INTRODUCTION

Electron transfer is the process by which an electron moves from one atom or molecule to another atom or molecule. Electron transfer is a mechanistic description of the thermodynamic concept of redox, where in the oxidation states of both reaction partners change. Redox reactions between metal ion centers involving transfer of electron from reductant to oxidant have been studied in detail in past and also reviewed by several groups of workers.

The first electron transfer reactions that were studied self-exchange electron transfer reactions of inorganic ions in aqueous solution. The inter valence absorption of metal complexes in solution and isotope effects were used. The understanding of organic charge transfer complexes started in the late 1940’s early 1950’s with the reports of Benesi and Hildebrand (1940), who observed new absorption bands in solutions of aromatic hydrocarbons and iodine and the idea of partial charge transfer in the ground-state of Brackman. The Mulliken mode (1952) for electron-donor acceptor complexes, and the discovery of excimer formation by Forster and Kaspar in 1954 were essential steps that have led to the extensive developments in the field of electron-donor acceptor system in the last decades.

Induced electron transfer by various kinds of operations on the ligand and one such induced electron transfer reaction has been the pioneering work from Taube’s laboratory in the year 1960. The reaction which fall into this category are those in which a metal ion complex (one electron oxidizing metal ion complex) such as pentaamminecobalt(III) complex, with a bound organic ligand suffered a net two-electron oxidation initiated by the attack of an external one-electron oxidant, such as Ce(IV), Mn(III) etc, yielding a radical-cation intermediate which by an intermolecular
electron transfer reduced the internal oxidant. As the reduced from of Cobalt(III) (Viz.,), Cobalt (II), is substitution labile, if an induced electron transfer occurs in Co$^{\text{III}}$-L bond will be served at the very act of electron transfer to Co$^{\text{III}}$ bound will be served at the very act of electron transfer to Co$^{\text{III}}$ center, making the product analysis simpler and effective.

Electron transfer processes are fundamentally important to many branches of chemistry and biology. Kinetic studies are expected to provide information on how the electron transfer event is affected by the hydrophobic and electrostatic interactions in the organized media. Electron transfer processes in micellar system can be considered as models to get insight in electron transport occurring in biological phenomenon.

If the action of the external oxidant takes place independently of the internal electron transfer act, this study will be powerful tool for probing the mechanism of oxidant by the external oxidant, or whether a two electron transfer occurs (so that the bound ligand gets oxidizing without disturbing Co$^{\text{III}}$ center. Work with systems of this kind has not progressed very far but enough attempts have been made to project this apparent approach possible. In what follows, a brief survey of the earlier but limited reports on induced electron transfer reactions in Co$^{\text{III}}$-L system.

Cobalt(III) complexes, by virtue of their abundance and diversity, have played a fundamental role in our understanding of the structural, spectroscopic, and electrochemical properties of coordination compounds. We have been interested in the synthesis and micelle-forming properties of cobalt(III) complexes containing lipophilic ligands for a long time$^{1-4}$. In recent times, there are some reports from various research groups on metallo-surfactants of a various nature and their micelle forming
properties\textsuperscript{5-8}. Electron transfer in a restricted geometry system such as micelles, reverse micelles and vesicles attract a great deal of interest, because of their potential to prolong the lifetime of charge-transfer states, a goal of electron-transfer studies aiming to utilize solar energy\textsuperscript{9-10} and as molecular switches\textsuperscript{11}. We have been interested in the synthesis and micelle-forming properties of many surfactant-metal complexes for a long-time\textsuperscript{12}. The electron transfer in PentaammineCobalt(III) amino acids with Ce(IV) has been already reported\textsuperscript{13-19}. It as the diagnostic tool to find out the fraction proceeding by synchronous cleavages of N-H and C-C bonds in micelles medium\textsuperscript{20-24}.

Induced electron transfer, wherein the interaction of a one-electron oxidant with a metal complex leads to the formation of the one-electron reduced metal center, remains an intriguing mechanistic problem\textsuperscript{25}. Manganese(III) acetate dihydrate was prepared by following the procedure in the literature\textsuperscript{26} and the sample was of 99\% purity as evidenced from the estimation of the purity of a solution in acetic acid by an iodometric procedure. In the case of manganese (III) perchlorate, specific rates were evaluated spectrophotometrically from the decrease in absorbance at 380nm\textsuperscript{27}.

Surfactant molecules self-aggregate into super molecular structures when dissolved in water or oil. The simplest aggregate of these surfactant molecules is called a micelle; and the dispersion of the aggregates in water or oil is referred to as a micelles solution\textsuperscript{28-31}. Hence, micelles solutions exhibit interesting properties on addition of salts or with change in temperature. For example, the micelles solutions of cetyltrimethylammonium bromide (CTAB) become extremely viscous on addition of small quantities of sodium salicylate\textsuperscript{32-34}. Reaction kinetics can be studied in terms of fractal dimensions of the reaction medium\textsuperscript{35,36}. Micelles are known membrane mimetic system\textsuperscript{37-39} which functions in many ways.
A study of the kinetic of oxidation of cobalt(III) bound α-amino acids is important both from the mechanistic point of view and its bearing on the mechanism of amino acid metabolism. The effect of organized assemblies on the equilibrium and rates of reactions has attracted increasing attention in recent years. This interest is based on the realization that many biochemical processes proceed in a micro heterogeneous system which contains an aqueous and a lipophilic moiety. Among the biochemical functions, the redox processes, in which electron transport occurs, represent reactions of primary importance. The investigation of electron-transfer processes in micelles system has been carried out by examining properly selected reactions.

Several surfactants are able to aggregate in non-aqueous solvents to yield reverse micelles, in which the polar head groups of the surfactant monomers cluster to form a micellar core and are directed towards the centre of the assemble, and the hydrophobic tails extend outwards into the bulk organic phase. Several transition metal complexes have been used for studying electron-transfer reactions. Several transition metal complexes have been used for studying electron transfer of different environments such as micelles, vesicle, DNAs. Electron transfer in these restricted geometry systems attracts great deal of interest because of their potential to prolong the lifetime of charge-transfer states, a goal of electron-transfer studies aiming to utilize solar energy and as molecular switches. Studies on the chemistry of electron transfer reactions of cobalt(III) complexes have received a sustained high level of attention for past decades due to their relevance in various redox processes in biological systems.
Surfactant-metal complexes are a special type of surfactants, where the coordination complex, containing a central metal ion with surrounded ligands coordinated to the metal, acts as the surfactant. Like any other well-known organic surfactant these surfactant-metal complexes also from micelles at a specific concentration called critical micelle concentration (CMC) in aqueous solution. We have been interested in synthesis, micelles forming properties and electron transfer reactions of many surfactant-metal complexes for a long time\textsuperscript{64-67}.

Cationic surfactants have become important because of their bacteriostatic properties. They have been introduced into several commercial products including antiseptic agents in cosmetics and as germicides\textsuperscript{68}. Cationic surfactants have also found a wide range of applications because of their unique solution properties (e.g., detergency, solublization and surface wetting capabilities) in diverse areas such as the mining, petroleum and the pharmaceutical industries, chemical as well as biochemical research\textsuperscript{69}, and as catalysts for several organic and inorganic reactions\textsuperscript{70}. Most of the chemical reactions investigated were for simple organic and inorganic system. On the other hand, relatively few works have been carried on electron-transfer reactions for transition metal ions complexes with lipophilic ligands\textsuperscript{71-76}. We have been interested for a long time in the synthesis and micelle forming properties of many metal complexes containing lipophilic ligands (metallosurfactants)\textsuperscript{77,78}.

For decades, studies on the chemistry of electron transfer reaction of Cobalt(III) surfactant complexes have received a sustained high level of attention from the scientific community due to their relevance to various redox processes occurring in biological systems and their abilities to act as antitumor\textsuperscript{79}, anthelmintic\textsuperscript{80}, antiparasitic\textsuperscript{81}, antibiotic\textsuperscript{82} and antimicrobial agents. The study of micellar solutions is
of interest both from the point of view of basic research and applications of surfactants. A variety of experimental techniques have been used for studying the micellar system. The surfactant molecule consists of a polar hydrophilic head group and a non-polar hydrophobic tail. A variety of surfactant molecules have been synthesized. Surfactants molecules are classified as ionic or non-ionic depending on whether the head group has a net charge or not. The ionic surfactants are further classified as cationic or anionic depending on whether the head group is positively or negatively charged. CTAB is an example of a cationic surfactant and NaLS that of an anionic surfactant.

Speciation study of essential metal ion complexes is useful to understand the role played by the active site cavities in biological molecules and the bonding behavior of protein residues with the metal ion. Cobalt acts as catalysts in a variety of enzyme system functions and as coenzymes in several biochemical processes. Cobalt is essential for the production of red blood cells. In this respect its role ranges from weak ionic enzymatic cofactors to highly specific substances known as metalloenzymes.

The role of micelles is simple, but vital resulting in compartmentalization of the energy transfer partners. By binding the metal ions electrostatic alloy to the negatively charged micellar surface, their effectively concentration is substantially increased. The concentration of these counter cations in the micellar surface has been estimated to be around 3M.

In characteristic conversions involving induced electron transfer, a ligand bound to a reducible metal ion react with an external 1e oxidant, forming a metal bound radical intermediate. Internal electron transfer then achieves a net 2e oxidation of the ligand, yielding two reduced species. One derived from the ligand metal and the
other from the external oxidant\textsuperscript{86,87}. A study of the kinetic of oxidation of cobalt(III) bound \(\alpha\)-amino acids is important both from the mechanistic point of view and its bearing on the mechanism of amino acid metabolism. Recently, we have shown that a series of one and two-electron reduced heteropolyanions of the Keggin and Dawson series convert quantitatively NO and N\(_2\)O in acidic aqueous media\textsuperscript{88}. Unsubstituted and lacunary heteropolyanions, as well as the heterometal-substituted heteropolyanions of these two groups, prove active for this purpose.

The electronic structures and the interaction between manganese centers are thus of some considerable interest, and the synthesis and characterization of manganese complexes with well-defined and simple bridging ligand systems seem to be especially so. Such a transition state can be envisaged only when the C-H bond fission occurs in the slow step with hydride ion transfer. The absence of formation of Co(II) rules out the synchronous C-C bond fission and electron transfer to Co(III). Oxidation is an important process in organic chemistry and introduction of new economic and effective reagents for oxidation under mild and anhydrous conditions constitutes a standing challenge. Imidazolinium dichromate is an oxidant which is non-hydroscopic, non-photosensitive, stable yellow solid which is freely soluble in water acetic acids, N-N-dimethyl formamide etc\textsuperscript{89-91}. The little work has been done on Imidazolinium dichromate as oxidant in micellar media\textsuperscript{92,93}.

The kinetics of reduction of Co(III) complexes is free from complications arising due to reversible electron transfer, aquation, substitution and isomerisation reactions. Dieble and Taube\textsuperscript{94}, Watts et al\textsuperscript{95,96} and other researchers\textsuperscript{97} have studied the kinetics and mechanism of reduction of Co\textsuperscript{III} by Fe\textsuperscript{II} in aqueous and non-aqueous medium. Various effects on this reaction are reported\textsuperscript{98}. Besides this, many
researchers\textsuperscript{99-101} have been studying the micellar and reverse micellar effect on the rate of different types of reactions. Oxidation is an important process in organic chemistry and use of new economic and effective oxidants under mild and anhydrous conditions constitutes a standing challenge. H$_2$O$_2$ is an oxidant\textsuperscript{102-104}, which is non-hygroscopic non-photosensitive, stable yellow orange solid, freely soluble in water, acetic acid, N,N-dimethylformamide etc. only few works have been done on H$_2$O$_2$ with Cobalt(III) complexes as oxidant in micellar media\textsuperscript{105-106}. In recent years there has been a great upsurge of interest on mechanistic studies of reactions of amino acids with transition metal complexes, due to their biological relevance\textsuperscript{107-112}. Pyridinium Fluorochromate (PFC) is an efficient reagent for oxidation of primary and secondary alcohols to carbonyl compounds. A large class of organic compounds were oxidized by PFC has been reported\textsuperscript{113-117}. Since induced electron transfer in pentaamminecobalt(III) complexes of $\alpha$-hydroxyacids with various oxidants have been studied\textsuperscript{118-123}. The extent of PFC oxidation of pentaamminecobalt(III) complexes of $\alpha$-hydroxyacids in micellar medium as an oxidisable hydroxyl group is separated from carbonyl bound to Co(III) centre by a saturated fragment namely C-C bond\textsuperscript{124}.

The reaction of hydrazine’s with most oxidants give the corresponding acids\textsuperscript{125} and in some cases\textsuperscript{126} esters or amides. Thallium(III) salts are well known oxidants\textsuperscript{127} in organic synthesis. The oxidation of cyclopropane by thallium(III) acetate in acetic acid leads to cleavage of C-H bonds\textsuperscript{128}. The chemical literature has described thallium induced splitting of carbon-nitrogen bond\textsuperscript{129} no mechanistic investigation has been carried out. The effects of cyclodextrin inclusion on the kinetics and mechanism of ligand substitution\textsuperscript{130,131} and electron transfer reactions of transitions metal
complexes in aqueous solution have received considerable attention in recent years. Recently we have reported a study on the outer-sphere electron transfer reaction of some surfactant cobalt(III) complexes with Fe(II) ion. In many systems it has been observed that metal ions, through present in small amounts, may alter the kinetics and even the course of oxidation-reduction. Induced electron transfer reactions, in which a Co\textsuperscript{III}-bound organic ligand suffers a net two electron oxidation initiated by an external oxidant such as Ce\textsuperscript{IV}, yielding a carbon radical intermediate, have been studied in detail by Taube and co-workers. The cation radical formed subsequently increase an intermolecular second one-electron transfer, resulting in the reduction at the cobalt (III) center without altering the carbon skeleton of the ligand. Pyridinium hydrobromide perbromide (PHPB) has been extensively used in organic synthesis as a mild and selective bromination agent and as an oxidant, but kinetic and mechanistic aspects of its reaction have not been studied much.

Ce (IV) oxidation of Oxalatopentaamminecobalt (III) complex:

The oxidation of (NH\textsubscript{3})\textsubscript{5}CoC\textsubscript{2}O\textsubscript{4}H\textsuperscript{2+} by Ce(IV) was reported as the pioneering work on induced electron transfer reaction but the report was confined to product analyses only as the reactions were sluggish. For the consumption of one mol of Ce(IV), one mol of Cobalt(III) complex was reduced yielding Co\textsuperscript{III} and CO\textsubscript{2} quantitatively as shown in eq.1

\[
(NH\textsubscript{3})\textsubscript{5}CoC\textsubscript{2}O\textsubscript{4}H\textsuperscript{2+} + Ce(IV) + 4H\textsuperscript{+} \rightarrow Co\textsuperscript{2+} + Ce\textsuperscript{3+} + 2 CO\textsubscript{2} + 5 NH\textsubscript{4}\textsuperscript{+} ---(1)
\]

This was accounted for by a mechanism involving oxalate ion radical, formed by the reaction of the external oxidant, Ce(IV) and the bound oxalate ligand, which then by intermolecular electron transfer reduced Cobalt(III) to Cobalt(II). As the intermediate, [(NH\textsubscript{3})\textsubscript{5}Co\textsuperscript{III}C\textsubscript{2}O\textsubscript{4}], could not be trapped, the mode of electron transfer
between the external and internal oxidant through the bound organic ligand was less certain. However, Cobalt (III) would not have assisted in the oxidation process, because the rate of reaction of the complex was much slower than that of the free oxalate. Recent reports on the activation parameters of this reaction have confirmed the earlier mechanism suggested\textsuperscript{143-144}.

**Ce(IV) oxidation of Captive Trioxalatocobalt(III)complex\textsuperscript{145}:**

In aqueous H\textsubscript{2}SO\textsubscript{4} medium, Ce(IV) was reported to react directly with [Co(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}]\textsuperscript{3-}, as well as with oxalate species produced by acid-promoted decomposition of the trioxalatocomplex\textsuperscript{146}. The reaction sequence proposed suggests reduction at the Cobalt (III) center (e.g. 2 - 5)

\[
\text{Co}^{\text{III}}(\text{C}_2\text{O}_4)_3^{3-} + \text{Ce}^{\text{IV}} \underset{\text{Fast}}{\overset{\text{Fast}}{\rightleftharpoons}} \text{Co}^{\text{III}}(\text{C}_2\text{O}_4)_3^{3-} - \text{Ce}^{\text{IV}} \quad \text{-----}(2)
\]

\[
\text{Co}^{\text{III}}(\text{C}_2\text{O}_4)_3^{3-} - \text{Ce}^{\text{IV}} \underset{\text{slow}}{\overset{\text{slow}}{\rightleftharpoons}} \text{Co}^{\text{II}}(\text{C}_2\text{O}_4)_3^{2-} - \text{Ce}^{\text{III}} \quad \text{-----}(3)
\]

\[
\text{Co}^{\text{II}}(\text{C}_2\text{O}_4)_3^{2-} - \text{Ce}^{\text{III}} \rightarrow \text{Co}^{\text{II}}(\text{C}_2\text{O}_4)_3^{2-} + \text{Ce}^{\text{III}} \quad \text{-----}(4)
\]

\[
\text{Co}^{\text{II}}(\text{C}_2\text{O}_4)_3^{2-} \overset{\text{Fast}}{\rightarrow} \text{Co}^{\text{II}} + 2\text{C}_2\text{O}_4^{2-} + 2\text{CO}_2 \quad \text{-----}(5)
\]

**Induced electron transfer in 4-formylbenzatopentaammineCobalt(III) complex\textsuperscript{147}:**

When the 4-formylbenzatopentaammine Cobalt(III) ion was oxidized by Cl\textsubscript{2} or H\textsubscript{2}O\textsubscript{2} \{catalyses by Mo(VI)\}, the corresponding terephalato complex was formed as product, but when Co\textsuperscript{3+} (aq), S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-} (Catalyzed by Ag\textsuperscript{+}) or alkaline permanganate was used, the oxidation of the ligand led to reduction of cobalt(III), apparently suggesting the 2e\textsuperscript{-} oxidizing agent did not involve the cobalt(III) center, but 1e\textsuperscript{-} oxidizing agent
did. The net change for the latter class of an induced electron transfer system was represented as eg.6.

\[
[(\text{NH}_3)_5\text{Co}^{	ext{III}}-\text{O-CO}<\text{O}-\text{CO-H}]^{2+}\text{M}^{3+} + \text{H}_2\text{O} + 4\text{H}^+ \\
\text{Co}^{2+} + \text{M}^{2+} + \text{HOOC}-\text{COOH} + 5\text{NH}_4^+ \quad \text{-------(6)}
\]

As with the oxalate complex, the question as to whether the reduction of the Cobalt (III) center takes place simultaneously with that of the external oxidizing agent or whether a radical ion of finite life-time is formed was not settled by the experiments but they provided evidence for an electron transfer through the organic molecule.

**Permanganate oxidation of formatopentaamminecobalt(III) complex**

Permanganate ion oxidation of formatopentaamminecobalt (III) complex provided evidence for an intermediate formation. Both Co\(^{2+}\) and \([(\text{NH}_3)_5\text{Co}^{	ext{III}}(\text{OH}_2)]^{3+}\) were products of the reaction and the ratio in which they were formed depended on permanganate concentration. The observations were accounted for by the mechanism.

\[
[(\text{NH}_3)_5\text{Co}^{	ext{III}}\text{O}_2\text{CH}]^{2+} + \text{MnO}_4^- \longrightarrow \text{Int} \quad \text{-------(7)}
\]

\[
\text{Int} \longrightarrow \text{Co}^{2+} \quad \text{-------(8)}
\]

\[
\text{Int} + \text{MnO}_4^- \longrightarrow [(\text{NH}_3)_5\text{Co}^{	ext{III}}(\text{OH}_2)]^{3+} \quad \text{-------(9)}
\]

Through the question of identify of the intermediate was not settled an important conclusion arrived at was that an intermediate was generated by the action of the external oxidant of the substrate complex and that only after the formation of the intermediate, the choice was made between forming Co\(^{II}\) or \([(\text{NH}_3)_5\text{Co(OH)}_2]^{3+}\) as products. If cobalt(III) assisted in the oxidation of the bound ligand by the external agents, which should have been reflected in an increased rate of reaction for the ligand
complexes by cobalt(III), compared to the rate of oxidation of unbound ligand, which has not been observed in the presence reaction.

Ce (IV) oxidation of Pyridinmethanolpentaamminecobalt(III) Complex:\textsuperscript{149}

The induced electron transfer effect has been most extensively investigated with \([(\text{NH}_3)_5\text{Co}^{\text{III}}-\text{N} \overset{\text{CH}_2\text{OH}}{\cdot} \text{CH}_2\text{OH}]\), a similar system as previous one, possessing a ligand with an oxidisable group separated from the Co\textsuperscript{III} center by a conjugated fragment. When this complex is oxidized by Ce (IV), Co\textsuperscript{III} or Ag(II), probably through one-electron charge, Co\textsuperscript{II} result as one of the products; but with oxidizing agent as Cl\textsubscript{2}, H\textsubscript{2}O\textsubscript{2} (catalysed by Mn(VI)) or Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2-} in acid solution, the aldehyde, \([(\text{NH}_3)_5\text{Co}^{\text{III}}-\text{N} \overset{\text{CH=O}}{\cdot} \text{CH}_2\text{OH}]^{3+}\) is formed as the product by a two-electron transfer. With increasing concentration of Ce(IV), Pentaammine(4-Pyridinmethanol)-cobalt(III) or Pentaammine(4-Pyridinmethanol)cobalt(III) or Pentaammine(3-Pyridinmethanol) cobalt(III) undergoes oxidation yielding both, the aldehyde complexes of Co\textsuperscript{III} and (Co\textsuperscript{2+} free aldehyde) but the product ratio, \{[Co\textsuperscript{II}]/[Co\textsuperscript{III}-CHO]\} decrease, indicating again the partitioning of reaction paths. The studies also indicate that the two intermediates are formed by parallel rather than interrelated events. The reported stoichiometries of the reactions are

\[2\text{Ce(IV)} + [(\text{NH}_3)_5\text{Co}^{\text{III}}-\text{N} \overset{\text{CH}_2\text{OH}}{\cdot} \text{CH}_2\text{OH}]^{3+} \rightarrow 2\text{Ce}^{3+} + [(\text{NH}_3)_5\text{Co}^{\text{III}}-\text{N} \overset{\text{CHO}}{\cdot} \text{CHO}]^{3+} + 2\text{H}^+ \] \quad \text{-------(10)}

\[\text{Ce(IV)} + [(\text{NH}_3)_5\text{Co}^{\text{III}}-\text{N} \overset{\text{CH}_2\text{OH}}{\cdot} \text{CH}_2\text{OH}]^{3+} + 4\text{H}^+ \rightarrow \text{Ce}^{3+} + \text{Co}^{2+} + 5\text{NH}_4^+ + [\text{HN} \overset{\text{CHO}}{\cdot} \text{CHO}]^+ \] \quad \text{-------(11)}
Oxidation of α-amino acids and pentaamminecobalt(III) complexes of α-amino acids:

The Oxidation of α-amino acids by Co\textsuperscript{III} salt\textsuperscript{150} in aqueous perchloric acid yielding ammonia and the corresponding aldehyde as per the following reaction scheme. Through α-amino acids are known to form a complex with Co\textsuperscript{III}, no kinetic evidence has been provided for such a complex formation.

In the cerium (IV) oxidation of α-amino acids\textsuperscript{151} the carboxylate radical is formed in the rate-determining step, while the C-C and N-H fissions were assumed to occur in a subsequent fast step.

\[
\begin{align*}
R-CH-COOH + Ce^{IV}(so_4)_2 & \xrightarrow{\text{slow}} R-CH-COO^0 + H^+ + Ce(III) \quad -----(12) \\
R-CH-COO^0 & \xrightarrow{\text{Fast}} R-C^\parallel H-NH_2 + CO_2 \quad -----(13)
\end{align*}
\]

In the Ag\textsuperscript{+} Catalyzed peroxydisulphate oxidation of benzoylglycine the products obtained were benzoic acid, formaldehyde and ammonia\textsuperscript{152}. As the reaction mixture initiated acrylonitrile polymerization, the reaction sequence involved radicals. The stoichiometry of the reaction in aqueous medium is given by eq.14.

\[
\begin{align*}
H_5C_6-CO-NH-CH_2-COOH + 2S_2O_8^{2-} + 2H_2O & \xrightarrow{\text{Ag}^+} \\
H_5C_6COOH + HCHO + NH_3 + CO_2 + 2HSO_4^{-} + 2SO_4^{2-} & \quad -----(14)
\end{align*}
\]

Though the metal ion oxidants with α-amino acids yielding aldehyde as one of the products, N-chlorotoluene-p-sulphonamide (Chloramines-T-{CAT}) oxidation of α-amino acids seems to give the final product as the corresponding nitrile through...
the intermediacy of N-chloramines acid\textsuperscript{153}. According to Ramachandran et al the stoichiometry for the chloramines-T oxidation of threonine is

\[ \text{R'}-\text{CH-COO}^- + 2\text{RNNaCl} \rightarrow \text{R'}-\text{CN} + 2\text{RNH}_2 + \text{CO}_2 + 2\text{NaCl} \quad \text{----(15)} \]

\[ + (\text{NH}_3) \]

Also a qualitative study of the oxidation of \(\alpha\)-amino acids by potassium bromate (ie) Br(V) has been studied\textsuperscript{154} and the formation of respective aldehyde and ammonium ion has been explained with rate-determining cleavage of the N-H and C-C bonds. When potassium bromate was used as an oxidant for the cobalt(III) bound\textsuperscript{155} and unbound \(\alpha\)-amino acid, Viz, glycine from the products of Br(V)-induced electron transfer in the cobalt(III) complex (Viz, Cobalt(II), CO\textsubscript{2} and other products of the reaction) suitable mechanistic schemes have been proposed. A semi quantitative estimate of the reaction proceeding by one-electron transfer to Br(V) and cobalt(III) in a nearly synchronous manner has also been made.

**Polyoxometalates:**

Polyoxometalates (POM)\textsuperscript{156} are a class of inorganic compounds with a remarkable degree of molecular and electronic tenability that impact disciplines as diverse as catalysis\textsuperscript{157}, medicine\textsuperscript{158} and material science\textsuperscript{159}. These compounds are molecular metal oxides mainly based on V, Mo, Mn and W ions in their highest oxidation states. Because of the cluster structure, POM is especially useful as model systems for the studies of magnetic and electronic interactions. Indeed, many of these structures allow the inclusion of well-isolated clusters of paramagnetic ions with various nuclearities and definite topologies and geometries\textsuperscript{160}. On the other hand, they permit the controlled injection of electrons, giving rise to mixed-valence species in which delocalized electrons, may coexist and interact with localized magnetic
moments. In this context, they provide unique systems for the development of new theories in the mixed valence area. Some typical structural types are the Linguist\textsuperscript{161} ($\text{Mo}_6\text{O}_{19}^{2-}$, M=Mo, W), Keggin\textsuperscript{162} ($\text{XMo}_{12}\text{O}_{40}^{m-}$, X=P, Si, Co, Ni), and Dawson-Wells\textsuperscript{163}. The Keggin structure is constituted of four edge-sharing triads of $\text{MO}_6$ octahedral arranged around the X atom in such a way that the resulting species has a tetrahedral symmetry. The Keggin structure can also be viewed as formed by a $\text{XO}_4^{m-}$ clathrate encapsulated into a neutral $\text{M}_{12}\text{O}_{36}$ sphere based on corner sharing $\text{MO}_5$ square-pyramids whose apical oxygen atoms point outside the sphere\textsuperscript{164,165}. They are sometimes noted as $\text{XO}_4^{m-} = \text{M}_{12}\text{O}_{36}$.

Today the series of compounds ($\text{XMo}_{12}\text{O}_{40}^{n-}$) are known as Keggin anions. In recent review, Ketosis described the large number and important of the POM applications, which depend primarily on their redox properties, ionic charge, conductivity, etc. Most of them are related to the special ability of the Keggin framework to accept electrons without decomposing. In reality, the Keggin core is a reservoir of electrons that can undergo many electron-reduction processes\textsuperscript{166} without significantly deformation the framework.

An important property of the poly oxoetalte anions is that their identity is usually preserved by reversible redox processes, forming hetero poly blues are hetero poly browns reduction products by addition of various electrons which are delocalized over the sphere\textsuperscript{167}. Experimentally, it has been found that when the reduced species contain an even number of delocalized electrons, their spins is always completely paired, even at room temperature. This result is general and has found not only in the Keggin structure but also in the other ones. It was initially attributed to a very strong
anti ferromagnetic coupling via a multi route super exchange mechanism\textsuperscript{168}, but more recently and electron delocalization can also stabilized the singlet ground state\textsuperscript{169}.

Heteropolyoxometalates (POMs) are those anions and their derivatives made of an assembly of MO\textsubscript{6} octahedrons. These octahedrons contain a central tetrahedron, XO\textsubscript{4}, in which X is a main group element (P\textsuperscript{V}, Si\textsuperscript{IV}, Al\textsuperscript{III}, Ge\textsuperscript{IV}, etc…) or a transition metal ion (Fe\textsuperscript{III}, Co\textsuperscript{II}, Co\textsuperscript{III}, Cu\textsuperscript{I}, Cu\textsuperscript{II}, Mn etc…). Heteropolyanions involving manganese are very common and of great important both biologically and industrially. Some of the major biological roles of Mn-bound enzymes and proteins are generation of O\textsubscript{2} in photosynthesis, essentially involving splitting of H\textsubscript{2}O, and destroying the superoxide ion radical, O\textsubscript{2} (by the Mn-enzyme superoxide dismutase) formed as a product of oxidation by O\textsubscript{2} in biological systems. Manganese enzymes are also involved in diverse metabolic pathways including DNA synthesis, sugar metabolism and protein modification, to mention a few. The knowledge and information that has accumulated on the nature of such Mn containing species and their biological roles are as a result of research done mostly in the last three decades.

From the viewpoint of atmospheric chemistry, the oxides of iron, manganese and titanium are considered to be the most important as they are always present in air bone suspended particulate matter and in solid effluents like fly ash. MnO\textsubscript{2} is known to oxidize sulphur(IV) into sulphate. In suspended particulate matter, the combustion processes are likely to be major source of MnO\textsubscript{2} as such processes are known to release the metal in their highest oxidation states. In natural aqueous systems, the formation of Manganese(IV) oxides occurs mostly via the oxidation of manganese(II) and subsequent precipitation of oxides from solution, oversaturated with Manganese(III,IV), Manganese(III) and Manganese(IV) so formed are present as
sparingly soluble oxides and hydroxides, whereas Manganese(II) is in the soluble phase.

Both Manganese(II) and Manganese(IV) are important in atmospheric chemistry of pollutants in general and sulphur dioxide in particular. The role of Manganese(II) as catalyst in the autoxidation of aqueous SO$_2$ has been subject of several studies with MnO$_2$ has been studies by Bassett and Parker$^{170}$. Halperin and Taube$^{171}$, who carried out an isotopes tracer study on his heterogeneous solid-liquid system, suggested the binding of the sulphite ion at the surface of MnO$_2$ through the oxygen atom. 

Recently the MnO$_2$ catalyzed autoxidation of sulphur(IV) in buffered and unbuffered solution has been reported. Dioxygen oxidation of manganese(II) complexes to manganese(IV) is unusual but not known. Schiff base ligand formed from salicyaldehyde when coordinated to Mn(II) lead to the O$_2$ oxidation to Manganese (IV) state$^{172-175}$.

Other dimeric Mn (IV)-Mn(IV) complexes have been prepared by H$_2$O$_2$ oxidation of the manganese(III) species unlike these imines systems, the present amine system is expected to stabilized better the manganese(IV) state. The Oxygen-Evolving Complex (OEC) of photo system II (PS II) contains a $\alpha$-oxo-bridged manganese tetramer that can carry out the four-electron oxidation of water to O$_2$. In soil and sediment environments, Manganese(IV) oxide is among strongest oxidizing agents that may be encountered in the absence of molecular oxygen. Mn substituted heteropolyanions were first reported in 1970$^{176}$.

Pope and coworkers have oxidized some Mn(II) substituted polyoxotungstenate $\text{XW}_{11}\text{O}_{39}\text{Mn(II)}$ H$_2$O (X=Si, P, B and Zn) chemically and
electrochemically and characterized the species by spectroscopy\textsuperscript{177}. They proposed that the corresponding Manganese complex is oxidized to the Mn\textsuperscript{IV}(OH) complex rather than to Mn\textsuperscript{V}O. Jonson studied the oxidations of alkyl aromatic hydrocarbon by \([\text{Ni}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}\) and \([\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}\) in aqueous acetic acid. The heteroatom’s like Ni(IV) and Mn(IV) in \{\([\text{Ni}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}\) and \([\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}\)\}\textsuperscript{178-180} are readily reduced by two electrons probably irreversibly. This work has been aimed at stabilizing the manganese (IV) ion in the polyacid \([\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}\) and studying the kinetics using \(\alpha\)-hydroxy acid as the reductant.

**Micellar Catalysis:**

**Micelles Catalyzed Oxidation Reactions:**

Ionic amphiphillic substances, such as long chain hydrocarbon quaternary ammonium sulphate and carboxylate salts, behave like strong electrolytes even in dilute aqueous solution of concentration less than \(10^{-4}\) M. at higher concentration, however a pronounced deviation from ideal behavior, has been observed and physical properties such as electrical conductivity, specific heat, pH, density interfacial tension, optical and spectroscopic properties change in a well designed manner at (or) after a particular concentration, which can be attributed to the association of amphiphiles forming aggregate micelles. The concentration at which the micelle appears is known as critical micelle concentration or CMC. The physical and chemical behavior of surfactant in aqueous solution are tread extensively in books and reviews\textsuperscript{181,182}.

Depending on the chemical structure of the surfactant, its micelle can be cationic, anionic, ampholytic or nonionic. As micelles exist in a dynamic equilibrium, the kinetic of micelle dissociation have been measured for several surfactant by stopped flow\textsuperscript{183,184} and by other high speed technique such as temperature jump and
pressure jump. Micelles have average radii of 12-30Å and contains 20-100 monomers. The hydrophobic part of the aggregate forms the core of the micelle while the polar head groups are located at the micelle-water interface in contact with and hydrated by a number if water molecules. From esr\textsuperscript{185} and nmr\textsuperscript{186} spectroscopic studies, the interior of micelle has been inferred to be hydrocarbon like. The changed head group and relatively small counter ions of the ionic micelle are located in a compact region, known as the Stern Layer which extends form the core to within a few angstron of the shear of the micelle.

The narrow range of concentration at which micelles first become detectable is the critical micelle concentration, CMC and for detergent containing long-chain hydrocarbon groups. The value of CMC is usually between $10^{-4}$ and $10^{2}$ M. The number of carbon atoms $n$, is empirically related to logarithm of CMC by long CMC-A-Bn where A and B are constants\textsuperscript{187}. The geometry of the micelle land size are determined by the number of monomers, the aggregation number $N$ and it is usually in the range of 10-100 in aqueous media. In turn, the effectiveness of micelle catalysis depends on micelles size and geometry\textsuperscript{188}. For an understanding of micelles catalysis, knowledge of the location of the solubilisate in the micelle is necessary. The solubilisate may be trapped in the hydrocarbon core of the micelle, be oriented radically in the micelle with its polar group buried (deep penetration) or be absorbed on the surface of the micelle. Solubilisation is a dynamic equilibrium process and life time is of the order of $10^{-10}$ sec. to $10^{-6}$ sec\textsuperscript{189}. The micelle substrate binding constants for several system range from $10^{3}$ to $10^{5}$ M$^{-1}$. The extent of solubilisation of the substrate in micelle surface has been determined my several physical methods such as solubility and distribution studies.
**General Feature of Micelles Catalysis:**

Due to distribution of the substrate between aqueous and micelles phases, the rate of the reaction of the substrate are different. Basically, these rate effects can be attributed to electrostatic and hydrophobic interactions between the substrate and the surfactant aggregate and in some cases to change in structure of the surrounding water. On simple electrostatic consideration, Hartely\textsuperscript{190} predicated that cationic micelles enhance the rate of reaction of nucleophilic anions with unchanged substrate while anionic micelle retard them but catalyze reactions involving cations. Uncharged and zwitterionic micelles will have little or no reaction rate. For example, the hydrolysis of esters which involves \( \text{OH}^{-} (\text{H}_2\text{O}) \) is catalyzed by cationic micellar surfactant and inhibited by anionic ones\textsuperscript{191}, whereas the converse is true for the hydrolysis of ortho ester which involves \( \text{OH}^{+} (\text{H}_2\text{O}) \textsuperscript{192,193}. \) The fact that uncharged and zwitterionic micelles have significant effects on the rate of many reactions indicates that simple electrostatic considerations are insufficient to account for all the observed rate effects and micelle-substrate interactions. In the reactions of triphenylmethane dyes (Carbonium ions) and Pyridinium ions in cationic micelles solutions, hydrophobic interactions over come electrostatic repulsion.

Micelles catalysis trends to be more pronounced for surfactants having long alkyl chains (i.e) froth that are more hydrophobic\textsuperscript{194}. This can be rationalized by postulating increased charge density of the ions of the surface of the micelle with increasing carbon chain length which in turn would increase the electric field of the reaction site. Micelles catalysis seems to be specific and varies with substrate structures. For example, the hydrolysis of methyl orthobenzoate is catalyzed by
micelles sodium dodecylsulphate while that of methyl formate is unaffected\textsuperscript{195} and this is probably due to greater hydrophobic of the orthobenzoates.

Micelles catalyzed reactions are inhibited by counter ions and larger the ion, the grater the effects\textsuperscript{196,197}. The behavior has been rationalized by assuming competition between the reactants and the electrolyte for a binding site on or in the micelle. But micelles catalysis of the decarboxylation of 6-nitrobenzoxazole-3-carboxylate ion is enhanced by electrolytes\textsuperscript{198,199} and this may be due to change in micelles structure by adding salts. Investigation of aqueous micelles system and their influence on the rate of reactions have led to assumption that they mimic enzymatic reactions.

Both micelle and globular proteins have similar X-ray structure\textsuperscript{200}. Proteins denaturing agents such as urea and guanidinium salts disrupt the micelle and increase the CMC and both micelles and enzymes bind substrates with almost similar binding constants. Also micellar catalyzed reactions obey Michaelis-Menton type kinetic and the added inhibitors behave in a similar fashion with both micellar and enzymatic catalyses.

Like most model systems, aqueous micellar system has their own limitations the catalysis be aqueous micelles in rarely greater than 100 and the reasons for the poor catalytic power is related to the dynamic equilibrium existing between momeric and micellar surfactant species. Furthermore, the hydrophobic hydrocarbon chain which forms the core contains various amount of water. Naturally occurring micellar systems, such as phospholipids and bile salts as well as synthetic surfactants affect the rate of numerous chemical reactions, in vivo and invitro\textsuperscript{201} and the influence
of micellisation of enzymatic reactions and other biochemical processes have been discussed by Elworthy et.al\textsuperscript{202}, Jencks\textsuperscript{203} and Mysels\textsuperscript{204}.

**Formation of reversed micelles and their catalysts:**

Micellisation has been observed in a variety of solvents whose polarity ranges from completely polar through dipole aprotic to polar. The dramatic rate enhancement observed in non-aqueous solvents suggests a unique micro environment which might be considered as the model for the cell membrane and there in vivo and in vitro interactions many review articles, summaries and original articles have appeared on this topic\textsuperscript{205-207}.

The aggregation of surfactant molecule in non-aqueous solvent has been discussed in term of the theory of regular solutions of non electrolyte\textsuperscript{208,209}. The principle of hard and soft acids and bases\textsuperscript{210-214} and hydrogen bonding\textsuperscript{215}. In non polar solvents, the micelle structure are generally the inverse of those formed in water, with polar head groups the interior while the hydrophobic hydrocarbon portion of the surfactants in contact with polar solvent. The aggregation number varies from 3-10, 25-30 and 155-10000 monomers depending upon the nature of the surfactant. The CMC of surfactant used varies with the dielectric constant of the medium\textsuperscript{216}. The activity of solubilisate is decreased by the surfactant and both species subsequently remain solution\textsuperscript{217}. The effect of solubilisate on micelles parameters vary with nature of surfactant and solvent. The water molecules trapped in surfactant solvent system may catalyze certain reactions as the chemical potential of water in micelles phase will be higher than either H\textsubscript{2}O (or) H\textsubscript{3}O\textsuperscript{+}.

Investigation of reactions in polar can provide information relevant to enzymatic and cell membrane interactions, organic and inorganic reactions.
Mechanism is small and large industrial processes. Reversed micelles catalytic systems are essentially analogue to those utilized for aqueous micelles ones but for a few exceptions the polar substrates are more likely to be solubilisate in the polar interior of the reversed micelle and substrate specificity is for in excess. Kinetic and spectral investigation involving reversed micelles has been made on several systems such as aromatic electrophilic and nucleophilic and electron transfer and isomerisation reactions.

The kinetics and mechanism of diphenyl sulphide, Methyl phenyl sulphides and α-hydroxy acids in presence of perchloric acid medium by Nicotinium dichromate (NDC) have been studied. Since induced electron transfer in pentaamminecobalt(III) complexes of α-hydroxy acids has been also reported and there were some inconsistencies and the work has incomplete. The extent of Nicotinium dichromate (NDC) oxidation of pentaammine cobalt(III) complexes of α-hydroxy group is separated from carboxyl bound to Co(III) centre by a saturated fragment namely C-C bond. The cation radical formed due to the oxidation of hydroxyl group by NDC should in nearly synchronous fashion transfer electron resulting in a C-C and O-H bonds fission and reduction at cobalt(III) centre. Micellar systems are convenient to use because they are optically transparent, readily available and stable.

The organized molecular assemblies such as micelles are used in spectroscopic measurements due to their possible effects on the systems of interest. In the fields of metal ion complexation, at concentrations above the critical micelles concentration (CMC), micelles form a ternary complex with advantageous properties, such as hyperchromic and bathochromic displacement, that can modify sensitivity of
the method by affecting the interference and matrix effects\textsuperscript{229}. The ability of micelles system to solubilized slightly insoluble or even very insoluble complexes and/or ligands has been used to enhance the analytical merit of given methods\textsuperscript{230-232}. The ability of micelles to solubilized complexes in aqueous solution can eliminate the need for non-aqueous extraction step in a given analysis\textsuperscript{233-235}. This reduces the cost and toxicity of the method.

The chemical competition studies for the nitrous acid assisted removal of azide ion from Co(NH\textsubscript{3})\textsubscript{5}N\textsubscript{3}\textsuperscript{2+} on the one hand with those derivable from measurements of the rates of anatine of Co(NH\textsubscript{3})\textsubscript{5}H\textsubscript{2}O\textsuperscript{3+}, Haim and Taube\textsuperscript{236} concluded that a common intermediate is formed in the two kinds of reactions. By extending this kind of measurements to reactions in which NO\textsubscript{3}\textsuperscript{-} is the leading group, Pearson and Moore\textsuperscript{237} showed that the product distributions are sensitive to the nature of the leaving group. Thus the agreement recorded by Haim and Taube for two different leaving groups, which formed the basis for their conclusion, must be regarded as fortuitous, or to have an explanation other than that advance.

Electron transfer reactions of cysteine can proceed through either inner or outer sphere mechanism. In the inner-sphere mechanism, a long lived cysteine-metal complex is formed prior to the electron transfer step. Thus, Legrum\textsuperscript{238} noticed that when cysteine is added to vanadate, a new optical band appears in the 700-770nm region. The intensity of this band decreases with time. Similar observations were reported in the Cr (IV) and Fe(III) oxidations of cysteine\textsuperscript{239,240}. With substitutionally inert oxidants such as ocacyanomolybdate(V) and heteropoly12-tungstocobaltate (III), the electron transfer reaction proceeds via an outer-sphere mechanism\textsuperscript{241-243}. 
Electron transfer reactions have been of general interest since the mild-1950s, after establishment of their basic theoretical treatment by Marcus\textsuperscript{244}. Since then, the field of electron transfer reactions has grown\textsuperscript{245}, due to this kind of process being related to many areas of both practical and theoretical interest. In particular, in the last few years there has been an increasing interest in the study of electron reactions under conditions globally referred to as restricted geometry conditions\textsuperscript{246}, that is, under conditions in which one, or both, reactants are limited in movement. These types of conditions are composed of situations produced when the reactants are forced to remain at the surface of micelles\textsuperscript{247-258} or in the cavity of cyclodextrins and related compounds\textsuperscript{259}. The study of the rates and mechanism of electron-transfer reactions is fundamental to the understanding of many important biological redox sequences, including the respiratory chain and photosynthesis\textsuperscript{260}. At the basis of these biological processes is the controlled sequential transfer of electrons between protein molecules that contain specific redox-active sites.

Induced electron transfer, wherein the interaction of a one-electron oxidant with a metal complex leads to the formation of the one-electron reduced metal center, remains an intriguing mechanistic problem\textsuperscript{261}. Among the systems studied are a series of Co(III)(NH\textsubscript{3})\textsubscript{5}X complexes where X=carbinol pyridine;\textsuperscript{262} oxidation by Ce(IV), Ag(II), or S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-} result in the formation of Co\textsuperscript{2+} (aq), Albert in less-than-quantitative yields. The proposed mechanism involves the formation of a one-electron oxidized ligand radical coordinated to the Co(III) center which can engage in ligand-to-metal intermolecular electron transfer to form Co\textsuperscript{2+}(aq) and the free two-electron oxidized ligand in competition with further interaction with the oxidant.
Quinolinium dichromate was found to be a mild reagent for the oxidation of organic compounds. Oxidation kinetic of primary, secondary and allylic alcohols$^{263}$, substituted benzyl alcohols$^{264}$, aliphatic aldehydes$^{265}$, aromatic aldehydes$^{266}$, heterocyclic aldehydes$^{267}$, cyclohexanones$^{268}$, $\beta$-diketones$^{269}$, aliphatic and aromatic carboxylic acids$^{270}$, styrenes$^{271}$, substituted cinnamate$^{272}$, and 2-naphthols$^{273}$, were carried out by various authors. The mildness of Quinolinium dichromate was demonstrated effectively in the oxidation of diols$^{274}$ where a single hydroxyl group was oxidized to give carbonyl compound as the product. The determination of isoniazid in the pure form and in pharmaceutical formulations was carried out by Kulkarni et al$^{275}$. Oxidation of $\alpha$-hydroxy acids by Quinolinium dichromate was carried out by Chimatader et al$^{276}$ and Aruna et al$^{277}$ in various organic solvent. A mechanism involving the C-C bond cleavage leading to the formation of aldehydes as the product was proposed. The formation of ketoacids by the C-H cleavage of the $\alpha$-hydroxyacids was reported with much chromium(VI) oxidants$^{278}$.

Recent reported preparation of solutions having workable concentrations of indium(I)$^{279}$, germanium(II)$^{280}$ and gallium(I)$^{281}$ have allowed us to extent the current inorganic electron transfer picture (which is based largely on the reactions of d- and f-electron donors$^{282}$) to include reactions of these uncommon s$^2$ centers.

Heteropolyanions are a special class of compounds of V(V), Nb(V), Ta(V), Mo(VI) and W(VI). When the anions contain only transition metal and oxygen such as Mo$_7$O$_{24}$$^{6-}$ and Nb$_6$O$_{19}$$^{8-}$ they are known as isopolyanions, whereas when the anions contain additional metal or non metal, they are known as heteropolyanions, such as [Co$_{12}$W$_{12}$O$_{42}$]$^{8-}$. The heteropolyanions in which Mn(II), Mn(III) and Mn(IV) are present as one of the addenda atom with Nb, W or Mo as metal atom have been
reported\textsuperscript{283}. Most of the Mn(III) compounds are fairly unstable and usually disproportionate into Mn(II) and Mn(IV). The standard oxidation potentials for Mn(III)/Mn(II) system are given below\textsuperscript{284}:

\[
\begin{align*}
\text{Mn}^{2+}_{(aq)} + e^- &\rightarrow \text{Mn}^{3+}_{(aq)} \quad E^0 = -1.5 \text{ V} \\
\text{Mn}^{2+}_{(aq)} + 2\text{H}_2\text{O} &\rightarrow \text{MnO}_2 + 4\text{H}^+ + e^- \quad E^0 = -1.239 \text{ V} \\
\text{Mn(OH)}_2 + \text{OH}^-_{(aq)} &\rightarrow \text{Mn(OH)}_3 + e^- \quad E^0 = +0.2 \text{ V}
\end{align*}
\]

The hydrated Mn(III) ion is an oxidizing agent and unstable with respect to Mn(II) and Mn(IV). Mn(III) is stable only in highly acidic solution\textsuperscript{285}. Kinetic studies show that a rapid equilibrium is established for the disproportionation reactions of Mn(III) in aqueous medium according to the following reaction\textsuperscript{286,287}.

\[
2\text{Mn}^{3+} \leftrightarrow \text{Mn}^{4+} + \text{Mn}^{2+}
\]

Mn(III) is also stable in solutions containing large excess of phosphoric acid, due to the formation of phosphates\textsuperscript{288}. The majority of Mn(III) complex ion are octahedral and high spin. A very few low spin octahedral complexes such as hexacyanomanganese(III) ion and dimethylaminotroponimintromanganese(III) are known\textsuperscript{289}. The heteropoly ions containing Mn(III) are generally very stable in solid state and in solution over a pH range to 1 to 7\textsuperscript{290,291}. The use of inorganic electron acceptors, such as Br\textsuperscript{2}, MnO\textsuperscript{4} and inorganic peroxides\textsuperscript{292}, is often encountered in polyoxometalates synthesis. Taking advantage of the oxidative stability of many polyoxometalates anions, researchers have also used ozone in this respect\textsuperscript{294}. The Co(III) ion in [Co\textsuperscript{III} W\textsubscript{12}O\textsubscript{40}]\textsuperscript{5-} is substitutionally inert. Thus it is reasonable to except that this ion will be reduced via outer sphere pathways\textsuperscript{295}.
Thermal electron transfer reaction between coordination compounds has been extensively investigated. An electron exchange between two metal centers may not be achieved by thermal activation but also by an optical charge transfer transition from one metal to another. However, it has not yet been observed to our knowledge that light-induced intervalence transfer does lead to a permanent and detectable change in the valency of the participating transition metals. Apparently fast radiations transitions restore the thermodynamically stable oxidation states which existed prior to intervalence transfer excitation.

But under favorable conditions it should be possible to observe a photochemical redox reaction initiated by intervalence transfer excitation of a complex containing two transition metal centers. We have explored this possibility and have found that the irradiation of aqueous \( [(\text{NH}_3)_5\text{Co(III)NCRu(II)(CN)}_5^-] \) leads to a redox reaction under formation of \( \text{Co}^{2+} \) and \( \text{Ru(CN)}_6^{3-} \). We believe that this photochemical redox reaction is initiated by a direct optical electron transfer from Ru(II) to Co(III). If Ru(II) is replaced by Fe(II) the redox reaction occurs as a thermal process. In our opinion these photochemical and thermal redox reactions are closely related processes which find a common explanation on the basis of a theory advanced by N. S. Hush.

The oxidation of glycols, \( \alpha \)-hydroxy acids, \( \alpha \)-hydroxyl ketones, and several other organic substrates by manganese(III) pyrophosphate are well documented. Also manganese(III) sulfate was used as an oxidant in the reactions with formic acid, formaldehyde, and \( \alpha \)-hydroxy acids. Wherein it has been shown that it behaves as a carbon-carbon bond cleaving agent. The report on the oxidation of glycolic acid by the \( \text{Mn}^{3+} \) ion also lends support for such a bond-cleavage action. But the reports of reactions with manganese(III) acetate as oxidant are limited and
its behavior toward hydrazine\textsuperscript{315} has been shown to be exceptional. One of the products of manganese(III) induced electron transfer in cobalt(III) complexes of \(\alpha\)-hydroxy acids, Co(II), was estimated after 9 half-lives, by diluting the reaction mixture by a factor of 10 with concentrated HCl, allowing the evolution of chlorine to cease, and then measuring the absorbance of chloro complex of cobalt(II) at 692nm\textsuperscript{316}.

Kinetic patterns for reductions by Cu\textsuperscript{+} and V\textsuperscript{2+} suggest\textsuperscript{317,318} that Pearson’s description of donors and acceptors as hard and soft reagents\textsuperscript{319} may have some applicability to electron-transfer reactions and that inner –sphere paths are most favored when the lead in donor atom (or a nearby chelating center) and the reducing center are complementary donor acceptor pairs.

Chromium oxidation continues to be topic of current interest for organic chemists as evidenced by the development of new techniques and procedures reported in the literature\textsuperscript{320-323}. Chromium oxidation is a simple process which can be easily performed in the laboratory and scaled up in industry as well. Chromium(VI) reagents are used in the oxidation of almost every oxidisable functional group. Kinetic of chromic acid oxidation of substituted mandelic acids in acetic acid-water was followed by Sundaram and Venkatasubramanian\textsuperscript{324}. The effect of various substituents and the structural influence has been analyzed with the help Hammett equation. Paul and Pradhan\textsuperscript{325} proposed novel mechanism for the oxidative decarboxylation of mandelic acid based on a study of deuterium labeling, solvent isotopic effect and kinetic isotopic effect. The study reported herein is an outcome of our long standing interest in the reactions of S\textsuperscript{IV} with transition metal ions and their complexes\textsuperscript{326-327}. 