Chapter

Introductory Chapter: Redox - An Overview

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1. Redox

The term "redox" is the combination of two different terms that describe two totally different chemical processes, i.e., "reduction" and "oxidation." The abbreviation "red" has been taken to distinguish reduction from oxidation that is "ox." The reduction is a process wherein any chemical entity gets reduced. It is different from oxidation, which is opposite of the reduction because the chemical entities are oxidized. These two processes or reactions which simultaneously take place in a system are abbreviated as "redox."

1.1 General introduction

Oxidation-reduction was primarily used to describe the reaction(s) of combination and/or removal of oxygen with or from chemical substances, respectively. Simultaneously, the removal and/or the addition of hydrogen were also used to differentiate among oxidation and reduction, respectively. The definitions were extended to a broader level, and the changes in the oxidation number or oxidation state of elements were considered to define oxidation and reduction. The increase in the oxidation number leads to oxidation and its alternative process yields reduction. This vast definition encompasses the recent and exact interpretation of "redox" reactions that is acceptance and donation of the electron(s) between the reacting entities. Consequently, the redox phenomenon indicates a simple reaction, formation of carbon dioxide as a consequence of the oxidation of carbon and/or formation of methane by the reduction of carbon, for example, and the complex reaction consisting of a number of electron transfer reactions during the oxidation of sugar in the human body to produce energy.

The redox reaction(s) involves an oxidant or oxidizing agent and a reductant or reducing agent. The oxidant takes the electron(s) and oxidizes the reductant. The reductant, however, donates the electron(s) and reduces the oxidant.

Redox reactions are the key to make many desired chemical changes and/or processes reality to get maximum benefit out of it. A simple overview to surface the vital need of these reactions revolves around combustion, metabolic reactions, extraction of metals from their ores, manufacture of countless chemicals, and reactions occurring in our natural environment. For example, a cell either battery and/or biological cell involves redox processes [1–3]. Research that involves the biological systems interprets that the electronic and the structural environment of the substance(s) are the key factors that control chemical transformations such as electron transfer mechanisms in DNA molecules, which may appear through the exposure of cells to radiations that may have the power of ionization to cause

biologically deleterious effects such as inactivation, transformation, and mutagenesis [4–6]. The water molecules are ionized by some specific radiations and form radicals in the vicinity of DNA that contribute to the significant damage in DNA and chemical modifications to DNA, consequently. Of these radicals, the hydroxyl radical is thought to be the most damaging and produces the consequences for DNA strand breakage by the redox dependence of the rate of interaction of hydroxyl radical adducts of DNA nucleobases with oxidants [7].

Redox reactions mainly follow second-order kinetics with a series of intermediate reactions in a range of mechanisms such as entity transfer mechanisms that involve electron, atom, or group transfer and ligand addition, substitution, or dissociation.

Redox phenomenon in terms of electron transfer (ET) reactions and their mechanisms is catered for the interest of readers of this book. Essentials of only the electron transfer reactions of coordination or transition metal complexes and advanced oxidation processes for water treatment are being focused in a brief and narrative way.

1.2 Redox reactions of transition metal complexes

An enormous number of studies unfolded the characteristics and effect of the structural geometries on the kinetics and mechanisms of the redox reactions of various transition metal complexes [8–25]. The literature review helped to summarize that the redox reactions of the transition metal complexes undergo two types of mechanisms. These types are classified as the *outer-sphere and inner-sphere mechanisms*, which lead the electron transfer processes of the transition metal complexes.

1.3 Schematic representation of the mechanistic pathways

The fundamental distinction between the two mechanistic routes of electron transfer is the simplicity of the outer-sphere mechanism over the inner-sphere mechanism. The outer-sphere redox reactions are simple in nature and undergo electron transfer in a very simple way. The outer-sphere mechanism is further classified into the self-exchange and cross-exchange reactions. This classification is based upon the oxidation state of coordination compounds. In the self-exchange reactions, the same coordination compounds with different oxidation states reduce and oxidize each other. However, in the cross-exchange reactions, different coordination compounds with either of the same and/or different oxidation states or numbers reduce and oxidize each other in the vicinity. However, in the inner-sphere mechanism of electron transfer, the substitution of ligand or atom prior to electron transfer plays a key role. The difference between the two mechanisms is represented in **Figure 1** [13].

One cannot easily propose the operated mechanism of electron transfer under specific cases beside the simple and apparent difference between the two reaction pathways. There are two reasons for this. It may usually be possible to suppose without any doubt that the inner-sphere mechanism is operating the electron transfer process in favorable cases, but in many reactions where the reactants or the products and/or both of them are substitution labile, the mechanism through the inner-sphere process becomes suspected. In such reactions, the exact nature of the real reacting entities that are taking part in the reactions and the products which form initially becomes impossible to recognize without proper experimental and technical treatments. The other reason for ambiguity in recognizing the reliable electron transfer mechanism appears when the nature of the outer-sphere mechanism is considered, which does not need any re-arrangement of the structure of the reacting entities rather it only needs the transfer of an electron between the oxidizing

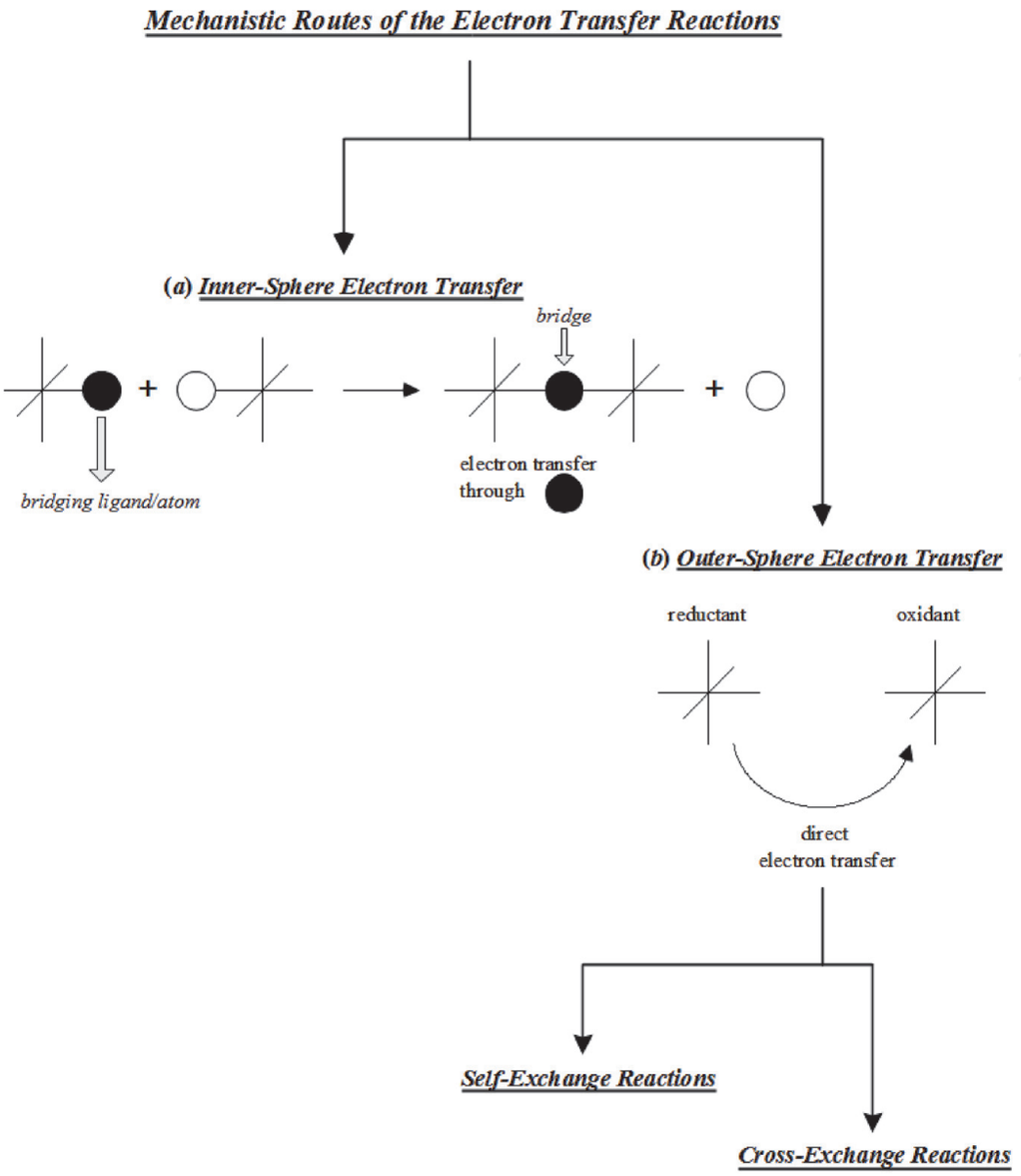

Figure 1.
Schematic representation of the redox mechanism. (a) The inner-sphere mechanism. (b) The outer-sphere mechanism.

and the reducing agents. To suggest or propose an outer-sphere mechanism one needs credible evidence with proof of unavailability of the alternative inner-sphere mechanistic pathway. Consequently, there are a large number of reactions that are clearly defined to be operated through inner-sphere mechanism. However, many reactions follow outer-sphere mechanism and an uncomfortably big number of reactions operates by inner-/outer-sphere mechanism i.e., in between [26].

1.4 Experimental approach: kinetics and mechanisms of some selected transition metal complexes of Fe(II) and Fe(III)

The redox reactions of a few selected coordination compounds of the transition metal, iron, in its two oxidation states, i.e., +2 and +3, are briefly discussed. The mixed ligand complexes such as dicyanobis(phenanthroline)iron(III) and dicyanobis(bipyridine)iron(III) oxidize hexacyanoferrate(II), acetylferrocene, and 1-ferrocenylethanol by outer-sphere mechanism [8–11, 13] in the aqueous-organic media. The effect of optimized parameters on the kinetics of the redox reactions helped to propose the operated mechanism and rate laws (**Figures 2–5**) [8, 10].

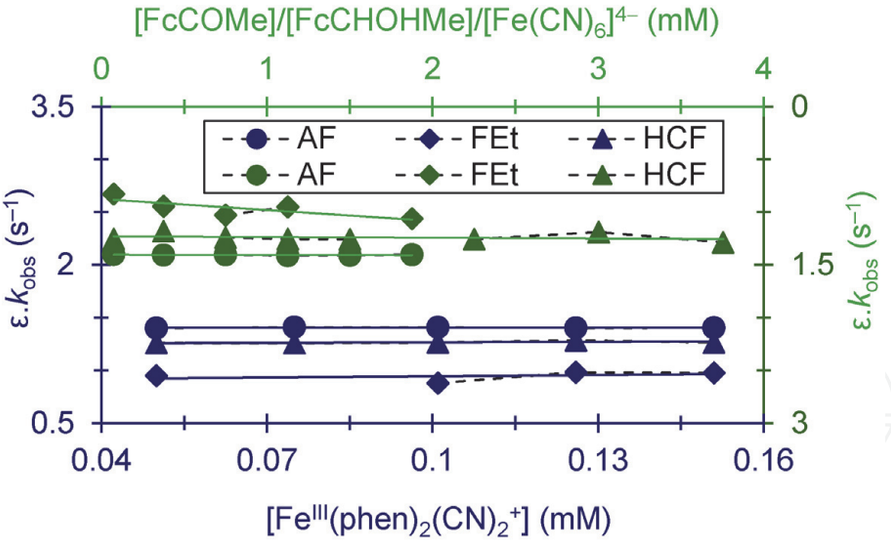

Figure 2.
Kinetics of the redox reaction between Fe(III) and Fe(II) complexes. The abbreviations; ε.K_{obs}/AF/FEt/HCF, correspond to the multiplication product of the molar absorptivity of [$Fe^{II}(phen)_2(CN)_2$] and observed zero-order rate constant/acetylferrocene/1-ferrocenylethanol/hexacyanoferrate(II).

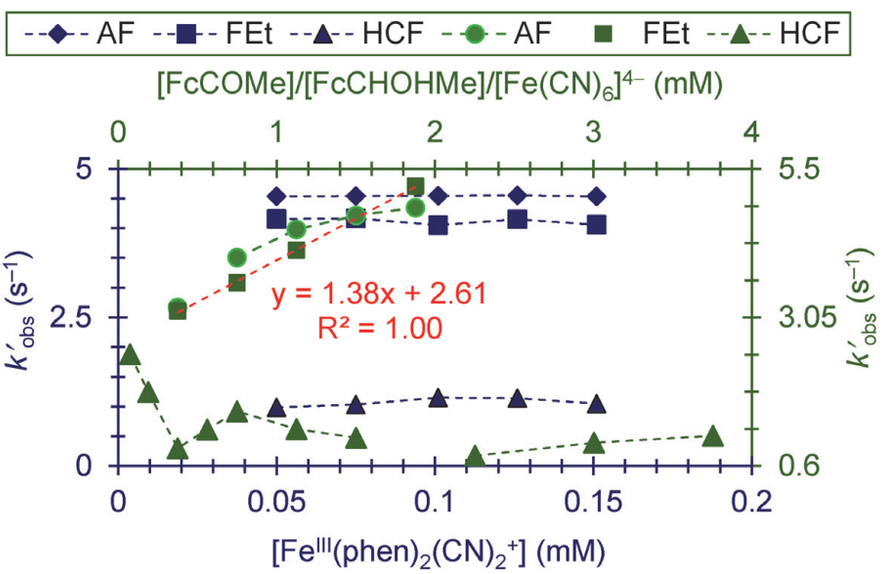

Figure 3.
Kinetics of the redox reaction between Fe(III) and Fe(II) complexes. The abbreviations; k′$_{obs}$/AF/FEt/HCF, correspond to the observed pseudo-first-order rate constant/acetylferrocene/1-ferrocenylethanol/hexacyanoferrate(II).

An outer-sphere electron transfer mechanism was proposed for each reaction because the oxidants and reductants are substitution inert and outer-sphere reactants.

Meanwhile, the oxidation of tris(bipyridine)iron(II) by ceric and bromate ions in aqueous-acidic media was reported to follow an outer-sphere mechanism with a second-order rate law (**Figures 6** and 7) [12, 14]. The iron complexes of the chelating agents such as 1,10-phenanthroline and 2,2′-bipyridine and the ligand such as cyanide ion are either good outer-sphere oxidants and/or reductants and show high stability towards ligand substitution [27, 28].

Protein as a nutrient is an important structure and is critical to aerobic life because of its control of oxygen reduction reactions. This management is crucial either to avoid or to minimize the production of destructive products such as hydroxyl radicals, peroxide, and superoxide as a result of the destructive reduction

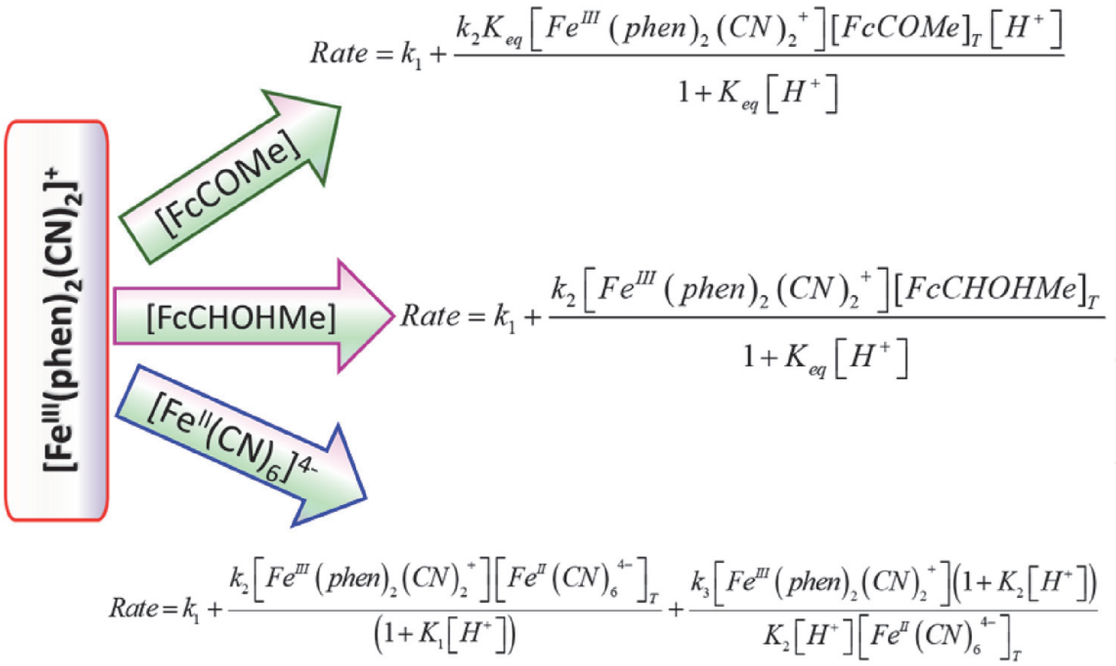

Figure 4.
Proposed rate laws: reduction of $[Fe^{III}(phen)_2(CN)_2]^+$ by acetylferrocene, 1-ferrocenylethanol, and hexacyanoferrate(II) [8].

$$-\frac{d\left[Fe(II)\right]}{dt} = k_1 + k_2\left[Fe(III)\right]\left[Fe(II)\right]_T + \frac{k_3\left[Fe(III)\right]}{K_2\left[H^+\right]\left[Fe(II)\right]_T}$$

Figure 5.
Proposed rate law: oxidation of $[Fe^{II}(CN)_6]^{4-}$ by $[Fe^{III}(phen/bpy)_2(CN)_2]^+$ [10].

$$-\frac{d\left[Fe^{II}(bpy)_3^{2+}\right]}{dt} = \frac{k K_1 K_d\left[Fe^{II}(bpy)_3^{2+}\right]\left[Ce^{IV}\right]_T\left[SO_4^{2-}\right]_a}{K_d^2 + \left[SO_4^{2-}\right]_a\left[K_d\left(K_1 + [H^+]_a\{K_2 + K_1K_3\}\right) + \left(K_4[H^+]_a\left[SO_4^{2-}\right]_a\right)(K_2 + K_1K_3)\right]}$$

Figure 6.
Proposed rate law: oxidation of $[Fe^{II}(bpy)_3]^{2+}$ by ceric sulfate in the aqueous-acidic media [13–14].

$$Rate = k_1\left[Fe(2,2'-bipy)_3^{2+}\right][HBrO_3] + \frac{k_2K_{ip}\left[Fe(2,2'-bipy)_3^{2+}\right][H_2BrO_3^+]}{(1+K_{ip}[H_2BrO_3^+])}$$

Figure 7.
Proposed rate law: oxidation of $[Fe^{II}(2,2'\text{-bipy})_3]^{2+}$ by bromate ion in the aqueous-acidic media [12].

and/or to optimize the utilization of oxygen in an effective way to transport and storage. Hemeproteins are those structures which maintain and control these oxygen reduction reactions. Such management and control of protein was surfaced by studying the mechanism of the redox reaction of aquopentacyanoferrate(II) ($[Fe^{II}(CN)_5H_2O]^{3-}$) with coordinated dioxygen of human oxyhemoglobins (HbO_2) [29]. This reaction yielded hydrogen peroxide (H_2O_2) and aquomethemoglobin (metHb•H_2O) and the oxidation product of aquopentacyanoferrate(II), i.e., $[Fe^{III}(CN)_5H_2O]^{2-}$. The reaction was found to undergo overall second-order

kinetics with a first order in each oxidant (HbO_2) and reductant ($[Fe^{II}(CN)_5H_2O]^{3-}$), respectively. The results declared that the structures of the reactants such as protein and external donor control the kinetics of the electron transfer with an inner-sphere mechanism that involves direct electron transfer from the aquopentacyanoferrate(II) to bound dioxygen that yields peroxide, subsequently. Another study surfaced the effect of binding sites and protonation on the kinetics of the electron transfer reaction (s) of blue copper proteins [30]. The oxidants with different binding sites such as $[Co^{III}(4,7\text{-DPSphen})_3]^{3-}$, $[Fe^{III}(CN)_6]^{3-}$, and $[Co^{III}(phen)_3]^{3+}$ were used to oxidize parsley plastocyanin. In each reaction, regardless of the binding sites, and prior to electron transfer, a strong association between protein and complex occurs. The variation in the binding sites varied the reduction potential and affected the rate of electron transfer, consequently. The reductant (plastocyanin) is a copper protein that consisted of type 1 copper, which is involved in electron transport from photosystem II to photosystem I at the surface of the thylakoid membrane. A single copper here utilizes oxidation states I and II. The structure of poplar plastocyanin PCu^{II} contains Cu(II) coordinated with two histidines, one cysteine, and one methionine in a distorted tetrahedral arrangement.

It has always been of interest to probe the details of the transfer of electron(s) and proton(s) because of successfully unveiling strategies of energy conversion in both of the fields, biology and chemistry. The energies as well as mechanism are strongly influenced by the coupling of electron and proton transfer. This defines the need to build up multiple redox equivalents to carry out those reactions that involve multielectrons. This also explains those mechanistic pathways through which electron and proton transfer occur simultaneously to avoid intermediates of high energy [31]. The theoretical background of the proton-coupled electron transfer reactions in solutions and proteins and electrochemistry was reviewed and discussed [32]. The theoretical treatment was based on the calculations of multistate continuum theory wherein the solvent provides dielectric continuum, the solute is treated as a multistate valence bond model, and quantum mechanical approach is used for transferred proton or hydrogen nucleus. The rate expression of electronically nonadiabatic electron transfer and proton-coupled electron transfer depends upon the reorganization energies of solute (inner-sphere) and solvent (outer-sphere) and also upon electronic coupling. For proton-coupled electron transfer, this is the average of the proton vibrational wave functions of the reactants and the products. The compensation of the smaller outer-sphere solvent reorganization energy for proton-coupled electron transfer by the larger energy needed to coupling for electron transfer appears with a similar rate for both electron transfer and proton-coupled electron transfer in calculations. A comparative theoretical study supported the reviewed outcomes through the proton-coupled electron transfer, single proton transfer, and single electron transfer reactions in iron bi-imidazoline complexes [33].

1.5 Advanced oxidation processes for water treatment

The oxidation of organic compounds by a number of oxidants either of inorganic nature or organic nature has been of interest. These redox reactions are usually catalyzed by transition metals. The kinetics of the oxidation of pyridinecarbaldehyde isonicotinoyl hydrazone to isonicotinoyl picolinoyl hydrazine was studied, and the mechanism was proposed in the view of results obtained in aqueous solution [34]. The reaction was catalyzed by iron(III). Advanced oxidation processes (AOPs) are used to remove pollutants/contaminants such as organic and inorganic compounds from water and wastewater by oxidation of these unwanted compounds. The process involves a number of chemical reactions consisting of

oxidants such as ozone (O_3), hydrogen peroxide (H_2O_2), and UV light with the addition of catalysts that may lead to yield hydroxyl radical ($^{\bullet}OH$) which degrades such pollutants, dyes and organic compounds, for example [35–40].

2. Conclusion

This concise review of the redox reactions and their applications surfaced the crucial role of redox processes. The importance of redox processes is undoubtedly tremendous. The applications encompass energy production, technological development to treat and maintain water resources, and advances in materials chemistry. These advances may lead the life to its standard in an economic and cost-effective way. Redox reactions are also an important facet of biological and biochemical world to carry out life and its routine practices. For example photosynthesis, respiration and digestion are among the common ones. Precisely, we can sum up with one sentence that "redox" is basically the key to sustaining life on this planet.

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