

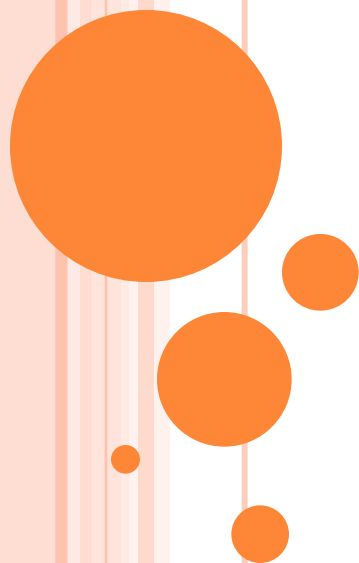
Course Code: CHEM4007
Course Name: Inorganic Chemistry-II

Unit: 2
(Electron Transfer Reaction)
(Lecture-Part 2)

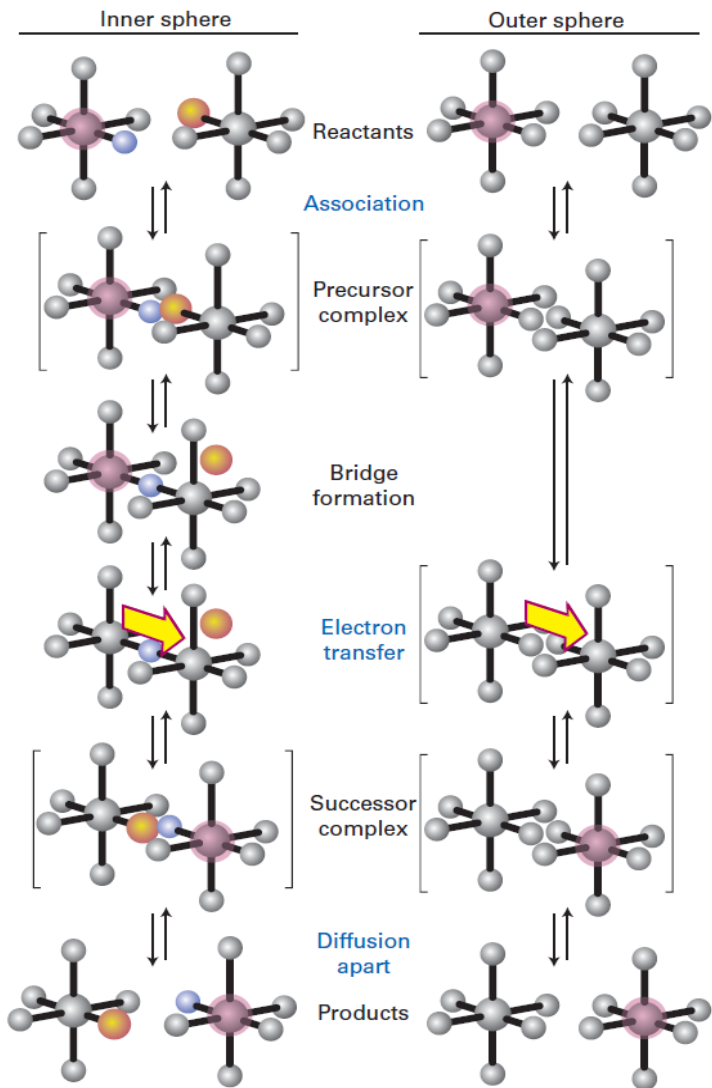
For
M.Sc.
Semester: II

By

Dr. Abhijeet Kumar
Department of Chemistry
Mahatma Gandhi Central University



Different Steps involved in Inner-Sphere Mechanism: A Schematic Representation

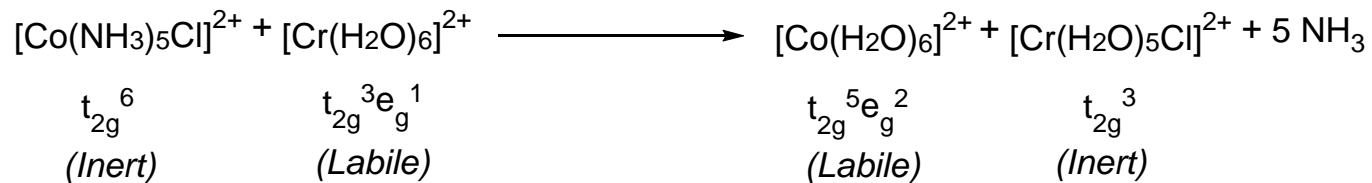


➤ Different Steps are as follows:

- (a) **Precursor complex:** *The very first step in the electron transfer reaction is the formation of precursor complex which are common to both type of mechanisms. As it can be seen in Figure 1 that reactants comes in close proximity and interact with each other to form **Precursor complex**.*
- (b) **Bridged Binuclear Intermediate formation:** *As the reaction progresses, one of the ligand of one reactant coordinates with other metal centre by substituting one ligand attached to it to form bridged binuclear intermediate.*
- (c) **Electron Transfer:** *In case of inner-sphere mechanism, reactions use the tunneling phenomenon with a bridging ligand as the conduit (a channel to transfer something). It means in this step, electron transfer occurs to form **Successor complex**.*
- (d) **Product formation:** *Finally products separate out.*

Figure 1: Schematic representation of both types of mechanisms

Evidences to support the role of bridging Ligand



Scheme 1: Reduction of $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ by $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$

- Prof. Henry Taube received Nobel Prize in Chemistry in 1983 for *his work in the mechanisms of electron-transfer reactions, especially in metal complexes.*
- Taube and co-workers observed the role of bridging ligand in the electron transfer reaction.
- In one classical example showed in scheme 1, they observed that Cl atom connects two metal centre and acts as bridging ligand which facilitate the electron transfer process and thereby affecting the rate of reaction drastically.
- Other ligands such as SO_4^{2-} , H_2O , and OH^- were also found to act as bridging ligands and affects the rate of electron transfer reaction.

Taube, H.; Myers, H.; Rich, R. L.; *J. Am. Chem. Soc.* **1953**, *75*, **4118**.

Taube, H.; Myers, H.; *J. Am. Chem. Soc.* **1954**, *76*, **2103**.

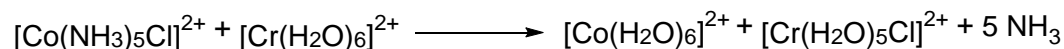


Continued..

Different Steps involved in Inner-Sphere Mechanism

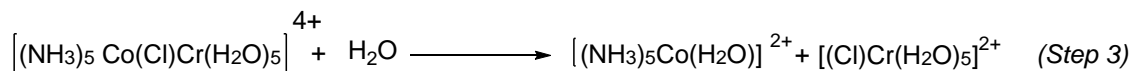
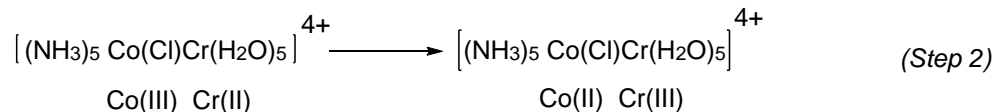
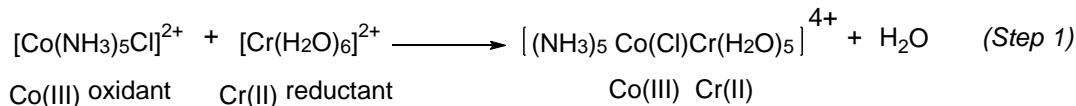
➤ Overall Reaction follows three following steps:

- (a) A substitution reaction that leaves the oxidant and reductant linked by a bridging ligand.
- (b) The electron transfer, frequently accompanied by transfer of the ligand.
- (a) Separation of the products occurs at the final step.

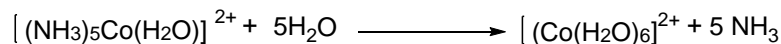


Scheme 1: Reduction of $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ by $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$

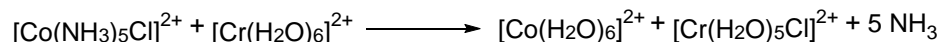
➤ The reaction written in scheme 1 could further be elaborated as:



These are followed by formation of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ because Co(II) is labile:



So overall:



➤ As it could be seen that in step 1, precursor complex formed. In step 2, bridging intermediate formation followed by electron transfer took place and in the final step 3, successor complex separated to form products.

Effect of Bridging Ligand on Rate Of Redox Reaction

➤ **Table 1:** Second-order rate constants for selected inner-sphere reactions with variable bridging ligands

Entry	Oxidant	Reductant	Bridging Ligand	$k_r / (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$
1.	$[\text{Co}(\text{NH}_3)_6]^{3+}$	$[\text{Cr}(\text{OH}_2)_6]^{2+}$	None	8×10^{-5}
2.	$[\text{CoCl}(\text{NH}_3)_5]^{2+}$	$[\text{Cr}(\text{OH}_2)_6]^{2+}$	Cl^-	6.0×10^5
3.	$[\text{CoF}(\text{NH}_3)_5]^{2+}$	$[\text{Cr}(\text{OH}_2)_6]^{2+}$	F^-	2.5×10^5
4.	$[\text{CoI}(\text{NH}_3)_5]^{2+}$	$[\text{Cr}(\text{OH}_2)_6]^{2+}$	I^-	3.0×10^5

Data adapted from Chapter 21, "Shriver & Atkins Inorganic Chemistry" (5th edition); Publisher: W. H. Freeman and Company New York; Authors: P. Atkins, T. Overton, J. Rourke, M. Weller, F. Armstrong, M. Hagerman.

- As it is clear from the table 1 that, the value of rate constants drastically increases in presence of one bridging ligand such as F^- , Cl^- , I^- etc.
- These drastic enhancement in the rate of reaction in the presence of bridging ligands in case of the reduction of Co(III) complexes indicate its role in the electron transfer reactions.
- It means reaction could be considered to follow inner-sphere mechanism if bridging is possible between two metal centres.



Continued..

Effect of Bridging Ligand on Rate Of Redox Reaction

➤ Similarly the reaction between $[\text{Co}(\text{CN})_5]^{3-}$ and Co(III) oxidants ($[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$) that have bridging ligands to form the product $[\text{Co}(\text{CN})_5\text{X}]^{3-}$ could be considered to follow an inner-sphere mechanism as evident by rate constant values.

Table 2: Rate constant value for reaction with $[\text{Co}(\text{CN})_5]^{3-}$

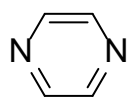
Entry	Oxidant	k ($M^{-1} s^{-1}$)
1	$[\text{Co}(\text{NH}_3)_5(\text{F})]^{2+}$	1.8×10^3
2	$[\text{Co}(\text{NH}_3)_5(\text{OH})]^{2+}$	9.3×10^4
3	$[\text{Co}(\text{NH}_3)_5(\text{NCS})]^{2+}$	1.1×10^6
4	$[\text{Co}(\text{NH}_3)_5(\text{Cl})]^{2+}$	5×10^7
5	$[\text{Co}(\text{NH}_3)_5(\text{NH}_3)]^{3+}$	8×10^4

➤ In entry 5, one could see that there is no bridging ligand still the rate of reaction is fairly high. But lack of bridging ligand indicates that reaction proceed via outer-sphere mechanism.

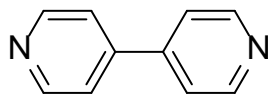
➤ In entry 3, reactions with thiocyanate as bridging groups show interesting behavior. The N-bonded $[\text{Co}(\text{NH}_3)_5(\text{NCS})]^{2+}$ reacts by bridging *via* the free S end of the ligand.

Prediction for inner-sphere mechanism

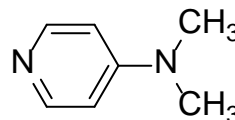
- Inner-sphere reactions should always be suspected when *ligand transfer occurs* as well as *electron transfer*, and if *good bridging groups* such as Cl, Br, I, N₃, CN, SCN etc. are present.
- Organic ligands such as pyrazine, 4,4'-bipyridine, and 4-dimethylaminopyridine (Figure 2) with two donor sites could also act as bridging ligands and could facilitate inner-sphere mechanism.



Pyrazine



4, 4'-Bipyridine



4-dimethylaminopyridine

Figure 2: Examples of organic bridging ligands

- Although in all the examples of bridging ligands discussed above, one could see the presence of lone pair of electrons. But it is not an essential requirement for a ligand to form bridge. **The carbon atom of a methyl group can also act as a bridge** between OH⁻ and I⁻ in the hydrolysis of iodomethane, so it can act as a bridge between Cr(II) and Co(III) in the reduction of methylcobalt species by Cr(II)



Topics and questions to be addressed in Next Lecture

- *Different types of organic ligands in the role of bridging ligands and their effect on rate of reaction.*
- *Does inner-sphere mechanism always end with transfer of ligand?*
- *Out of three major steps (Precursor complex formation, bridged intermediate formation followed by electron transfer and product formation) which one is the rate determining step?*



References

Student may also consult following books:

- *Chapter 21, “Shriver & Atkins Inorganic Chemistry” (5th edition); Publisher: W. H. Freeman and Company New York; Authors: P. Atkins, T. Overton, J. Rourke, M. Weller, F. Armstrong, M. Hagerman.*
- *Chapter 12, “Inorganic Chemistry” (5th edition); Publisher: Pearson Education India; Authors: G. L. Miessler, P. J. Fischer, D. A. Tarr.*
- ***Rest of the topics of this unit will be discussed in next part of the lecture.***

