Outer sphere and Inner Sphere Electron Transfer

The transfer of electrons between molecular compounds is an extremely important phenomenon. We will discuss here the electron transfer between inorganic complexes.

There are two mechanisms by which inorganic complexes transfer electrons.

1. **Outer sphere mechanism**
When electron transfer occurs between complexes that do not undergo substitution. No new bonds are broken or formed.

2. **Inner sphere mechanism**. Electron transfer occurs between complexes via a bridging ligand. At least one of the complexes needs to be labile to allow the bridge to form. Bonds are broken and formed.

1. Outer sphere mechanism: In this mechanism one reactant is reduced and other is oxidized by involving three steps

Outer sphere electron transfer

$$M^{(a+1)+}L_x + M'^{b+}L_y \rightleftharpoons M^{a+}L_x + M'^{(b+1)+}L_y$$

oxidant (O) is reduced — reductant (R) is oxidised

Mechanism

1. Formation of precursor complex

$$M^{(a+1)+}L_x + M'^{b+}L_y \overset{K_{eq}}{\rightleftharpoons} \{M^{(a+1)+}L_x \cdots M'^{b+}L_y\} \quad \text{Precursor complex}$$

2. Activation/reorganisation of precursor complex. Electron transfer. Relaxation to successor complex

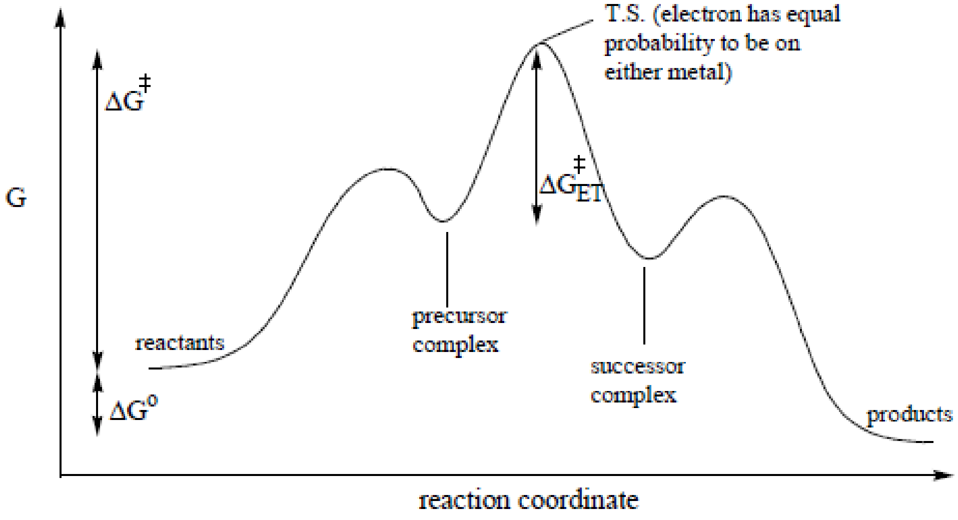
$$\{M^{(a+1)+}L_x \cdots M'^{b+}L_y\} \xrightarrow{k_{ET}} \{M^{a+}L_x \cdots M'^{(b+1)+}L_y\} \quad \text{Successor complex}$$

3. Dissociation of successor complex

$$\{M^{a+}L_x \cdots M'^{(b+1)+}L_y\} \xrightarrow{k_{diss}} M^{a+}L_x + M'^{(b+1)+}L_y$$

Formation of precursor complex and dissociation of successor complex are fast. Electron transfer slow

The energy change can be expressed by the following plot



Some examples of outer sphere mechanism are

remember from thermodynamics, driving force $\Delta G^o = -nF\Delta E^0$

$$[Ru^*(NH_3)_6]^{2+} + [Ru(NH_3)_6]^{3+} \xrightarrow[{[Ru(NH_3)_6]^{3+/2+}\ E^0 = +0.051V}]{k = 6.7 \times 10^3\ M^{-1}s^{-1}} [Ru^*(NH_3)_6]^{3+} + [Ru(NH_3)_6]^{2+}$$

$$[Co^*(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+} \xrightarrow[{[Co(NH_3)_6]^{3+/2+}\ E^0 = +0.058\ V}]{k = 10^{-9}\ M^{-1}s^{-1}} [Co^*(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+}$$

Self exchange reactions (M and M* are isotopes). $\Delta G^o = O$

$$[V(H_2O)_6]^{2+} + [Ru(NH_3)_6]^{3+} \xrightarrow[{[V(H_2O)_6]^{3+/2+}\ E^0 = -0.255\ V}]{k = 1.3 \times 10^3\ M^{-1}s^{-1}} [V(H_2O)_6]^{3+} + [Ru(NH_3)_6]^{2+}$$

Cross reaction

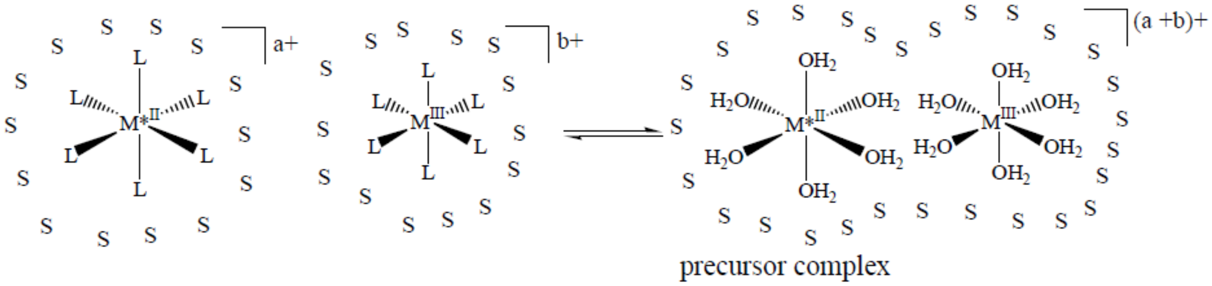
Factors affecting outer sphere mechanism

$$\Delta G^\ddagger = \underbrace{\Delta G_t^\ddagger}_{\text{energy to bring reactants together (including overcoming coulombic repulsion)}} + \underbrace{\Delta G_o^\ddagger}_{\text{energy needed for solvent reorganisation}} + \underbrace{\Delta G_i^\ddagger}_{\text{energy required for reorganisation of bond lengthening/compression to make interacting orbitals the same energy}}$$

The effect of solvent ($\triangle G_0^\ddagger$)

More is the interaction with solvent, difficult is the electron transfer and therefore the rate of reaction would be slow.

Solvent those interact strongly with complexes (such as by Hydrogen bonding) will reduce the rate of electron transfer



Energy required for reorganization of bonds $\triangle G_i^{\ddagger}$:

Metal-ligand bond lengths will change when the oxidation state of the metal changes. The Frank-Condon principle states that because nuclei are much more massive than electrons, an electronic transition occurs much faster than the nuclei can respond. Complexes must adjust their M-L bond lengths before electron transfer.

Example: Here Fe(III)-O and Fe(II)-O bond length are different in the reactant, but in the transition state identical bond length make the electron transfer possible

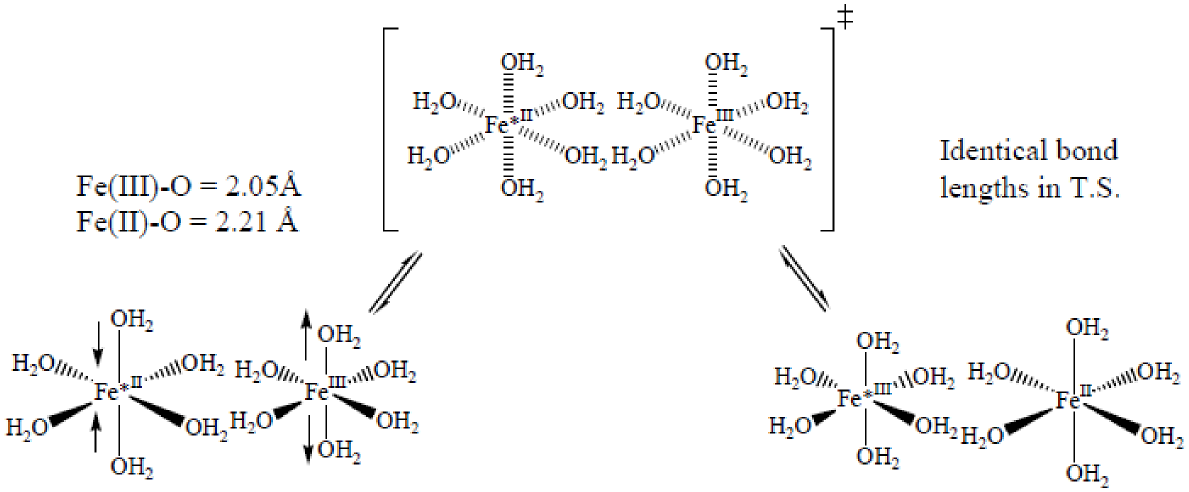


Fig. Transition state for outer sphere electron transfer

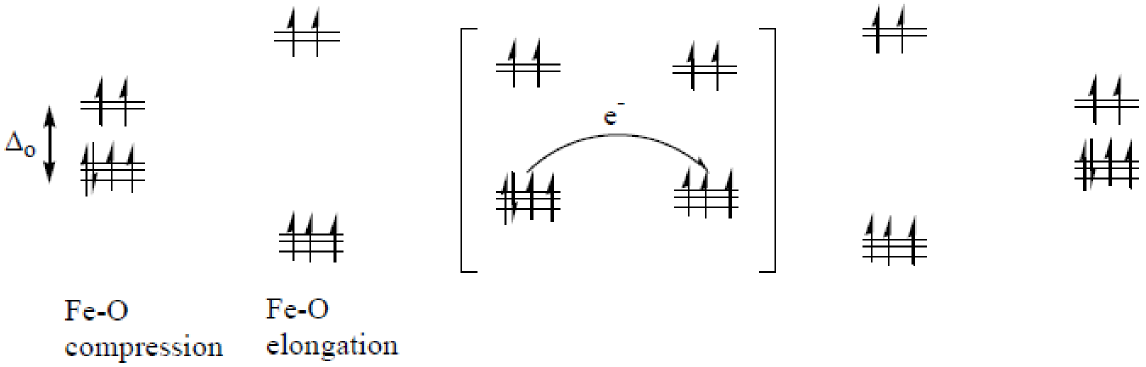
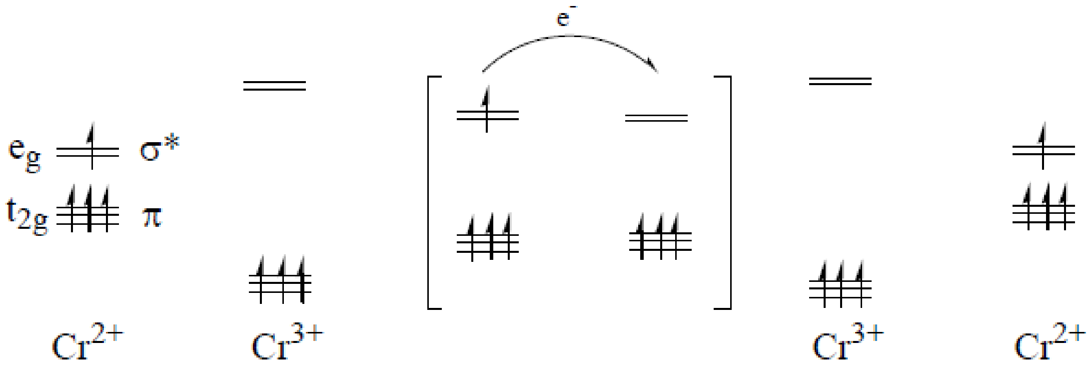


Fig. Outer sphere electron transfer

Electron transfer requires orbital overlap and occurs between orbitals of the same symmetry

Self Exchange Reaction	Configuration	k (M^{-1} s^{-1})	Δr Å
$[Cr(H_2O)_6]^{2+}$ / $[Cr(H_2O)_6]^{3+}$	$t_{2g}^3e_g^1$ / $t_{2g}^3e_g^0$	10^{-5}	0.3
$[V(H_2O)_6]^{2+}$ / $[V(H_2O)_6]^{3+}$	$t_{2g}^3e_g^0$ / $t_{2g}^2e_g^0$	10^{-2}	0.2
$[Fe(H_2O)_6]^{2+}$ / $[Fe(H_2O)_6]^{3+}$	$t_{2g}^4e_g^2$ / $t_{2g}^3e_g^2$	4	0.15
$[Ru(H_2O)_6]^{2+}$ / $[Ru(H_2O)_6]^{3+}$	$t_{2g}^6e_g^0$ / $t_{2g}^5e_g^0$	4×10^3	0.05
$[Fe(phen)_3]^{2+}$ / $[Fe(phen)_3]^{3+}$	$t_{2g}^6e_g^0$ / $t_{2g}^5e_g^0$	10^3	0.01



If the electron transition is occurring from e_g to e_g in Oh field

large change in bond length (M-L) has to occur in sigma type of orbital, therefore the electron transfer would be **Slow.** Also the steric hindrance due to ligand is there.

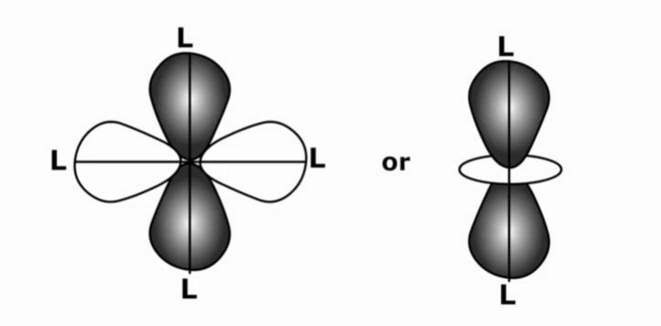
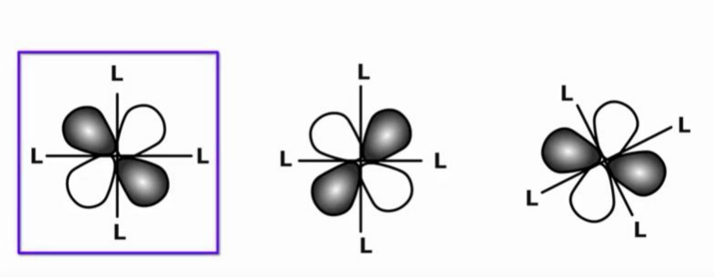


Fig. sigma type symmetry orbital $d_{x^2-y^2}$ and d_z2

If the electron transition is occurring from t_{2g} to t_{2g} in Oh field

In O_h field t_{2g} is $\pi-\pi^*$: t_{2g} t_{2g} transition = small change in bond length. 'Fast' electron transfer



Overlap

2nd and 3rd row metals generally undergo fast electron transfer than 1st row due to better overlap of 4d and 5d orbitals.

Ligands that have extended π-systems e.g. Phen, bipy etc can assist electron transfer.

2. Inner sphere electron transfer: It is mediated by a bridging ligand

i) Reductant and oxidant share a ligand in the precursor and successor complex.
ii) On activation the electron is transferred between the metals.
iii) The ligand **may** transfer between complexes.

$$\underset{O}{M^{III}L_5X} + \underset{R}{M^{II}Y6} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \{L_5M^{III}-X-M'^{II}Y_5\} + Y$$

$$\{L_5M^{III}-X-M'^{II}Y_5\} \xrightarrow{k_{ET}} \{L_5M^{II}-X-M'^{III}Y_5\}$$

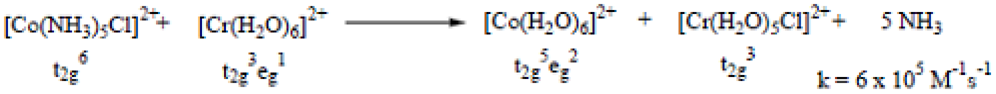
$$Y + \{L_5M^{II}-X-M'^{III}Y_5\} \xrightarrow{k_d} L_5M^{II}Y + XM'^{III}Y_5$$

$$\text{or} \quad Y + \{L_5M^{II}-X-M'^{III}Y_5\} \longrightarrow L_5M^{II}X + M'^{III}Y_6$$

Change of Inner sphere mechanism to outer sphere mechanism

Example of Inner sphere mechanism:

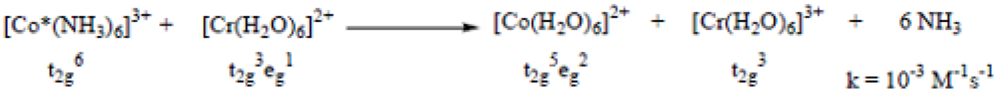
The labile group is needed always in this type of reaction. Here Cl is the labile group



$$\underset{t_{2g}^{6}}{[Co(NH_3)_5Cl]^{2+}} + \underset{t_{2g}^{3}e_g^{1}}{[Cr(H_2O)_6]^{2+}} \longrightarrow \underset{t_{2g}^{5}e_g^{2}}{[Co(H_2O)_6]^{2+}} + \underset{t_{2g}^{3}}{[Cr(H_2O)_5Cl]^{2+}} + 5\,NH_3 \qquad k = 6 \times 10^{5}\ M^{-1}s^{-1}$$

Example of Outer sphere mechanism:

If we replace the Cl by NH_3 in the reaction then outer sphere mechanism is followed

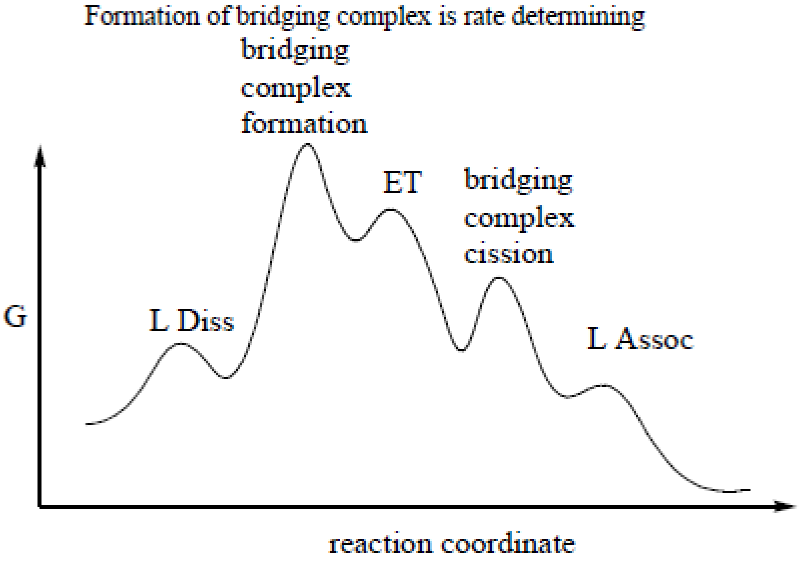


$$\underset{t_{2g}^{6}}{[Co^{*}(NH_3)_6]^{3+}} + \underset{t_{2g}^{3}e_g^{1}}{[Cr(H_2O)_6]^{2+}} \longrightarrow \underset{t_{2g}^{5}e_g^{2}}{[Co(H_2O)_6]^{2+}} + \underset{t_{2g}^{3}}{[Cr(H_2O)_6]^{3+}} + 6\,NH_3 \qquad k = 10^{-3}\ M^{-1}s^{-1}$$

outer sphere mechanism

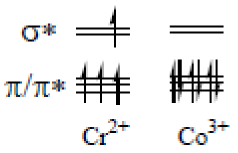
Factors that affect the rate of inner sphere electron transfer reactions

i) Formation of the bridging complex can be the rate limiting step (k_a). This will be dependent on how inert or labile the complexes are. (k_{ET} vs k_a). It is also possible that dissociation (k_d) is the rate limiting step.

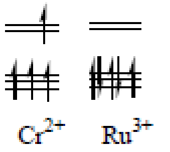


(ii) Electronic configurations. σ* (‘e_g’) orbitals interact strongly with bridging ligand. Orbital symmetries of metal σ* and bridging ligands facilitate electron transfer. Massive acceleration in rates from outer to inner sphere can be achieved.

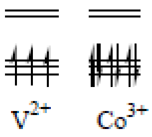
Reaction	HOMO	LUMO	Acceleration IS/OS
$Cr^{2+} + Co^{3+}$	$\sigma*$	$\sigma*$	~ 10^{10}
$Cr^{2+} + Ru^{3+}$	$\sigma*$	$\pi*$ (π)	~ 10^{2}
$V^{2+} + Co^{3+}$	$\pi*$	$\sigma*$	~ 10^{4}
$V^{2+} + Ru^{3+}$	π	π	All OS



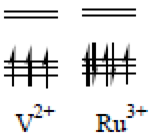
Large reorganisation for Co^{3+} OS. IS much faster



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

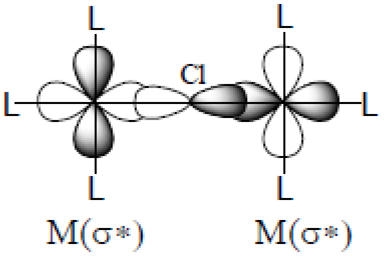


Co^{3+} Reorganisation IS faster



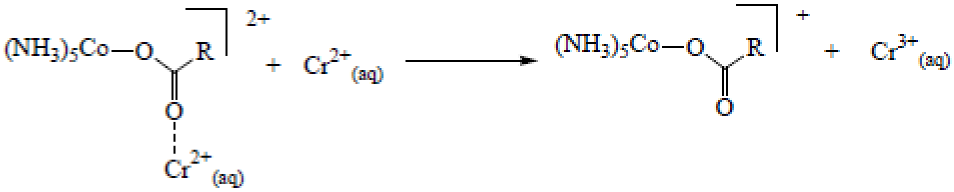
Easily go OS.
No reorganisation

e.g.



iii) Bridging ligand. Inner sphere electron transfer is very sensitive to bridging ligand.

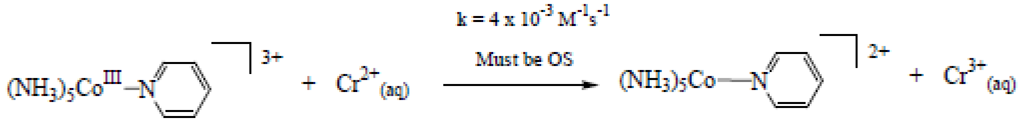
1) The bridge connects the two metals.

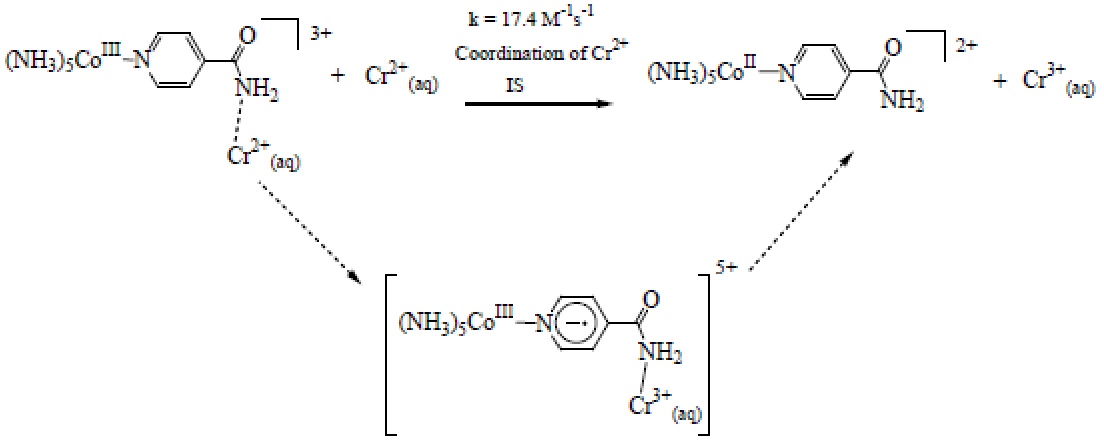


	R= H	Me	Ph	^{t}Bu
k $M^{-1}s^{-1}$	7.2	0.35	0.15	9.6×10^{-3}

Increasing bulk of R slows binding of Cr^{2+} to bridge

2) Transfer can be a two step process from metal to ligand then ligand to metal. This circumvents the simultaneous reorganisation energy of both complexes that is required for outer sphere.





ligand mediates electron transfer