

Course Code: CHEM4007
Course Name: Inorganic Chemistry-II

Unit: 2
(Electron Transfer Reaction)
(Lecture-Part 1)

For
M.Sc.
Semester: II

By

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General Introduction

- As the topic itself suggests that in electron transfer reaction, electron will be transferred from one species to other. It means one will be oxidized whereas reduction will take place in case of other. It means overall the different modes of the transfer of electron will be discussed for this redox reaction.
- Previously we have discussed about the kinetics and mechanism of substitution reaction in case of different types of complexes (tetrahedral, square-planar, octahedral). So before moving to this part once again go through those topics).
- Terms such as inert, labile complexes and parameters to identify them, needs to be revised.
- Overall unit-I should be revised before moving to this part.



Redox Reaction: An Introduction

- Redox (Reduction as well as Oxidation): It means both the process will take place during the reaction.
- Redox reaction could occur by the **direct transfer of electrons** (as in some electrochemical cells and in many solution reactions) or **by the transfer of atoms and ions**.
- In cases of coordination complexes, two reacting complexes could come together by a bridging ligand so electron transfer could also occur through this one. But it may not be the case in all types of redox reactions i.e. it is not mandatory that for redox reaction to occur, there must be an involvement of bridging ligand. It means that we will be discussing different types of mechanisms to discuss redox reactions.
- Because redox reactions in solution involve both an oxidizing and a reducing agent, they are usually bimolecular in character.
- But in few exceptional cases one molecule has both oxidizing and reducing centres.



Classification of Redox Reactions

- In the 1950s, Prof. Henry Taube who received Nobel Prize in Chemistry (1983) "*his work in the mechanisms of electron-transfer reactions, especially in metal complexes.*"
- He identified two different mechanisms of redox reactions for metal complexes:
 - (a) **Inner-Sphere Mechanism:** In an inner-sphere mechanism, the coordination spheres of the reactants *share a ligand transitorily* and form a bridged transition state.
 - (b) **Outer-Sphere Mechanism:** In an outer-sphere mechanism, the complexes come into contact *without sharing a bridging ligand* and the electron tunnels from one metal atom to the other.
- Although the mechanisms of some redox reactions have been definitively assigned as inner- or outer-sphere.
- The mechanisms of a vast number of reactions are unknown because in order to study or figure out the reaction pathway there should be sufficient time. But in case of labile complexes (According to Taube, a reaction half-life (*the time it takes for the concentration of the initial compound to decrease by one half*) of one minute or less as the criterion for lability).
- So where the half life is less than one minute it would be difficult to make unambiguous assignments that whether the electron transfer takes place through inner-sphere or outer-sphere mechanism.



Various steps involved in both types of mechanisms: A Schematic Representation

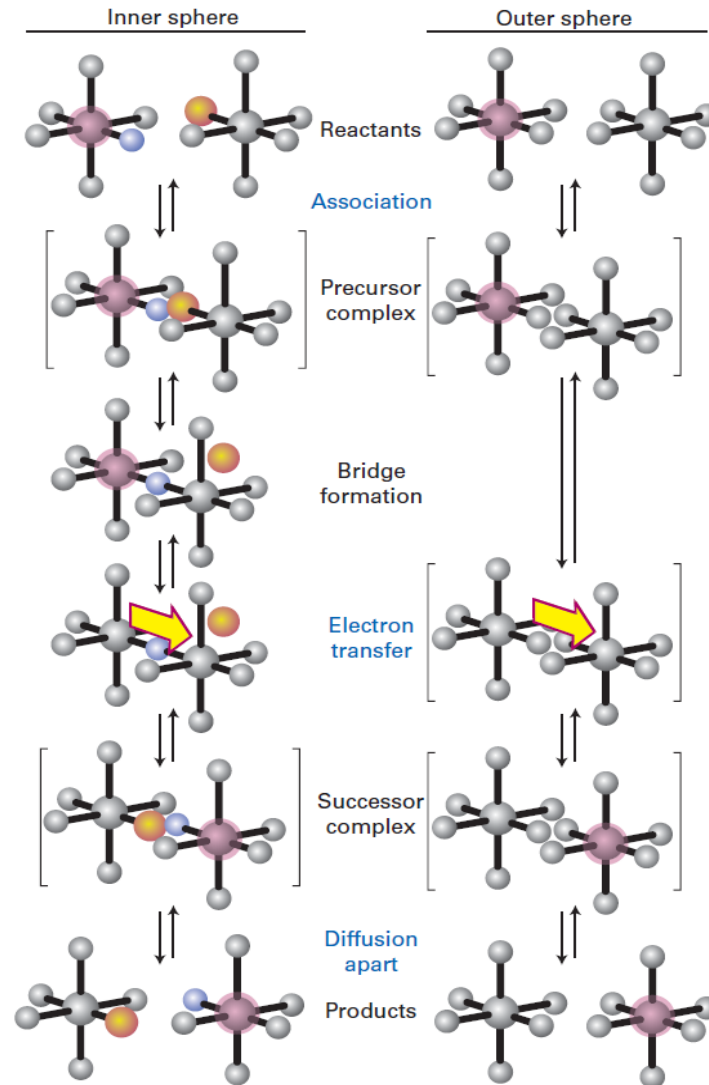


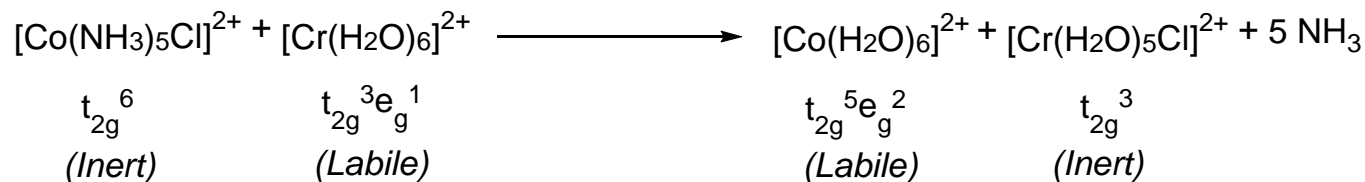
Figure 1: Schematic representation of both types of mechanisms

(Picture adapted from Chapter No. 21, "Shriver & Atkins Inorganic Chemistry" 5th edition)



Inner-Sphere Mechanism

- **Inner-Sphere Mechanism:** In an inner-sphere mechanism, the coordination spheres of the reactants *share a ligand transitorily* and form a bridged transition state.
- At least one of the complexes needs to be labile to allow the bridge to form. Bonds are broken and formed.
- The inner-sphere mechanism was first confirmed for the reduction of the nonlabile complex $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ by $\text{Cr}^{2+}(\text{aq})$ (Scheme 1).

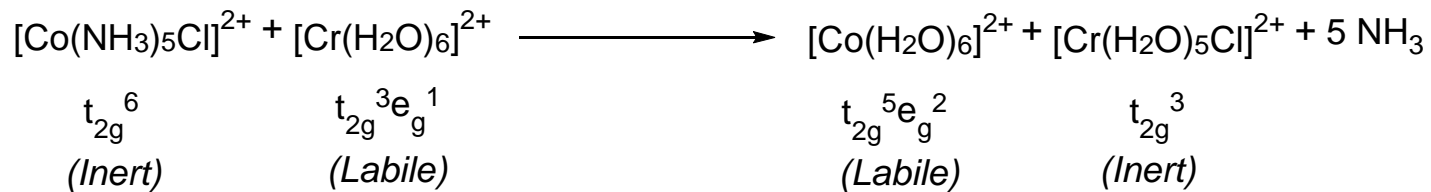


Scheme 1: Reduction of $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ by $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$

Question: What are the evidences available to support this pathway?



Evidences to support Inner-Sphere Mechanism in Scheme 1



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

➤ **Observation:**

Addition of $^{36}\text{Cl}^-$ to the solution did not lead to the incorporation of any of the isotope into the Cr(III) product.

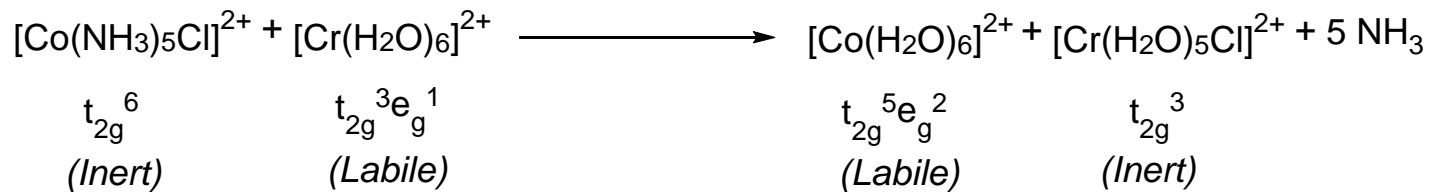
➤ **Discussion:**

- (a) *It means that the Cl^- attached to the Cr(III) on the product side has been received from the reactant itself and not from any external sources.*
- (a) *It further indicates that for the transfer of Cl^- from Co(III) to Cr(III), bridge formation must have occurred as indicated in the inner-sphere mechanism (Figure 1) otherwise some amount of product with $^{36}\text{Cl}^-$ would also have formed.*



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Evidences to support Inner-Sphere Mechanism in Scheme 1

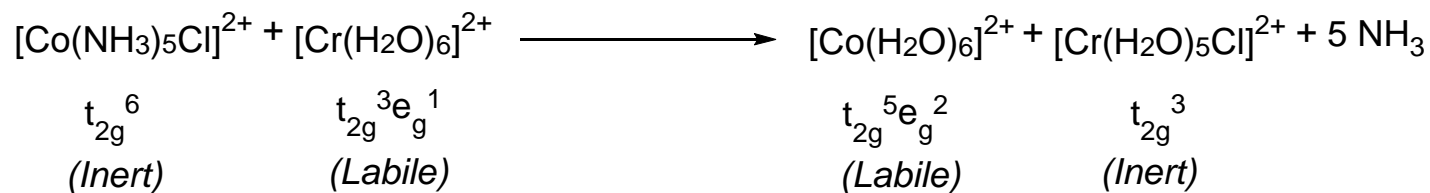


Scheme 1: Reduction of $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ by $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$

- **Observation:** *The rate of this reaction (Scheme 1) is much faster than reactions which involves removal of Cl^- from nonlabile $\text{Co}(\text{III})$ or addition of Cl^- into the nonlabile $[\text{Cr}(\text{OH}_2)_6]^{3+}$ complex.*
- **Discussion:** *It means that the presence of Cl^- in close proximity as in the case of inner-sphere mechanism, facilitates the transfer process and therefore enhances the rate of reaction.*
- **Conclusion:** *These observations suggest that Cl has moved directly from the coordination sphere of one complex to that of the other during the reaction. The Cl attached to $\text{Co}(\text{III})$ can easily enter into the labile coordination sphere of $[\text{Cr}(\text{OH}_2)_6]^{2+}$ to produce a bridged intermediate as shown in Figure 2.*



Structure of Bridged intermediate formed in case of inner-sphere mechanism (Scheme 1)



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

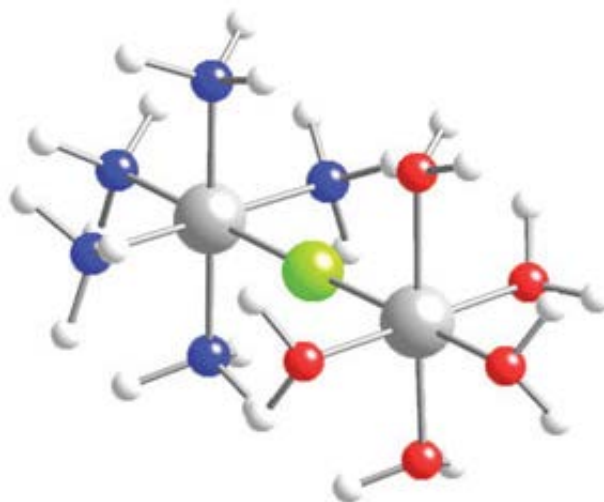


Figure 2: Structure of Bridged intermediate formed during reaction shown in scheme 1

(Picture adapted from Chapter No. 21, "Shriver & Atkins Inorganic Chemistry" 5th edition)



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.***

