CHAPTER I

GENERAL INTRODUCTION

Although most chemical reactions are extremely complex and the rate equations are often baffling in interpretation, there is a growing realization that the complexity is due mainly to the presence of many simple unimolecular or bimolecular steps which are going on successively or simultaneously or in opposition to each other. The great hope for advances in chemical kinetics lies in the fact that these simple unimolecular or bimolecular steps can be understood and calculated. The challenge is to put these various steps together to give the overall reaction and predict its rate. One of most intriguing areas of chemistry is that which deals with the mechanism of a reaction. The mechanism is a mental model devised to explain the facts.

Reaction rate is of great practical interest in both laboratory and industry. The reaction that takes years to become sensibly complete is particularly useful in making its products, but reactions that complete in fraction of seconds include hazardous explosion. Therefore, it becomes necessary for a kinetician to understand the factors controlling the rates. For synthetic purpose, knowledge of reaction mechanism will often allow the reaction condition to be selected for maximum product yields. Finally, it is an area of chemistry where the practical application of theory lacks far behind the realm of experiment, yet at several points, theory has not proved to be success.
Kinetic studies are receiving much importance in the recent years since they provide us the most powerful method of investigating the detailed reaction mechanisms. It is one of the most intriguing and challenging areas of chemistry, which deals with the mechanisms of reactions. To many chemists the real heart of chemistry is the study of mechanisms. Thus, chemical kinetics can be defined as that branch of chemistry concerned with the study and prediction of time dependent systems. To understand the mechanism of any reaction we must know a reaction as a function of time, the exact positions of all the atoms as the reactants are converted into product molecules. Virtually all information regarding reaction mechanism comes by inference of indirect evidence. Hence, it is the important job of chemists to device the proper experiments to generate most conclusive evidence.

The experimental part of the subject deals with ways of measuring precisely the rates of reactions at various varying conditions of the experiments. The interpretation of results leads to an understanding of the mechanism of the reaction. The combination of the results of a large number of experiments gives rise to general theories of chemical reactivity. The important steps in any kinetic investigations are; (1) collection of kinetic data (2) establishment of relationships between the rate and reaction mixture composition (3) study of structural effects and (4) interpretation of the collected data to arrive at reaction mechanism.

The award of Nobel prize for the year 1992 to Prof. R. A. Marcus on the "Electron Transfer Reactions" and 1999 Nobel prize to Prof. Ahmed Zewail for
discovery of “Femtochemistry” and 2001 Nobel prize to Profs. William Knowles, K.Barry Sharpless and Royji Noyori for their work on “Chirally Catalysed Hydrogenation Reactions” emphasize the importance of field of reaction kinetics. Electron transfer reactions play a central role in physical, chemical and biological processes. Because of the ubiquity of electron transfer processes, the study of electron transfer reactions, perhaps more so than that of any other area of chemistry is characterized by a strong interplay of theory and experiment. Nonetheless the importance of electron transfer in transition metal redox chemistry has been recognised and more recently it has become increasingly obvious that many reactions in organic chemistry once thought to be concerted in nature also occur via sequential one electron steps.

The kinetic data will be the source of a great deal of detailed insight into the mechanism of a reaction. Although, other types of experimental evidences are also sought for purpose of formulating a reaction mechanism, the study of reaction kinetics generally forms the backbone of a thorough mechanistic investigation.

The work of Henry Taube in redox systems unequivocally demonstrated the transport of electron from reductant to oxidant. This discovery certainly added many important features in the syntheses of coordination complexes and organometallics. It is such a subject, which has manifestations in almost all walks of life. As a result, oxidation-reduction reaction needs at least two reactants, one capable of gaining electrons (oxidant) and the other capable of losing electrons...
(reductant), i.e., a reducing agent (reductant) by losing electrons, gets oxidised and an oxidising agent (oxidant), by gaining the electrons, gets reduced.

The reaction thus consists of transfer of electrons from a reducing agent to an oxidising agent, so that there cannot be an oxidation without concomitant, reduction. Such cases where oxidation and reduction are involved are commonly termed as redox reactions; and such a redox system involves a redox potential. It follows automatically, that any oxidation-reduction reaction must involve two redox couples that differ in their affinity for electrons. This affinity of atoms for electrons is conferred to them by their particular atomic structure and it is expressed in terms of reduction potential or redox potential. Reduction potential of a redox couple is its tendency to get reduced from one oxidation state to another oxidation state. Redox reactions are also defined as involving changes in oxidation states or oxidation numbers. In a redox reaction, the oxidation number of the oxidant decreases and that of the reductant increases. The transfer of electrons is a book keeping device for effecting the changes in oxidation states and for balancing the equations.

Particularly in aqueous solutions, it is usually possible to imagine atom or group transfer, rather than electron transfer, as occurring in a redox reaction. For example, iron(II) ion may act as a reducing agent by transferring a hydrogen atom from its hydration shell to a substrate:

\[
\text{Fe(H}_2\text{O)}_6^{2+} + \text{RH} \rightarrow \text{Fe(H}_2\text{O)}_5\text{OH}^{2+} + \text{R}^\cdot
\]
Iron(III) ion may act as an oxidising agent by transferring hydroxyl radical to a substrate:

\[
\text{Fe (H}_2\text{O)}_6^{3+} + \text{R}' \rightarrow \text{Fe (H}_2\text{O)}_5^{2+} + \text{H}^+ + \text{ROH}
\]

In general, transfer of a positive group or atom is equivalent to the transfer of electrons and transfer of a negative group or atoms is equivalent to the taking up of electrons. The problem, then, in studying the mechanism of an oxidation–reduction reaction, is to find out whether atom transfer or electron transfer occurs, which atoms are transferred, and what intermediates, stable or unstable species are formed. A complete study would include a detailed picture of the transition state for all steps involved. Not only the composition but also the geometry of the transition state is desired.

**OXIDATION-REDUCTION IN INORGANIC REACTIONS**

Two general classes of transition states emerge for redox reactions involving metal complexes, the so called *outer-sphere* and *inner-sphere types*. In the first of these, the inner coordination shells of both the metal ions are intact in the transition state. In the second case, the two metal ions are connected through a bridging ligand common to both the coordination shells. From *Franck-Condon principle*, it follows that before electron transfer between two ions is possible, the energy of the electron must be the same in the two sites. There must also be sufficient orbital overlap between the two sites to provide for a reasonable probability of a transfer.
In the case of reaction of outer-sphere type, the electron must wait for appropriate fluctuation of the ions and their coordination spheres, without in any way being able to influence the changes required in the site to which it will be transferred. For reactions of inner-sphere type, an activated complex of the type \( L_x M^{n+1} - X - M^n W_x \) may be formed, where \( L, X \) and \( W \) are ligands. In arriving at a configuration having \( X \) as a bridging group, either \( M^{n+1} \) or \( M^n \) (or both) has undergone substitution in the first coordination sphere. Delocalisation of an electron over two sites will lower the energy needed for the formation of the activated complex and the electron will be able to affect the energy required to produce a fluctuation at the site to which it is going to be transferred.

Presumably the reaction is consummated by the fluctuation, which causes the separation of \( M^{n+1} \) and \( M^n \) and may well require other changes in the coordination spheres as well. A feature of the bridged activated complex is that the bridging group may move from the oxidising agent to the reducing agent.

The most conclusive evidence for the mechanism comes from isolation of the products, which is possible only if the appropriate solvolysis reaction occurs slowly. However, the reaction of Cr(II) and some of the reactions of V(II) and Fe(II) are convincingly characterized as following the inner-sphere mechanism. In the latter case, the immediate \( V(III) - X \) or \( Fe(III) - X \) products have often been detected spectrophotometrically, prior to their dissociation. Therefore, probably the inner-sphere mechanism is the most favorable provided, (a) a suitable ligand is available in the coordination sphere of the oxidising complex and (b) substitution
of a water molecule in the reducing agent occurs sufficiently rapidly to permit the transition state M-X-M' to form rapidly.\textsuperscript{9a} The most common instances of outer-sphere mechanism are found when nature of the coordination sphere of one reeductant of other contains ligands unsuited for bridging or when exchange occurs too slowly to permit bridge formation. Among such reactions\textsuperscript{9b} are Co(NH\textsubscript{3})\textsubscript{6}\textsuperscript{3+} oxidations and Cr(bipy)\textsubscript{2}\textsuperscript{2+} reductions; certain reactions of V(H\textsubscript{2}O)\textsubscript{6}\textsuperscript{2+}, which undergo substitution more slowly than most divalent ions; electron exchange of Fe(C\textsubscript{5}H\textsubscript{5})\textsubscript{2} and Fe(C\textsubscript{5}H\textsubscript{5})\textsubscript{2}\textsuperscript{+}; and reactions such as electron exchange of Fe(CN)\textsubscript{6}\textsuperscript{3-} and Fe(CN)\textsubscript{6}\textsuperscript{4-}.

**OXIDATION-REDUCTION IN ORGANIC REACTIONS**

The oxidation-reduction concepts, however, are not so clearly applicable in organic chemistry, for when carbon compounds are oxidised their component atoms are very seldom deprived of their surrounding complete electron shells. Covalent bond fission is an essential feature of organic reactions and it can be effected by two different pathways,\textsuperscript{10} viz., \textit{Homolytic reactions} in which electron pairs are symmetrically disrupted and \textit{Heterolytic reactions} in which electron pairs are transferred from one molecule to another as an undivided entity.

Electron removal by these two pathways has clearly distinguishable characteristics.

In homolytic oxidations electrons are removed singly from organic molecules by active atoms such as chlorine, or by active free radicals. Though, molecules containing unshared electrons can be oxidised in this way, homolytic
oxidations usually involve the removal from an organic molecule of one electron together with a hydrogen atom e.g.,
\[
R_3C-H + Cl^- \rightarrow R_3C^* + HCl
\]
The initial organic product necessarily has unpaired electron and so must perforce undergo a reaction of similar type e.g.,
\[
R_3C^* + Cl-Cl \rightarrow R_3C-Cl + Cl^-
\]
or must combine with another free radical before stable entities alone result. Thus, chain reactions, dimerisations or disproportionations e.g.,
\[
2 C_2H_5^* \rightarrow C_2H_6 + C_2H_4
\]
are typical homolytic reactions.

All homolytic electron transfer reactions, such as above require very much less activation energy than needed for direct breakage of a covalence. Hence, homolytic oxidations, when once started, proceed very rapidly indeed. The traces of free radicals required for the initiation of homolytic oxidation may be formed by thermal dissociation of molecules which have weak covalence’s, by disruptions of molecules by exposure to radiant energy, high energy particles (α-particles) or electrons (β-particles) or by single electron transfer, from ions of transition elements which can have incomplete inner electron (d—) shells. Consequently oxidations, which are demonstrably prone to catalysis in these ways, are homolytic in type.

Heterolytic oxidations involve the attack on organic compounds of electrophilic reagents, which can, by a single process gain control of a further
electron pair. Heterolytic oxidants therefore attack the exposed electron pairs of atom such as oxygen, nitrogen or sulphur or the loosely held π-electrons of olefins, rather than buried electron pairs of C–H, O–H or N–H bonds. Again, heterolytic reactions yield stable molecular or ionic products in one or at most two consecutive stages and very seldom lead to chain reactions. On the other hand, they usually require higher activation energy than homolytic reactions and so tend to be slower processes. Use of catalyst lowers the activation energy in such cases. When heterolytic reactions are subjected to catalysis, the mechanism of catalysis is largely different from the catalysis involved in the case of homolytic reactions.

PROBABLE WAYS OF ELECTRON TRANSFER REACTIONS

Oxidation-Reduction reaction may involve one or more electron transfer. Depending upon the number of electrons transferred between oxidant and reductant, the reaction may proceed in one or more steps. Transition metals such as iron and cobalt and several others usually exhibit stable oxidation states differing by one electron and react with each other through one equivalent steps. However, the stable oxidation states in post transition elements such as arsenic, antimony etc., differ by two electrons. Thus, on the basis of their pattern of reactivity, the reactions of these elements are classified into two main categories.4,11-16
COMPLEMENTARY AND NON-COMPLEMENTARY REACTIONS

Complementary Reactions

Complementary reactions are those in which oxidant and reductant both undergo two-equivalent changes or one-equivalent change. These reactions generally obey a bimolecular rate equation and the electron transfer can take place in a single step or in two steps of one electron each. In $\text{Tl(I)} \rightarrow \text{Tl(III)}$ exchange reactions, electrons are transferred in a single step as the formation of the intermediate, $\text{Tl(II)}$, is not detected. On the other hand, the oxidations of $\text{As(III)}^{17}$ and $\text{Sb(III)}^{18}$ by $\text{Tl(III)}$ are other reactions where no evidence for the formation of $\text{Tl(II)}$ has been obtained. The evidence obtained for the formation of $\text{As(IV)}$ in pulse radiolytic studies indirectly supports one-equivalent steps in $\text{As(III)}$ oxidations. However, such an evidence in the reaction of $\text{As(III)}$-$\text{Tl(III)}$ has not been observed. It is assumed that $\text{As(IV)}$ is formed in the reaction (i) then it is very much likely that the two intermediates $\text{Tl(II)}$ and $\text{As(IV)}$ react with each other before they can diffuse out of the solvent cage in which they are found.

$$\text{As(III)} + \text{Tl(III)} \rightleftharpoons \text{Tl(II)} + \text{As(IV)} \quad (i)$$

A large number of complementary reactions have been explained by assuming the formation of bridged activated complex between oxidant and reductant further facile transfer of electron through the bridging ligand.
Non-Complementary Reactions

Non-complementary reactions are those in which oxidant and reductant undergo unequal equivalent changes such as one-equivalent oxidant interacts with two equivalent reductant and two-equivalent oxidant interacts with one-equivalent reductant. There are a number of possibilities of electron transfer in non-complementary reactions and these are related to the nature of both oxidant and reductant.

MULTI EQUIVALENT REACTIONS

Oxidising agents such as Cr(VI) and Mn(VII) undergo net changes of 3 and 5 units in oxidation number respectively during their reactions in acidic solution. For the most part, these reactions occur by one or two electron steps, with the necessary intervention of unstable intermediate oxidation states of Cr or Mn. The reactions of Cr(VI) with transition metal complexes generally proceed by sequential one-electron step, but with post transition metal ions and with non-metallic compounds, two electron steps appear to be preferred.

Electron transfer reactions are found to be governed by two classical principles

(a) Michaelis Principle of Compulsory Univalent Oxidation Steps

(b) Shaffer’s Principle of Equivalent Change

Michaelis hypothesis involves the principle that an oxidation-reduction reaction takes place in one or more successive single electron transfer steps. This principle evolved from a considerations of restricted field of redox reactions, of which the
oxidation of hydroquinones to quinones through semiquinone intermediate is
typical and is now generally recognised as being without universal validity. Apart
from the reactions involving metal ions, many two equivalent redox reactions are
now known which proceed in one step through the transfer of hydride ion or an
oxygen atom.\textsuperscript{22, 23}

\[ \text{E.g., } \ \text{NO}_2^- + \text{OCl}^- \rightarrow \text{NO}_3^- + \text{Cl}^- \]

The second principle\textsuperscript{20, 21} refers to the observation that non-complementary
reactions are often slow compared with complementary one's. Examples are the
slow reduction of Ti(III) by Fe(II) or Ce(IV) by Ti(I) as compared to the rapid
reduction of Ti(III) by Sn(II) and Ce(IV) by Fe(II).

One of the implications of the comparison on which the principle of
equivalence change is based is that reactions between 2-equivalent oxidants and
2-equivalent reductant occur by a concerted 2-equivalent step. This may well be
the case for reactions such as the Ti(I) $\leftrightarrow$ Ti(III) exchange.\textsuperscript{24-26} The observation
expressed by Shaffer, for non-complementary reactions, is based on the low
probability of termolecular mechanisms as one possibility or the formation of the
unstable valence states as the other possibility.\textsuperscript{15} Another expected feature of
these reactions will be the frequent occurrence of catalysis since the normal paths
will be slow.

**UNSTABLE OXIDATION STATES**

The formation of unstable oxidation states during the course of non-complementary reactions has been now anticipated in a number of such reactions
with sufficient proofs. For example, the reductions of Tl(III) by Fe(II)\textsuperscript{27,29}, V(III) or V(IV)\textsuperscript{30-33} and Cr(VI) by Tl(I)\textsuperscript{34} can only be explained through the formation of unstable Tl(II) species. Similar unstable oxidation states have been observed in other studies.\textsuperscript{32,33} The interconversions between Cr(III) and Cr(VI) always appear to involve the unstable states Cr(IV) and Cr(V).

In a classic study, King and Tong\textsuperscript{35} have worked out the details of the redox reactions between Ce(IV) and Cr(III) in aqueous sulphuric acid. The rate law was found to be as in equation (ii), which is very reasonably explained by the mechanism involving steps of equation (iia) to (iic).

\[
\text{Rate} = K \times k \times [\text{Ce(IV)}]^2 \times [\text{Cr(III)}]/ [\text{Ce(III)}] \quad (\text{ii})
\]

The first step is a rapid equilibrium, and a second step, the interconversion of Cr(IV) to Cr(V) is rate determining.

\[
\begin{align*}
\text{Ce(IV)} + \text{Cr(III)} & \rightleftharpoons \text{Ce(III)} + \text{Cr(IV)} \quad \text{fast:} \quad K \\
\text{Ce(IV)} + \text{Cr(IV)} & \longrightarrow \text{Ce(III)} + \text{Cr(V)} \quad \text{slow} \quad k \\
\text{Ce(IV)} + \text{Cr(V)} & \longrightarrow \text{Ce(III)} + \text{Cr(VI)} \quad \text{fast}
\end{align*}
\]

Excellent support comes from the study of related reactions such as the oxidation of vanadyl ion by acid chromate ion\textsuperscript{36} (HCrO\textsubscript{4}) and the analytical important oxidation of ferrous ion by acid chromate.\textsuperscript{37} It is significant that in the above example the change over from Cr(IV) to Cr(V) or vice versa, is rate determining. This may be related to the likelihood that, at this stage, a change in coordination number from 6 to 4 occurs.\textsuperscript{35} The stoichiometric examination of the reaction between acid chromate and Fe(II) or VO\textsuperscript{2+} in presence of iodide leads to the
conclusion that the rapid oxidation of iodide is because of its reaction with Cr(V). A related phenomenon is seen in the oxidation of As(III) by peroxodisulphate ion. This slow reaction is accelerated or oxidation is induced by adding Fe(II) and the reaction is postulated to go by the formation of As(IV) from the reaction (iiiia, iiib).

\[
\begin{align*}
\text{Fe(II)} + \text{S}_2\text{O}_8^{2-} & \rightarrow \text{Fe(III)} + \text{SO}_4^{2-} + \text{SO}_4^2 \quad \text{(iiiia)} \\
\text{As(III)} + \text{SO}_4^2 & \rightarrow \text{As(IV)} + \text{SO}_4^{2-} \quad \text{(iiib)}
\end{align*}
\]

As mentioned earlier, another feature of these unstable oxidation states is the frequent occurrence of catalysis. A number of studies of the catalysis by platinum metals of oxidation reactions have been made. The catalysis by Ag(I), Cu(II), Mn(II) and Cr(III) in oxidation–reduction reactions are also found to occur through formation of unstable oxidation states.

**ACTIVE SPECIES**

If a particular substance (oxidant, reductant or catalyst) is capable of existence in several forms in aqueous solution, all the species existing may not be active. Those species, which are involved in a slow step, will influence the reaction. The reaction conditions will determine the nature of the active species.

Moore and Anderson have reported that three or four species of Ce(IV) exist in sulphuric acid depending on its strength and the main active species in dilute solutions is Ce(SO₄)²⁻. Hardwick and Robertson have given the following equilibria amongst various species of Ce(IV) in sulphuric acid solutions. The
concentration of H\(^+\), HSO\(_4^-\) and SO\(_4^{2-}\) would determine the nature of the active species.

\[
\begin{align*}
\text{Ce}^{4+} + \text{HSO}_4^- & \rightleftharpoons \text{CeSO}_4^{2+} + \text{H}^+ \\
\text{CeSO}_4^{2+} + \text{HSO}_4^- & \rightleftharpoons \text{Ce(SO}_4)_2 + \text{H}^+ \\
\text{Ce(SO}_4)_2 + \text{HSO}_4^- & \rightleftharpoons \text{HCe(SO}_4)_3^- \\
\text{HCe(SO}_4)_3^- + \text{HSO}_4^- + \text{H}^+ & \rightleftharpoons \text{H}_3\text{Ce(SO}_4)_4^- 
\end{align*}
\]

To formulate the reaction rate as a function of species concentration, therefore, requires knowledge of the existence of such equilibria and generally speaking, the knowledge of determination of one or more equilibrium constants. The distinction between the species and laboratory concentrations is particularly critical in the cases of partially displaced equilibria, because the rate equations, if cast in the form of reaction rate as a function of laboratory concentration, quite often resemble the equations applicable to different mechanisms.

**EFFECT OF IONS ON THE RATE**

The rate of redox reactions of complex ions is highly sensitive to the presence of other ions in the solution. Usually, added anions have the greater influence on the reaction of two cat ions each other and added cat ions influence the rate of two anions with each other. Large effects of anions on the rate are usually attributed to the formation of bridged species if labile complexes are involved.

In the redox reaction between two cat ions, if the reducing agent is complexed first, it will be more stabilized in the oxidized form and hence the reaction is speeded up in the presence of anion. Also a negative ion should enable
to positive ions to approach each other more easily. This will be more effective if the negative ion is between the two cat ions in the transition state.

If the oxidising agent is complexed first the anion may stabilize it and slow down its rate of reaction. For example, the rate of reactions of Ce(IV) oxidations are reduced strongly by forming sulphate complexes in presence of sulphate. This shows, in agreement with the theory that the coumbic repulsions between reactants do not play a dominant role. The conclusions to be drawn are not that electrostatic factors do not exist, but that other factors are of greater importance. Some significant effects of chloride ions are particularly noticeable in redox reactions. The redox reactions in which the reductant is able to form complexes with chloride are Tl(I), Pd(II), Sn(II) and Sb(III).

**CATALYSIS**

Any substance, other than reactants which influences the rate of chemical reaction and itself remains unchanged chemically at the end, is called a catalyst. The phenomenon of rate alteration is designated as catalysis. Catalysts influence the reactions by changing the reaction path. Such catalytic influences arise as consequences of lowering of the energy of activation.

In solution involving inorganic oxidations, the catalysts are ions having unstable oxidation states. This case is a particular example of homogeneous catalysis where the catalyst present in the same fields as a part of reactants. Though, the mechanism of catalysis depends on the nature of the substrate,
oxidant and other experimental conditions, it has been shown that metal ion acts as catalyst by one of the following paths.

(a) The catalyst is first oxidised by the oxidant to its higher oxidation states, which in a subsequent step oxidises the substrate.

(b) The catalyst forms a complex with oxidant, the complex then oxidises the substrate either in the rate determining or in a fast step.

(c) The catalyst itself first oxidises the substrate in a slow step and the reduced form of the catalyst is oxidised by the oxidant in a fast step.

(d) The catalyst traps the radical produced as intermediates and oxidises them at faster rate.

**Importance of Catalysis**

Catalyst development and synthesis have become a wide spread research field because of the increasing global demand for better systems in chemical industry. Catalysis is also most effective and most rational of all the means for accelerating the chemical reactions. Catalytic processes are extensively used in industry and their use is continually increasing. Most of the technological processes introduced recently in chemical industry incorporate catalytic reactions. In presence of catalyst the rates of reactions are accelerated thousands and millions of times and they take place at low temperature, which is an economical advantage. Catalysis is utilized in manufacturing some of the most important inorganic products such as hydrogen, ammonia etc. Catalysis is widespread in synthetic chemistry as in the synthesis of high polymers viz. synthetic rubber, plasticizers and also...
intermediates for synthesis of dyes, insecticides etc. The successful exploitations of a material as a catalyst will give value-added products with improved yields and also eliminate or minimise environmental pollutants.

Osmium(VIII) is a case in point as it has been utilized\(^\text{10}\) as catalyst for hexacyanoferrate(III) oxidation of organic and inorganic substrates. The catalysis is understood to be due to the intervention of intermediate oxidation states of osmium. The detailed picture of its catalytic action has been reviewed by Upadhaya et al.\(^\text{45}\)

Often, very small quantities of catalysts like Os(VIII)\(^\text{46}\), Pd(II)\(^\text{47}\), Cr(III)\(^\text{48}\), Ru(III),\(^\text{49}\) V(V)\(^\text{50}\) etc., causes appreciable rate accelerations of particular reactions.\(^\text{39,40}\)

**STUDY OF FAST REACTIONS**

The study of fast reaction is on the threshold of exciting developments, since so many of the reaction of complexes, especially of transition series and biological processes are rapid. The impact of results on the understanding of inorganic, analytical and biological processes can be imagined.

**PRESENT WORK**

In the present thesis, some redox reactions in alkaline medium as detailed below have been studied. Reactions were followed conveniently by Spectrophotometer in the UV-Vis. region. The details of such studies are given below.

The thesis comprises eight chapters including the general introduction about chemical kinetics as follows.
1. **General Introduction**

This chapter introduces about the kinetics and mechanisms of reactions in general.

**PART I**

**MECHANISMS OF UNCATALYSED REACTIONS**

2. **Kinetics and Mechanism of Oxidative Degradation of L-proline by Alkaline Diperiodatonickelate(IV)—A Free Radical Intervention and Decarboxylation**

The kinetics of oxidation of L-proline by diperiodatonickelate(IV) (DPN) in aqueous alkaline medium at a constant ionic strength of 0.50 mol dm$^{-3}$ was studied spectrophotometrically. The reaction is of first order in [DPN], zero order in [Alkali] and less than unit order in [L-proline]. A mechanism involving the diperiodatonickelate(IV) as the reactive species of the oxidant has been proposed. The reaction constants involved in the different steps of mechanism are calculated. The isokinetic temperature was determined and discussed. The reaction follows a 1:2 stoichiometry as given below,

\[
\text{COOH} + 2\text{Ni}^{(IV)} + 2\text{OH}^- \rightarrow \text{H}_2\text{N} \text{COOH} + 2\text{Ni}^{(II)} + 2\text{H}^+ + \text{CO}_2
\]

3. **Kinetic and Mechanistic Investigation of Oxidative Degradation and Deamination of Atenolol by Diperiodatonickelate(IV) in Aqueous Alkaline Medium**

The kinetics of oxidation of atenolol (ATN) by diperiodatonickelate(IV) (DPN) in aqueous alkaline medium at a constant ionic strength of 1.0 mol dm$^{-3}$ was studied spectrophotometrically. The reaction is of first order in [DPN], less than unit order
in [Alkali] and zero order in [ATN]. Addition of periodate has no effect on the reaction. Effect of added products, ionic strength and dielectric constant of the reaction medium have been investigated. The main products were identified by IR, NMR and Mass spectral studies. A suitable mechanism is proposed. The reaction constants involved in the different steps of mechanism are calculated. The thermodynamic activation parameters with respect to slow step of the mechanism are computed and discussed.

4. Kinetic and Mechanistic Study of Oxidation of Sulfamethoxazole by Diperiodatocuprate(III) in Aqueous Alkaline Medium

The kinetics of oxidation of sulfamethoxazole (SMZ) by diperiodatocuprate(III) (DPC) in aqueous alkaline medium at a constant ionic strength of 0.10 mol dm$^{-3}$ was studied spectrophotometrically. The reaction between diperiodatocuprate(III) and sulfamethoxazole in alkaline medium exhibits 2:1 stoichiometry. The reaction is of first order in [DPC], less than unit order in [Sulfamethoxazole] and [Alkali]. Periodate has retarding effect on the rate of reaction. Decrease in the dielectric constant of the medium decreases the rate of reaction. The main products were identified by IR and NMR. A mechanism involving the monoperiodatocuprate(III) as the reactive species of the oxidant has been proposed. The rate law is given by,

$$\text{Rate} = \frac{d[DPC]}{dt} = \frac{k K_4 K_5 K_6 [\text{SMZ}][\text{OH}^\text{-}]}{[\text{H}_2\text{I}_2\text{O}_6^\text{3-}]} + K_4 \text{[OH]}[\text{H}_2\text{I}_2\text{O}_6^\text{3-}] + K_4 K_5 [\text{OH}] + K_4 K_5 K_6 [\text{SMZ}][\text{OH}^\text{-}]}$$
5. Mechanistic and Spectral Investigation of Oxidation of 4-Hydroxycoumarin by Aqueous Alkaline Permanganate by Stopped Flow Technique

The kinetics of oxidation of 4-hydroxycoumarin (HDC) by permanganate in aqueous alkaline medium at a constant ionic strength of 0.40 mol dm$^{-3}$ was studied spectrophotometrically using a rapid kinetic accessory. The reaction between permanganate and HDC in alkaline medium exhibits 6:1 stoichiometry. The reaction is of first order in [Permanganate], less than unit order in [HDC] and [Alkali]. The main products were identified by spot test, IR and NMR. A suitable mechanism is proposed. The reaction constants involved in the different steps of mechanism are calculated. The activation parameters with respect to slow step of the mechanism are computed and discussed and thermodynamic quantities are also determined.

PART II
MECHANISMS OF CATALYSED REACTIONS

6. Mechanistic and Spectral Studies for Ruthenium(III) Catalysed Oxidation of Sulfanilic acid by Alkaline Hexacyanoferrate(III) by Stopped Flow Technique

The kinetics of ruthenium(III) catalysed oxidation of sulfanilic acid (p-aminobenzenesulfonic acid) (SNA) by hexacyanoferrate(III) in alkaline medium at a constant ionic strength of 2.5 mol dm$^{-3}$ has been studied spectrophotometrically using a rapid kinetic accessory. The reaction exhibits 2:8 stoichiometry (SNA: HCF(III)). The experimental rate law is given by
The active species of HCF(III) and ruthenium(III) are understood as $[\text{Fe(CN)}_6^{3-}]$ and $[\text{Ru(H}_2\text{O)}_5\text{OH}]^{2+}$ respectively. Reaction rate increases with increase in ionic strength.

A mechanism involving the formation of a complex between sulfanilic acid and hydroxylated species of ruthenium(III) has been proposed.


The kinetics of ruthenium(III) catalysed oxidation of atenolol by permanganate in alkaline medium at a constant ionic strength of 0.30 mol dm$^{-3}$ has been studied spectrophotometrically using a rapid kinetic accessory. The reaction between permanganate and atenolol in alkaline medium exhibits the stoichiometry eight moles of $\text{MnO}_4^-$ were consumed by one mole of atenolol as given by equation,

$$\text{OH} \quad \text{CH}_2\text{CH} - \text{CH}_2\text{NH} - \text{HC} \quad \text{CH}_3$$

$$+ 8 \text{MnO}_4^- + 9 \text{OH}^- \underset{\text{Ru(III)}}{\longrightarrow} \text{O} - \text{CH}_2\text{COOH}$$

The reaction shows first order dependence on [Permanganate] and [Ruthenium(III)] and apparent less than un t order in both atenolol and alkali concentrations. Reaction rate decreases with increase in ionic strength and increases with decreasing dielectric constant cf the medium. The active species of
ruthenium(III) is understood as $[\text{Ru(H}_2\text{O}_2\text{OH}]^{2+}$. A suitable mechanism is proposed. The reaction constants involved in the different steps of mechanism are calculated. The activation parameters with respect to slow step of the mechanism are computed and discussed and thermodynamic quantities are also calculated.

8. **Kinetics and Mechanistic aspects of Reduction of Ruthenium(III) Catalysed Diperiodatonickelate(IV) Complex by Paracetamol in Aqueous Alkaline Medium by Stopped Flow Technique**

The kinetics of ruthenium(III) catalysed oxidation of paracetamol by diperiodatonickelate(IV) (DPN) in aqueous alkaline medium at a constant ionic strength of 1.0 mol dm$^{-3}$ was studied spectrophotometrically using a rapid kinetic accessory. The reaction exhibits 1:2 stoichiometry. The reaction shows first order dependence on [DPN] and [Ruthenium(III)] and apparent less than unit order in both [Paracetamol] and [Alkali] under the experimental conditions. However, the order in [Paracetamol] and [Alkali] changes from first order to zero order as the concentrations change from lower to higher concentrations respectively. Addition of periodate has retarding effect on the reaction. The main products were identified by spot test, IR and NMR. A mechanism involving the monoperiodatonickelate(IV) as the reactive species of the oxidant has been proposed. The active species of ruthenium(III) is understood as $[\text{Ru(H}_2\text{O}_3\text{OH}]^{2+}$.

$$
\begin{align*}
\text{HO-C-CH}_3 + 2 \text{[Ni(OH)]}_2\text{(H}_2\text{IO}_5\text{)}^\text{2-} + \text{NaOH} & \rightarrow \text{HO-C-CH}_3 + 2 \text{Ni(OH)}_2 + 2 \text{H}_2\text{IO}_5^- + \text{CH}_3\text{COONa} + \text{H}_2\text{O} \\
\text{Ru(III)}
\end{align*}
$$
REFERENCES

1. J.J.Zuckerman,

2. Sir.G.Wilkinson,

3. R.A.Sheldon and J.K.Kochi,

4. H.Taube,

5. H.Taube,
D.Banerjee,

6. H. J.Price and H.Taube,

7. J.H.Espenson,

8. A.Haim and N.Sutin,
9. J.H. Espenson,

10. W.A. Waters,

11. N. Sutin, F. Basolo and R.G. Pearson,

12. A.G. Sykes,

13. D. Benson,

14. J. Halpern,

15. F. Basolo and R.G. Pearson,

16. N. Sharma, R. Varadrajan, S.K. Mishra and P.D. Sharma,
17. P.D.Sharma and Y.K.Gupta,

18. P.D.Sharma and Y.K.Gupta,

19. L.Michaelis,
    Trans. Electrochem. Soc., 71, 107 (1937);

20. P.A.Shaffer,

21. J.Halpern,

22. M.Anabar and H.Taube,

23. R.Stewart,

24. R.J.Prestwood and A.C.Wahl,

25. G.Harbottle and R.W.Dodson,

26. S.W.Gilks and G.Nord-Waind,
27. C.E. Johnson, Jr.,

28. K.J. Ashurst and W.C.E. Higginson,

29. S.A. Chimatadar and J.R. Raju,

30. W.C.E. Higginson, D.R. Rosseinsky, J.B. Stead and A.G. Sykes,

31. G.A. Hiremath, P.L. Timmanagoudar and S.T. Nandibewoor,

32. S.M. Tuwar, S.T. Nandibewoor and J.R. Raju,

33. S.M. Tuwar, S.T. Nandibewoor and J.R. Raju,

34. G.S. Gokavi and J.R. Raju,
    Polyhedron, 6, 1721 (1987).

35. E.L. King and J.Y. Tong,

36. J.H. Espenson,

37. J.H. Espenson and E.L. King,
38. F.H. Westheimer,

39. U.S. Mehrotra and S.P. Mushran,
   S.A. Chimatadar, S.T. Nandibewoor and J.R. Raju,

40. S.K. Mishra and Y.K. Gupta,
    J. Inorg. Nucl. Chem., 30, 2991 (1968);
    S.A. Chimatadar, S.T. Nandibewoor, M.I. Sambrani and J.R. Raju,

41. R.L. Moore and R.C. Anderson,

42. T.J. Harwick and E. Robertson,

43. P. George and D.H. Irvine,

44. P. Veersomaiah, K. Balreddy, B. Sethuram and T. Navaneeth Rao,

45. S.K. Upadhaya and M.C. Agarwal,

46. S.A. Chimatadar, S.B. Koujalagi and S.T. Nandibewoor,
    Transition Met. Chem., 26, 241 (2001);
S.M. Desai, N.N. Halligudi and S.T. Nandibewoor,
*Int. J. Chem. Kinet.*, 31, 583, (1999);
D.L. Kamble and S.T. Nandibewoor,

47. S.A. Chimatadar, S.B. Koujalagi and S.T. Nandibewoor,
*Transition Met. Chem.*, 27, 62 (2002);
G.A. Hiremath, P.L. Timmanagoudar and S.T. Nandibewoor,
S.A. Chimatadar, S.B. Koujalagi and S.T. Nandibewoor,

48. R.M. Kulkarni, D.C. Bilehal and S.T. Nandibewoor,
*Transition Met. Chem.*, 28, 199 (2003);
V.A. Morab, S.M. Tuwar and S.T. Nandibewoor,
*Z. Phys. Chem. (Munich)*, 210, 141 (1999);
P.D. Pol, R.T. Mahesh and S.T. Nandibewoor,
*React. Kinet. Catal. Lett.* 81, 113 (2004);
S.T. Nandibewoor and V.A. Morab,

49. D.C. Bilehal, R.M. Kulkarni and S.T. Nandibewoor,
*Can. J. Chem.*, 79, 1926 (2001);
P.D. Pol, C.P. Kathari and S.T. Nandibewoor,
*Transition Met. Chem.*, 28, 209 (2003);
S.T. Nandibewoor, G.A. Hiremath and P.L. Timmanagoudar,

50. D.L. Kamble and S.T. Nandibewoor,