CHAPTER I

INTRODUCTION

Electron transfer is undoubtedly the most fundamental reaction in life processes and is found to be involved in numerous chemical systems of vast technological and biological importance such as information storage, energy conversion, photosynthesis, respiration etc. The importance of electron transfer lies in the fact that it is often immediately followed by several other reactions like hydrogen atom and proton transfer reactions. Thus, biological processes involve complex reactions dominated by electron and hydrogen movement. Proteins have metal ions capable of existing in different oxidation states and the metal ions are embedded in an environment that responds to change in the oxidation states by transfer of electrons from one part to another. Though the electron transfers are manifested in catalytic conversion processes like photosynthesis and redox processes in metalloenzymes, they have also been implicated in DNA damage and repair [1,2].

Electron transfer reactions are one among the most important types of chemical reactions associated with the processes having potential industrial application along with various fields of research with considerable chemical and biological relevance. When systems with different capacity to hold the electrons are allowed to interact or molecules containing chromophoric groups are irradiated by light of suitable wavelength, electron transfer takes place from the ground to the excited electronic state. The rate of these electron transfer reactions are of prime importance and can be studied using spectroscopic methods which probe the energetic and spin states of electrons in molecules. The solvent medium also plays a very important role in the rate of electron transfers. Several techniques and methods allow the measurement of rates of these
reactions and reliable theoretical frameworks are also used for interpreting the contributions of various factors which determine the efficiency of electron transfer and to explore how different structural and electronic factors mediate electron transfer.

Sulfur is one of the essential elements required for normal physiological functions and it plays a major role in energy transduction, enzyme action and as a necessary constituent in certain biomaterials such as vitamins, cofactors and hormones [3]. Sulfur as thiol moiety is abundant in cells in the form of aminoacids, proteins, enzymes etc., and low molecular weight thiols protect cells from oxidative processes and free radical attack. Thus organic sulfides serve pivotal role in biological macromolecules, organic polymers and xenobiotics [4,5]. Chiral sulfoxides are useful building blocks in asymmetric synthesis of organic compounds and they are found in biologically and pharmaceutically important molecules [6-8].

The importance and complexity of biological electron transfer systems and the vital role of sulfur compounds in particular, sulfur centered radicals in biological systems lead to the focus on the study of electron transfer reactions with regard to sulfur compounds and metal ions. The multifaceted involvement of these systems in metabolic pathways also highlights the importance and the development of several electron transfer systems which can mimic functions of redox enzymes [9-11].

1.1. Phenylsulfinylacetic acid - A general survey

Phenylsulfinylacetic acid (PSAA) is an ambident ligand [12] which has three donor sites: the sulfur atom, oxygen atom of the SO group and oxygen atom of the carboxylate group. Thus, it is a potential chelating agent which forms a five membered chelate ring if the carboxylate oxygen and sulfur atoms are involved and a six membered chelate ring if the oxygen atoms of the carboxylate group and the SO group are involved.
With Cd(II) it forms a dihydrate, \( \text{Cd}(C_6H_5\text{SOCH}_2\text{CO}_2)_{2} \cdot 2\text{H}_2\text{O} \) and a tetra coordinate complex \([\text{Cd}(\text{H}_2\text{O})_4]^{2+} \ [\text{Cd}(C_6H_5\text{SOCH}_2\text{CO}_2)_4]^{2-}\) while with Pt(II) it gives a five membered complex (I) in which both sulfur of SO group and oxygen of carboxylate group are bonded to the metal and another binuclear complex with chlorine bridged structure (II).

![Chemical Structures](image)

The ionization constants of several phenylsulfinylacetic acids were determined in ethanol-water and dioxane-water solvent systems by Pasto and Kent [13]. They showed an inversion of the relative acidities of phenylsulfinylacetic acid and phenylsulfonyl-acetic acid in different solvents: the phenylsulfinylacetic acid being the weaker acid of the two in pure water becomes a stronger acid in highly non-aqueous solvent systems. This behaviour was explained on the basis of the predominant existence of the following conformational structure (III) without intra-molecular hydrogen bonding.

![Chemical Structure](image)

The resonance and inductive interaction of the sulfinyl group in PSAA was studied by Pasto et al. [14] and they reported that the sulfinyl group is a less effective group for the transmission of inductive effect compared to mercapto and sulfonyl groups.
The transmission of the inductive effects by the sulfinyl group may be partially shunted into the highly polar sulfur-oxygen bond instead of being directed entirely through the methylene group to the carboxyl group, thus reducing the over-all effects. Besides, they reported that the extent of electron donation by $p$-fluoro and $p$-methoxy groups to the d-orbitals of sulfur is less significant in the phenylsulfinyl- and phenylsulfonylacetic acid series.

Direct characterization of arylsulfinyl radicals formed from the photolysis of several aromatic sulfinyl compounds (Scheme 1.1) was done by Darmanyan et al. [15] using nanosecond laser photolysis method in various solvents. The study provides direct evidence for the $\alpha$-cleavage which is the predominant primary photochemical process. The photolysis of aromatic sulfinyl compounds resulted in carbon-centered radical and arylsulfinyl radical. The cleavage is followed by recombination to form sulfenic ester (eq.1.2) [16] or hydrogen abstraction by the arylsulfinyl radical [17] to form sulfenic acid and alkene (eq.1.3).

\[
\begin{align*}
\text{ArSO}_2\text{R} + \text{hv} &\rightarrow \text{ArSO}^- + \text{R}^+ \quad (1.1) \\
\text{ArSO}^- + \text{R}^+ &\rightarrow \text{ArSOH} + \text{Alkene} \quad (1.2, 1.3)
\end{align*}
\]

Scheme 1.1

The crystal structure of phenylsulfinylacetic acid was determined by Leiserowitz et al. [18]. The compound has space group P212121 with lattice parameters: $a = 10.21 \ \text{Å}$, $b = 10.07 \ \text{Å}$, $c = 8.47 \ \text{Å}$ and $Z = 4$. The effect of molecular structure on
optical properties of phenyl- and (m-bromophenyl)sulfinylacetic acids were studied by Janczewski et al. [19].

Phenylsulfinylacetic acid is known to undergo a facile cleavage to benzenethiol and glyoxylic acid in the presence of mineral acids. According to Kenney et al. [20] benzenethiol and glyoxylic acid recombined to form phenylmercaptohydroxyacetic acid (Scheme 1.2).

\[
\begin{align*}
C_6H_5SCH_2COOH & \xrightarrow{H^+} C_6H_5SCH_2COOH^+ + C_6H_5SH + OHCOCOOH \\
C_6H_5SCH_2COOH & \xrightarrow{H^+} C_6H_5SCHCOOH + C_6H_5SH + OHCOCOOH
\end{align*}
\] (1.4)

Scheme 1.2

On the other hand Pummerer [21] and Walker et al. [22] suggested that phenylmercaptohydroxyacetic acid was formed prior to the formation of benzenethiol and glyoxylic acid in the presence and absence of \( H^+ \) according to eq.1.6 and eq.1.7 respectively.

\[
\begin{align*}
C_6H_5SCH_2COOH & \xrightarrow{H^+} C_6H_5S=CHCOOH \rightarrow C_6H_5SCHCOOH \rightarrow C_6H_5SH + OHCOCOOH \\
C_6H_5SCH_2COOH & \xrightarrow{H^+} C_6H_5SCHCOOH \rightarrow C_6H_5SH + OHCOCOOH
\end{align*}
\] (1.6)

During acid disproportionation reaction of PSAA [20] sulfur atom is reduced and the \( \alpha \)-carbon atom is oxidized. For this disproportionation to occur the \( \alpha \)-carbon to the sulfoxide group must possess a hydrogen atom. In the case of PSAA series \( p-\text{CH}_3 \) group promotes the disproportionation whereas a \( p-\text{NO}_2 \) group retards it.
The kinetic results obtained in the esterification of substituted PSAAs [23] indicated that electron-withdrawing groups accelerate the rate of esterification while reverse is the case with electron-donating groups. The reaction series obey the Hammett equation excellently for meta- and para-substituted compounds. The ortho-substituents are found to transmit the electrical effect almost to the same extent as the para-substituents with negligible steric effect.

Recently, Subramaniam et al. [24] have reported the oxidative decarboxylation of PSAA with oxo(salen)chromium(V) complexes catalyzed by pyridine bases such as imidazole, 1-methyl imidazole and pyridine. Both the electron-donating and electron-withdrawing substituents in PSAA accelerate the reaction rate. The Hammett plots for the three oxo(salen)chromium(V) complexes with three nitrogen bases display a nonlinear upward curvature. The Hammett parameter $\rho$ changes from large negative to small positive values as the substituents change from electron-donating to electron-withdrawing groups. A mechanism involving direct oxygen transfer from oxo(salen)chromium(V)-nitrogen base adduct to PSAA with simultaneous decarboxylation to yield methyl phenyl sulfone is proposed.

Phenylsulfinylacetic acid is a versatile synthetic agent used in the synthesis of cyclic ketones [25,26], tribenzyltinphenylsulfinyl acetate [27] and methyl ester of 2-benzenesulfinyl-hexanoic acid. Ethyl phenylsulfinylfluoroacetate a derivative of PSAA is a new and versatile reagent for the preparation of $\alpha$-fluoro-$\alpha,\beta$-unsaturated carboxylic acid esters [28]. PSAA provides a new approach to the synthesis of triphenylphosphorane ylide precursors from alkyl halides [29]. It is also used in the synthesis of bactericides, cephalosporin and in the development of photographic material with high sensitivity and improved image stability.
1.2. Chromium as an oxidizing agent

Chromium is a metal widely distributed in nature and exists in different oxidation states viz., +2, +3, +4, +5 and +6. Among them Cr(VI) and Cr(III) are the most common stable forms of chromium. The most probable Cr(VI) species in aqueous solution are $H_2CrO_4$, $HCrO_4^-$, $HCrO_3^+$, $CrO_4^{2-}$ and $Cr_2O_7^{2-}$. The relative distribution of these species depends mainly on the pH of the medium and Cr(VI) concentration [30].

Although chromium is found to be a carcinogen, the mechanism underlying the uptake and metabolism are crucial. Many researchers have established that the Cr(V) species formed as a result of oxidation of intracellular reductants by Cr(VI) plays a major role in DNA-damage. In spite of its carcinogenicity chromium is widely used as a synthetic oxidizing agent [31-34] for the oxidation of a variety of organic compounds in aqueous and non-aqueous media. The potent oxidant Cr(VI) is unique because it satisfies the basic requirements of an oxidant like lower cost, higher yields, better selectivity, easier preparations, higher solubility and shorter reaction times [35-37].

1.2.1. Mechanistic pathways for Cr(VI) oxidation

In the oxidation of organic substrates by Cr(VI) different mechanisms have been proposed depending on the conditions, nature of the substrate and Cr(VI) species. Watanabe and Westheimer [38] proposed a mechanism which involves the formation of a complex between the substrate (S) and Cr(VI) in a reversible step followed by its decomposition leading to Cr(IV) and organic product as shown in Scheme 1.3.

$$\text{Cr(VI)} + S \rightleftharpoons \text{Cr(VI)-S (Complex)} \quad (1.8)$$

$$\text{Cr(VI)-S} \rightarrow \text{Cr(IV)} + \text{Product} \quad (1.9)$$

Scheme 1.3
Depending on the substrate and conditions, in some cases the formation of Cr(VI)-S complex (eq.1.8) is the slow rate-determining step and the complex then undergoes dissociation very rapidly (eq.1.9) while in some other cases, both the steps (eq.1.8 and eq.1.9) are considered to be important as rate-determining steps and are represented as Michaelis-Menten kinetics [39-42]. Both the cases lead to different rate laws. In the first case the rate law depends on the first power of the substrate and the plot of 1 / \( k_1 \) vs. 1 / [substrate] is linear which passes through the origin whereas in the second case the order dependence on substrate is fractional and the plot of 1 / \( k_1 \) vs. 1 / [substrate] has a definite intercept value. The Cr(IV) species formed undergoes disproportionation to Cr(III) in fast steps via formation of Cr(V) [43,44].

In the oxidation of alcohols, aldehydes and hydroxy acids very often the rate-determining step involves the breaking of a C-H bond in a cyclic transition state of chromate ester. The cleavage of C-H bond in all these cases is demonstrated by the positive primary kinetic isotopic effect by comparing the reactivity of C-H bond and C-D bond [45-49]. The structure of the transition state formed in the oxidation of aliphatic primary alcohols (IV) by quinolinium bromochromate (QBC) [45], cyclic alcohols (V) [50] and benzaldehydes (VI) [51] by quinolinium dichromate and D-gluconic acid (VII) by Cr(VI) [52] are shown below.

![Diagram](Image)

(IV)  

(V)
A common mechanism with the formation of ester like Cr(VI)-thiol complex followed by electron transfer has been suggested for the oxidation of different thiols by Cr(VI) (Scheme 1.4). The Cr(VI)-thioester then experience a one-electron transfer giving rise to the Cr(V) intermediate and thiy radical (eq.1.11) or react with a second thiol molecule to produce a Cr(IV) intermediate and disulfide through two-electron transfer (eq.1.12) [53,54].

\[
\begin{align*}
\text{Cr(VI)} + \text{RSH} & \rightleftharpoons \text{Cr(VI)-SR} + \text{H}^+ \quad (1.10) \\
\text{Cr(VI)-SR} & \rightarrow \text{Cr(V)} + \text{RS}^\cdot \quad (1.11) \\
\text{Cr(VI)-SR} + \text{RSH} & \rightarrow \text{Cr(IV)} + \text{RSSR} + \text{H}^+ \quad (1.12)
\end{align*}
\]

Scheme 1.4

In the oxidation of organic sulfur compounds by Cr(VI) two different mechanisms, one involving single-electron transfer (SET) to Cr(VI) leading to the formation of Cr(V) at the rate-determining step [55,56] and the other involving the S_N2 type nucleophilic attack of sulfide on chromium to form Cr(VI)-S adduct have been proposed [57]. In some cases the actual mechanism may be a continuum between these two extreme possibilities, S_N2 and SET mechanisms [58].
1.3. Kinetics of Cr(VI) oxidation of sulfur compounds

The oxidations of sulfur containing biomolecules by the metal ions play a key role in several metabolic processes. The intracellular sulfur containing compounds in proteins in the form of thiols and thioethers are potential Cr(VI) reductants amply involved in the pathways leading to the malfunction of biomolecules. Many reducing agents present in cell cytoplasm reduce Cr(VI) to the ultimate product Cr(III) via generation of hyperactive Cr(V), Cr(IV) and free radical intermediates which are mostly stabilized by the intracellular ligands.

1.3.1. Oxidation of sulfides and sulfoxides

A mechanism with the formation of sulfonium cation radical intermediate by one-electron transfer from sulfur atom to Cr(VI) in the rate-determining step (Scheme 1.5) has been proposed for the oxidation of alkyl aryl and diphenyl sulfides [55].

\[
\begin{align*}
\text{Me} & \quad \text{Ar-S-CH}_3 \\
& \quad \text{Cr(VI)} \\
\text{Me-S} & \quad \text{Ar-S-CH}_3 \\
& \quad \text{Cr(V)} \\
\end{align*}
\]

A similar single-electron transfer mechanism has also been postulated [59] for the oxidation of aryl methyl sulfoxides and diaryl sulfoxides based on the observed low \( \rho \) values of -0.8 and -0.48 respectively. The formation of sulfonium ion intermediate is confirmed by the observed rate acceleration by electron-releasing groups and rate retardation by electron-withdrawing groups. In all these cases a good correlation exists
between log $k_2$ and Hammett $\sigma$ constants. Khan et al. have studied the kinetics and mechanism of the oxidation of dimethyl sulfoxide (DMSO) by Cr(VI) [60].

Different oxidizing species and mechanisms have been proposed for the Cr(VI) oxidation of N-substituted phenothiazines by Pitchumani et al. [57]. The nucleophilic attack of sulfur atom of phenothiazine on chromium atom of HCrO$_3^+$ (eq.1.16) followed by ligand coupling is suggested for N-acetylphenothiazine while nucleophilic attack of phenothiazine on oxygen atom of H$_2$CrO$_4$ (eq.1.17) followed by solvolysis to yield sulfoxide is proposed for N-methylphenothiazine.

\[
\begin{align*}
\text{Ac} & \quad \text{Cr} \quad \text{OH} \\
\text{Me} & \quad \text{H}_2\text{CrO}_4 \\
\end{align*}
\]

A comparative study on the kinetics of the redox reaction of dialkyl sulfides with Cr(V) and Cr(VI) in aqueous CH$_3$CN has been carried out by Ganesan et al. [58]. The rate of the reaction with Cr(V) is two orders more than Cr(VI). Based on the substituent and solvent effects an outer sphere electron transfer mechanism has been proposed for Cr(V) oxidation. Two different mechanisms one involving nucleophilic attack of sulfide
on chromium (Scheme 1.6) and the other a single-electron transfer from sulfide to chromium have been proposed for the Cr(VI) oxidation.

\[
R_2S + \text{Cr(IV)} \rightarrow \text{Cr(VI)} \quad (1.18)
\]

\[
\text{Cr(VI)} \rightarrow \text{Cr(III)} \quad (1.19)
\]

**Scheme 1.6**

### 1.3.2. Oxidation of sulfur containing aminoacids

The oxidation of biologically important sulfur compounds, L-cysteine and related thiols by chromium(VI) were characterized by a pre-redox equilibrium involving the formation of a 1:1 thio ester of chromium(VI) \([53,54]\) followed by competitive redox decomposition of the intermediate by reaction with either H\(^{+}\) or RSH.

Reduction of Cr(VI) to Cr(III) by L-cysteine in neutral aqueous solution was studied by Lay et al. \([61]\) and proposed the mechanism which includes: i) formation of a Cr(VI) complex with two cysteine ligands; ii) its conversion to a precursor Cr(III) complex by sequential one-electron reductions with three cysteine molecules and iii) intra-molecular rearrangement of the precursor Cr(III) complex leading to the final product.

From the magnetic moment data along with the ESR measurements Bose et al. \([62]\) unequivocally established that Cr(IV) is the dominant long-lived intermediate and Cr(V) accounts for < 5% of the intermediate in the Cr(VI)-glutathione reaction. These
intermediates were formed by two parallel pathways: an internal electron transfer process within a Cr(VI)-thioester precursor and a bimolecular reaction between the precursor complex and glutathione. They also proposed that rapid ligand exchange or rearrangement takes place prior to the rate-limiting reduction of Cr(VI) by the tripeptide.

Perez-Benito et al. [63] studied the formation, decomposition and reactivity of chromium(VI)-glutathione thioester intermediate in neutral and slightly acidic aqueous solutions. They proposed a mechanism explaining the catalytic effects of both the buffer (citrate and phosphate) and Zn$^{2+}$ ion with the involvement of Cr(II) as an unstable intermediate. Mansour [64] observed Michaelis-Menten kinetics with respect to substrate in the Cr(VI) oxidation of L-methionine to its sulfoxide via the formation of a transient protonated methionine intermediate.

### 1.3.3. Oxidation by onium dichromates and halochromates

Onium dichromates and halochromates are excellent classes of oxidizing agents of Cr(VI) used for the oxidation of a variety of functional groups [65-70]. Different types of mechanisms have been proposed with different oxidizing agents in partially aqueous, non-aqueous and in aqueous media. In majority of the cases, organic sulfides viz., alkyl phenyl, dialkyl and diphenyl sulfides are oxidized to yield the corresponding sulfoxides whereas in some cases other products are also reported. Among the halochromates, oxidation by fluorochromates are found to be faster than others and this can be explained on the basis of high electron-withdrawing power of fluorine.

Rajasekaran et al. [71] have proposed a reaction mechanism involving a three-membered electron-deficient cyclic transition state (Scheme 1.7) for the oxidation of para-substituted phenyl methyl sulfides (MPS) with pyridinium chlorochromate (PCC) to yield sulfoxides. In protic solvents the reaction follows a second-order rate law and the
formation of the complex is the rate-limiting step while the decomposition of the complex by Michaelis-Menten kinetics is the rate-determining process in aprotic solvents.

\[
\begin{align*}
\text{Ph} & \quad \text{S} \quad \text{Me} \quad \text{O} & \quad \text{Cr} & \quad \text{Cl} \\
\text{S} & \quad \text{Me} & \quad \text{O} & \quad \text{Py} \quad \text{H}^+ \\
K & \quad \text{Ph} & \quad \text{S} \quad \text{Me} & \quad \text{CrO}_2 & \quad \text{Py} \quad \text{H}^+ \quad \text{Cl}^- \\
& \quad k_1
\end{align*}
\]

(Scheme 1.7)

A common mechanism involving the formation of an oxidant-sulfide intermediate followed by its decomposition in a slow step by Michaelis-Menten kinetics has been proposed for the oxidation of diphenyl sulfide (DPS) by dichromate and seven chromium(VI) complexes in glacial acetic acid [72]. The oxidation of MPS by bispyridinesilver(I) dichromate (BPSDC) [73] is also found to proceed via Michaelis-Menten type of kinetics with respect to MPS.

A mechanism involving one-step electrophilic oxygen transfer from pyridinium fluorochromate (PFC) / butyltriphenylphosphonium dichromate (BTPPD) to the sulfide via a polar transition state has been proposed for the oxidation of a number of mono-substituted aryl methyl, alkyl phenyl, dialkyl and DPSs by PFC [74] and BTPPD [75] to their sulfoxides. The nucleophilic attack of sulfide sulfur on oxygen was viewed as an \(S_N2\) process.

Based on the negative polar reaction constants that indicate the involvement of electron deficient sulfur center, a mechanism involving the formation of a sulfonium
cation intermediate in the slow rate-determining step has been proposed for the oxidation of organic sulfides by morpholinium chlorochromate [76], QBC [77] and bipyridinium chlorochromate [78]. In all these cases, it is found that electron-releasing groups accelerate the reaction rate while electron-withdrawing groups decelerate the rate. Alhaji et al. [79] analysed the kinetic observations in favour of a $S_N2$ type of mechanism in the imidazolium fluorochromate (IFC) oxidation of MPS in acetonitrile-H$_2$O (1:1) mixture. The oxidations of organic sulfides by tetraethylammonium chlorochromate [80] and cetyltrimethylammonium dichromate [81] have also been reported. Recently, new halochromate reagents viz., tripropylammonium fluorochromate (TPAFC) [82], benzimidazolium dichromate [83] and tetrahexylammonium bromochromate [84] have been used for the oxidation of methionine.

The oxidation of thioglycollic, thiolactic and thiomalic acids to their disulfides by quinolinium fluorochromate (QFC) [85], PFC [86], PCC [87] and IFC [88] proceeds through a two-electron transfer via Michaelis-Menten kinetics. These reactions involve the formation of a thioester in a pre-equilibrium step and its subsequent decomposition to a sulfonium ion in the slow step.

Kabilan et al. [89] have studied the kinetics of oxidation of phenylthioacetic acid (PTA) by PFC in aqueous acetic acid medium and proposed a mechanism involving the formation of phenylsulfanylacetic acid as an intermediate which then undergoes Pummerer type rearrangement followed by disproportionation to yield thiophenol as the final product. Whereas with PCC [90] the formation of protonated arylsulfanylacetic acid intermediate in the slow step has been proposed which then undergoes intra-molecular rearrangement leading to the formation of thiophenol (Scheme 1.8). The oxidations of S-phenylmercaptoacetic acid by piperidinium chlorochromate [91] and quinoxalinium dichromate [92] have also been reported recently.
1.4. Oxidation of sulfides and sulfoxides by Cr(V) complexes

The study of Cr(V) complexes received much attention in recent years because of their ability to act both as a structural and a biomimetic model for a range of Cr(V) species which are believed to be generated in vivo during the intracellular reduction of Cr(VI). Such type of important model complexes of Cr(V) are oxochromate, salen, porphyrin and corrolato chromium complexes.

Ganesan et al. [58,93] have studied the oxidation of dialkyl sulfides and alkyl aryl sulfides by sodium bis(2-hydroxy-2-methylpropionato)oxochromium(V), sodium bis(2-hydroxy-2-methylbutyrate)oxochromium(V) and sodium bis(2-hydroxy-2-ethylbutyrate) oxochromate(V) complexes. They interpreted the kinetic results in terms of a mechanism involving an outer-sphere electron transfer from sulfide to Cr(V) as the rate-determining step.

Rajagopal and co-workers [94] reviewed the role of salen complexes as catalysts for the oxygenation of several organic compounds containing hetero atoms. The direct oxygen atom transfer from the oxidant to the substrate (Scheme 1.9) rather than electron transfer is envisaged in the selective oxidation of organic sulfides by
oxo(salen)chromium(V) complexes [95,96]. The higher reactivity of dialkyl sulfides compared to aryl methyl sulfides also rules out the operation of electron transfer mechanism. The mechanism involves the direct electrophilic attack of oxygen of the oxo(salen)chromium at the electron rich sulfur center of the substrate and the transition state is represented as shown in VIII.

\[
[(\text{salen}) \text{Cr}^V \cdot \text{O}]^+ \xrightarrow{\text{slow}} \left[ (\text{salen}) \text{Cr}^{\text{III}} - \text{O} + \overset{\text{R}}{\overset{\text{S}}{\text{S}}} \overset{\text{R'}}{\text{S}} \right]^+ \xrightarrow{\text{fast}} [(\text{salen})\text{Cr}^{\text{III}}] + \text{RSOR}'
\]  

(Scheme 1.9)

(VIII)

The oxidation of sulfoxides by oxo(salen)chromium(V) complexes [96] involve an initial formation of an adduct by the binding of sulfoxide to the chromium center of the oxidant followed by oxygen atom transfer from oxidant-sulfoxide adduct to the substrate (Scheme 1.10). The binding of organic sulfoxides with Cr(V) ion has been observed from the shift in the \(\lambda_{\text{max}}\) of Cr(V) and sharpening of the peak.
In both sulfides and sulfoxides, the electron-releasing substituents introduced in the para-position of the phenyl ring accelerate the rate appreciably and electron-withdrawing groups decelerate the rate. The observed order of rate constants clearly indicates the operation of a pronounced electronic and steric effects in both sulfide and sulfoxide oxygenation reactions. The oxidation of methionine by oxo(salen)-chromium(V) in aqueous acetonitrile medium [97] involves the initial binding of water to oxo(salen) to form [O=Cr\(^V\)(salen)-H\(_2\)O\(^+\)] followed by direct oxygen atom transfer from [O=Cr\(^V\)(salen)-H\(_2\)O\(^+\)] to the sulfur center of methionine.

Venkataramanan et al. [98] found that the oxygenation of organic sulfides by oxo(salen)chromium(V) is accelerated by ten to twenty times in the presence of added donor ligand oxides (LO) like pyridine-N-oxide, 4-picoline-N-oxide, 4-phenyl pyridine-
N-oxide and triphenyl phosphine oxide. The catalytic activity is explained by the mechanism involving the electrophilic attack of [(salen)Cr^{V}=O]^+ -LO adduct formed as a result of strong binding of donor ligands to the oxo(salen)chromium(V) ion on the sulfur atom of organic sulfides. The binding of LO to the oxo(salen)chromium(V) ion weakens the Cr=O bond in the complex and facilitates the attack of oxygen atom on sulfides to form sulfoxides as the product.

Corroles are a class of contracted porphyrin that inspire great interest as synthetic targets because of the preparation of metal complexes in which the metal generally rests stably in a higher valence state in the corrin-like macrocyclic skeleton [99-101]. The general ease of synthesis of meso-A_{3}-triarylcorroles has allowed the study of various synthetic metallo-oxo species as model systems [102-105]. Detailed research in the area of oxo-metal species of corroles has been performed by Gross and co-workers [102] in which the tris(pentafluorophenyl)corrolatochromium system was studied in four formal oxidation states. The corrole-based Cr^{V}O/Cr^{III} cycle allows for aerobic oxidation of the substrate in which the mild oxidative power of Cr^{V}O may be beneficial for catalytic processes in biological systems [106].

It is noted that oxo-metal species obtained on the basis of A_{3}-triarylcorroles and variation of the meso substituents at the periphery of the corrole macrocyclic ring can significantly influence the properties of the final compounds. Churchill and co-workers [107] prepared the first meso-ABC-corrolatochromium(V) complex, oxo[5-(4-bromophenyl)-10-(pentafluorophenyl)-15-(2-thianaphthyl)corrolato] chromium (V) with different electron-withdrawing capacity. Meunier [108] reviewed the oxidations catalyzed by metalloporphyrins and characterization of high valent metal-oxo porphyrin complexes including chromium-oxo porphyrins.
1.5. **Co-oxidation studies of organic substrates by Cr(VI)**

Hasan and Rocek [109] reported a dramatic rate acceleration in the Cr(VI) oxidation of a mixture of isopropyl alcohol and oxalic acid compared to the Cr(VI) oxidation of either of these substrates. They attributed this rate acceleration to the phenomenon called co-oxidation wherein both the substrates undergo oxidation simultaneously and this behaviour is of entirely different in nature than the familiar catalyzed oxidation reactions. Oxalic acid was found to accelerate the rate of many chromic acid oxidations in a rapid co-oxidation reaction yielding CO$_2$ as one of the products and Cr(VI) was reduced directly to Cr(III) in the rate-limiting step [109-111]. A detailed analysis of the co-oxidation reaction has revealed the following features: i) the transition state contains one molecule each of the substrate, oxalic acid and Cr(VI) which offers the reaction a more favorable pathway than the oxidation of a single molecule ii) a total suppression of the rate-accelerating effect of oxalic acid by aluminium nitrate and iii) the rate-limiting step is the decomposition of a termolecular complex in a three-electron redox process thus avoiding the formation of the energetically unfavorable Cr(IV) [109].

Gurumurthy et al. [112] carried out the co-oxidation of S-phenylmercaptoacetic acids (PMA) by chromic acid in the presence of oxalic acid in 50% aqueous acetic acid. The electron-releasing substituents in the phenyl ring of PMA accelerate the rate while the electron-withdrawing ones retard it. The formation of a ternary complex between oxalic acid, chromic acid and PMA in a fast step followed by the hydrolysis in a subsequent slow rate-limiting step yielding the sulfoxide is proposed as the mechanism. The susceptibility of the reaction to the steric effect of *ortho*-substituents has been analyzed using Taft's steric energy relationships.
The enhanced reactivity due to co-oxidation of MPS and oxalic acid by Cr(VI) [113] was explained by considering the rate-determining formation of a ternary complex among sulfide, oxalic acid and Cr(VI). The kinetics of co-oxidation of several substituted phenyl methyl sulfoxides and oxalic acid with Cr(VI) have also been carried out by Srinivasan et al. [114] in the presence of perchloric acid. The products of co-oxidation reaction are phenyl methyl sulfones and carbon dioxide. Electron-releasing groups in the phenyl ring accelerate the rate while electron-withdrawing groups retard it and the Hammett correlation yields a reaction constant of -0.93. Diaryl sulfoxides also behave in an analogous manner in the co-oxidation. They proposed that chromic acid forms a cyclic 1:1 neutral complex with oxalic acid. The complex then reacts with a molecule of sulfoxide producing a ternary complex in the rate-determining step. The ternary complex on solvolysis yields the products sulfone, carbon dioxide and Cr(III) species. This mechanism involves a two-electron oxidation of the sulfoxide and a simultaneous one-electron oxidation of the oxalic acid part in the ternary complex.

The co-oxidation of DMSO and oxalic acid by Cr(VI) in aqueous acid media occurs much faster than that of the two substrates alone under the experimental condition [115]. In the mixture both the substrates undergo oxidation simultaneously via a ternary complex of Cr(VI) through a three-electron transfer step. For the reaction the micellar effect has been considered as a probe for the three-electron transfer in a single step.

The co-oxidation of formic acid [116] and aromatic anils [117] in the presence of oxalic acid by chromium(VI) occur through a three-electron transfer from Cr(VI) leading to the formation of Cr(III). Here both the substrates undergo oxidation simultaneously via the formation of a ternary complex with Cr(VI). In the co-oxidation of benzhydrols and phenylmethylicarbinols by Cr(VI) in the presence of oxalic acid Nagarajan et al.
have observed that the reaction is sensitive to the polar effects of substituents in the phenyl ring.

Basheer Ahamed has proposed two different mechanisms for the chromic acid oxidation of acetanilides and benzanilides with oxalic acid [119]. The oxidation kinetics of acetanilide and \( p \)-substituted acetanilides follow zero-order and second-order dependence on [substrate] and [oxalic acid] respectively yielding azobenzenes and acetaldehyde (Scheme 1.11) while the oxidation kinetics of benzanilide and \( p \)-substituted benzanilides follow fractional-order each in [substrate] and [oxalic acid] yielding the corresponding azobenzenes and benzaldehyde (Scheme 1.12). In the proposed mechanism the rate-limiting step involves the direct reduction of Cr(VI) to Cr(III).

\[
(COOH)_2 + H_2CrO_4 \rightleftharpoons \quad \text{(Scheme 1.11)} \quad (1.29)
\]

\[
\text{O} \quad \text{O} \\
\text{C} \quad \text{O} \\
\text{C} \quad \text{O} \\
\text{O} \quad \text{O} \\
\text{O} \quad \text{O} \\
\text{C} \quad \text{C} \\
\text{N} \\
\text{C}_6H_5 \\
\text{O} \\
\text{H}
\]

\[
C_6H_5\tilde{\text{N}}: + \text{CH}_3\text{CHO} + \text{Cr(III)} + \text{O}=\text{C}=\text{O} + \text{O} \quad \text{fast} \quad C_6H_5\text{N} \equiv \text{N} \quad C_6H_5 \\
(1.31)
\]
A three-electron oxidation of a mixed substrate system of propanaldehyde and isobutyl alcohol by chromic acid was investigated by Jagannatham and co-workers [120]. They observed the first-order dependence of rate on [Cr(VI)] and fractional-order dependence on both the substrates. The proposed mechanism involves the formation of a diester of chromic acid with neutral molecules of aldehyde and alcohol in two successive equilibrium steps followed by its decomposition in a slow step to the products.

1.5.1. Co-oxidation involving other Cr(VI) reagents

Though considerable work on co-oxidation by Cr(VI) has been reported only a limited work on co-oxidation using other Cr(VI) reagents is available. Raju and co-worker [121] studied the co-oxidation of oxalic acid and arsenic(III) by chlorochromate in aqueous acetic acid and reported that the reaction proceeds through the formation of a cyclic intermediate. The oxidation of phenoxyacetic acid by PFC in
the presence of oxalic acid proceeds through PFC-oxalic acid complex and the reaction involves three-electron transfer [122].

The mechanism of the co-oxidation of benzaldehyde and oxalic acid by PCC [123] was investigated in 50% acetic acid medium and the products were found to be benzoic acid and carbon dioxide respectively. The involvement of cyclic ternary complex in the rate-determining step was proposed. Meenakshisundaram et al. [124] observed enhanced reactivity in the QFC co-oxidation of cycloalkanones and oxalic acid. They found that oxalic acid reacts ca.70 times faster than the reaction with cyclohexanone alone. The enol form of the cycloalkanone is identified as the active substrate and π-complex formation has been envisaged to explain the acceleration of rate in cycloalkanones oxidation. The presence of oxalic acid results in the suppression of a ring-cleavage reaction yielding cyclohexane-1,2-diones as the main product. Mn(II) catalyzes the co-oxidation process at its higher concentrations.

The mechanism of co-oxidation of S-phenylmercaptoacetic acid (PMA) and oxalic acid by PCC [125] in aqueous acetic acid is explained by Rocek’s mechanism involving a ternary complex. Formation of a ternary complex between the reactants at low concentrations and decomposition of the complex at higher concentrations of PMA are considered as rate-limiting steps on the basis of the observed first-order and fractional-order dependence of PMA at low and high concentrations respectively.

1.6. Ligand catalyzed Cr(VI) oxidations

The rate of chromium(VI) oxidation of various organic compounds were found to enhance significantly in the presence of ligands like ethylenediaminetetraacetic acid (EDTA) and pyridine bases viz., picolinic acid (PA), 2,2’-bipyridine (Bpy), 1,10-phenanthroline (Phen) etc., They act as chelating agents and form Cr(VI)-ligand
complexes which are found to be more reactive than Cr(VI) itself. The Cr(VI)-ligand complex then undergo nucleophilic attack by the substrate to form a ternary complex which subsequently undergoes redox decomposition through one-electron or two-electron transfer leading to products. Depending upon the kinetic conditions and nature of the substrate either the formation of the ternary complex or its decomposition is identified as the rate-determining step.

The electron transfer reaction of Cr(VI) with organic sulfides is facilitated by added Bpy, Phen, PA and pyridine-2,6-dicarboxylic acid (PDA) [126]. The added bases form more reactive oxidizing species, Cr(VI)-base adducts carrying positive charge. To account for the spectral and kinetic results Cr(V) species is proposed as the intermediate and the reaction in the presence of added ligands proceeds via one-electron transfer mechanism (Scheme 1.13). The reactions in the absence and presence of pyridine bases follow reactivity-selectivity principle.

\[
\text{HCrO}_4^- + n\text{H}^+ + \text{Ligand} \quad \overset{K}{\longrightarrow} \quad \text{Cr(VI)-ligand complex} + \text{H}_2\text{O} \quad (1.36)
\]

\[
\text{Cr(VI)-ligand complex} + \text{S}^\cdots\text{Ar}^-\cdots\text{S}^\cdots\text{Me} \quad \overset{k_1}{\longrightarrow} \quad \text{S}^\cdots\text{Ar}^-\cdots\text{Me} + \text{ligand} \quad (1.37)
\]

\[
\text{ligand} \quad \overset{O^-}{\longrightarrow} \quad \text{Cr(V)} \quad + \quad \text{S}^\cdots\text{Ar}^-\cdots\text{S}^\cdots\text{Me} \quad \longrightarrow \quad \left[\begin{array}{c}
\text{Ar}^+ \quad \text{S} \cdots \text{O}^- \cdots \text{Cr(IV)} \cdots \text{ligand} \\
\text{Me}^+ \quad \text{O}^- \\
\end{array}\right] \quad (1.38)
\]

\[
\left[\begin{array}{c}
\text{Ar}^+ \quad \text{S} \cdots \text{O}^- \cdots \text{Cr(IV)} \cdots \text{ligand} \\
\text{Me}^+ \quad \text{O}^- \\
\end{array}\right] \quad \longrightarrow \quad \text{ArS(O)Me} + \text{Cr(IV)} \longrightarrow \text{ligand complex} \quad (1.39)
\]

\[
\text{Cr(IV)} \quad \text{ligand complex} + \text{ArSMe} \quad \overset{\text{several steps}}{\longrightarrow} \quad \text{ArS(O)Me} + \text{Cr(III)} \longrightarrow \text{ligand complex} \quad (1.40)
\]

**Scheme 1.13**
The PA catalyzed Cr(VI) oxidation of alkyl aryl and DPSs in aqueous acetic acid medium have been investigated by Srinivasan et al. [127]. A good Hammett correlation exists for both alkyl aryl and DPSs. They proposed three different mechanisms (Scheme 1.14) which involve the formation of radical cation intermediate as a result of single-electron transfer (eq.1.41) or nucleophilic attack of sulfide on oxygen atom of Cr(VI)-PA complex (eq.1.43) or nucleophilic attack of sulfide on chromium of Cr(VI)-PA complex (eq.1.44) in the rate-limiting step. Studies with alkyl phenyl sulfides demonstrate that steric effect plays a significant role in the PA catalyzed oxidation.

\[
\text{Scheme 1.14}
\]
The kinetics of oxidation of ortho-substituted MPSs by Cr(VI) is significantly influenced by localized and delocalized effects both in the presence and absence of PA while steric effect plays a minor role in the reaction [128].

In the PA promoted Cr(VI) oxidation of DMSO [129] the Cr(VI)-PA complex formed at the pre-equilibrium step undergoes a nucleophilic attack by the O or S atom of DMSO followed by oxygen transfer or ligand coupling leads to the product dimethyl sulfone (Scheme 1.15). Similar mechanism has also been reported [130] in the Cr(VI) oxidation of DMSO catalyzed by Bpy.

![Scheme 1.15](image)

(IX) \[ \overset{k_1}{\underset{k_2}{\longrightarrow}} \]

(IX) \[ \overset{k}{\longrightarrow} \text{Me}_2\text{SO}_2 \ + \ Cr(IV)-PA \text{ complex} \]

(Scheme 1.15)

The oxidation of (S)-phenylmercaptoacetic acids (PMA) by Cr(VI) has been performed in 50% aqueous acetic acid in the presence of EDTA by Sathiyarayanan et al. [131]. A mechanism involving the formation of a ternary complex (XII) comprising of EDTA-Cr(VI) and PMA in a fast step followed by its hydrolysis in a subsequent slow step yielding the sulfoxide is proposed (Scheme 1.16). The participation
of water in the rate-controlling step is confirmed from the decrease in reactivity with $D_2O$ and formation of highly structured transition state is inferred from high negative entropy value.

The kinetics of oxidation of DL-methionine to its sulfoxide by Cr(VI) has been studied in aqueous acetic acid in the presence of EDTA [132]. In this reaction Cr(VI)-EDTA complex is proposed as the active electrophile. The reversible formation of a ternary intermediate with methionine and its decomposition are envisaged as Michaelis-Menten kinetics which explains the enhanced reactivity with EDTA. Similar mechanism involving decomposition of termolecular complex in a slow step has been proposed for the PA catalyzed Cr(VI) oxidation of phenoxyacetic acid [133] and for the
BPSDC oxidation of dibenzyl sulfoxide [134] catalyzed by Bpy, Phen, imidazole and OxH₂ where the order of catalytic efficiency is OxH₂ > Bpy > Phen > imidazole.

The catalytic activities of Phen, OxH₂ and PA in the Cr(VI) oxidation of trans-stilbene have been investigated by Meenakshisundaram et al. [135] where Cr(VI)-Phen/OxH₂/PA complex is suggested as the probable reactive electrophile. The mechanism involves the nucleophilic attack of the ethylenic bond on Cr(VI)-Phen/OxH₂/PA complex and the formation of a ternary complex. Comparison of the catalytic efficiencies of various complexing agents revealed that the effect is more pronounced in the case of oxalic acid.

The kinetics of PA catalyzed quinaldinium chlorochromate oxidation of phenol [136] in 60% acetic acid-water (v/v) medium shows unit-order dependence each with respect to oxidant, PA and substrate. The reaction is catalyzed by acid and low dielectric constant of the medium. A mechanistic study of the EDTA and Bpy assisted one-step two-electron oxidation of lactic acid by Cr(VI) was carried out by Khan et al. [137] where the chromate-ester experiences a redox-decomposition in the rate-determining step. In EDTA and Bpy catalyzed paths Cr(VI)-EDTA and Cr(VI)-Bpy complexes respectively have been suggested as the active oxidants. The kinetics of Cr(VI) oxidation of DMF in the presence of EDTA and Bpy was investigated in aqueous HClO₄ [138]. The reaction rate increases with increasing [EDTA] while added Bpy has negligible effect on the reaction rate. The first-order kinetics with respect to EDTA at low concentration shifts to zero-order at higher concentrations. The reaction is considered to proceed through the formation of a stable Cr(VI)-DMF-EDTA complex. Recently, Cr(VI) oxidation of several alcohols [139-143] and organic acids [144,145] catalyzed by Bpy have also been reported.
Rajagopal and co-workers [146] substantiated that pyridine bases PA, Bpy, Phen, imidazole and N-methyl imidazole efficiently catalyzed the carboxylato bound chromium(V) oxidation of aryl methyl sulfides. The catalysis is explained in terms of formation of Cr(V)-catalyst and Cr(V)-catalyst-substrate intermediate complexes. The products, sulfoxide and Cr(III) are formed as a result of ligand coupling between O atom of Cr(VI) and S center of sulfide.

1.7. Surfactants and micelles

Surfactants constitute an important class of industrial chemicals with a wide range of applications in chemical and technological areas including production and processing of foods, agrochemicals, pharmaceuticals, personal care and laundry products, petroleum and oil recovery, mineral processing, fuel additives and lubricants, paints, coatings and adhesives and in photographic films. They can also be found use in a wide spectrum of medical applications, soil remediation techniques and other environmental, health and safety applications [147-149]. By nature surfactants are amphiphilic molecules containing both hydrophilic and hydrophobic moieties. Based on their functional groups they are classified as anionic, cationic, zwitterionic and nonionic surfactants. Gemini or dimeric surfactants are amphiphilic compounds with hydrophobic chains connected by a spacer group [150].

The amphiphilic character of surfactants allows self-association or micellization among different molecules to form clusters called micelles, whereby the hydrophilic head groups exist in the micellar surface and the hydrophobic hydrocarbon chains occupy mainly the micelle interior. Thus micelles have polar exterior and nonpolar interior regions. Considerable leeway normally exists with regard to the location and positioning of solubilizates during the course of any interaction between two roughly defined regions. The hydrophilic part of the micelle normally achieves its solubility
either by ionic interactions or by hydrogen bonding. For nonionic surfactants, however, the hydrocarbon chain attraction is opposed by the requirements of hydrophilic groups for hydration and space.

The repulsive forces arising due to electrostatic and/or steric interactions between the polar head groups limit the micelle size while attractive forces favour the micelle growth. The formation of micelles by ionic surfactants is ascribed to a balance between the short-range attractive forces among hydrophobic groups and the repulsive forces among hydrophilic groups. The net charge of micelles is always less than the degree of micellar aggregates indicating that large fraction of counter ions remain associated with the micelle; these counter ions form the Stern layer at the micellar surface.

Micelle formation is usually explained by two models. One is mass action model in which a kind of dynamic equilibrium is considered between monomeric species and the micelles (eq.1.51). The other is phase separation model in which micelles are thought to form new phase in the system above the cmc.

\[ n \, S \xrightarrow{\text{eq.1.51}} S_n \]  

where n shows the number of monomer units present in the micelle i.e., the aggregation number, S stands for any surfactant and \( S_n \) shows micelle formed from the surfactant monomers.

Hartley [151] proposed that micelles are spherical with charged groups situated at the micellar surface. Bain [152] suggested that lamellar and spherical forms coexist. X-ray studies by Harkins et al. [153,154] suggested the sandwich or lamellar model. Later, Debye and Anacker [155] proposed that micelles are rod-shaped rather than spherical or disk like. The cross section of such a rod would be circular with the polar heads of the detergent lying on the periphery and the hydrocarbon tails filling the
interior. Though different shapes have been proposed for micelle, the spherical form is generally accepted as the actual structure.

1.7.1. Critical micelle concentration

The micellization characteristics of a surfactant are understood by determining the values of its micellization parameters such as critical micelle concentration (cmc), aggregation number etc., Micelles are the most prevalent aggregate structure in surfactant solutions and they form over a narrow range of surfactant concentration called the critical micelle concentration. Micelle formation involves a fairly specific number of surfactant molecules. Above the cmc, surfactant solutions show an abrupt change in physical properties such as electrical conductivity, surface tension, osmotic pressure, density, light scattering or refractive index [156].

The value of cmc depends on a large number of parameters. In a given homologous series of surfactants, longer the carbon chain length of the surfactant the lower is the cmc [157]. Zana [158] has attributed that the decrease of charge upon increasing number of carbon atoms reduce the electrostatic repulsion on the micellar surface. The more the ionized groups present in the surfactant, the higher the cmc due to the increase in electrostatic repulsion to form the micelles. The detailed study of the nature of the polar head group of ionic surfactants on the micelle properties has been reported by Anacker and his co-worker [155]. Since electrical repulsion is absent in non-ionic surfactants, aggregation is facilitated and hence their cmc values are much lower than the ionic surfactants.

The additives showed marked influence in cmc values of both ionic and nonionic surfactants [159]. The effect of added substances on the cmc depends greatly on whether the additive is solubilized in the micelles or in the intermicellar solution. The addition of
electrolytes to ionic surfactant in water decreases the cmc of ionic detergents and results in established linear dependence of log (cmc) on the concentration of added salt [157,160]. For nonionic surfactants electrolyte addition has little effect on cmc values. The cmc also depends upon the nature of the solvent: Berr [161] has shown that CTAB forms large micelles in D$_2$O than in H$_2$O.

A close relationship has been observed by Shirai et al. [162] between the association of counter-ions and cmc. Smaller the cmc stronger is the tendency towards the association of the counter-ions. Knowledge of these and other factors which alter the cmc is desirable and necessary in order to design meaningful kinetic experiments in the investigations of micellar catalysis and inhibition.

1.7.2. Micellar effects and kinetic models

The micellar effects have been explained by considering the hydrophobic and electrostatic interaction between the surfactants and reactants as well as the partitioning of the reactants in both aqueous and micellar media. Different models have been proposed by different researchers to explain the micellar effect and to determine the kinetic parameters. According to Berezin et al. [163,164], the surfactant solution above the cmc may be considered as a two-phase system consisting of an aqueous phase and a micellar pseudo-phase. The reactants, A and B may be distributed as shown in the Scheme 1.17.

\[
\begin{align*}
A_w & \xrightarrow{K_A} A_m \\
B_w & \xrightarrow{K_B} B_m
\end{align*}
\]

\[
\begin{align*}
A_w + B_w & \xrightarrow{k_w} \text{product} \\
A_m + B_m & \xrightarrow{k_m} \text{product}
\end{align*}
\]

(Scheme 1.17)
A quantitative rate expression for a bimolecular reaction according to Scheme 1.17 is given by,

\[ \frac{k_{\text{exp}}}{k_m P_A P_B CV + k_w (1-CV)} = \frac{1}{(1 + K_A C) (1 + K_B C)} \]  

(1.54)

where \( k_{\text{exp}} \) is the observed second-order rate constant in aqueous micellar system, \( C \) is the total surfactant concentration minus cmc i.e., \( C = [D] - \text{cmc} \), \( V \) is the partial molar volume of the surfactant in the micelle, \( CV \) and \( (1-CV) \) stand for the fractions by volume of the micellar phase and aqueous phase, \( k_m \) and \( k_w \) are the rate constants for the reaction occurring in the micellar phase and aqueous phase respectively. The binding constants (K) are related to their partition coefficients (P) as: \( K_A = (P_A - 1) V \) and \( K_B = (P_B - 1) V \). For the dilute surfactant solutions, where the volume fraction of the micellar phase is small (i.e. \( 1 \gg CV \)), the eq. 1.54 reduces to,

\[ \frac{k_{\text{exp}}}{k_m P_A P_B CV + k_w} = \frac{1}{(1 + K_A C) (1 + K_B C)} \]  

(1.55)

The Menger-Portnoy model [165-168] considers the partitioning of only one reactant say \( A \), between the micellar and aqueous phase (Scheme 1.18).

\[ A_m + B \xrightarrow{k_m} \text{product} \]  

(1.56)

\[ A_w + B \xrightarrow{k_w} \text{product} \]  

(1.57)

(Scheme 1.18)

The Scheme 1.18 leads to the rate law,

\[ k_w = \frac{k_m K_A C + k_w}{(1 + K_A C)} \]  

(1.58)
where $K_A$ is the binding constant in terms of the micellized surfactant, $k_m$ and $k_w$ are the first-order rate constants in the micellar and aqueous phase, $C$ is the concentration of the micelle.

A kinetic model (Scheme 1.19) analogous to the Hill model proposed for enzyme catalyzed reactions was developed by Piszkiewicz [169-171] to explain the micellar effect. It considers that the substrate (S) and detergent (D) molecules aggregate to form the active micelle ($D_n S$). To explain the rate-retarding effect of the detergent at its higher concentrations, formation of the kinetically inactive micelle through the aggregation of surfactant molecules has been considered.

\[
\begin{align*}
D_n S & \xrightarrow{k_m} \text{product} \\
S & \xrightarrow{k_w} \text{product}
\end{align*}
\]

(Scheme 1.19)

The observed rate constant is,

\[
k_{\text{obs}} = \frac{k_m [D]^n + k_w K_D}{K_D + [D]^n}
\]

where $K_D$ is the dissociation constant of the micelle back to its free components, $k_m$ is the rate of reaction within the micelle and $k_w$ is the rate constant of reaction in the absence of micelle.

In the pseudo-phase ion-exchange model [164,172], the micellar surfaces are treated as selective ion-exchangers saturated with the counter-ions. If the reactant is a di-positive species, $R^{2+}$ then in the presence of SDS micelles, both the $R^{2+}$ and $Na^+$ ions will
compete for micellar binding and the pseudo-phase ion-exchange equilibrium will be established (Scheme 1.20). The equilibrium will be shifted in the direction favouring an increase in the number of reactant species in the aqueous phase with increasing [Na\(^+\)]. In this model, the ion-specificity for binding has not been considered. If there is a significant ion-specific interaction, then this model will not be applicable. Sometimes, binding of the counter-ions may perturb the micellar structure and then also the simple ion-exchange model will not be applicable.

\[
\begin{align*}
R^{2+}_w + 2 \text{ Na}^+_m & \xrightleftharpoons{K_{ex}} \text{ R}^{2+}_m + 2 \text{ Na}^+_w \\
\text{product} & \quad \text{product}
\end{align*}
\]

\[(\text{Scheme 1.20})\]

1.7.3. Kinetic studies in micellar medium

Kinetic studies in micellar media can provide mechanistic details about hydrophobic and electrostatic interactions not only in chemical redox reactions but also in biological electron transfers which take place on membrane surfaces and at protein-substrate interfaces. Kinetic and mechanistic studies of a variety of chemical reactions in presence of micellar aggregates have been carried out to understand the nature of interactions existing between reactant molecules, intermediates and micelles. Micellar aggregation number, cmc values and extent of incorporation of counter-ions are very important in the kinetic studies of reactions carried out in micellar media.

Micellar effect on the kinetics and mechanism of chromium(VI) oxidation of organic substrates has been reviewed by Das [173]. The anionic surfactant SDS accelerates the Cr(VI) oxidation of DMSO in presence of PA monotonically while
cetylpyridinium chloride retards the reaction continuously [129]. The observed micellar effects have been explained by considering the hydrophobic and electrostatic interaction between the surfactants and reactants. The pseudo-phase ion-exchange model has been applied to explain the micellar effect and the Piszkiewicz model has been applied to determine the kinetic parameters.

The redox reactions of dialkyl sulfides with Cr(VI) [174] following a mechanism involving the rate-determining nucleophilic attack of sulfide on chromium of oxidizing species followed by fast ligand coupling between O\(^{-}\) and S\(^{+}\). The catalytic role of H\(^{+}\) and development of positive charge on S due to electron transfer from sulfur favour the reaction in the anionic micelle, SDS and disfavour in the cationic micelle, cetyltrimethylammonium chloride.

Bharathy et al. [175] studied the rate of electron transfer from organic sulfides to [Cr\(^{V}(ehba)_{2}\)]\(^{-}\) (ehba-2-ethyl-2-hydroxybutyric acid) in micellar medium. The micellar inhibition observed in the presence of SDS is explained on the basis of decrease in the polarity of the medium, the electrostatic repulsion faced by the anionic oxidant from the anionic micelle and the partition of the hydrophobic substrate between the aqueous and micellar phases. The micellar catalysis in the presence of CTAB is attributed to the increase in the concentration of both the reactants in the micellar phase. This catalysis is contrary to the enormous micellar inhibition observed with IO\(^{4-}\), HSO\(^{5-}\) and HCO\(^{4-}\) oxidation of organic sulfides.

Rate acceleration by anionic surfactant while retardation by cationic surfactant have been observed in the Cr(VI) oxidation of DMSO [173-177] and dialkyl sulfides [174]. The catalytic role of SDS is explained in terms of preferential concentration of H\(^{+}\) ion in the anionic micellar phase. Further in SDS the sulfate head group can stabilize the
positive charge on S in the transition state. The cationic surfactant inhibits the reaction because the approach of $\text{H}^+$ ion to the cationic micellar surface (in which both the reactants are preferentially concentrated) is unfavourable due to the electrostatic repulsion. Similar accelerating effect is observed in the Cr(VI) oxidation of dialkyl sulfides in the presence of SDS [174], where the reaction proceeds through ET mechanism. But rate inhibition was noticed in the oxidation of organic sulfides with other oxidants in the presence of SDS [178-180].

1.8. Linear free energy relationships

Linear free energy relationships are empirical relationships between thermodynamic quantities and are known as extra-thermodynamic equations [181]. Linear free energy relationships are attempts to develop quantitative relationships between structure and reactivity. When a series of reactions are carried out by varying the substituents in a substrate with a range of electronegativities, the reaction rate changes. Successful correlations between structure and reactivity not only aid the understanding of the reactions but also allow predicting the nature of transition state and mechanism of chemical reactions.

To summarize the effects of meta- and para-substituents on the rate constants in aromatic reactions, Hammett [182] developed a direct quantitative correlation between the rate constants for a series of reactions and a constant $\sigma$ called substituent constant, which depends only on the electronic effects of substituent relative to that of hydrogen and is independent of the reaction. The equation which correlates the above two quantities is known as the Hammett equation (eq.1.64).

$$\log \left( \frac{k}{k_o} \right) = \rho \sigma$$  \hspace{1cm} (1.64)

where $k_o$ is the rate constant of reaction for the unsubstituted compound, $k$ is for substituted compound and $\rho$ is the reaction constant.
The substituent constant $\sigma$ is a measure of the total polar effect exerted by the substituents in the meta- and para- positions on the reaction center whereas $\rho$ is the slope of the line correlating $\log k$ with the sigma values of the substituents and is the measure of the susceptibility of the reaction towards the electronic effects. The reaction constant $\rho$ depends on the nature of the reaction including conditions such as solvent and temperature. The magnitude of $\rho$ measures the extent of transmission of electronic effect of substituents. The negative $\rho$ value is an indication of the development of positive charge in the transition state while the positive $\rho$ value specifies the development of negative charge at the reaction center which leads to rate acceleration by electron-withdrawing groups.

1.8.1. Modifications of the substituent constants

Though Hammett treatment can be used to correlate an enormous amount of data for many reactions, there are instances in which the rate data do not fit with Hammett equation. There are reactions where the substituents are in direct resonance interaction with the reaction site, such type of resonance interaction is called ‘cross conjugation’ or ‘through resonance’. Brown and Okamato [183] derived a new set of substituent constants based on the ionisation constants of substituted anilinium ions designated as $\sigma^+$, for correlating reactions in which an electron-deficient reaction site can directly conjugate with electron-donating substituents. Likewise, for electron-withdrawing substituents entering into direct conjugation with electron rich reaction center $\sigma^-$ constants [184] were proposed based on the ionisation constants of phenols.

The Hammett equation and its modified forms [185,186] all collectively known as linear free energy relationships (LEFR) have been found useful for correlating reaction rates and equilibrium constants for side chain reactions in meta- and para-substituted derivatives. The existence of a linear relationship indicates the operation of a single
mechanism throughout the reaction series. *Ortho* isomers and aliphatic compounds do not exhibit this relationship due to increased crowding in the transition state of o-isomers and flexibility of aliphatic compounds because of the weak relation between their structure and equilibrium positions.

**1.8.2. Isokinetic relationship**

Variation in rate within a reaction series may be caused by changes in either or both the enthalpy and the entropy of activation. According to Leffler [187] for a reaction series which follows Hammett’s LFER, the reaction must be either isoentropic or $\Delta T S$ should vary linearly with $\Delta T H$ according to the eq. 1.65.

$$\Delta T H = \Delta T H_o + \beta \Delta T S$$  \hspace{1cm} (1.65)

This relationship is called isokinetic relationship and $\beta$ is the isokinetic temperature which can be calculated from the slope of the linear correlation between $\Delta T H$ and $\Delta T S$. The isokinetic temperature is the temperature at which the effect of substituent on rate of the reaction vanishes and all the substituted compounds in a given series have the same reactivity. According to Petersen and co-workers [188] the isokinetic relationship between $\Delta T H$ and $\Delta T S$ is significant only if the range of observed $\Delta T H$ ($\Delta \Delta T H$) should exceed twice the maximum possible error ($\delta$) in $\Delta T H$. According to Bunnett [189] if the experimental temperature is above the isokinetic temperature in a reaction series obeying isokinetic relationship, then the reaction having the highest entropy has the highest rate.

For the reactions where excellent correlation is not obtained with eq.1.65, Exner showed an alternative method of correlation to determine the isokinetic temperature. According to Exner [190] a good linear log-log plot of the rate constants at two different temperatures by employing eq.1.66 is an indication of the existence of an isokinetic relationship.
\[
\log k_2 = a + b \log k_1 \quad (1.66)
\]

The slope of the plot of \( \log k_2 (T_2) \) vs. \( \log k_2 (T_1) \), \( T_2 > T_1 \) affords the slope, \( b \) and applying the value of ‘\( b \)’ in eq.1.67 the isokinetic temperature is calculated.

\[
\beta = \frac{T_1T_2(b-1)}{(bT_2 - T_1)} \quad (1.67)
\]

### 1.9. Reactivity-selectivity principle

The inverse relationship which exists between the increasing reactivity of a reagent and its selectivity is called reactivity-selectivity principle (RSP). Various definitions and modifications have been proposed by Exner [191] for RSP. When two similar reagents react in analogous reactions with various substrates of a given set, the reagent which reacts faster should show smaller differences in reaction rates within the set i.e., lower selectivity. The difference in reactivity between the sets should be larger than within the sets. Further extensions of RSP are possible in which the two reagents are replaced by one reagent in two different solvents or under different conditions or both the reagents and conditions are varied.

The experimental basis for the verification of RSP is based on a set of rate constants when two reagents (fast, \( F \) and slow, \( S \)) react with a series of similar substrates. Then the similarity of the reactions requires an approximate, more or less precise linear relationship between the two series as in eq.1.68. The precision of eq.1.68 is tested using correlation coefficient and standard deviation from the regression line.

\[
\log k_{Fi} = a + b \log k_{Si} + \varepsilon_i \quad (1.68)
\]

where \( \varepsilon_i \) is a random variable with zero mean value i.e., the error of eq.1.68 and \( i = 1, 2, 3, \ldots n \). For valid RSP the slope \( b \) must be positive but less than 1 \((0 < b < 1)\). While choosing the reagent and substrates the rate difference between the reagents
should be greater than that between the substrates. When the difference in reactivity is almost zero or extremely large one must expect that the difference in selectivity is almost zero. Since the difference between the reagents is variable along the series of substrates, it is advisable to define the mean difference $\Delta$ as in eq.1.69.

$$\Delta = \left( \sum \log k_{F_i} - \sum \log k_{S_i} \right) / N$$  \hspace{1cm} (1.69)

When $\log k_{F_i}$ values are plotted against $\log k_{S_i}$ values, according to this principle four types of graphical representation can be seen. The four anticipated types of behaviour are valid RSP, anti RSP, indifferent behaviour and crossing.

i. The RSP is valid when the slope $b$ is significantly less than unity and $\Delta$ is not too small (greater than the range of $\log k_{F_i}$) and the case is noted as RSP (+).

ii. When $b$ is greater than unity the reversal of RSP takes place and is RSP (-).

iii. No decision is possible when the slope $b$ is not significantly different from unity. The reason may be either equal selectivity of the two reagents or an insufficiently precise linearity and this case is denoted as RSP (?).

iv. When $\Delta$ is too small it may be that the regression line intersects the straight line $y = x$. then the validity of RSP is changed since the terms, fast reagent and slow reagent will exchange and is denoted as RSP(±).

When measurements are made with more than two reagents, the linear relationship between $\log k_{F_i}$ and $\log k_{S_i}$ values in the graphical representation shows family of straight lines intersecting at one point, $y_0$. In the field of RSP this point is termed as ‘magic point’ which represents some limiting value of reactivity in which for a particular substrate the reaction rate is independent of the reagent and vice versa. When RSP holds this point should be situated on the side of high reactivity.
1.10. Scope of the present investigation

One of the most prevalent types of chemical processes is the electron transfer reaction as they mimic the reactions taking place in biological systems. Chromium(VI) is established as a versatile oxidant for many types of substrates varying from metal ions to several organic compounds and it paves way for the synthesis of variety of useful compounds. The study of Cr(VI) oxidations create considerable interest due to the existence of different chromium(VI) species, involvement of different intermediates Cr(IV) and Cr(V) and the tendency of final product chromium(III) to form a variety of complexes. Therefore different attempts are required to confirm the intermediacy of different oxidation states of chromium by use of competition experiments.

Sulfur compounds involved in metabolic reactions serve as both fuels and respiratory oxygen replacing materials. The covalent bonds of sulfur between peptide chains confer extra toughness and rigidity. Transition metal-sulfur bonds are ubiquitous not only in metalloenzymes but also present in man-made functional materials and in catalysts with various architectures of structural interest. Since chromium-sulfur interaction is of biologically important and the mechanistic aspects of oxidation of organic sulfur compounds by Cr(VI) differ significantly, efforts have to be made to understand the mechanism of such reactions.

Thioacids rapt the attention of researchers since, they possess versatile synthetic possibilities and valuable properties as building blocks for the synthesis of sulfoxides and sulfones. They turn out to be convenient models for studying the optical properties of sulfoxide systems. Even though the researchers focused their study on sulfur containing acids like phenylmercaptoacetic acid and phenylsulfonylacetic acid, no systematic investigation has yet been reported on the kinetics of oxidation of phenylsulfinylacetic acid, PSAA. The literature scanning and the applicability of PSAA
in pharmaceuticals prompted to undertake the present study of oxidation of phenylsulfinylacetic acid by Cr(VI). Various ligands were used in the reaction to identify their effects in the Cr(VI) oxidation. The possible roles played by such ligands are, they may either undergo oxidation leading to a radical mechanism or act as catalysts without undergoing any change. As the electron transfer reactions in micellar media resemble the enzyme catalyzed reactions, the micellar effects also have been studied to substantiate the proposed reaction mechanism. Hence the experiments were designed to meet the following objectives.

i) To get an insight into the mechanism of oxidation of PSAA by Cr(VI) in aqueous acetonitrile media and document the kinetic and spectral proofs.

ii) To accomplish the above reaction in the presence of oxalic acid in order to observe the role of oxalic acid, either as a catalyst or a co-reductant and to propose the relevant mechanism.

iii) To corroborate and compare the catalytic activity of nitrogenous ligands viz., PA, PDA, Bpy and EDTA in the Cr(VI) oxidation of PSAA and to investigate the respective mechanisms.

iv) To probe the effect of different micelles on the Cr(VI) oxidation of PSAA.

v) To study the substituent effects in the above oxidations in order to get a perception about the mechanism of the reaction.

With these in mind several *para*- and *meta*-substituted phenylsulfinylacetic acids were synthesized and the rate measurements were carried out under different conditions.
1.11. References


