

Inorganic Redox Reactions and Mechanism

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Abstract

In this review, the importance, different types of redox reactions and their applications in different field mainly, in biological system have been explored. Examples and mechanisms of Outer-sphere, inner-sphere and PCET (proton coupled electron transfer) redox reactions are also discussed.

Keywords: Redox, Outer-sphere, Inner-sphere, Electron transfer, Proton transfer.

1. Introduction

The improvement of knowledge on mechanism of reactions of d-block metal complexes started with the basic researches by Jorgenson¹ and werner². The first quantitative study in 1911 was done by Lamb³. These great scientists choose substitution and isomerisation reactions as their research interest. As days goes, followers paid more intense attention on redox reaction as this kind of reaction is the basis of photosynthesis, respiration and other biological processes.

Redox reactions may proceed with or without a net chemical change. Self exchange processes (e.g.1) are most widely known examples for redox reactions without a net chemical change.



2. Different Types of Redox Reactions

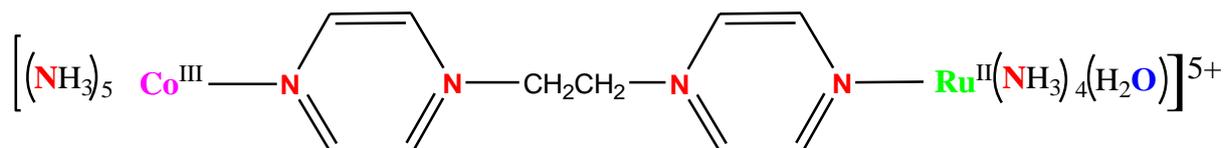
Redox reactions are of very wide types, they may be classified as

- a) The outer-sphere reactions
- b) The inner-sphere reactions
- c) The proton coupled electron transfer (PCET) reactions

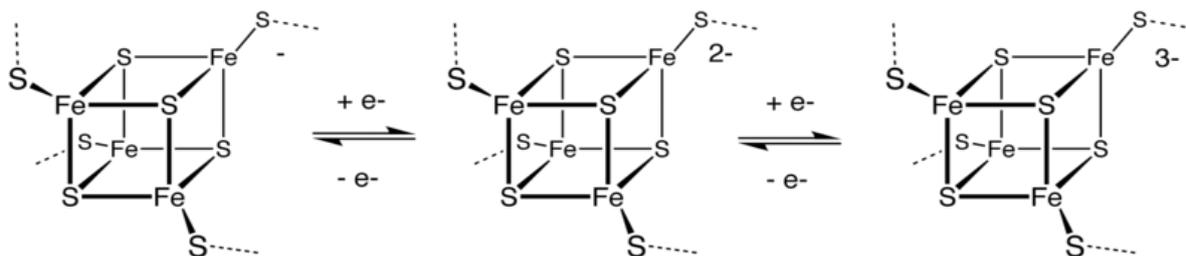
2a. The Outer-Sphere Reactions

Outer sphere refers to an electron transfer (ET) event that occurs between chemical species that remain separate intact before, during, and after the ET event⁴. In contrast, for

inner sphere electron transfer the participating redox sites undergoing ET become connected by a chemical bridge. Because the ET in outer sphere electron transfer occurs between two non-connected species, the electron is forced to move through space from one redox center to the other. This is why in outer-sphere mechanism there is very little electronic interactions between reagents. Even a bridged intermediate may undergo outer sphere electron transfer if the bridge is insulated, does not transmit electron and inhibits the inner sphere path. In the following example, electron transfer from Ru(II) to Co(III) in the bridged complexes is outer-sphere⁵.



Outer sphere ET is the basis of the biological function of the iron-sulfur proteins. The Fe centers are typically further coordinated by cysteinyl ligands. The $[\text{Fe}_4\text{S}_4]$ electron-transfer proteins ($[\text{Fe}_4\text{S}_4]$ ferredoxins) may be further subdivided into low-potential (bacterial-type) and high-potential (HiPIP) ferredoxins. Low- and high-potential ferredoxins are related by the following redox scheme.



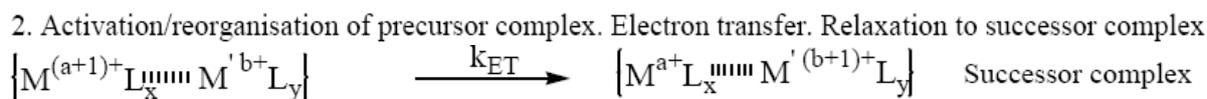
Because of the small structural differences between the individual redox states, ET is rapid between these clusters.

Mechanism:

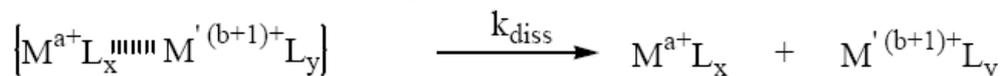


This is a general example of outer-sphere electron transfer reaction, where oxidant (O) is reduced and reductant (R) is oxidized. At first step oxidant (O) and reductant (R) come close to form a precursor complex $[\text{O} \cdots \text{R}]$, in next step this complex is to be activated to form activated precursor complex $[\text{O} \cdots \text{R}]^*$ and electron transfer and relaxation to successor complex $[\text{O} \cdots \text{R}^+]$ happens. At last the successor complex dissociates to products.

1. Formation of precursor complex



3. Dissociation of successor complex



Among the above three steps, formation of precursor complex and dissociation of successor complex is fast. Electron transfer step is slow i.e. rate determining step. The free energy vs. reaction coordinate graph looks like:

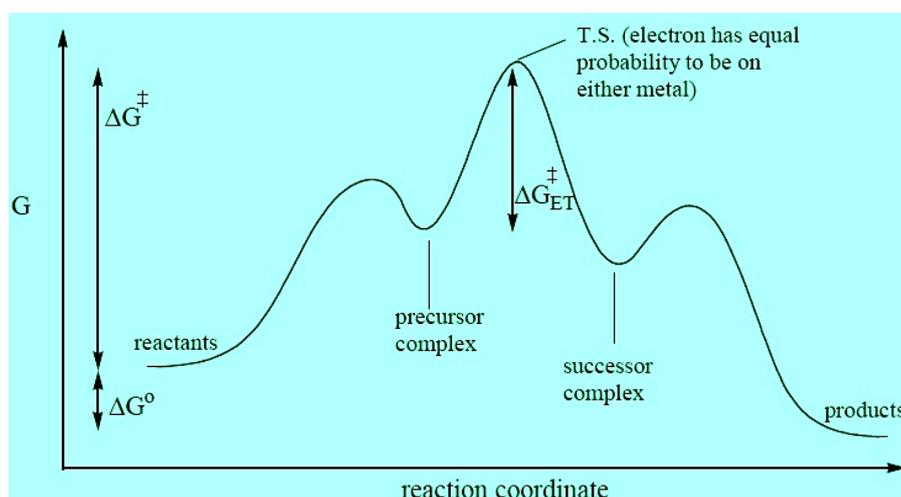


Figure 1: The free energy vs. reaction coordinate graph of outer-sphere reaction

The free energy related to activation of precursor complex is expressed as sum of three free energy terms:

$$\Delta G^\ddagger = \Delta G_t^\ddagger + \Delta G_o^\ddagger + \Delta G_i^\ddagger$$

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

2b. The Inner-Sphere Reactions

Inner sphere or bonded electron transfer⁶ is a redox chemical reaction that proceeds via a covalent linkage - a strong electronic interaction between the oxidant and the reductant. In Inner Sphere (IS) electron transfer (ET), a ligand bridges the two metal redox centers

during the electron transfer event. Inner sphere reactions are inhibited by large ligands, which prevent the formation of the crucial bridged intermediate. Thus, IS ET is rare in biological systems, where redox sites are often shielded by bulky proteins. Inner sphere ET is usually used to describe reactions involving transition metal complexes. In inner-sphere reaction not only electron transfer occurs but also bonds are broken and made⁷.

The most important example⁸ of this type of mechanism is the reduction of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ by $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ as given below.



Where both metal centers (Co^{III} & Cr^{III}) are inert but both the Co^{II} & Cr^{II} are labile. The chloride anion, strongly bonded to inert Co^{III} ion can very fastly replace a H_2O molecule from labile Cr^{II} via a bridged intermediate, $[(\text{NH}_3)_5\text{Co}-\text{Cl}-\text{Cr}(\text{H}_2\text{O})_5]^{4+}$. After ET the intermediate leading to form reduced Co^{II} and oxidized Cr^{III} .

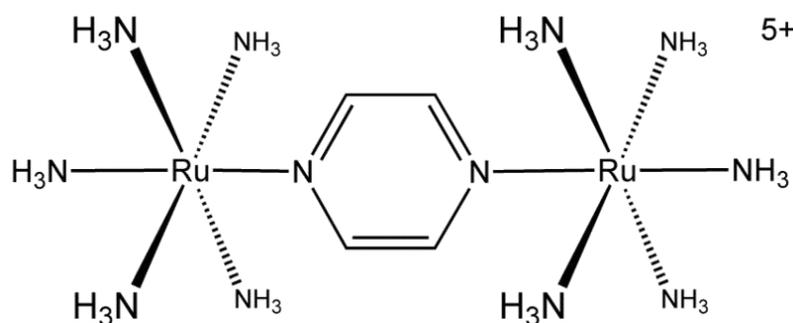


Figure 2: Structure of "Creutz Taube complex"

In the preceding example, the occurrence of the chloride bridge is inferred from the product analysis, but it was not observed. One complex that serves as a model for the bridged intermediate is the "Creutz Taube complex" $[(\text{NH}_3)_5\text{RuNC}_4\text{H}_4\text{NRu}(\text{NH}_3)_5]^{5+}$. This species is named after Carol Creutz, who prepared the ion during her Ph. D studies with Henry Taube. The bridging ligand is the heterocycle pyrazine, 1,4- $\text{C}_4\text{H}_4\text{N}_2$. In the Creutz-Taube Ion, the average oxidation state of Ru is 2.5^+ . Spectroscopic studies, however, show that the two Ru centers are equivalent, which indicates the ease with which the electron hole communicates between the two metals⁹. The significance of the Creutz-Taube ion is its simplicity, which facilitates theoretical analysis, and its high symmetry, which ensures a high degree of delocalization. Many more complex mixed valence species are known both as molecules and polymeric materials.

The bridging ligand could be virtually any entity that can convey electrons. Typically, such a ligand has more than one lone electron pair, such that it can serve as an electron donor to both the reductant and the oxidant. Common bridging ligands include the halides and the pseudohalides such as hydroxide and thiocyanate. More complex bridging ligands are also

well known including oxalate, malonate, and pyrazine. Prior to ET, the bridged complex must form, and such processes are often highly reversible. Electron transfer occurs through the bridge once it is established. In some cases, the stable bridged structure may exist in the ground state; in other cases, the bridged structure may be a transiently-formed intermediate, or else as a transition state during the reaction.

2c. The Proton Coupled Electron Transfer (PCET) Reactions

Electron transfer (ET) and proton transfer (PT) are most important processes of redox reactions in different energy conversion processes of chemistry and biochemistry. Proton-coupled electron transfer (PCET) is a redox reaction in which the concerted transfer of an electron and proton to or from a substrate is happened¹⁰. In PCET, the proton and the electron (i) start from different orbital and (ii) are transferred to different orbital. They transfer in a concerted elementary step. PCET contrast to step-wise mechanisms in which the electron and proton are transferred sequentially.

ET (electron transfer): Step-wise mechanism



PT (proton transfer): Step-wise mechanism



PCET (proton coupled electron transfer): Concerted mechanism



PCET is thought to be persistent in redox reactions that appear to be net hydrogenations and dehydrogenations. Relevant examples include water oxidation in photosynthesis, nitrogen fixation and oxygen reduction in many pathways for respiration. Inorganic chemists often study simple reactions to test this mechanism, one example being the comproportionation of a Ru(II) aquo and a Ru(IV) oxo reactants:

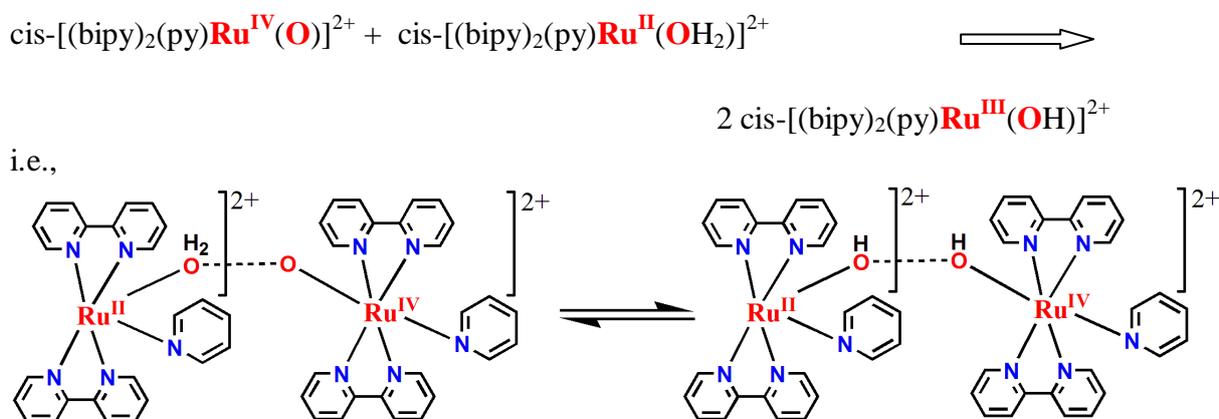


Figure 3: Comproportionation reaction of Ruthenium complexes

PCET is also often invoked in electrochemical reactions where reduction is coupled to protonation or where oxidation is coupled to deprotonation¹¹.

Although it is relatively simple to demonstrate that the electron and proton begin and end in different orbital, it is more difficult to prove that they do not move sequentially. General sequential pathways are lower in energy than concerted pathways. The main evidence that PCET exists is that a number of reactions occur faster than expected for the sequential pathways. In the initial electron transfer (ET) mechanism, the initial redox event has a minimum thermodynamics barrier associate with the first step. Similarly, the initial proton transfer (PT) mechanism has a minimum barrier associated with the protons initial pKa. Variations on these minimum barriers are also considered. The important finding is that there are a number of reactions with rates greater than these minimum barriers would permit. This suggests a third mechanism lower in energy; the concerted PCET has been offered as this third mechanism. This assertion has also been supported by the observation of unusually large kinetic isotope effects (KIE). A typical method for establishing PCET pathway is to show that the individual ET and PT pathways operate at higher activation energy than the concerted pathway¹⁰. In some literature, the definition of PCET has been extended to include the sequential mechanisms listed above. This confusion in the definition of PCET has led to the proposal of alternate names including electron transfer-proton transfer (ETPT), electron-proton transfer (EPT), and concerted proton-electron transfer (CPET).

3. Conclusion

Transition metal complexes which are taking part in outer-sphere redox mechanism are usually kinetically inert and there must be quantum mechanical tunneling of electron between metal centers. In this type of mechanism most important factors are (a) complexes are must come close together for tunneling (b) bond lengthening and shortening must occur (c) Franck-Condon principle must be obeyed. Whereas in inner-sphere redox mechanism important factors are (a) substitution to form a bridge between oxidant and reductant (b) actual electron transfers (c) separation of the products (often with transfer of the bridging ligand). An increasingly common and biologically important Proton-coupled electron transfer (PCET) is a redox reaction in which the concerted transfer of an electron and proton to or from a substrate is happened.

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