Department of Chemistry
Institute of Science
Banaras Hindu University, Varanasi - 221 005
M.Sc. Sem.-II (CHM-202); Inorganic Chemistry

Reading Material on Electron Transfer Reactions

Introduction:

If we have a look on some of the introductory inorganic chemistry books available in our library, we can see that in general, these include a chapter on redox reactions, the reactions leading to formal change in the oxidation state of the involved substances.

An examination of the redox reactions reveal that they fall in two broad categories: (i) reactions involving simple electron transfer, and (ii) atom transfer reactions with and without electron transfer.

An example of reaction that truly occurs by electron transfer between two different oxidation states of the osmium complex is shown below.

$$\underset{\Lambda}{[Os(N\text{–}N)_3]^{3+}} + \underset{\Delta}{[Os(N\text{–}N)_3]^{2+}} \rightarrow \underset{\Delta}{[Os(N\text{–}N)_3]^{2+}} + \underset{\Lambda}{[Os(N\text{–}N)_3]^{3+}} \quad (k \geq 5\text{x}10^4\ M^{-1}\ sec^{-1})$$

(N–N =2,2’–bipy)

The complexes $[Os(N\text{–}N)_3]^{2+/3+}$ exist in isomeric Δ and Λ forms and are optically active. If far apart, these do not racemize. However, upon mixing racemization occurs with rapid loss of optical activity. This loss in optical activity is due to electron transfer from one form to other. Soon you will see that many reactions occur by direct electron transfer.

On the other hand, if we examine the reactions shown below:

$$NO_2^- + OC1^- \rightarrow NO_3^- + C1^-$$

$$3SO_3^{2-} + ClO_3^- \rightarrow 3SO_4^{2-} + C1^-$$

In nitrite to nitrate conversion, oxygen atom is transferred from $OC1^-$ to NO_2^- so that it becomes NO_3^-. In the mean-time nitrogen oxidises to (+V) from (+III) while Cl gets reduced to -1 oxidation state. In sulphite to sulphate conversion too, oxygen is transferred from $C1O_3^-$ and the reaction is followed by oxidation of sulphur to (+VI) from (+IV) and Cl gets reduced to -1.

These reactions involve atom as well as electron transfer. The change in formal oxidation states takes place because electrons that were formally non–bonding (N or S lone pair) now become bonding (N–O or S–O a bond pair) while those previously bonding (O–Cl bond pair) now turn to non–bonding (the Cl– lone pair).

In transition metal chemistry too, redox reactions can occur by atom transfer. For example reduction of $[Co^{III}(NH_5)_3Cl]^{2+}$ with $[Cr^{II}(H_2O)_6]^{2+}$ under **acidic conditions** occurs in the following manner:

$$[Co^{III}(NH_3)_5Cl]^{2+} + [Cr^{II}(H_2O)_6]^{2+} \rightarrow [(NH_3)_5Co^{III}\text{–}Cl\text{:} \rightarrow Cr^{II}(H_2O)_5]^{5+} + H_2O$$

$$\downarrow$$

$$[Co^{II}(H_2O)_6]^{2+} + [Cr^{III}(H_2O)_5Cl]^{2+} + 5NH_4^+ \leftarrow [(NH_3)_5Co^{III} \leftarrow \text{:}Cl\text{–}Cr^{II}(H_2O)_5]^{5+}$$

In this reaction too, Cl is transferred from Co(III) to Cr(II) and electron from Cr(II) to Co(II). <u>These represent atom transfer with electron transfer reactions.</u>

If we analyse the following reaction:

$$[Ir^{IV}Cl_6]^{2-} + [Cr^{II}(H_2O)_6]^{2+} \rightarrow [Ir^{III}Cl_6]^{3-} + [Cr^{II}(H_2O)_6]^{3+}$$

in this reaction electron is being transferred from Cr(II) to Ir(IV), but atom is not being transferred. This represents electron transfer without atom transfer.

We have already discussed about "Oxidative Addition" and "Reductive Elimination Reactions" while introducing the subject matter in the first unit dealing with reactions undergone by octahedral complex.

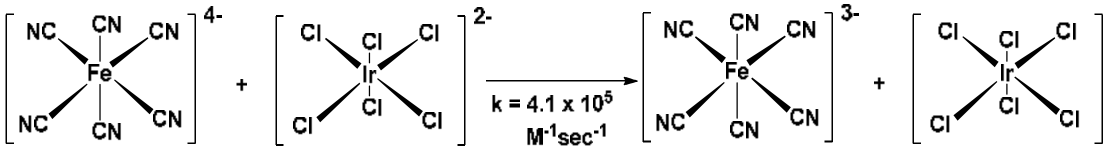
Types of Electron Transfer Reactions

After having general discussion on the electron transfer reactions we should have an idea about types of these reactions. The electron transfer reactions can be classified as:

(i) outer sphere, and (ii) inner sphere electron transfer reactions

i. Outer Sphere Electron Transfer Reactions

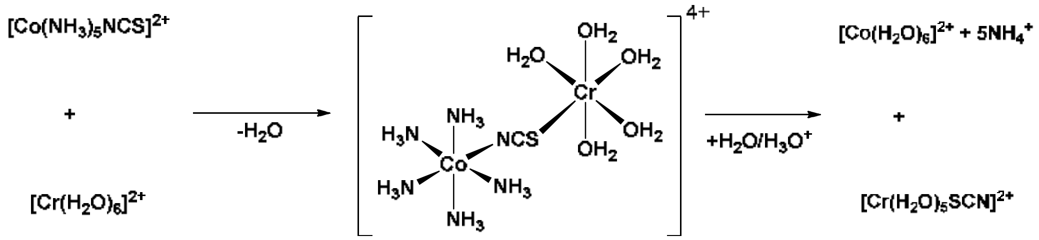
When the electron transfer takes place in such a way that inner coordination shells or spheres of the involved complexes remains intact i.e. there is no change in the inner sphere of the reductant and oxidant, we call it an ***Outer Sphere*** electron transfer reaction. Such a reaction usually occurs when rapid electron transfer takes place between two substitutionally inert complexes. For example, in the reaction between $[Fe(CN)_6]^{4-}$and $[IrCl_6]^{2-}$:



electron is transferred from Fe(II) to Ir(IV), but inner spheres for both the complexes are unchanged.

i) Inner Sphere Electron Transfer

In this type of reaction there is a change in inner spheres of both the oxidant and reductant. If we examine the reaction between $[Co^{III}(NH_3)_5NCS]^{2+}$ with $[Cr^{II}(H_2O)_6]^{2+}$ under acidic conditions:



we can see that inner sphere about both the Co and Cr gets altered. Interestingly, reaction passes through an intermediate bridged complex. The ligand NCS^- while linked to oxidant (Co^{III}), concurrently establishes a bond with the reductant (Cr^{II}) metal centre and bridges the two metal ions.

There two pre–requirements for an inner sphere mechanism to be operative:

1) First requirement is that one reactant (usually, oxidant) must have one ligand capable of linking the two metal ions simultaneously. Such a ligand is called a bridging ligand (**BL**).

2) The second requirement is that a ligand on one of the reactants (most often reductant) must be labile; i.e. it should be easily replaced by the bridging ligand.

In the inner sphere electron transfer reactions, usually bridging ligand is transferred from oxidant to reductant.

However, transfer of the **B**L is not a must in such reactions. For example, in the reaction:

$$[Ir^{IV}Cl_6]^{2-} + [Cr^{II}(H_2O)_6]^{2+} \rightarrow [Ir^{III}Cl_6]^{3-} + [Cr^{II}(H_2O)_6]^{3+}$$

electron transfer occurs *via* inner sphere mechanism, but ligand transfer is not taking place.

General Considerations for Electron Transfer Reactions

Before we begin with detailed discussion of the electron transfer mechanisms, let us have some general idea about the electron transfer reactions. There are several notions which apply to both outer and inner sphere electron transfer reactions.

1. The electron is transferred from highest occupied molecular orbital (HOMO) of the Reductant to lowest unoccupied molecular orbital (LUMO) of theOxidant.

2. Usually before chemical reaction the reactants (reductant and oxidant) are brought into proper orientation for reaction by chemical activation process. In electron transfer reactions the electron is transferred from HOMO of the reductant to LUMO of the oxidant. Thus, for effective electron transfer these orbitals must be of the same type.

Soon you will realize that efficient outer sphere electron transfer occurs when both donor and receptor MO's are π * orbitals, while inner sphere reactions requires donor and receptor MO's to both be π^* or σ^*.

In case of symmetry mismatch, for effective electron transfer greater chemical activations involving both structural deformation and electron configuration changes are required.

3. Regarding chemical activation, one may think that electron transfer reactions involve an intermediate. It is not at all clear whether the activation occurs as a discrete step prior to electron transfer or the activation takes place as a blurred part of the overall electron transfer process.

4. There is a thermodynamic influence on the activation energy barrier. You will see that reactions which may require a HOMO and/ or LUMO change can have lower barriers than predicted, because the reaction has a negative free energy change.

Mechanism of Outer Sphere Electron Transfer Reactions

The outer sphere mechanism involves three elementary steps:

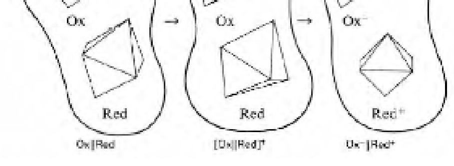
First step is **formation of a precursor** (cage) complex. In this step the reactant metal centres are brought at such a distance that electron transfer can take place, but at this stage their relative orientations and internal structures do not permit electron transfer. This step can be shown as:

$$\text{Ox} + \text{Red} \leftrightarrow \text{Ox II Red}$$

Second step involves **chemical activation of the precursor complex, transfer of electron and relaxation to the successor complex**. This step involves changes in the solvent cage and structural changes in the precursor. Oxidant and reductant are brought in proper orientation and structural changes defining chemical activation for electron transferoccurs in this step.

$$\text{Ox II Red} \leftrightarrow {}^{-}\text{Ox II Red}^{+}$$

Fig. 1



Here you can see that **oxidant enlarges in size** as it accepts an electron and while **reductant contracts** as it loses the electron. Summarily, **partial bond-breaking occurs in the oxidant, while partial bond-making follows in the reductant.**

The third and last step of the outer sphere process is **cleavage of the successor complex** to the final products. It can be shown as follows:

$${}^{-}\mathrm{Ox}\ \mathrm{II}\ \mathrm{Red}^{+} \leftrightarrow \mathrm{Ox}^{-} + \mathrm{Red}^{+}$$

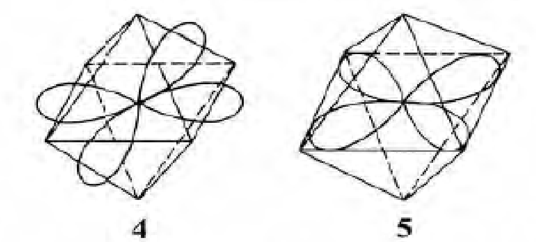
One should be very clear that measurement of a rate constant for an outer sphere electron transfer reaction usually gives an idea about overall rate of the reaction. It is not possible to measure rate constant for any elementary steps because the first and the last steps are assumed to be rapid equilibria relative to the second step. It can be concluded from the following reaction.

Factors influencing the outer sphere electron transfer reactions

(a). Chemical Activation and Electron Transfer

Rate of the electron transfer reactions are usually determined by π^* or σ^* nature of the electron donor MO (HOMO) of the reductant and receptor MO (LUMO) of the oxidant. One can expect more facile electron transfer when both donor and receptor mo are of π^* type due to small reductant/ oxidant activation (change in M–L bond distance) in $d\pi^*$ than for a change in $d\sigma^*$ electron density.

Further, **ease of electron transfer depends on overlap and mixing of the donor and receptor MO's**. Electron transfer is easier if overlap and mixingof donor and receptor mo is large. Considering orientation of $d\pi^*$(**4**)/ $d\sigma^*$(**5**) electrons in octahedral complexes, it may be concluded that $\pi^* \rightarrow \pi^*$ electron transfer should be faster than $\sigma^* \rightarrow \sigma^*$ transfer.



4 **5**

Fig. 2 Showing disposition of $d\pi^*$(**4**)/ $d\sigma^*$(**5**) orbitals in octahedral complexes

Thus we can simply say that ***if orbital overlap and mixing is appreciable and electron is being transferred from $\pi^* \rightarrow \pi^*$, small activations are required and the reactions are relatively fast on the other hand, if changes are required greater activations are involved and reactions are rather slow.***

An examination of the Table 1 dealing with rates of outer sphere electron transfer reactions show that first four examples require little chemical activation for a M(ll) → M(III) electron exchange because these do not pass through a change in σ^* orbital configuration in either complex.

Reaction			Rate Constant k ($M^{-1}sec^{-1}$)
		NET $\pi^* \rightarrow \pi^*$	
$Fe(H_2O)_6^{2+}$ $(\pi^*)^4(\sigma^*)^2$	+	$Fe(H_2O)_6^{3+}$ $(\pi^*)^3(\sigma^*)^2$	4.0
$Fe(phen)_3^{2+}$ $(\pi^*)^6$	+	$Fe(phen)_3^{3+}$ $(\pi^*)^5$	$\geq 3 \times 10^7$
$Ru(NH_3)_6^{2+}$ $(\pi^*)^6$	+	$Ru(ND_3)_6^{3+}$ $(\pi^*)^5$	8.2×10^2
$Ru(phen)_3^{2+}$ $(\pi^*)^6$	+	$Ru(phen)_3^{3+}$ $(\pi^*)^5$	$\geq 10^7$
		NET $\sigma^* \rightarrow \sigma^*$	
$Co(H_2O)_6^{2+}$ $(\pi^*)^5(\sigma^*)^2$	+	$Co(H_2O)_6^{3+}$ $(\pi^*)^6$	~5
$Co(NH_3)_6^{2+}$ $(\pi^*)^5(\sigma^*)^2$	+	$Co(NH_3)_6^{3+}$ $(\pi^*)^6$	$\leq 10^{-9}$
$Co(en)_3^{2+}$ $(\pi^*)^5(\sigma^*)^2$	+	$Co(en)_3^{3+}$ $(\pi^*)^6$	1.4×10^{-4}
$Co(phen)_3^{2+}$ $(\pi^*)^5(\sigma^*)^2$	+	$Co(phen)_3^{3+}$ $(\pi^*)^6$	1.1

Table 1. Second order rate constant for some outer sphere electron transfer reactions

For example, if we see the reaction involving Ru(III)/Ru(II) systems, change in M–L bond distances is very small (0.04 Å) due to $\pi^* \rightarrow \pi^*$ exchange, therefore small activations are required and reactions are fast. It **do not involve any σ* changes** (Fig. 3).

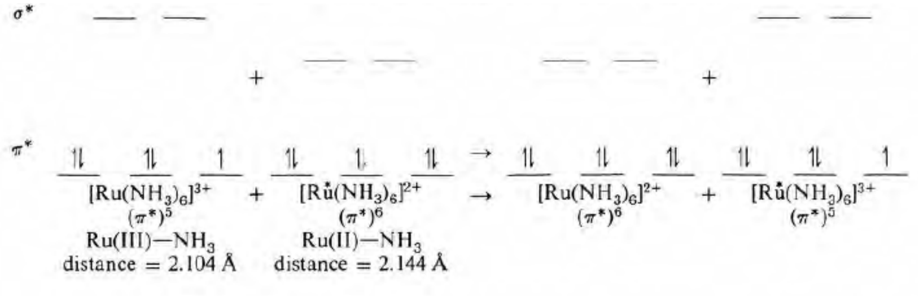


Fig. 3

On the other hand, Co(III)/Co(II) exchanges are rather slow relative to Fe(II)/ Fe(III) and Ru(II)/ Ru(III) systems. The slow rate is related to changes in high-spin/ low-spin conditions for the reductant and oxidant (Fig. 4).

Further. change in Co–NH_3 distance is 0.178 A, which is almost four times relative to analogous Ru(II)/Ru(lll) exchange indicating greater activations.

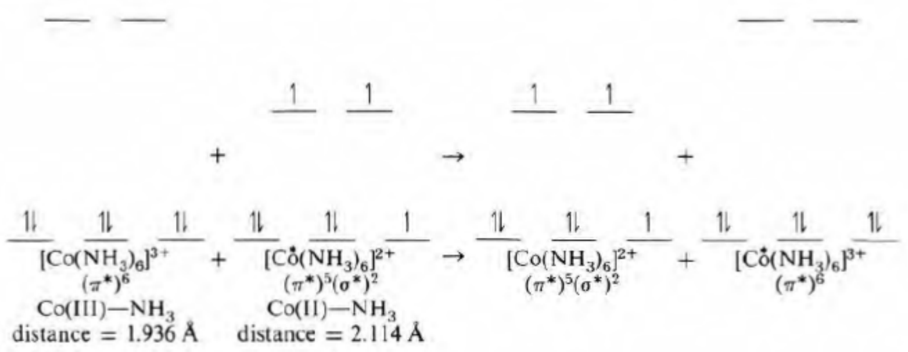
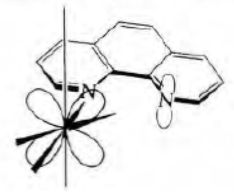


Fig. 4

Another important observation that can be made from Table–1 is related to rate enhancement in presence of a ligand like o–phenanthroline (Fig. 5). Being a *π*– acceptor ligand it may lead to delocalization of the complex *π** mo's onto its skeleton causing greater donor-receptor mixing without severe inter-complex orientation requirements. The overlap of oxidant/ reductant *π** MO's to greater extent leads to higher electron transfer rate.



o–phenanthroline

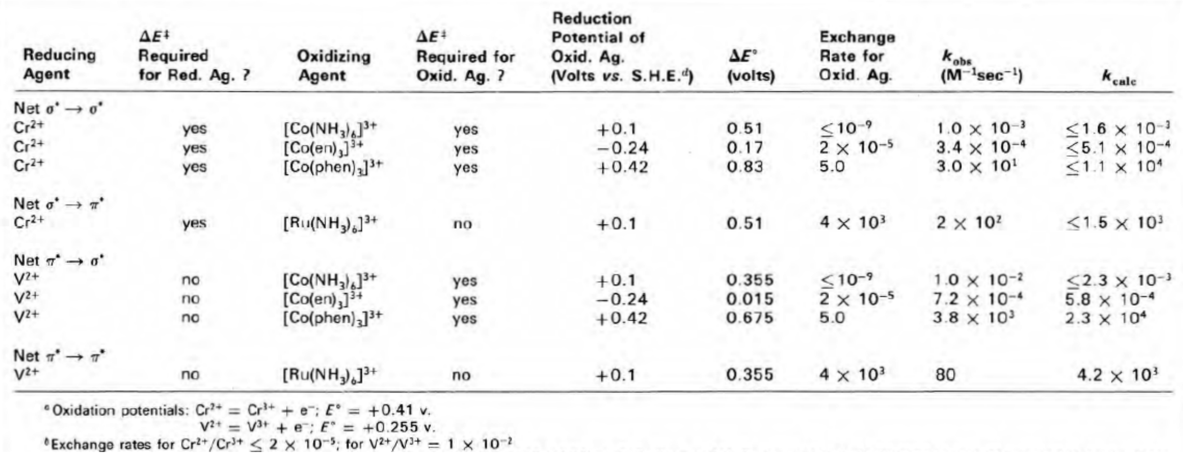
Fig. 5 Showing delocalization of metal *dπ** onto ligand orbitals

Cross Reactions

So far, we have discussed self–exchange reactions wherein **ions of the same metal in two different oxidation states are involved in the exchange process**. The reactions wherein **two different metal ions are involved in the exchange process are called "Cross Reactions"** The obvious question arises in what way the rates cross reactions are different from self–exchange reactions.

Also, we know that to achieve maximum rate in a exchange reaction one should have systems that affect π* → π* electron transitions.

Table 2. Kinetic parameters for some outer sphere reactions



Reducing Agent	$\Delta E^{\ddagger}$ Required for Red. Ag. ?	Oxidizing Agent	$\Delta E^{\ddagger}$ Required for Oxid. Ag. ?	Reduction Potential of Oxid. Ag. (Volts *vs.* S.H.E.[d])	ΔE° (volts)	Exchange Rate for Oxid. Ag.	k_{obs} ($M^{-1}sec^{-1}$)	k_{calc}
Net $\sigma^* \rightarrow \sigma^*$								
Cr^{2+}	yes	$[Co(NH_3)_6]^{3+}$	yes	+0.1	0.51	$\leq 10^{-9}$	1.0×10^{-3}	$\leq 1.6 \times 10^{-3}$
Cr^{2+}	yes	$[Co(en)_3]^{3+}$	yes	−0.24	0.17	2×10^{-5}	3.4×10^{-4}	$\leq 5.1 \times 10^{-4}$
Cr^{2+}	yes	$[Co(phen)_3]^{3+}$	yes	+0.42	0.83	5.0	3.0×10^{1}	$\leq 1.1 \times 10^{4}$
Net $\sigma^* \rightarrow \pi^*$								
Cr^{2+}	yes	$[Ru(NH_3)_6]^{3+}$	no	+0.1	0.51	4×10^{3}	2×10^{2}	$\leq 1.5 \times 10^{3}$
Net $\pi^* \rightarrow \sigma^*$								
V^{2+}	no	$[Co(NH_3)_6]^{3+}$	yes	+0.1	0.355	$\leq 10^{-9}$	1.0×10^{-2}	$\leq 2.3 \times 10^{-3}$
V^{2+}	no	$[Co(en)_3]^{3+}$	yes	−0.24	0.015	2×10^{-5}	7.2×10^{-4}	5.8×10^{-4}
V^{2+}	no	$[Co(phen)_3]^{3+}$	yes	+0.42	0.675	5.0	3.8×10^{3}	2.3×10^{4}
Net $\pi^* \rightarrow \pi^*$								
V^{2+}	no	$[Ru(NH_3)_6]^{3+}$	no	+0.1	0.355	4×10^{3}	80	4.2×10^{3}

[a] Oxidation potentials: $Cr^{2+} = Cr^{3+} + e^-$; $E^{\circ} = +0.41$ v.
$V^{2+} = V^{3+} + e^-$; $E^{\circ} = +0.255$ v.

[b] Exchange rates for $Cr^{2+}/Cr^{3+} \leq 2 \times 10^{-5}$; for $V^{2+}/V^{3+} = 1 \times 10^{-2}$

It has been observed that cross reactions are rapid despite an otherwise large chemical activation because large $\Delta E^{\#}$ is neutralized by an attendant free energy change. From Table–2 which deals with standard electrochemical cell potentials, one can see that there is a rough correlation between the rate of reaction and free energy change $\Delta G^{\circ} = - nFE^{\circ}$.

General Features of Cross Reactions

For self–exchange reactions $\Delta G^{\circ} = 0$ (i.e. reactants and products lie at the same level).

For cross reactions $\Delta G^{\circ} < 0$ (reactants lie at high energy than the products), and all other things being equal there is a distortion in energy profile diagram so as to lower $\Delta E^{\#}$.

In the simplest possible terms, thermodynamic spontaneity supports electron transfer earlier in the chemical activation process (less oxidant /reductant structure deformation) (Fig. 6).

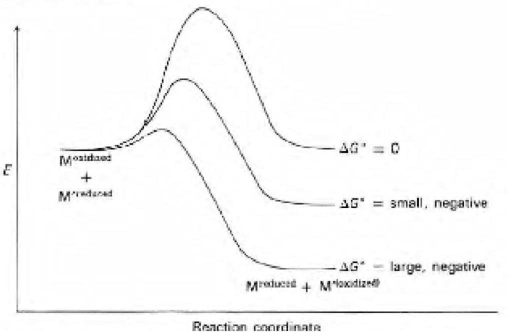


Fig. 6 Activation energy profile for an electron transfer reaction in which the free energies of the products may be less than those of the reactants.

Table 2 dealing with outer sphere reductions of $[Ru(NH_3)_6]^{3+}$ and $[Co(NH_3)_6]^{3+}$ by Cr(II) and V(ll) gives some insight into the thermodynamics of the activation process.

The Cr(II) outer sphere reductions should require greater ΔE^* relative to V(ll) because high spin ion $[Cr(H_20)_6]^{2+}$ with a $(\pi^*)^3(\sigma^*)^1$ configuration requires activation toward low spin $(\pi^*)^4$ configuration.

On the other hand, little activation should be required for $[V(H_20)_6]^{2+}$ $[(\pi^*)^3]$, as there is no change in σ^* occupation on electron transfer. This expectation is realized in Cr(II)/ Cr(III) exchange ($k < 10^{-5}$ s^{-1}) compared with V(II)/ V(III) exchange ($k \sim 10^{-2}$ s^{-1}), and is generally seen in outer sphere Cr(1l) and V(1l) cross reactions even though ΔGo for Cr(II) reductions is more negative than for V(II).

The rate constants for cross reactions are given by Marcus Hush equation:

$$k_{12} = (k_{11}.k_{22}.K_{12}f)^{1/2}$$

where k_{12} is the rate constant for cross reaction, k_{11} and k_{22} represent the rates for self-exchange reactions and K_{12} is for equilibrium constant for cross reaction. Parameter f is usually close to 1 and given by the equation:

$$\log f = (\log K_{12})^2 / 4 \log (k_{11}.k_{22}/z^2)$$

where z is a measure of collision frequency of two uncharged particles in solution and is taken as 10^{11} m^{-1}.

If we consider the following cross reaction, equilibrium constant K_{12} is given by:

$$[Fe(CN)_6]^{4-} + [Mo(CN)_8]^{3-} \rightarrow [Fe(CN)_6]^{3-} + [Mo(CN)_8]^{4-};\ K_{12} = 1 \times 10^2$$

The rate of self-exchange k_{11} for the reaction involving Fe(II)/Fe(III) is given by:

$$[Fe(CN)_6]^{4-} + [Fe^*(CN)6_8]^{3-} \rightarrow [Fe(CN)_6]^{3-} + [Fe(CN)6_8]^{4-};\ k_{11} = 7.4 \times 10^2 M^{-1}s^{-1}$$

Similarly, the rate of self-exchange for reaction involving Mo(V)/Mo(IV) k_{22} can be given by

$$[Mo(CN)_8]^{4-} + [Mo^*(CN)_8]^{3-} \rightarrow [Mo(CN)_6]^{3-} + [Mo^*(CN)_8]^{4-};\ k_{22} = 3 \times 10^4\ M^{-1}s^{-1}$$

Here, you can see that k_{12} shows dependence on K_{12}, As K_{12} increases, the reaction rate also increases and thus, we can conclude that *Markus* ***equation connects thermodynamics and kinetics.*** Thus, outer sphere reactions which are thermodynamically more favourable tend to proceed faster than those which are less favourable.

The simplified Marcus equation presented here, breaks down when K_{12} becomes large. The complete theory reveals that rate increases rapidly with increasing spontaneity, achieves maximum when the change in free energy is equal to the sum of reorganisation energies, and then decreases as the driving force increases further.

Inner Sphere Electron Transfer Reaction

It is well known that reduction of $[Co^{III}(NH_3)_6]^{3+}$ with $[Cr^{II}(H_2O)_6]^{2+}$ under **acidic conditions** takes place very slowly ($k = 10^{-3}\ M^{-1}s^{-1}$) by an outer sphere mechanism:

$$[Co^{III}(NH_3)_6]^{3+} + [Cr^{II}(H_2O)_6]^{2+} \rightarrow [Co^{II}(H_2O)_6]^{2+} + [Cr^{III}(H_2O)_6]^{3+} + 5NH_4^+$$

However, if an ammine ligand in cobalt complex $[Co^{III}(NH_3)_6]^{3+}$ is replaced by Cl^-, rate appreciably enhances to ($k = 6 \times 10^5\ M^{-1}s^{-1}$), One can say with certainty that the reaction is now following different mechanism:

$$[Co^{III}(NH_3)_5Cl]^{2+} + [Cr^{II}(H_2O)_6]^{2+} \rightarrow [Co^{II}(H_2O)_6]^{2+} + [Cr^{III}(H_2O)_5Cl]^{2+} + 5NH_4^+$$

H. Taube who was conferred on Nobel prize for his work on electron transfer reactions clearly showed that an inner sphere mechanism is operative in the reduction of $[Co(NH_3)_5Cl]^{2+}$with $[Cr^{II}(H_2O)_6]^{2+}$; Herein, the Cl^- ligand, while still attached to Co(III), replaces an H_20 at Cr(ll) to give an intermediate shown below and electron transfer follows

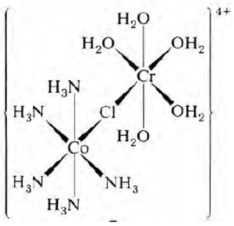


Fig. 7

It can be understood in the following manner:

The reductant $[Cr^{II}(H_20)_6]^{2+}$ and reduced oxidant $[Co^{II}(H_20)_6]^{2+}$ are substitutionally labile while the chloro-complexes $[Co^{III}(NH_3)_5Cl]^{2+}$ and $[Cr^{III}(H_20)_5Cl]^{2+}$ are inert. Thus, the only possibility by which chloride could be transferred from Co(III) to Cr(ll) is through some complex resulting by attack of $CoC1^{2+}$ on Cr^{2+}. With the help of tracer studies i.e. by external addition of radio–chloride Taube showed that an inner sphere mechanism can be clearly assigned when both the oxidant and the oxidized reductant are substitution inert and ligand transfer from oxidant to reductant is accompanied by electron transfer.

In such reactions electron transfer is followed by ligand transfer in the opposite direction

$$Co^{III}\text{-}Cl{:} + Cr^{II} \rightarrow [Co^{III}\text{-}Cl{:} \rightarrow Cr^{II}] \rightarrow Co^{II} + {:}\,Cl\text{-}Cr^{III}$$

It is very clear that for an inner sphere electron transfer process to follow the reductant must be substitutionally labile and the oxidant must have a bridging ligand which can establish linkage between the two metal ions simultaneously. The ligand transfer may or may not take place in such a reaction. For example, reduction of Ir(IV) by Cr(ll) involves electron transfer, but bridging ligand is not transferred from the oxidant to reductant.

$$[IrC1_6]^{2-} + [Cr(H_20)_6]^{2+} \rightarrow [IrC1_6]^{3-} + [Cr(H_20)_6]^{3+}$$

The reaction passes through formation of a bridge between the two reactant metal ions, the bond between lr(III)-Cl] is stronger relative to [Cr(III)-Cl], therefore Cr-Cl bond is broken and reaction proceeds without transfer of the bridging ligand.

Mechanism of the Inner Sphere Electron Transfer Reaction.

The elementary steps involved in an inner sphere mechanism can be represented by:

First step is the **formation of precursor complex**, in this step the oxidant and reductant are brought close to each other via linkage by the bridging ligand so that electron transfer can take place

$$Ox–X + Red\,(H_2O) \leftrightarrow [Ox–X\cdots Red] + H_2O$$

Second step involves **chemical activation, electron transfer and relaxation to the successor complex**. In this step activation of the precursor complex occurs which is followed by electron transfer.

$$[Ox–X\cdots Red] \leftrightarrow [^{-}Ox^{\cdot}\cdots X–Red^{+}]$$

In the third step the **bridged species dissociation to separated** products

$$[^{-}Ox\cdots X–Red^{+}] + H_2O \leftrightarrow Ox(H_2O)^{-} + RedX^{+}$$

Ih has been observed that such a reaction follows second order kineticsand for a reaction like the one shown below

$$Ox\text{-}X + Red \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Ox\text{- }X\text{- }Red] \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Ox^{-} + RedX^{+}$$

rate of the reaction is given by the equation:

$$Rate = [k_1k_3/(k_2 + k_3)].[Ox\text{-}X][Red]$$

Herek_3 is overall rate constant for the second and third steps.

It has been found that in some cases $k_3 >> k_2$ and rate determining step is simply formation of the precursor complex. Therefore, rate law reduce to $Rate = k_1[Ox–X][Red]$.

However, there are many instances wherein rate determining step is rearrangement and electron transfer within the intermediate, or fission of the successor complex. This means that $k_3 < k_2$ and the rate law becomes $Rate = Kk_3[Ox–X][Red]$.

Factors influencing the rates of Inner Sphere Electron Transfer

Now, let us have a look on the factors determining rates of inner sphere electron transfer reactions.

Formation of the precursor complex: We have already discussed about substitution reactions at octahedral metal centres in the first unit. **You have seen that a *d^3* metal ion is relatively inert to substitution, while high spin *d^4* and *d^5*complexes are labile**.

Further, usually in inner sphere electron transfer reactions $V^{2+}[(\pi^*)^3(\sigma^*)^1]$, Cr^{2+} [$(\pi^*)^3(\sigma^*)^1$], and Fe^{2+} $[(\pi^*)^4(\sigma^*)^2]$ are employed as reductants.

An examination of the substitution rates for

$[V(H_2O)_6]^{2+} + H_2O^* \rightarrow [V(H_2O)_5(H_2O^*)]^{2+} + H_2O$ ($k = 1 \times 10^2\ s^{-1}$)

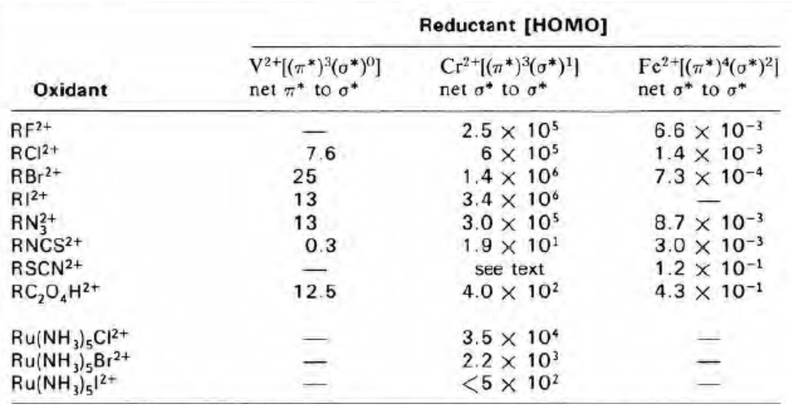
$[V(H_2O)_6]^{2+} + NCS^{-}\rightarrow [V(H_2O)_5NCS]^{+} + H_2O$ ($k = 28\ M^{-1}s^{-1}$)

$[Cr(H_2O)_6]^{2+} + H_2O^* \rightarrow [Cr(H_2O)_5(H_2O^*)]^{2+} + H_2O$ ($k = 10^9\ s^{-1}$)

$[Fe(H_2O)_6]^{2+} + H_2O^* \rightarrow [Fe(H_2O)(H_2O^*)]^{2+} + H_2O$ ($k = 10^6\ s^{-1}$)

shows that here are marked differences in their rates.

In inner sphere electron transfer reaction the very first step is formation of precursor complex wherein a labile ligand from reductant is replaced and bridged complex is formed. Thus, the rate at which this ligand is given out will control relative rate of the electron transfer reaction.



Oxidant	Reductant [HOMO]		
	$V^{2+}[(\pi^*)^3(\sigma^*)^0]$ net π^* to σ^*	$Cr^{2+}[(\pi^*)^3(\sigma^*)^1]$ net σ^* to σ^*	$Fe^{2+}[(\pi^*)^4(\sigma^*)^2]$ net σ^* to σ^*
RF^{2+}	—	2.5×10^5	6.6×10^{-3}
RCl^{2+}	7.6	6×10^5	1.4×10^{-3}
RBr^{2+}	25	1.4×10^6	7.3×10^{-4}
RI^{2+}	13	3.4×10^6	—
RN_3^{2+}	13	3.0×10^5	8.7×10^{-3}
$RNCS^{2+}$	0.3	1.9×10^1	3.0×10^{-3}
$RSCN^{2+}$	—	see text	1.2×10^{-1}
$RC_2O_4H^{2+}$	12.5	4.0×10^2	4.3×10^{-1}
$Ru(NH_3)_5Cl^{2+}$	—	3.5×10^4	—
$Ru(NH_3)_5Br^{2+}$	—	2.2×10^3	—
$Ru(NH_3)_5I^{2+}$	—	$<5 \times 10^2$	—

Table 3. Second order rate constant for the inner sphere reduction of various Co(III) complexes and some Ru(III) complexes at 25 °C

Available data on V(ll) reductions presented in the above Table 3 clearly shows that when this ion is employed as an inner sphere reductant the reaction rate is controlled by rate at which water is given out from the coordination sphere of $[V(H_2O)_6]^{2+}$. It has been concluded on the basis of similarity rate of electron transfer reaction with the rate of water substitution on V(ll) ion, and independence of the rate on the nature of the bridging ligand available on the oxidant.

On the other hand, rates involving Cr(II) and Fe(II) reductions are significantly less than their rates of water substitution.

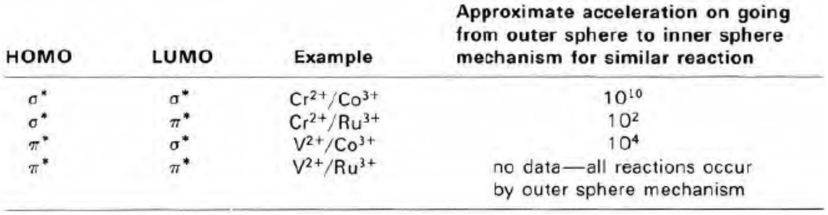
Rearrangement of the Precursor Complex and Electron Transfer

In the introductory part related to inner sphere electron transfer reactions you have seen that usually formation of the reactant pair is very fast and reversible. Further, rate of such reactions are governed by the rearrangement and electron transfer step. The rate of an inner sphere electron transfer may depend on the nature of the oxidant, the reductant, and the bridging ligand.

Electronic structure of the Oxidant and Redcurtant

From the Taube's experiment it was concluded that reduction of $[Co^{III}(NH_3)_6]^{3+}$ with $[Cr^{II}(H_2O)_6]^{2+}$ under acidic conditions occur by an outer sphere mechanism while reaction is accelerated if an ammine ligand in $[Co^{III}(NH_3)_6]^{3+}$is replaced by Cl and follows an inner sphere mechanism.

The rate enhancement is related to symmetries of the reductant orbital from which electron is given out and the oxidant orbital into which the electron moves. After careful examination of a number of outer sphere and inner sphere reactions, following general observations have been made:



HOMO	LUMO	Example	Approximate acceleration on going from outer sphere to inner sphere mechanism for similar reaction
σ^*	σ^*	Cr^{2+}/Co^{3+}	10^{10}
σ^*	π^*	Cr^{2+}/Ru^{3+}	10^2
π^*	σ^*	V^{2+}/Co^{3+}	10^4
π^*	π^*	V^{2+}/Ru^{3+}	no data—all reactions occur by outer sphere mechanism

Table 4

From the Table 4 it can be concluded that while some rate acceleration has generally occurred on going from an outer sphere to an inner sphere mechanism in comparable reactions, the effect is most prominent when both HOMO and LUMO are σ*. In such reactions bridging group facilitates the inner sphere pathway.

The Nature of the Bridging Ligand

The nature of bridging ligand plays an important role in determining the rates of inner sphere electron transfer reactions.

Haim recently pointed out, "***The role of the bridging ligand [in an inner sphere mechanism] is ... dual. It brings the metal ions together (thermodynamic contribution) and mediates the transfer of the electron (kinetic contribution)."*** The thermodynamic contribution is related to the stability of the intermediate complex, and kinetic to factors such as oxidant-reductant reorganization and matching of donor and receptor molecular orbitals.

As far as bridging ligands (BL) are concerned, both inorganic and organic ligands have extensively been utilized in the inner sphere electron transfer reactions.

While studying electron transfer reactions one major problem is how to ascertain that reaction is following an inner or outer sphere mechanism?

In this regard a simple test that can be applied in some of the cases is carrying out a reaction of the type:

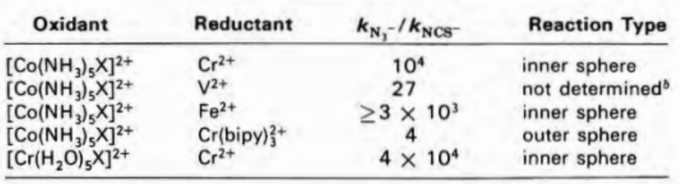
$$[Co^{III}(NH_3)_5X]^{2+} + [Cr^{II}(H_2O)_6]^{2+} \xrightarrow{H^+} [Co^{II}(H_2O)_6]^{2+} + [Cr^{III}(H_2O)_5X]^{2+} + 5NH^{4+}$$

utilizing the N_3^- or NCS^- as bridge ligand X.

For such a reaction the is $k^{os}_{N3-}/k^{os}_{NCS-} \approx 1$, while $k^{is}_{N3-}/k^{is}_{NCS-} >> 1$(see Tables 4 and 5).

It may be related to preferential formation of the intermediate in inner sphere mechanism by one bridging ligand or the other.

Some data related to this is given in the Table 5 given below.



Oxidant	Reductant	$k_{N_3^-}/k_{NCS^-}$	Reaction Type
$[Co(NH_3)_5X]^{2+}$	Cr^{2+}	10^4	inner sphere
$[Co(NH_3)_5X]^{2+}$	V^{2+}	27	not determined[b]
$[Co(NH_3)_5X]^{2+}$	Fe^{2+}	$\geq 3 \times 10^3$	inner sphere
$[Co(NH_3)_5X]^{2+}$	$Cr(bipy)_3^{2+}$	4	outer sphere
$[Cr(H_2O)_5X]^{2+}$	Cr^{2+}	4×10^4	inner sphere

Table 5. Relative rates of reduction of azido and thiocyanato complexes.

As NCS is an ambidentate ligand, it can form a bond with the metal centres through either end.

When NCS^- is S-bound to a oxidant, $[Co(NH_3)_5SCN)]^{3+}$ nitrogen end of the ligand can be attacked by the reductant $[Cr(H_2O)_6]^{2+}$ and rate of this reaction is comparable to azide as the bridge (NCS^-, $=1.9 \times 10^5$ $M^{-1}s^{-1}$; N_3^-, 3.0×10^5 $M^{-1}s^{-1}$).

The bent S-bound thiocyanate can also be attacked by the reductant at sulphur atom directly bound to the oxidant metal ion because it possesses two lone pairs of electron.

When attack occurs at S- bound to oxidant we call it ***adjacent*** and when remote N atom is attacked by the reductant we call it ***remote*** attack.

Thus, both remote attack at nitrogen and adjacent at sulphur is possible, and notably, these occur at almost the same rates at least with $[Cr(H_20)_6]^{2+}$as the reducing agent

A lot of information has been acquired on inner sphere electron transfer reactions using organic bridging agents. It has been observed that rate of such reactions are controlled by:

i) Bridge steric effects

ii) the point of attack by reductant on the bridge, and ii) electronic structure of the bridge along with its reducibility.

Most of such studies have been made on carboxylate complexes and amine complexes of the type:.

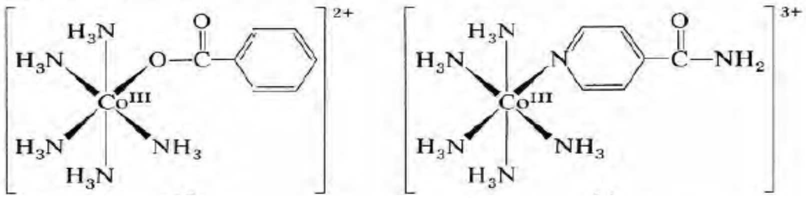


Fig. 8

These follow second order kinetics and proposed mechanisms involve attack at a ***remote site*** rather than at the atom directly bonded to the oxidant metal center.

The influence of steric crowing on rates of some reactions for $[Co^{III}(NH_3)_5X]^{2+}$ complexes as oxidant and $[Cr^{II}(H_2O)_6]^{2+}$ as reductant is shown below. In these reactions attack by the Cr(ll) ion occurs at the carbonyl oxygen of the carboxylate group.

Notably, the rate constants for reduction by $[Cr(H_2O)_6]^{2+}$decreases with increasing steric bulk of the organic compounds.

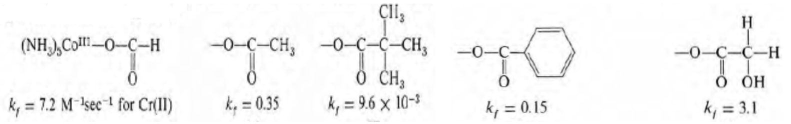


Fig. 9

Further, if another basic group is added on to the carboxylate moiety, chelation of the reductant [Cr(ll) in this case] is possible, and the rate constant increases.

Electron transfer is possible *via* attack at a site even more remote than the carboxylcarbonyl oxygen. It has been observed in the reactions of various Co(III) and Ru(lll) complexes based on substituted pyridines. For example, $[Co^{III}(NH_3)_5(py)]^{2+}$ reacts relatively slowly with Cr(ll)

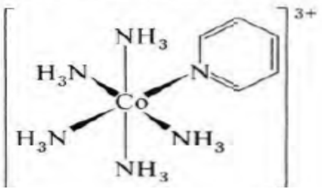


Fig. 10

($k = 4 \times 10^{-3}$ $M^{-1}s^{-1}$) to give $[Cr(H_2O)_6]^{3+}$ by an outer sphere pathway.

On the other hand, complex $[Co^{III}(NH_3)_5(\text{isonicotinamide})]^{2+}$ (Fig. 11) reacts rather rapidly ($k = 17.4$ $M^{-1}s^{-1}$) with $[Cr(H_20)_6]^{3+}$ to give 22 as the first Cr(III) product. This observation suggested that the attack of Cr(II) is at the remote carbonyl group in 21, not the -NR_2 group.

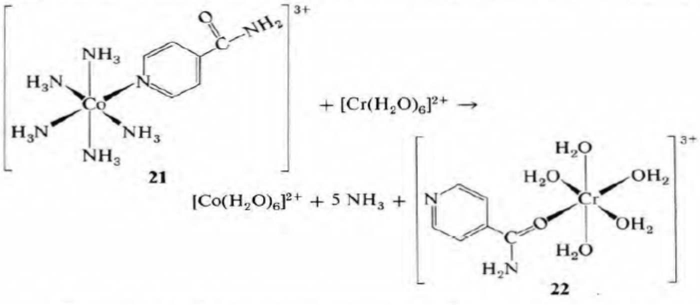


Fig. 11

Rates of the reduction of Co(III), Cr(III) and Ru(III) complexes with Cr(II) is shown in the Table 6.

An examination of the Table-6 shows that relative reduction rates of Co(lll) and Cr(III) complexes with a simple bridge (F^-, Cl^-, CH_3COO^-) varies to a greater extent. Contrarily the isonicotinamide complexes of Co(lll) and Cr(III) are reduced at analogous rates. It means that factors favouring the Co(lll) reductions over analogous Cr(lll) reductions are not at all important with isonicotinamideas a bridging ligand.

It may be attributed to reducibility of the bridges like isonicotinamide, and the reduction proceeds through such bridges via a chemical or radical mechanism. In such a mechanism after precursor formation, Cr(ll) activation $[(\pi^*)^3(\alpha^*)^1 \rightarrow (\pi^*)^4]$ an electron is transferred into a π• orbital of isonicotinamide, thereby forming Cr(lll) and the radical anion $H_2NC(O)C_5H_4N^-$. This step is thought to be rate-determining step. Convincing experimental evidence has been obtained to support the free radical nature of the bridge.

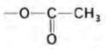
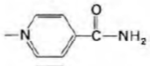
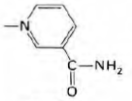
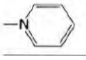
Bridging Ligand	**Oxidizing Agent**		
X	$[Co^{III}(NH_3)_5X]^{n+}$	$[Cr^{III}(H_2O)_5X]^{n+}$	$[Ru^{III}(NH_3)_5X]^{n+}$
F^-	2.5×10^5	2.64×10^{-2}	—
Cl^-	6×10^5	90	3.5×10^4
 $-O-\underset{\overset{\|}{O}}{C}-CH_3$	3×10^{-1}	10^{-4}	2.6×10^4
	1.74×10^1	1.8	3.9×10^5
	1.4×10^{-2} (outer sphere) 3.3×10^{-2} (inner sphere)	—	0.84×10^4 (outer sphere) 1.35×10^4 (inner sphere)
	4.0×10^{-3} (outer sphere)	—	3.4×10^3 (outer sphere)

Table 6. Rates of Reduction of Various Co(lll), Cr(lll), And Ru(lll) Complexes with $Cr^{2+}(aq)$. Second Order Rate Constants in Units of $M^{-1}sec^{-1}$

On the other hand, reductions of Co(III) and Cr(III) through simpler bridges such as Cl^- occur by the concerted mechanism, because these species are not reducible. Thus, reductions through simple inorganic bridges are generally controlled by oxidant activation and the thermodynamics of the reaction

<u>Fission of the Successor Complex</u>

While dealing with kinetics of the inner sphere electron transfer reactions you have gone through a limiting case wherein $k_3<k_2$ and the rate law becomes: rate = Kk_3, under such conditions overall rate of electron transfer reactions can be controlled by the rate of fission of the successor complex.

One of the most interesting examples is presented by the Ru(III)-nicotinamide complexes in Table XX.It has been observed that when $[Ru(NH_3)_5(isoamide)]^{3+}$reacts with $Cr(H_2O)_6]^{2+}$, precursorformation and electron transfer to give Ru(II) and Cr(III) are complete within time of mixing. However, the yellow-orange binuclear successor complex (23) isquite stable and decomposes only slowly to ultimatelygive [Ru(NH$_3$)$_5$(isoamide)]$^{2+}$and Cr(III) by three different routes depicted below.

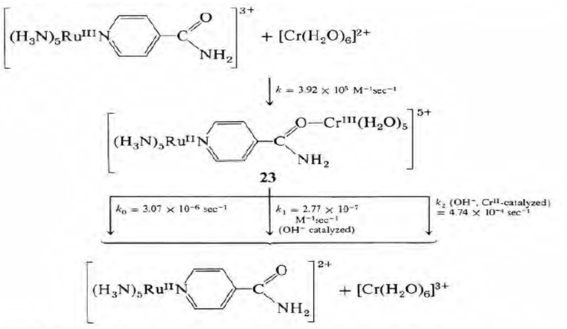


Fig. 12

The stability of intermediate complex 23 is due to substitutional inertness of Cr(III) and Ru(ll). As you have already seen that substitution reactions of octahedral transition metal complexes usually occur by dissociative activation, dissociation of the complex 23 and formation of final products are slow. Thus, due to substitutional inertness ofCr(III) the intermediate complex maydecompose by following three routes.

Thek_0 path presents spontaneous dissociation of the complex to give final products.

The k_1 path shows an inverse dependence on [H$^+$]. Accordingly, the intermediate complex 23 loses a proton from Cr(lll)-bound water to give 24, which then dissociates to products.

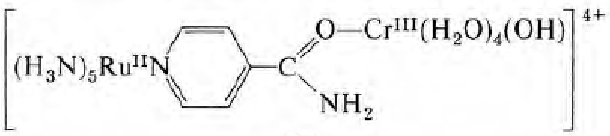


Fig. 13

The k_2 path also has an inverse dependence on [H$^+$] but also it isdirectly dependent on excess [Cr(II)].

It can be explained by assuming that OH-ligandin 24 functions as a bridge between 24 and unreacted Cr(ll). Thus, a bridgeof the type -C=0-Cr^{III}-0-Cr^{II} is formed and inner sphere electron transfer occurs from Cr(ll) to Cr(III). It means that a species like -C=0-Cr^{II}-O-Cr^{III}is formed and, since Cr(II) is more susceptible to substitutionthan Cr(III), complex 24 [which now contains Cr(ll) instead of Cr(III)] candecompose to products. Finally, due to catalysis by excess Cr(ll) the k_2 path is the most rapid among three decomposition paths.

Two Electron Transfer Reactions

After having discussed electron transfer reactions wherein one electron is transferred from reductant to oxidant.let us have a look on two electron transfer do occur. In this section we will examine how a two electron transfer reaction occurs and what is its mechanism?

One of the best understood two-electron transfer reactions in transition metal chemistry is the Pt(ll) catalyzed exchange of free Cl- for chloride bound to a Pt(IV). That is,

$$trans\text{-}[Pt(cn)_2C1_2]^{2+} + {}^*Cl^- \xrightarrow{[Pt(cn)_2]^{2+}} trans\text{-}[Pt(cn)_2{}^*ClC1]^{2+} + Cl^-$$

The rate law for this reaction is given by

$$\text{rate} = k[Pt(II)][Pt(IV)][Cl^-]$$

The mechanism can be understoodby considering rapid addition of free chloride to Pt(II) compound to form a five-coordinate, monopositive ion which subsequently interacts with the Pt(IV) to form asix-coordinate, inner sphere complex reactant. The platinumcentres in this intermediate complex are now in very similar environment. In this complextwo π* electrons transfer withanion transfer in the opposite direction, can readily occur.

The mechanism of this reaction has been established by using radio chloride and a chiral Pt(IV)complex. Fascinatingly exchange of radio chloride occurs at the same rate as change in optical rotation in the reaction of trans-$[Pt(\mathit{1}\text{-pn})_2Cl_2\ ]^{2+}$ with$[Pt(en)_2]^{2+}$. It advocated that the rate determining step of reaction involves both the initially free chloride and the chiral, six-coordinate Pt(IV) compound.

$$[Pt(en)_2]^{2+} + \textit{trans}\text{-}[Pt(\mathit{1}\text{-pn})_2Cl_2\ ]^{2+} \rightarrow [Pt(\mathit{l}\text{-pn})_2]^{2+} + \textit{trans}\text{-}[Pt(\mathit{e}n)_2Cl_2\ ]^{2+}$$

Creation of a symmetrical transition state is further supported by the fact that exchange is prevented when TMEA(tetramethylethylenediamine, $Me_2N\text{-}C_2H_4\text{-}NMe_2$)is used as ligand on Pt(IV), Apparently, very bulky ligand prevents approach of the Pt(ll) complex.

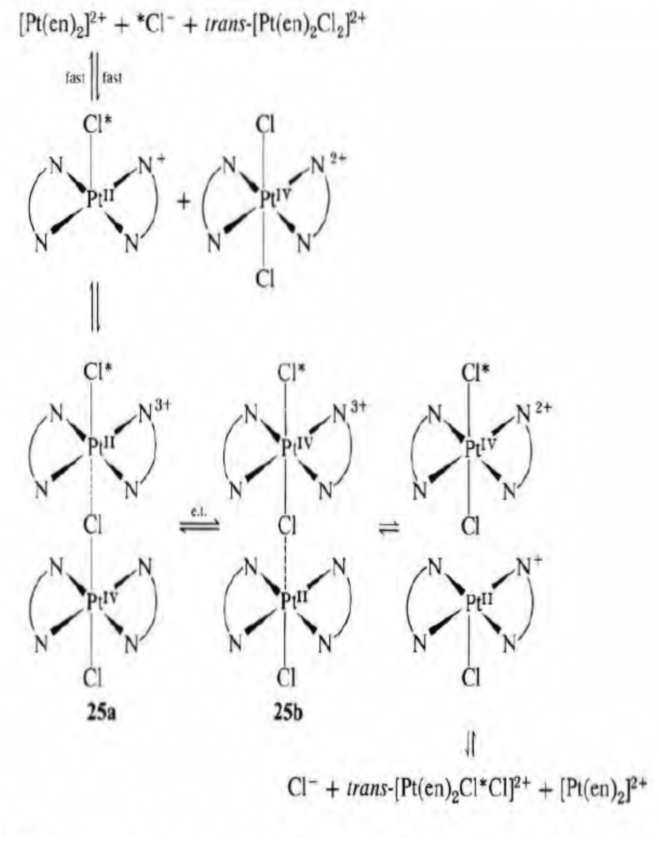


Fig. 14

Non Complementary reactions:

So far, we have discussed the reactions wherein formal oxidation states of the oxidant and reductantchange by the same number of units. These are called complementaryreactions. There are many reactions in whichformal oxidation states of the oxidant and reductant do not change by same number of units. Theseare termed as non-complementary processes such as

Mn(VII) + 5Fe(ll) →Mn(ll) + 5Fe(lll)

Cr(VI) + 3Fe(ll) → Cr(lll) + 3Fe(lll)

2Cr(ll) + Pt(IV) →2Cr(III) + Pt(ll)

Clearly in a non-complementary reaction, the oxidation states of the reactants change byunequal amounts and the stoichiometries are not 1: 1.One of the best example of non-complementary processes in transition metalchemistry presents chromate ion oxidations. It oxidation occurs in steps and in each step, involving a electron transfer.

$$\mathrm{Cr(VI)}\ [= \mathrm{HCrO_4^-}] + \mathrm{Red} \underset{k_{56}}{\overset{k_{65}}{\rightleftharpoons}} \mathrm{Cr(V)} + \mathrm{Ox}$$

$$\mathrm{Cr(V)} + \mathrm{Red} \xrightarrow[k_{54}]{} \mathrm{Cr(IV)} + \mathrm{Ox}$$

$$\mathrm{Cr(IV)} + \mathrm{Red} \xrightarrow[\text{fast}]{} \mathrm{Cr(III)} + \mathrm{Ox}$$

Such a mechanism follows the following rate law

$$-d[\mathrm{H\ Cr0^-_4})]/dt = k_{65}k_{54}[\mathrm{Cr(VI)}][\mathrm{Red}]^2/k_{54}[\mathrm{Red}] + k_{56}[0x]$$

Usually, this rate law is applicable with some modifications.If an inner sphere is operative e.g, with $[\mathrm{Fe(H_20)_6}]^{2+}$ or $\mathrm{V0^{2+}}$, the rate determining step is the second one; i.e., $k_{54}[\mathrm{Red}] << k_{56}[0x]$. it is due to slowness of the separation of the inner sphere complexafter electron transfer in the second step, and is related to the necessity for the Cr(IV) ion to change from a four-coordinate species in the inner sphere complex to a free, six-coordinate Cr(IV) ion.

However, if chromate oxidation occurs by substitution inert reducing agents, first step is rate determining and the ratelaw converges to $-d[\mathrm{HCr0^-_4}\ ]/dt = k[\mathrm{HCr0^-_4}\ ][\mathrm{Red}]$ as$k_{54}[\mathrm{Red}] >> k_{56}[0x]$. In this case the first step apparently has the least thermodynamic driving force of the three steps.

It has been observed for the reactions involving $[\mathrm{Fe(CN)_6}]^{4-}$ and $[\mathrm{Fe(bipy)_3}]^{2+}$as redu**c**tantsSuch a reaction do not give theproducts as expected.

$\mathrm{HCrO_4} + 3[\mathrm{Fe(CN)_6}]^{4-} + 7\mathrm{H^+} = \mathrm{Cr^{3+}} + 3[\mathrm{Fe(CN)_6}]^{3-} + 4\mathrm{H_20}$

Rather, the final product in the $[\mathrm{Fe(CN)_6}]^{4-}$ reaction is a bridged species$\mathrm{(H_20)_5Cr\text{-}N{=}{=}C\text{-}Fe(CN)_5}$. It is likely that the final step in the three-step sequenceinvolves inner sphere reduction ofCr(IV) and represents one of the example wherein the bridging ligand is supplied by the reductant in an inner sphere process.

Note: This lecture has been prepared by using following books:

1. **Inorganic Chemistry by Purcell and Kotz (All the tables and some of the Figures has been adopted from this book)**
2. **Inorganic Reaction Mechanisms by Martin L Tobe and John Burgess**
3. **Inorganic Chemistry: Principles of Structure and Reactivity by James E Huheey, Ellen A. Kaiter and Richard L. Keiter**
4. **My own experiences of teaching for past 28 years**