Introduction
INTRODUCTION

Electron transfer reactions have long been a central focus of mechanistic inorganic chemistry [1-12]. This interest stems partly from the fact that many transition metal complexes are versatile redox reagents. The wide range of oxidation states available over a comparatively narrow energy range often makes electron transfer reactions both thermodynamically and kinetically controlled.

Oxidation - reduction reactions between simple metal complexes have been extensively studied by inorganic chemists. The earliest contribution to literature in the field was a review by Taube [13]. The field of electron transfer reactions has grown enormously, both in chemistry and biology. Inorganic redox reactions are also of primary importance in biological systems. Indeed some of the most elegant work and intriguing data come from the area of inorganic biochemistry [11, 14-18].

Over the last two decades, a guiding principle for work on electron transfer has been the classical theory of electron transfer as developed by Marcus [19 -22], Hush [23,24] and others [25,26]. A number of excellent reviews and monographs on this work are available [4, 8-12]. However, within the past few years, increased theoretical and experimental studies have focused on non-classical aspects of electron transfer reactions, e.g. electron tunneling reactions [25-47].
Electron transfer processes are responsible even for the most fundamental of simple molecular transformations. This chapter will be confined to a survey of electron transfer reactions, involving organic and inorganic substrates.

All chemical reactions involve the transfer of electron, atom or group or energy transfer processes. Energy transfer reactions may also involve oxidation-reduction processes. The redox system consisting of an oxidant and reductant is said to form a redox couple. The driving force responsible for a redox process is the difference in the potential between the oxidant and the reductant.

The redox reactions may be classified in to two categories: (i) reactions involving simple electron transfer processes and (ii) reactions involving breakage and formation of covalent bonds.

The following reactions,

\[ \text{Fe}^{2+} + \text{Fe}^{3+} \text{ (exchange reaction) } \longrightarrow \text{Fe}^{3+} + \text{Fe}^{2+} \quad (1) \]

\[ \text{Fe}^{3+} + \text{Cu}^{+} \longrightarrow \text{Fe}^{2+} + \text{Cu}^{2+} \quad (2) \]

\[ \text{Fe}^{2+} + \text{Ce}^{4+} \longrightarrow \text{Fe}^{3+} + \text{Ce}^{3+} \quad (3) \]

come under the first category and such electron transfer reactions are limited in number \([7,8]\). Experimental and theoretical work in the electron - transfer
reactions have distinguished two types of mechanisms operative: (a) outer-sphere electron transfer and (b) inner-sphere electron transfer.

The early experiments in the electron transfer field were on "isotopic exchange reactions" (self exchange reactions) and later, "cross reactions". These experiments reflected two principal influences. One of them was the availability, after the second world war, of many radio active isotopes, which permitted the study of large number of isotopic exchange electron transfer reactions in aqueous solution such as depicted in reactions (4) and (5) where the asterisk denotes a radio active isotope.

\[ \text{Fe}^{2+} + \text{Fe}^{3+} \quad \leftrightarrow \quad \text{Fe}^{3+} + \text{Fe}^{2+} \quad \text{-------- (4)} \]

\[ \text{Ce}^{3+} + \text{Ce}^{4+} \quad \leftrightarrow \quad \text{Ce}^{4+} + \text{Ce}^{3+} \quad \text{-------- (5)} \]

The other factor involved in the growth of electron transfer field was the introduction of new instrumentation, which permitted the study of the rates of rapid chemical reactions. Simple electron transfer reactions are frequently rather fast compared to many reactions that involve breaking of chemical bonds and forming of new ones.

1.1 The Phenomena of Electron transfer reactions

Electrons are transferred from the reducing agents to the oxidizing agents in the actual oxidation-reduction processes. This leads to the following definition. Oxidation is the process, which results in the loss of one
or more electrons by atoms or ions. Reduction is the process, which results in the gain of one or more electrons by atoms or ions. An oxidizing agent is one that gains electrons and is reduced. A reducing agent is one that loses electrons and is oxidized. In all oxidation-reduction processes (or redox processes) there will be a reductant undergoing oxidation and an oxidant undergoing reduction. Since the two reactions are complementary to each other, one cannot take place without the other.

1.2 Classification of electron transfer reactions

All electron transfer reactions involve changes in the oxidation states of the reacting partners; some electron transfer processes are attended also by the transfer of atoms or groups from one center to another. The coupled electron and atom transfer reactions involve a certain transition state with special features, where often the electron donor and acceptor molecules are bridged by the groups being transferred. There are also reactions involving electron transfer through space without the mediation by any bridging group. Therefore, for the sake of convenience, electron transfer processes can be classified as "outer sphere" and "inner sphere" reactions [22,23].

In the outer sphere mechanism, each complex retains its own full coordination shell and the electron must pass through both. This, of course, is a purely formal statement, which does not imply that the "same" electron leaves one metal atom and arrives at the other. In the case of inner sphere
mechanism, the two reactants form an intermediate in which at least one ligand is shared, that is, the ligand belonging simultaneously to both coordination shells.

In some cases a reaction may proceed partly by each type of path. A documented example is

\[ V^{2+}(aq) + VO^{2+} \rightarrow 2 V^{3+}(aq) \]  

where at \(-25^\circ C\), an outer sphere path accounts for one-third of the product and an inner sphere path via a \([VOV]^4+\) intermediate accounts for the rest.

1.3 Outer sphere reactions

In this mechanism, direct transfer of an electron occurs. For this process to occur there is a critical requirement given by Franck-Condon principle which states that there can be no appreciable change of atomic arrangement during the time of an electronic transition.

\[ [Fe^{2+}(CN)_6]^4+ + [Fe^{3+}(CN)_6]^3- \rightarrow [Fe^{3+}(CN)_6]^3- + [Fe^{2+}(CN)_6]^4+ \]  

Ferrocyanide ion  Ferricyanide ion

The above reaction is fast and there is no heat change with reaction, since the same product is formed after electron transfer. When both the reactants are substitution-inert as in the present case, the close approach of
the metal atoms is impossible and hence the electron transfer takes place by
tunneling or outer sphere mechanism. Outer sphere electron transfer
reactions are more rapid for complexes containing ligands such as o-
phenanthroline and CN$^-$ ion than for corresponding complexes with ligands
like H$_2$O or NH$_3$.

Outer sphere exchange reactions between complexes having
different metal ions with different oxidation states, for example [Os$^{II}$(bpy)$_3$]$^{2+}$
[Mo$^{V}$(CN)$_8$]$^{3-}$ are usually faster than those between the complexes of the
same metal with different oxidation states. This means that, for such
reactions, the structure of the transition state is more like that of the
reactants and consequently the activation energy is decreased and the rate
is increased. The following reactions are some examples for outer sphere
transfer processes.

\[
\begin{align*}
[\text{Fe(CN)}_6]^{4-} + [\text{Mo(CN)}_8]^{3-} & \rightarrow [\text{Fe(CN)}_6]^{3-} + [\text{Mo(CN)}_8]^{4-} \quad (8) \\
[\text{Fe(H}_2\text{O)}_6]^{3+} + [\text{Fe(H}_2\text{O)}_6]^{2+} & \rightarrow [\text{Fe(H}_2\text{O)}_6]^{2+} + [\text{Fe(H}_2\text{O)}_6]^{3+} \quad (9)
\end{align*}
\]

1.4 Inner sphere reactions

In this type of reactions, a ligand is intimately involved in the transfer
of the electron from one metal into another. The first example of this type of
mechanism was provided by Taube and Co-workers [24]

\[
\begin{align*}
[\text{Co(NH}_3)_5\text{Cl}]^{2+} + [\text{Cr(H}_2\text{O)}_6]^{2+} & \rightarrow [(\text{NH}_3)_5\text{Co-Cl-Cr(H}_2\text{O)}_5]^{4+} + \text{H}_2\text{O} \quad (10) \\
[(\text{NH}_3)_5\text{Co-Cl-Cr(H}_2\text{O)}_5]^{4+} & \rightarrow [(\text{NH}_3)_5\text{Co}]^{2+} + [\text{Cr(H}_2\text{O)}_5\text{Cl}]^{2+} \quad (11)
\end{align*}
\]
The five coordinate Cobalt (II) species presumably immediately picks up a water molecule to fill its sixth coordination position and it is so labile and hydrolyses to \([\text{Co(H}_2\text{O)}_6]^{2+}\) rapidly.

If the bridging ligand contains more than one atom, the thermodynamically favoured isomer may not be the product obtained. The geometry of the bridge may result in a linkage isomer (remote attack) of the most stable product.

\[
[(\text{NH}_3)_5\text{Co(CN)}]^2^+ + [\text{Co(CN)}_5]^3^- \rightarrow [---\text{Co}≡\text{N}-\text{Co} ...]
\]

\[
[(\text{NH}_3)_5\text{Co}]^{2+} + [\text{CN}-\text{Co(CN)}_5]^3^- \hspace{1cm} (12)
\]

In at least one case [48] both linkage isomers form either through remote attack or through adjacent attack. In every redox process, the transfer of electron occurs and thereby the molecules either take up or donate one or more electrons when the energy necessary for the transfer is supplied (by any means like electromagnetic radiation, thermal, ion bombardment etc).

### 1.5 Inorganic peroxides as electron transferring agents

The following three inorganic peroxides are well known for their redox reactions [49-51] with various organic and inorganic compounds

- \(\text{H – O – O – H}\) Hydrogen peroxide \(E^0 = 1.77\) V
- \(\cdot\text{O}_3\text{S – O – O – SO}_3\cdot\) Peroxodisulphate \(E^0 = 2.01\) V
- \(\cdot\text{O}_3\text{S – O – O – H}\) Peroxomonosulphate \(E^0 = 1.82\) V
Peroxides are potentially electron acceptors and the ease with which they effect oxidation is due to the presence of peroxide linkage, -O–O-. The repulsion between electron pairs on the adjacent oxygen atoms of the peroxo bond makes the bond energy to be only \(\sim 138.07 \text{ kJ mol}^{-1}\).

On the basis of the mode of cleavage of the peroxide bond, the redox reactions involving the peroxides can be classified into two types:

1. reactions involving homolytic cleavage leading to the formation of free radicals as the intermediate.

For example, \(\text{S}_2\text{O}_8^{2-} \rightarrow 2\text{SO}_4^{2-}\)

2. reactions involving heterolytic cleavage occurring by ionic mechanism to form the product.

1.6 Halogens as electron transferring agents

Electron transfer reactions and formation of charge transfer complexes between a variety of electron donors and halogens are widely documented in the literature [52,53]. In general, the oxidizing capacity of halogens is well known and they are capable of attracting a single electron from one-electron reductants. The oxidation potentials of many organic molecules are low enough to permit the oxidation by halogens and many such reactions have been identified at radical cation stage [54-56].
1.7 Radical cations as electron transferring agents

Reports are available [57] on the oxidation of methyl viologen (MV) to methyl viologen radical cation (MV$^+$) by the inorganic peroxides. The simplest electron transfer reaction of a radical cation is the reaction with halide ions. In some cases, the reaction of I$^-$ with the radical cations are found to be an equilibrium process [56]. It is also known that the radical cations like perylene are reduced by Cl$^-$ and Br$^-$ [57]. Radical cations are some times used to oxidize other molecules to their radical cations by one electron–transfer [58].

\[
\begin{align*}
\text{Ar}_1 \text{H}^+ + \text{Ar}_2 \text{H} & \rightarrow \text{Ar}_1 \text{H} + \text{Ar}_2 \text{H}^+ \quad \text{-------- (14)}
\end{align*}
\]

Another very common electron transfer reaction of radical cation is the reaction with parent molecules as shown below:

\[
\begin{align*}
\text{R}_1^+ + \text{R}_2 & \rightarrow \text{R}_1 + \text{R}_2^+ \quad \text{-------- (15)}
\end{align*}
\]
These reactions have been studied by ESR technique with increasing concentration of parent species [59].

Radical cations react with a number of nucleophiles. Substitution often occurs, but there are many examples in which electron-transfer occurs either entirely or in part [60].

1.8 Reactions of hydrogen peroxide

In electron transfer reactions, hydrogen peroxide is a useful and versatile reagent and many of its reactions are available in literature [61-63]. Investigations were also made on the reduction mechanism using a semiconductor electrode (GaP) [64]. The redox potential of hydrogen peroxide ($E^0$) determined from the thermodynamic data is 1.77 V [49-51].

Redox reactions with hydrogen peroxide has been a subject of several investigations. Especially the electrochemical behaviour of $\text{H}_2\text{O}_2$ was of interest in connection with the electrochemical reduction and formation of oxygen. The reaction order in the reduction process of $\text{H}_2\text{O}_2$ on a dropping Hg-electrode was analysed [65].

In Advanced Oxidation Technology (AOT), hydrogen peroxide is used very much. The rates of degradation of different organic contaminants in water were found to be enhanced with the usage of the hydrogen peroxide [66-68]. Hydrogen peroxide traps the photogenerated electrons from
semiconductor photocatalysts more efficiently than oxygen [69] and in many highly toxic wastewater where degradation of organic pollutants is the major concern, the addition of hydrogen peroxide enhanced the degradation of pollutants effectively. The degradation of the pollutants finally leads to the formation of harmless products CO$_2$ and H$_2$O.

The solar photocatalytic mineralization of pentachlororophenol (PCP) was carried out in presence of hydrogen peroxide [70]. A total mineralization of this pollutant occurred at a faster rate than that observed in the absence of H$_2$O$_2$ [71-73]. Hydrogen peroxide could react with conducting band electrons to generate $\cdot$OH radicals, which are required for the photomineralization of organic pollutants:

$$\text{H}_2\text{O}_2 + e_{\text{cb}}^- \rightarrow \cdot\text{OH} + \cdot\text{OH} \quad \text{(16)}$$

$$\text{S (substrate)} + \cdot\text{OH} \rightarrow \cdot\text{S} - \text{OH} \quad \text{(17)}$$

$$\text{S} - \text{OH} \xrightarrow{\text{further reaction}} \text{Products.} \quad \text{(18)}$$

Azo dyes are biorecalcitrant compounds found in common industrial effluents in a wide concentration range. With the use of H$_2$O$_2$, Fe$^{3+}$ and visible radiation, azo dyes are effectively mineralized to CO$_2$ and H$_2$O [74 – 77].

1.9 Reactions of peroxomonomosulphate

Peroxomonomosulphate is found to undergo nucleophilic as well as electrophilic reactions. The nucleophilic or electrophilic behaviour of
peroxomonosulphate depends upon the pH of the medium [78] and the nature of the substrate used. It is reported that the electron population energy level of the highly occupied molecular orbitals of inorganic peroxo acids [79] increases in the order, \( \text{H}_2\text{O}_2, \text{H}_2\text{SO}_5, \text{H}_2\text{S}_2\text{O}_8 \), i.e., the nucleophilic character depends upon the highly occupied molecular orbital having the maximum number of electrons. According to the above statement, the nucleophilic character of peroxomonosulphate is in between \( \text{H}_2\text{O}_2 \) and \( \text{H}_2\text{S}_2\text{O}_8 \). The electrophilic character may be due to its lowest unoccupied molecular orbital than hydrogen peroxide and peroxodisulphate. The lowest unoccupied molecular orbital energy level is in the order of \( \text{H}_2\text{SO}_5 < \text{H}_2\text{O}_2 < \text{H}_2\text{S}_2\text{O}_8 \) and hence compared with the other two peroxides, peroxomonosulphate is more electrophilic. It is also inferred that there is intramolecular hydrogen bonding present in the peroxomonosulphate(\( \text{HSO}_5^- \)) i.e., the hydrogen bonding between -S=O and H-O-O- groups.

The standard electrode potential (\( E^0 \)) of PMS is reported to be 1.82 V [80] for the reaction,

\[
\text{HSO}_5^- + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HSO}_4^- + \text{H}_2\text{O}
\]

This high potential suggests the feasibility of PMS as a powerful oxidant and is brought out by its ability to oxidize many inorganic [81] and organic [82] compounds. A concise summary of the reactions involving peroxomonosulphate is given below.
1.10 Thermal decomposition of peroxomonosulphate (PMS)

Ball & Edwards [83] have investigated the thermal decomposition of PMS in aqueous solution. PMS was found to undergo both spontaneous as well as catalytic decomposition and the latter process was found to be eliminated by the addition of EDTA. The products of thermal decomposition were identified as oxygen and sulphate ion.

The Baeyer-Villiger reactions of Caro's acid (H$_2$SO$_5$) (PMS) with ketones to produce esters in alcoholic medium are usually conducted in acidic media since the ketone catalyzed decomposition of peroxomonosulphate was predominant in weakly alkaline solution [84]. Aqueous HSO$_5^-$ is reported to be catalytically decomposed to O$_2$ and HSO$_4^-$ by the dual catalysts Ag$^+$ and S$_2$O$_8^-$ [85].

1.11 Radiolytic chain decomposition of peroxomonosulphuric acid

Hart [86] has used a mixture of H$_2$S$_2$O$_8$, HSO$_5^-$ and H$_2$O$_2$ in the radiolytic decomposition of formic acid and has stated that peroxomonosulphuric acid is more reactive in the chain decomposition than peroxodisulphuric acid. Pulse-radiolytic studies [87] have shown that the reaction of e$^-$_aq with PMS takes two different courses,

\[
\begin{align*}
\text{HSO}_5^- + e^-_{aq} & \rightarrow \text{SO}_4^{2-} + \cdot \text{OH}^- \quad (20a) \\
\text{SO}_4^{2-} + \cdot \text{OH}^- & \rightarrow \text{HSO}_5^- + e^-_{aq} \quad (20b)
\end{align*}
\]
generating *OH radicals at a rate four times greater than that of SO₄²⁻. Moreover peroxomonosulphate was found to react with *OH relatively rapidly while S₂O₈²⁻ did not react with *OH radicals. A detailed study of the radiolytic chain decomposition revealed that G(-PMS), the amount of peroxomonosulphate decomposed for 100 eV energy absorption, increased from 10 at pH 1 to 60 at pH 12 in nitrogen saturated solution. The G values were found to be always higher for the N₂O saturated solution than that saturated with N₂. It was inferred that both e⁻aq and *OH were efficient in effecting the decomposition of peroxomonosulphate. The formation of SO₅⁻ and SO₄²⁻ as the radical products was identified by optical pulse radiolysis and O₂ as the molecular product identified by mass spectrometry.

1.12 Photochemical reactions

1.12.1 in-situ-photolysis esr-investigation of of peroxomonosulphate

An in-situ-photolysis-ESR-investigation of peroxomonosulphate was carried out [88] with light of 253.7nm wavelength, in aqueous solution in the pH range 1 to 8. The primary radical products, SO₄²⁻ and OH⁺ formed by the homolytic splitting of peroxomonosulphate,

\[
\text{HSO}_5^- \xrightarrow{h\nu} \text{SO}_4^{2-} + \text{OH}^+ \quad (21)
\]

were identified by spin-trapping agents, such as fumaric and maleic acids [89,90]. The coupling constants and the g values of the radicals (SO₄²⁻-adduct and OH⁺-adduct) were found to be in good agreement with the ESR
parameters of the radical adducts of fumaric and maleic acids with $\text{SO}_4^{2-}$ and $\text{OH}^+$ which are formed by uv photolysis of $\text{S}_2\text{O}_8^{2-}$ and $\text{H}_2\text{O}_2$ respectively. The formation of $\text{SO}_5^{2-}$ as a secondary radical product was also suggested due to the reactions,

\[
\begin{align*}
\text{HO-OSO}_3^- + \text{OH}^+ & \rightarrow \text{^\*O-OSO}_3^- + \text{H}_2\text{O} & \text{(22)} \\
\text{HO-OSO}_3^- + \text{SO}_4^{2-} & \rightarrow \text{^\*O-OSO}_3^- + \text{HSO}_4^- & \text{(23)}
\end{align*}
\]

1.12.2 Flash Photolysis of Peroxomonosulphate

It was reported [91] that sulphate radical anion and hydroxyl radical were produced by the flash photolysis of peroxomonosulphate and the sulphate radical formed was found to react with carbonate and bicarbonate anions to produce long-lived carbonate radical anion. Unsaturated monomers intercepted sulphate radical and the corresponding decrease in the absorption of carbonate radical anion at 600-630 nm suggested a tool for the study of all components of water-soluble or emulsion polymerization systems. The concentration of solute required to quench the reaction was said to be a measure of the rate constant for the interaction with sulphate radical anion. Rates of interaction for sulphate radical anion with unsaturated molecules were correlated with their ionization potential.

1.12.3 Photochemical decomposition of peroxomonosulphate in the presence and absence of isopropanol

Photolysis of peroxomonosulphate in aqueous solutions in presence and absence of 2-propanol under deaerated conditions, in the pH range 2.1-
9.0 was carried out [92] with 253.7 nm radiation. The Photochemical disappearance of PMS in presence or absence of 2-propanol at 25°C was found to obey an overall first order rate, \(-d[PMS]/dt = k_\Phi[PMS]\). In the absence of 2-propanol, the quantum yield, \(\Phi\), for the decomposition of PMS was found to depend upon the concentrations of PMS at \([PMS] \leq 2 \times 10^{-2} \text{ M}\) and is independent of concentration at \([PMS] > 2 \times 10^{-2} \text{ M}\). A maximum quantum yield, \(\Phi\), 1.18 was observed for the decomposition of PMS at \([PMS] = 6 \times 10^{-2} \text{ M}\) at pH 3.5 in the absence of 2-propanol. The \(\Phi\) in the presence of 2-propanol was found to be 3.03 at \([PMS] = 1 \times 10^{-2} \text{ M}\) and 4.45 at higher concentration of PMS. The proposed mechanism involves a chain mechanism to explain the quantum yields observed in this investigation.

1.13 Reactions involving inorganic substrates

Oxidation of halide ions with peroxomonosulphate was reported [93]. Peroxomonosulphate oxidizes halide ions to free halogens at markedly different rates. The reaction is found to be instantaneous with iodide, rapid with bromide and slow with chloride ions. Stopped flow transmittance method was used for following the oxidation of iodide ions [94] by peroxomonosulphate in aqueous solution at an ionic strength of 0.2 mol dm\(^{-3}\). A polar mechanism involving a nucleophilic attack by \(I^-\) on the external peroxidic oxygen leading to breaking of the oxygen-oxygen bond is proposed. Oxidation of nitrite ion [95], Chlorite ion [96] by peroxomonosulphate were carried out. The latter reaction was performed in the pH range 4.6-7.0 in phosphate buffered media, to minimize the self-
decomposition of ClO₂⁻ and peroxomonosulphate. The reaction was found to follow a total second order, first order each with respect to [HSO₅⁻] and [ClO₂⁻] and it was also observed that the reaction rate was unaffected in the pH range 4.6-7.0. The mechanism given is based on the nucleophilic attack by chlorine of ClO₂⁻ on the outer peroxide oxygen of the peroxomonosulphate. It is stated that ClO₂⁻ is a better nucleophile towards oxygen than Cl⁻ due to the "α-effect".

The reaction of thiocyanate [97] with peroxomonosulphate was found to be fast and hence the rate of reaction was measured by a Stopped flow conductance method, at pH 2 and 3.6. The reactants were found to be in equilibrium with intermediates, which decomposed to give sulphate, cyanide, cyanate and sulphur dicyanide as the products. The product proportions were dependent upon the pH and the ratio of the reactant concentrations.

Oxidation of Oxovanadium and peroxovanadium complexes were investigated by Thompson [98,99]. The reaction between HSO₅⁻ and VO²⁺ indicated the operation of a free radical mechanism involving SO₄⁻ radical as the intermediate. Oxidation of hypophosphite was carried out in acidic medium [100]. There was no detectable reaction occurring in the absence of H⁺, however the variation of [H⁺] did not affect the rate. This is explained as due to the complete protonation of hypophosphite even at the lowest H⁺ concentration. The reaction was found to obey a total second order, first order each with respect to [PMS] and [hypophosphite].
Oxidation involving azide and azidopentamminechromium(III) was carried out with peroxomonosulphate [101]. In the oxidation of azide, N₃⁻ was found to be the reactive species in acidic solution even though HN₃ is the predominant form. Cobaltous and ferrous complexes have been oxidized by peroxomonosulphate and the kinetics were followed by spectrophotometry [102]. Although the oxidation of cobaltous complexes are similar to those of H₂O₂ as oxidant, PMS is found to be a better reagent than H₂O₂ and produces a color of greater stability. As the cobaltic complexes formed are found to be very stable in acid medium, it is possible to separate them from other metals. The kinetics of oxidation of tris (1,10-phenanthroline) iron (II) sulphate and tris (2,2'- bipyridyl) iron (II) sulphate complexes have been carried out [103] in acidic, neutral and alkaline (pH = 9.0) media, spectrophotometrically by following the disappearance of the complexes at 510 nm (phenanthroline complex) and 525 nm (bipyridyl complex). Both the complexes are found to be oxidized by a first order process, first order with respect to [complex] and zero order with respect to [PMS] at all pH values, except the oxidation of [Fe(phen)₃]²⁺ at pH = 3.0 which obeys a total second order, first order each with respect to [complex] and [PMS].

1.14 Reactions involving organic substrates

A number of organic substances were used for the oxidation by peroxomonosulphate. Ogata and Tabushi have carried out [104] the kinetics of oxidation of dimethylaniline in aqueous solutions at various pH and
temperatures. Oxidation of ketones were also investigated [105]. Reports are available on the oxidation of DMSO, glycine, aniline, substituted aniline and amino acids [106-108]. Oxidation of aromatic aldehydes [109,110], aliphatic and the aromatic ketones were investigated [111]. In all the above reactions, a total second order kinetics was observed, first order each with respect to [PMS] and [substrate].

Free radical polymerization of water soluble acrylic monomers, with PMS as initiator has been studied extensively in aqueous media [112]. The efficiency of peroxomonomosulphate as a water soluble initiator for vinyl polymerization in the presence or the absence of reducing agents was investigated [113-115]. Vinyl polymerization of acrylonitrile initiated by peroxomonomosulphate with thiols, thioglycolic acid and ascorbic acid have been investigated [116]. It was inferred that in all the above polymerization reactions the percentage conversion of monomer increased with increase in time and temperature and a steady state was reached at approximately in 30 minutes. Free radical nature of the reaction was evident from the very high inhibiting effect of dissolved oxygen. Reports are also available in literature that water soluble initiators could be effectively used for bulk or solution polymerization, if they were used in conjunction with certain phase transfer agents like quarternary ammonium salts (Q’X’) [117,118].

1.15. Reactions of peroxodisulphate

The availability of selective oxidants for organic compounds and of simple sources of radicals for the use of selective syntheses are of
obvious importance to research in organic chemistry. Peroxodisulphate in several cases fulfills both requirements. Peroxodisulphate is one of the strongest oxidizing agents; the standard redox potential is estimated to be 2.01 V. Thermal, photochemical and radiolytic, reactions of $S_2O_8^{2-}$ provide the radical anion $SO_4^{2-}$, which appears to be a very effective electron transfer oxidizing agent.

The oxidation of many organic and inorganic substrates by peroxodisulphate were reported and have been reviewed by Wilmarth and Haim [119] and by House [120]. Oxidation of thiols to the corresponding disulfides and sulfoxides has been extensively investigated [121-127]. The kinetics and mechanism of reaction between aromatic amines and PDS have been studied [128,129]. Various oxidations effected by PDS in acetic acid medium were reported [130-133].

Oxidation of a variety of organic compounds, including alcohols, aldehydes, ketones, hydroxyl acids, phenols and amines were reported. Many peroxodisulphate oxidations are catalysed by silver ions [134-137]. With the majority of inorganic substrates, such oxidations are first order with respect to both peroxodisulphate and silver ion. The uncatalysed reactions of peroxodisulphate with ethylene glycol, glycerol and sorbitol were also investigated [138].
Kinetics of oxidation of 2,2-azinobis-(3-ethylbenzothiazole-6-sulphonate) (ABTS) was investigated [139]. The initial reaction between ABTS and $\text{S}_2\text{O}_8^{2-}$ generates very reactive $\text{SO}_4^{-}$ and ABTS$^+$, both of which undergo further reaction to form products. Spectroscopic stopped flow techniques have been adopted in this investigation as in the case of benzidine oxidation [140]. Fast kinetics of the formation and decay of the radical cations from 2,2-azinobis-(3-ethylbenzothiazole-6-sulphonate) (ABTS) in aqueous medium by PDS were also investigated [141].

1.16 Reactions of Ruthenium complexes

Sensitization of semiconductors by organic and inorganic dyes is found to be very much useful in solar energy conversion processes. In this respect, the role of Ru (II) complexes as photosensitizers in semiconductor photocatalysis is found to be highly promising. Photoexcitation of such Ru (II) complexes transfer electrons to semiconductors thereby effecting the conversion of light energy to photopotential or valuable fuel production such as hydrogen [142].

Homogeneous systems are convenient to understand the basic catalytic aspect of molecular catalysts. A few ruthenium complexes have been reported which can evolve oxygen from water in homogeneous system. Water oxidation catalysis by ammine coordinated ruthenium complexes was investigated in a homogeneous aqueous solution to evaluate the influence of structure on their catalytic activity and mechanism [143-148].
As far as the $[\text{Ru(bpy)}_3]^{2+}$ is concerned there are numerous reports available [149] especially on the role of it as solar harvesting unit. Recently $[\text{Ru(bpy)}_3]^{2+}$ and some of its polymer bound complexes have been investigated for visible light conversion to electricity [150]. The photochemical reactions of peroxodisulphate with $[\text{Ru(bpy)}_3]^{2+}$ have been individually reported by Boletta [151] and Gratzel [152]. Irvine has reported [153] the slow thermal oxidation of $[\text{Ru(bpy)}_3]^{2+}$ by peroxodisulphate. Venkatasubramaniam et al [154] made an investigation on the oxidation of tris(2,2′-bipyridyl)ruthenium complex with peroxomonosulphate and peroxodisulphate.

Kinetics of reduction of peroxodisulphate ion by $[\text{Rubpy}_3]^{2+}$ in aqueous solutions were studied under various conditions of temperature and ionic strength. Under equivalent conditions this reaction proceeds some 5,000 times faster than the peroxodisulphate oxidation of $[\text{Os(bpy)}_3]^{2+}$ and it was suggested that this arose from the difference in redox potentials of the $[\text{Ru(bpy)}_3]^{3+}/[\text{Ru(bpy)}_3]^{2+}$ and $[\text{Os bpy}_3]^{3+}/[\text{Os (bpy)}_3]^{2+}$ [155]. Reports based on the evolution of hydrogen using dye sensitizers are also available in the literature [156].

A number of reports on quenching phenomena and photoreactivity of the strongly luminescent complex tris (2,2′- bipyridine) ruthenium(II) have appeared [157-160]. Investigations on oxidative quenching of $[\text{Ru(bpy)}_3]^{2+*}$ or
excited dyes by 1,1'-dimethyl-4,4'-bipyridinium dication (paraquat or dimethyl viologen) (PQ$^{2+}$) in the presence of oxidizable substrates such as thiols, amines and organic oxygen compounds have been carried out [161-168]. In these systems the reaction sequence generally involves quenching by electron-transfer (eq.24-27) followed by the regeneration of the starting metal complex or dye through reduction by the scavenger.

$$\text{Ru(bpy)}_3^{2+} \xrightarrow{hv} \text{Ru(bpy)}_3^{2+} \quad \cdots \quad (24)$$

$$\text{Ru(bpy)}_3^{2+} + \text{PQ}^{2+} \rightarrow \text{Ru(bpy)}_3^{3+} + \text{PQ}^{**} \quad \cdots \quad (25)$$

$$\text{Ru(bpy)}_3^{3+} + \text{Scavenger} \rightarrow \text{Ru(bpy)}_3^{2+} + \text{Scavenger}_{ox} \quad \cdots \quad (26)$$

$$\text{Scavenger}_{ox} \rightarrow \text{stable products} \quad \cdots \quad (27)$$

Thus the scavenger is consumed and the reduced form of the oxidant, in this case, the radical cation PQ$^{**}$, accumulates [163]. Several reactions involving excited-state oxidation of metal complexes such as Ru(bpy)$_3^{2+}$ or RuL$_3^{2+}$ complexes as well as metalloporphyrins generate oxidants which are certainly powerful enough to oxidize water [163,169 -172]. Gorner et al [173] have reported about the photobleaching of the excited state [Ru(bpy)$_3$]$^{2+}$ by peroxodisulphate in the presence of DNA and a series of mononucleotides, polynucleotides and purine/pyrimidine bases. Electron transfer reactions of Ru (II) complexes with various oxidizing agents like phenol, methyl viologen and certain aromatic amines have been reported [174-176]. Investigations were made on the diffusion-controlled charge transfer from excited [Ru(bpy)$_3$]$^{2+}$ into colloidal TiO$_2$ stabilized in aqueous solution by EDTA. A systematic study of the luminescence, visible light absorption,
electrochemical and photoredox properties of Cis-X₂Bis(2,2′-bipyridyl-4,4′-dicarboxylate) ruthenium (II) complexes were reported by Nazeeruddin and co workers [177].

The spectroscopic and photophysical properties of ruthenium triazole complexes were also analysed [178]. A kinetic interpretation and comparison of the electrooptical properties of Ru((LL)₂(CN)₂ and Os(LLL)₂(CN)₂ derivatized surfaces with different sacrificial electron donors were reported [179].

The photoinduced electron transfer reaction between [RuL₃]⁴⁺ (L = batho phenanthroline disulfonate) and 2,2′-azinobis(3-ethylbenzothiazoline-6-sulphonate) which are electrostatically bound to positively charged alumina coated silica particles suspended in water were studied [180]. A comparative account of the efficiency and stability of photocatalytic systems in the presence of sacrificial agents were presented. Ru (II) complexes bearing the poly pyridyl ligands were used for the spectroelectrochemical studies [181].

Recent reports [182] on Ru (II) polypyridyl complexes also indicate that these complexes are prone to recognize and react with DNA and hence are good candidates for use as therapeutic agents. Ru (II) polypyridyl complexes were being reported [183] in a worthful manner for their anti-tumor and anti-HIV activities.
During the recent past, much attention has been paid towards synthesis and characterization of organometallic compounds of ruthenium in high formal oxidation states for the possible application of such compounds in homogeneous catalysis [184]. Binding of Ru (II) polypyridyl complexes with DNA were also reported [185].
References


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