of the reaction show that if the leaving group  $X^-$  is replaced by  $NO_3^-$ ,  $H_2O$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $N_3^-$ ,  $SCN^-$ ,  $NO_2^-$  and  $CN^-$ , the rates decrease in the order,  $NO_3^- > H_2O > Cl^- > Br^- > I^- > N_3^- > SCN^- > NO_2^- > CN^-$

3. Solvent Effect

Since in the solvent path, the solvent replaces directly, as the coordinating ability of the solvent increases, contribution made by this path to the overall rate of the reaction would also increase. The solvents can be divided into two,

- a) Good coordinating solvents like H<sub>2</sub>O, ROH etc which provide almost entirely a solvent path for exchange. For the reaction of Cl<sup>-</sup> with [Pt(py)<sub>2</sub>Cl<sub>2</sub>], rate of exchange does not depend on the nucleophile. i.e.  $k_s \gg k_{Cl} [Cl^-]$  or  $k_1 \gg k_2$ .
- b) Poor coordinating solvents like CCl<sub>4</sub>, C<sub>6</sub>H<sub>6</sub> contribute little to the overall rate of the reaction. Here rate of exchange depends on [Cl<sup>-</sup>]. i.e.  $k_s < k_{Cl} [Cl^-]$  or  $k_1 < k_2$ . The experimental results of the effect of solvent on the rate of exchange are,

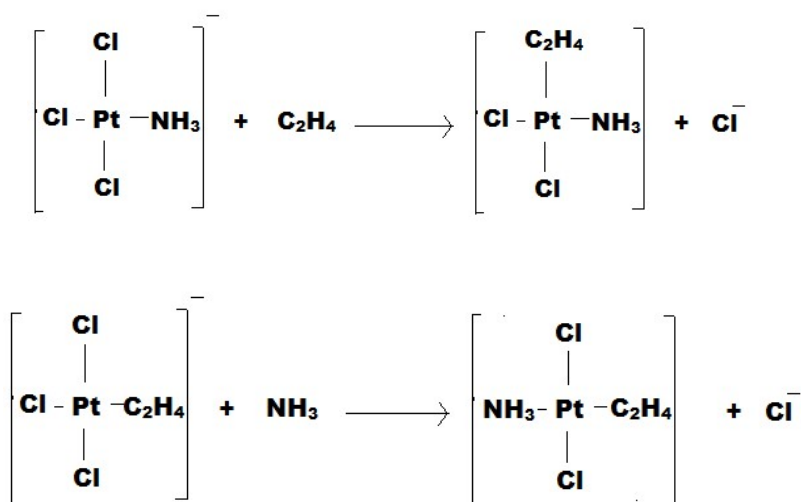
Solvents in which rate is independent of [Cl <sup>-</sup> ]	k <sub>obs</sub> (min <sup>-1</sup> )	Solvents in which rate is dependent on [Cl <sup>-</sup> ]	k <sub>obs</sub> (min <sup>-1</sup> )
H <sub>2</sub> O	2.1 x 10 <sup>-3</sup>	CCl <sub>4</sub>	1 x 10 <sup>-4</sup>
C <sub>2</sub> H <sub>5</sub> OH	8.5 x 10 <sup>-4</sup>	C <sub>6</sub> H <sub>6</sub>	2 x 10 <sup>-4</sup>
m- C <sub>3</sub> H <sub>7</sub> OH	2.5 x 10 <sup>-4</sup>	m-cresol	2 x 10 <sup>-4</sup>
(CH <sub>3</sub> ) <sub>2</sub> SO	2.3 x 10 <sup>-2</sup>	tert-C <sub>4</sub> H <sub>9</sub> OH	1 x 10 <sup>-3</sup>
CH <sub>3</sub> NO	1.9 x 10 <sup>-3</sup>		

#### 4. Effect of charge on the complex

The charge on the complex does not have appreciable effect on the rate of nucleophilic substitution of square planar complexes. For example, the rates of aquation reactions of [PtCl<sub>4</sub>]<sup>2-</sup>, [PtCl<sub>3</sub>NH<sub>3</sub>]<sup>-</sup>, cis [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] and [Pt(NH<sub>3</sub>)<sub>3</sub>Cl]<sup>+</sup> changes only by a factor of 2 whereas the charge of the complex changes from -2 to +1.

### TRANS EFFECT-THEORY AND APPLICATIONS

The ability of an attached group to direct substitution into a position trans to itself is called trans effect. Such a group has a marked influence (trans influence) on the rate of a reaction. For example, in the substitution reaction,

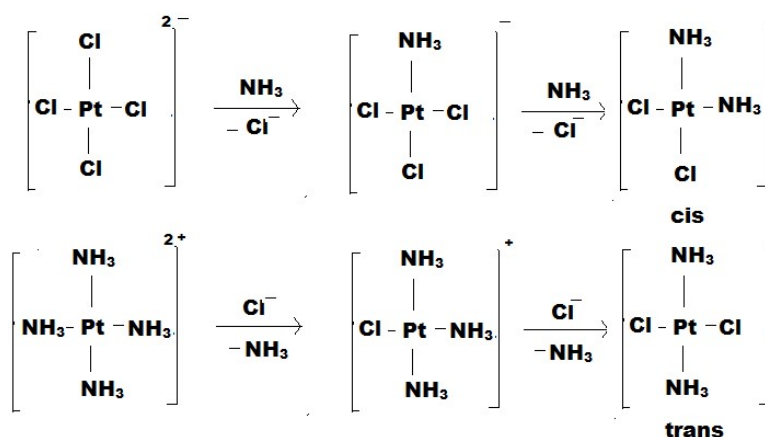


Since  $\text{Cl}^-$  has greater trans effect than  $\text{NH}_3$ , the  $\text{Cl}^-$  trans to  $\text{Cl}^-$  and not the one trans to  $\text{NH}_3$  is replaced by  $\text{C}_2\text{H}_4$ . Also,

Since  $\text{C}_2\text{H}_4$  has greater trans effect than  $\text{Cl}^-$ , the  $\text{Cl}^-$  trans to  $\text{C}_2\text{H}_4$  and not the one which is trans to  $\text{Cl}^-$  is replaced by  $\text{NH}_3$ . The approximate ordering of ligands in a trans directing series is,

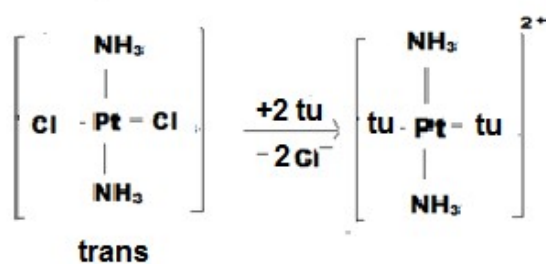
$\text{CN}^-$ ,  $\text{CO}$ ,  $\text{NO}$ ,  $\text{C}_2\text{H}_4 > \text{PR}_3$ ,  $\text{H}^- > \text{CH}_3^-$ ,  $\text{C}_6\text{H}_5^-$ ,  $\text{SC}(\text{NH}_2)_2$ ,  $\text{SR}_2 > \text{SO}_3\text{H}^- > \text{NO}_2^-$ ,  $\text{I}^-$ ,  $\text{SCN}^- > \text{Br}^- > \text{Cl}^- > \text{py} > \text{RNH}_2$ ,  $\text{NH}_3 > \text{OH}^- > \text{H}_2\text{O}$

Trans effect is used in synthesizing certain specific complexes. For example cis and trans diamminedichloro Pt(II) complexes have been synthesized separately as,



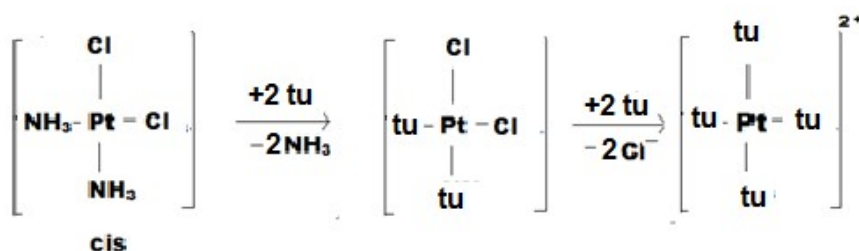
Another application of trans effect is in distinguishing cis and trans isomers of the formula  $[\text{PtCl}_2(\text{NH}_3)_2]$ . Addition of thiourea (tu) to the trans isomer results in the replacement of the two trans  $\text{Cl}^-$  ions. The reaction stops at this stage

because the trans  $\text{NH}_3$  molecules do not labilise each other.



But the addition of thiourea to the cis isomer results in the displacement of all the original ligands and gives  $[\text{Pt}(\text{tu})_4]^{2+}$  as the final product.

The trans effect of the ligands decreases in the order  $\text{tu} > \text{Cl}^- > \text{NH}_3$ . This method of differentiating the geometrical isomers is called the Kurnakov effect.



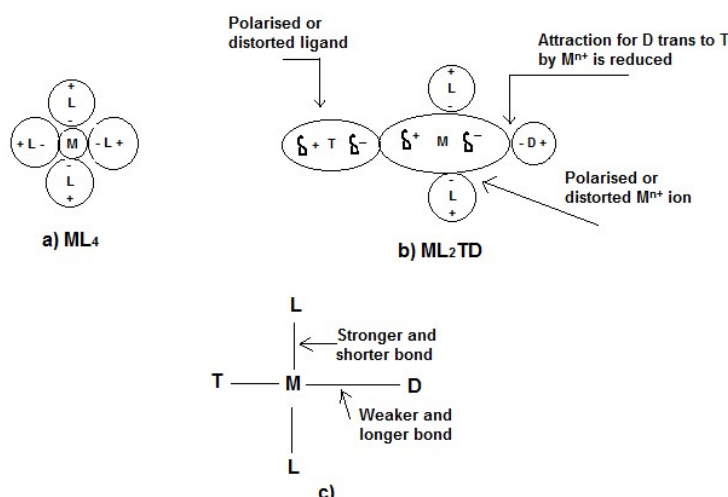


## Theories of trans effect

Several theories have been proposed for the explanation of trans effect.

### 1) Polarisation theory

This is a thermodynamic approach. According to this theory, the primary positive charge of  $M^{n+}$  induces a dipole in all the four ligands. If all the four ligands are identical as in (a), then the dipoles induced by the metal ions cancel each other and the resultant dipole is zero. None of the four ligands show trans effect. But if the four ligands are not identical, then the induced dipoles do not cancel each other. The two L ligands which are similar and trans to each other balance each other. But the other two trans ligands T and D, which are not similar do not balance each other. T is large and has greater polarisability than D. Polarisation takes place in such a way that the positive charge of  $M^{n+}$  central ion at a point trans to T is reduced. Hence the attraction of D for  $M^{n+}$  is also reduced and the bond trans to T is weakened and hence lengthened. This facilitates the replacement of D by E (entering ligand) at a point trans to T.



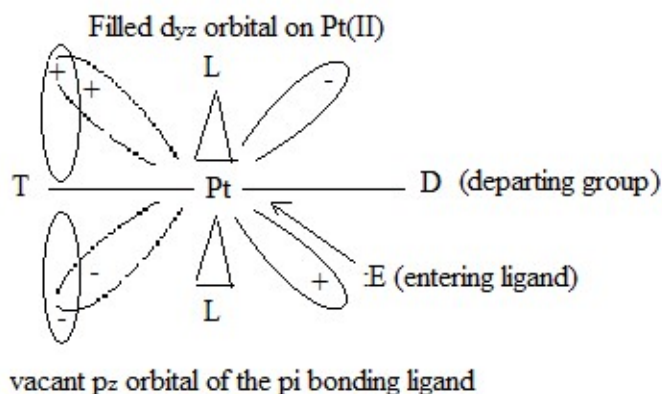
### Evidences:

- 1) The theory predicts that trans effect is important only when the central metal ion itself is polarisable and large in size. Actually, trans effect is observed predominantly in  $Pt(II)$  complexes than in  $Pd(II)$  or  $Ni(II)$  complexes.
- 2) If the ligand T is highly polarisable in  $[PtL_2TD]$  complex, then  $Pt-D$  bond trans to T is longer than  $Pt-L$  bond cis to T. The complex  $[Pt(C_2H_4)X_3]$  type where  $X = Cl^-$ ,  $Br^-$  and  $C_2H_4$  has large trans effect. The  $Pt-Cl$  or  $Pt-Br$  bond trans to  $C_2H_4$  is longer than that cis to  $C_2H_4$ .

**Defect:** The theory can well explain the ligands at the low end of the trans effect series like  $H_2O$ ,  $OH^-$ ,  $NH_3$  etc. However, this theory cannot explain the high trans effect of the pi bonding ligands like  $C_2H_4$ ,  $CN^-$ ,  $CO$  etc which lie at the other end of trans effect series.

## 2) Pi bonding theory

According to this theory, the vacant  $\pi$  or  $\pi^*$  orbitals of the pi bonding ligands accept a pair of electrons from the filled d orbitals of the metal ( $d_{xz}$  or  $d_{yz}$ ) to form M-L pi bond. In the case of Pt(II) square planar complex,  $[\text{PtL}_2\text{TD}]$  (T is the pi bonding ligand, D is the departing ligand trans to T), the filled orbital of Pt(II) overlaps with the empty orbital of the ligand T to form M-T pi bond. The formation of this pi bond increases the electron density in the direction of T and diminishes it in the direction of the ligand trans to T. The electron shift towards T facilitates the approach of the entering ligand E with its lone pair in the direction of trans directors.



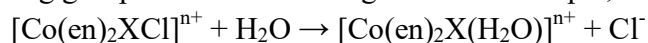
The formation of  $d_{\pi} - p_{\pi}$  bond between Pt(II) and the  $\pi$ - bonding ligand, T in the five coordinated transition complex.

## 3) Molecular Orbital approach

In this approach, there is the formation of a five coordinated intermediate with trigonal bipyramidal arrangement in which the more electronegative atoms occupy the axial positions. The loss of the ligand L from the triangular plane will take place from trans position to the least electronegative group T so that the entering group E is trans to T.

## Cis Effect

Certain ligands such as thiocyanate and hydroxide ions greatly accelerate the hydrolysis of a complex when they are cis to the leaving group as compared to the analogous reaction in which the leaving group is trans to these ligands. For example,

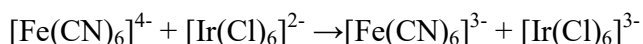


where X is a cis activating ligand like  $\text{OH}^-$ ,  $\text{SCN}^-$  etc. When  $\text{OH}^-$  is cis to the leaving  $\text{Cl}^-$ , the reaction rate is about ten times as great as that when it is in the trans position. The ligands that possess a strong cis effect are those that have unshared pairs of electrons in addition to the pair used in the sigma dative bond.

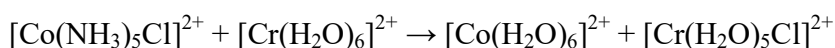
**ELECTRON TRANSFER REACTIONS**

Transition metals can undergo several oxidation- reduction reactions where in there is a change in oxidation state. There are formally two types of reactions of this type.

- Reactions involving simple electron transfer



- Reactions that can be considered as atom transfer reactions that occur with electron transfer



Simple electron transfer reactions involving transition metal complexes in solutions are complicated by the fact that the oxidised and the reduced species are often metal ions surrounded by shields of ligands and solvating molecules. No heat change is associated with the reaction. The reactions can be between two metal ions or between single element in different oxidation states (self exchange reactions). The electron transfer can be broadly divided into two mechanistic classes called outer sphere mechanism and inner sphere mechanism.

**OUTER SPHERE MECHANISM**

For transition metal complexes an outer sphere mechanism is established when rapid electron transfer occurs between two substituent inert complexes. (A substituent inert complex is one that undergoes substitution at a rate substantially less than the rate of electron transfer.) In this mechanism, the coordination shell of the reductant and oxidant stays intact. i.e the bonds are neither broken nor made. The electron effectively hops from one species to the other (also called tunnelling) and the ligands act as electron conduction media. An outer sphere electron transfer may be generally represented as,



$[\text{O}\cdots\cdots\text{R}] \rightarrow [\text{O}\cdots\cdots\text{R}]^* \rightarrow [\text{O}^-\cdots\cdots\text{R}^+] \text{ - chemical activation of precursor complex followed by electron transfer and relaxation to successor complex.}$

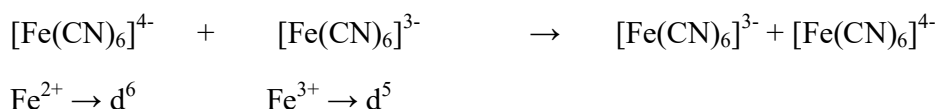


Here O is oxidant and R is reductant. First the oxidant and the reductant come together to form a precursor complex. Activation of the precursor complex which include reorganisation of solvent molecule and changes in metal –ligand bond length occur. Final step is the dissociation of the ion pair into products.

The salient features of electron transfer by outer sphere mechanism are,

1. Minimum electronic interactions by chemical bonding between the reactants.
2. The inner coordination spheres of the reactants remain unaffected.
3. The ligands in the two reactants remain as such and the bonds are neither made nor broken.
4. Rate is first order with respect to reactants.
5. Electron transfer from one stable complex to another with no breaking of M-L bond.
6. Rate depends on the size of the cations present in the solution.

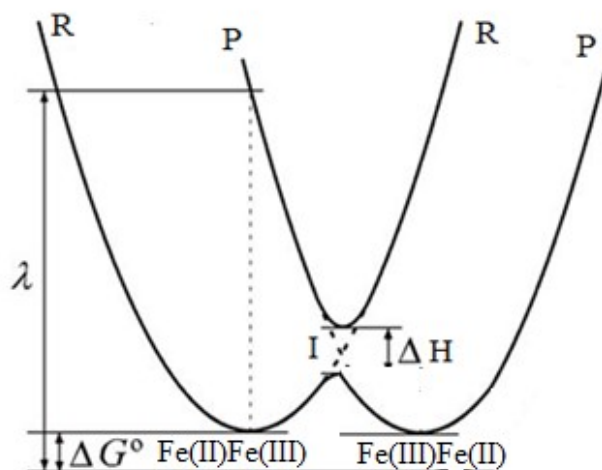
The exchange of  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  denotes a typical example of a process that takes place by direct electron transfer through an outer sphere activated complex. The rate of exchange can be studied by isotopic labelling of Fe.



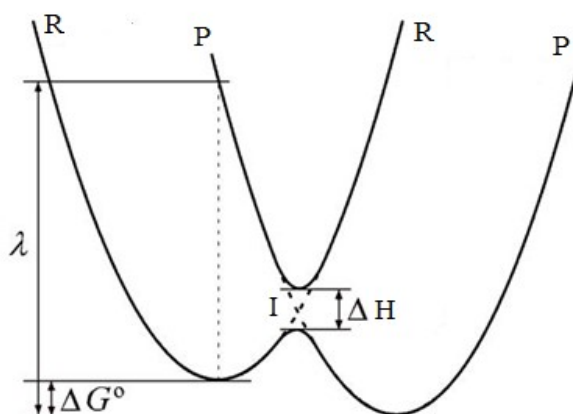
Fe-C bond longer      Fe-C bond shorter

The electron is transferred from a  $t_{2g}$  orbital of  $\text{Fe}^{2+}$  to  $t_{2g}$  orbital of  $\text{Fe}^{3+}$ . The bond lengths are unequal. i.e the energies of these orbitals are not equivalent. The probability of the reaction can be given by Franck Condon principle which states that there can be no appreciable change of atomic rearrangement during the time of electronic transition- the energies of the participating electronic orbitals must be same. Hence the ion- ligand bond length adjusts to intermediate value and then electron transfer takes place. Thus the actual process occurs with shortening of the bonds in  $\text{Fe}^{2+}$  and lengthening of bonds in  $\text{Fe}^{3+}$  complexes until participating orbitals are of same energy. Vibrational stretching and compression along M-L bonds allow this. In specific cases, there may be angular distortion of the ligand as well as solvent reorganisation to accommodate the precursor structural changes.

We assume that metal ligand stretching motion resemble a harmonic vibration and so the potential energy curve drawn as parabolas can be approximated as a harmonic potential well. The activated complex is located at the intersection of the two curves. However then the noncrossing rule states that, molecular potential energy curves of states of same symmetry does not cross but instead split into an upper and lower curve as shown.

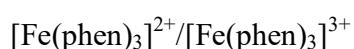
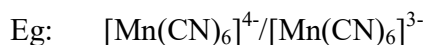


Potential energy diagram for a homonuclear electron transfer reaction. The activated complex is situated at I and  $\Delta E$  is the activation energy (Gibb's energy of activation). A general potential energy diagram for a heteronuclear electron transfer reaction can be drawn as,



### Correlation of rates with structure and electronic configuration

In outer sphere mechanism, the bond distortion magnitudes have an important role in the rates of the reaction. The rate seems to be relatively great for two ions of similar geometry so that little rearrangements are needed to symmetrise the transition state enhancing a strong coupling interaction. i.e low  $\Delta G_1^\ddagger$ . This will generally be the case for complexes differing by one electron in low energy  $t_{2g}$  orbitals used in ligand bonding.



The rates will be greatest if the ligands are unsaturated and pi bonding. This stabilises the lower valency state more than the higher and hence the geometries will be nearly equal. Thus  $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$  is faster than  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}/[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

If the geometry of the two ions is very different, the coupling interaction is very weak since large bond distortion is needed. This is the case for ions where the electrons to be transferred occupies one of the  $e_g$  orbitals used to hold a ligand.

Eg. Co(II)/Co(III), Cr(II)/Cr(III)

Qs: Why the electron transfer reaction of  $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$  is faster than  $[\text{Co}(\text{NH}_3)_6]^{2+}/[\text{Co}(\text{NH}_3)_6]^{3+}$

### **MARCUS THEORY**

Marcus gave a quantitative relation for the calculation of rate constant for electron transfer by outer sphere mechanism.

$k_{\text{et}} = \nu_{\text{N}} k_{\text{e}} e^{-\Delta G^\ddagger/RT}$  where  $k_{\text{et}}$  is rate for electron transfer and  $\Delta G^\ddagger$ , the Gibb's energy of activation, given by  $\Delta G^\ddagger = [\lambda (1 + \Delta_r G^0/\lambda)^2]/4$  where  $\Delta_r G^0$  is standard reaction Gibb's energy (obtained from the difference in standard potentials of the redox partners) and  $\lambda$  the reorganization energy, the energy required to move the nuclei associated with the reactant to the position they adopt in the product immediately before the transfer of the electron. This energy depends on the changes in metal-ligand bond lengths (innersphere reorganization energy) and orientation of solvent molecules around the complex (outersphere reorganization energy).

The preexponential factor has two components, the nuclear frequency factor  $\nu_{\text{N}}$ , and the electronic factor,  $k_{\text{e}}$ . The former is the frequency at which the two complexes having already encountered each other in the solution, attain the transition state. The electronic factor gives the probability on a scale from 0 to 1 that an electron will transfer when the transition state is reached; its precise value depends on the extent of overlap of the donor and acceptor orbitals.

A small reorganization energy and a value of  $k_{\text{e}}$  close to 1 corresponds to redox couple capable of fast electron self exchange. The first requirement is achieved if the electron is removed from or added to a nonbonding orbital, as the change in metal-ligand bond length is then least. It is also likely if the metal is shielded from the solvent. Simple metal ions such as aqua species typically have  $\lambda$  well in excess of 1 eV, whereas buried redox centres in enzymes, which are well shielded from the solvent can have values as low as 0.25 eV. A value of  $k_{\text{e}}$  close to 1 is achieved if there is good orbital overlap between the two components of the precursor complex.

For a self exchange reaction,  $\Delta_r G^0 = 0$  and therefore,  $\Delta G^\ddagger = \lambda/4$  and the rate of electron transfer is controlled by reorganization energy. For example in  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+/2+}$  self exchange reaction, an electron is transferred between antibonding  $\sigma^*$  orbitals which result in large innerspherereorganisation energy and hence a slow reaction. With Ru, V, Fe etc aqua complexes,

the electron is transferred between weakly antibonding or nonbonding  $\pi$  orbitals, the innersphere reorganization is less extensive and the reactions are faster.

The bulky hydrophobic ligands like bipyridyl acts as a solvent shield decreasing the outersphere reorganization energy. Bipyridyl and other pi acceptor ligands allow electrons in an orbital with pi symmetry on the metal ion to delocalize on to the ligand which lowers the reorganization energy.

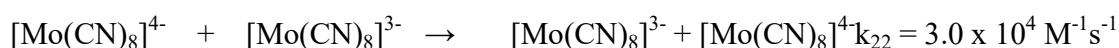
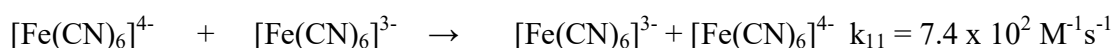
If we suppose that the reorganization energy for a redox reaction is the average for the two self exchange processes, we can write  $\lambda_{12} = (\lambda_{11} + \lambda_{22})/2$ , then Marcus equation breaks down to  $k_{12} = [k_{11}k_{22}K_{12}f_{12}]^{1/2}$  where  $k_{12}$  is the rate constant of overall heteronuclear reaction,  $k_{11}$  and  $k_{22}$  are rate constants for the two self exchange reactions,  $K_{12}$  is equilibrium constant for the overall reaction and  $\log f_{12} = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2)$ . Here  $Z$  is the collision frequency for the hypothetically uncharged reactant ions in solution. The factor  $f_{12}$  is described as a correction for the difference in free energies of the two reactants and is often close to unity. This relation called Marcus cross relation gives a relation for predicting the rate constant for heteronuclear outersphere redox reaction from self exchange rate constants for each partner and overall equilibrium constant.

The Marcus cross relation connects thermodynamics and kinetics as shown by the dependence of  $k_{12}$  on  $K_{12}$ . As  $K_{12}$  increases, the reaction rate increases. i.e.outersphere reactions that are thermodynamically more favourable tend to proceed faster. This relationship however breaks down when  $K_{12}$  becomes large.

For the reaction,



The self exchange reactions are,



$f_{12}$  can be calculated as 0.85 and  $K_{12} = 1.0 \times 10^2$

From Marcus equation,  $k_{12} = 4 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ . The experimental value is very close,  $3 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ .

The confidence in Marcus equation is so high that departures from Marcus equation is taken as a special feature in outer sphere mechanism like the barrier created by change in high spin to low spin or a change in symmetry. Alternatively, departure from Marcus equation indicate that the reaction is innersphere rather than outersphere.

### INNER SPHERE MECHANISM-TAUBE MECHANISM

Inner sphere reactions are more complicated than outer sphere reactions because in addition to electron transfer, bonds are broken and made. In this mechanism, the coordination spheres of

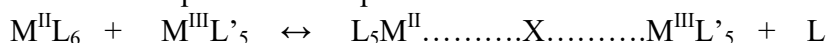
the reactants shares a ligand temporarily or transitorily and forms a bridged intermediate activated complex and the electron is transferred across the bridging group. In order for the electron transfer to occur, the molecular orbital from the reducing agent from which the donated electron originate and the molecular orbital in the oxidizing agent into which the electron is transferred must be of the same type ( $\sigma^*$ ).

The salient features of electron transfer by inner sphere mechanism are,

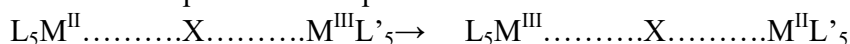
1. Oxidant and reductant attach to one another at some stage of the reaction.
2. At least one ligand should be capable of binding two metals.
3. The attachment between oxidant and reductant occurs through a bridging ligand.
4. The bridging helps in the transfer of electrons from reductant to oxidant.
5. The rate determining step may be the bridge formation or electron transfer process.

The elementary steps in this mechanism can be generalised as,

1. Formation of precursor complex



2. Activation of precursor complex and electron transfer

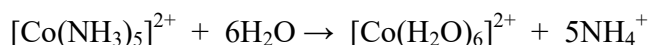


3. Dissociation to separated products



The first step involves substitution by bridging group X into the coordination sphere of the labile reactant (usually reductant) to form the precursor complex. This, then undergoes some kind of reorganisation followed by electron transfer to give the successor complex. In the last step, the successor complex breaks up to give the product.

Example for such a mechanism is the Taube reaction.



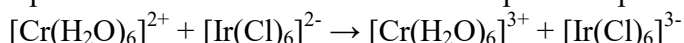
The role of the bridging ligand in an innersphere mechanism is dual. It brings the metal ions together (thermodynamic contribution) and mediates the transfer of electron (kinetic contribution). The thermodynamic contribution arises from factors important to the stability of the intermediate complex and the kinetic contribution arises from factors like oxidant reductant reorganisation and matching of donor and receptor molecular orbital types. The bridging ligands can be organic and inorganic in nature.

Two types of mechanisms have been proposed for the transfer of electron density from the reductant to the oxidant, once the bridged binuclear intermediate has been formed.



1) Chemical radical stepwise mechanism in which an electron is transferred from reductant metal to the bridging ligand reducing it to a radical anion. In a subsequent step, in an electron hopping process, the electron is transferred from reductant metal to the oxidant metal ion. 2) tunnelling resonance or exchange mechanism where the bridge acts simply as a mediator of electron flow. The electron simply passes by quantum mechanical tunnelling through the barrier constituted by the bridging ligand.

Though the bridging ligand is frequently transferred from oxidant to reductant in the course of electron transfer, this is not a requirement. The transfer or nontransfer of the bridging ligand depends on the relative stabilities of the products possible from the intermediate.



**There are two prerequisites for an innersphere mechanism to follow.**

- 1) One reactant (usually the oxidant) should possess at least one ligand capable of bonding simultaneously to two metal ions temporarily. If the bridging ligand contains only one atom (Cl) then both metal ions bond to it. However, if the bridging ligand contains more than one atom (eg. SCN<sup>-</sup>), the two metal atoms may or may not be bound to the same bridging ligand atom. The former is called adjacent attack and the latter, remote attack. Remote attack leads to linkage isomers.
- 2) One ligand of one reactant (usually the reductant) be substantially labile. i.e it must be capable of being replaced by a bridging ligand in a feasible substitution process. Thus the reduction of hexamine Co(III) by hexa aqua Cr(II) occurs slowly by outersphere mechanism. However when one NH<sub>3</sub> ligand is substituted by Cl<sup>-</sup>, the reaction occurs with a substantially greater rate. (Taube reaction)

### **Correlation of rates with structure and electronic configuration**

For an innersphere mechanism, a simple substitution reaction could be the rate determining step. i.e the rate of formation of the bridged species decides the rate of innersphere reaction to a greater extent. Furthermore, the rate of loss of coordinated water would put a limit on the rate of formation of a bridge. The order of reactivity for halides is I<sup>-</sup> > Br<sup>-</sup> > Cl<sup>-</sup> > F<sup>-</sup> for the known examples. The strength of the bridge formed could usually increase in the opposite order with F<sup>-</sup> giving the strongest bridge. i.e the ability to transmit an electron and to undergo homolytic bond breaking could be greater for I<sup>-</sup> and least for F<sup>-</sup>.

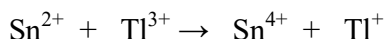
The rates of redox reactions are very sensitive to the presence of other ions in the solution. The mere presence of an anion should enable the cation to approach each other more easily. This will be most effective if the anion is between the two cations in the transition state. Thus the small anions may act as pseudo bridges even for reactions which go by electron transfer. In addition, if the anion complexes with reducing agents first, it will stabilise the oxidised form thus speeding up the rate of oxidation. Conversely, if the oxidising agent is complexed first, this may stabilise it and slow down the rate of reaction. For example, the rate of reaction between [Ru(bipy)<sub>3</sub>]<sup>2+</sup> and Ce<sup>4+</sup> is reduced strongly by SO<sub>4</sub><sup>2-</sup> present in solution by the formation of Ce(SO<sub>4</sub>)<sup>2+</sup>

**Doubly bridged inner sphere transfer**

Only a few examples are known for this type of reactions. Eg: reduction of  $\text{cis}[\text{Co}(\text{en})_2(\text{N}_3)_2]^+$  as its tetrammine analogue by  $\text{Cr}^{2+}$ . Approximately 1.2 to 1.4 azide ligands per Cr(II) are found in the respective products suggesting a doubly bridged intermediate.

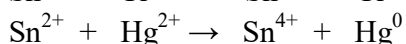
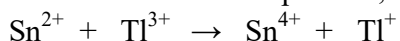
**Two electron transfer reactions**

In this case only one bridging ligand is involved but two electrons are transferred. This type of reactions occurs for elements having stable oxidation states which differ by two electrons without a stable one in between.



The two electron transfer reactions can be further categorised into complimentary and noncomplimentary reactions.

**Complimentary reactions** are those in which reductant loses and oxidant gains two electrons. For eg: in  $\text{Tl}^+ - \text{Tl}^{3+}$  system in aqueous medium containing  $\text{ClO}_4^-$  ions, the two electrons are transferred from  $\text{Tl}^+$  to  $\text{Tl}^{3+}$ . Other examples are,



**Noncomplimentary** reactions are those in which the no: of electrons released by the reductant is not equal to the no: of electrons accepted by the oxidant. They generally proceed through a multistep path.

