Physical-organic chemistry deals with studies on the mechanism of organic reactions by quantitative methods and related problems of the effect of structure and environment on the reactivity. Reactions involving oxidation-reduction are among the most common processes. Chemical kinetics provides information about how reactions take place, how one can trace the path of reaction. It also provides information about how individual molecules interact with each other, a topic of intense interest to those in pursuit of a deep understanding of chemical reactions. There have been monographs dealing with redox reactions, which are of fundamental importance.

The subject of reaction kinetics is concerned with the quantitative study of the rates of reactions and of the factors upon which they depend. The experimental part of the subject consists of measuring precisely the rates of reactions under varying conditions. Interpretation of these results leads to an understanding of mechanism of reactions. The important steps in any kinetic investigation are: (i) collection of kinetic data, (ii) establishment of relationship between the rate and reaction mixture composition, (iii) study of structural effects and (iv) interpretation of the collected data to arrive at reaction mechanisms.

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 had not able successes.

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 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. Finally, as an area of pure science in itself, the study of rates and mechanism is one of rich varieties, concerned with the chemistry of every element and full of experimental challenge.

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” and 2005 Nobel Prize to Prof. Robert Grubbs, Richard Schrock, and Yves Chauvin on their research achievements on “Matathesis Catalyst Technology” emphasize the importance of field of reaction kinetics. Electron transfer reactions play a significant 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 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:

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

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 type⁶, the electron must wait for appropriate fluctuation of the ions and their co-ordination 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 type⁶, 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 co-ordination 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.

**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 pathways⁷, viz., "Homolytic reactions" in which electron
pairs are symmetrically disrupted and "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.

**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.\textsuperscript{4, 5, 9}

**Complementary and non-complementary reactions:**

**Complementary reactions**

The oxidant and reductant change their oxidation state by an equal number of units. These are termed as complementary electron transfer reactions\textsuperscript{10}, e.g. (i) One equivalent – One equivalent reactions

These are the electron reactions in which there occurs the transfer of one electron from one species to the other. These simple reactions serve as models for more complicated systems and their study has proved invaluable in developing and understanding of the electron transfer in solution\textsuperscript{11}, e.g.,

\[
\text{Ce(III) + Co(III) } \rightarrow \text{Ce(IV) + Co(II)}
\]

(ii) Two-equivalent – Two-equivalent reactions\textsuperscript{11, 12}

\[
\text{U(IV) + Tl(III) } \rightarrow \text{U(VI) + Tl(I)}
\]
\[
\text{Sn(II) + Hg(II) } \rightarrow \text{Sn(IV) + Hg(0)}
\]

A large number of complementary reactions have been explained by assuming the formation of bridged activated complexes between the oxidant and the reductant for the 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 chromium(VI) and manganese(VII) undergo net changes of 3 and 5 units in oxidation number respectively during their reactions in acidic solution\(^1\). For the most part, these reactions occur by one or two electron steps, with the necessary intervention of unstable intermediate oxidation states of chromium or manganese. The reactions of chromium(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\(^1^4\)

(b) Shaffer's principle of equivalent change\(^1^5\)

Michaelis hypothesis states that an oxidation-reduction reaction takes place in one or more successive single electron transfer steps 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{16}.

E.g.,

\[
\text{NO}_2^- + \text{OCl}^- \rightarrow \text{NO}_3^- + \text{Cl}^-
\]

The second principle\textsuperscript{15} refers to the observation that non-complementary reactions are often slow compared with complementary one's. Examples are the slow reduction of thallium(III) by iron(II)\textsuperscript{17} or cerium(IV) by thallium(I)\textsuperscript{18} as compared to the rapid reduction of thallium(III) by tin(II)\textsuperscript{19} and cerium(IV) by iron(II)\textsuperscript{20}.

**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 thallium(III) by iron(II)\textsuperscript{17}, vanadium(III) or vanadium(IV)\textsuperscript{21,22} and chromium(VI) by thallium(I)\textsuperscript{23} can only be explained through the formation of unstable thallium(II) species. Similar unstable oxidation states have been observed in other studies\textsuperscript{24,25}. The interconversions between chromium(III) and chromium(VI) always appear to involve the unstable states, chromium(IV) and chromium(V).

In a classic study, King and Tong\textsuperscript{26} have worked out the details of the redox reactions between cerium(IV) and chromium(III) in aqueous sulphuric acid.
The rate law was found to be as in equation (i), which is very reasonably explained by the mechanism involving steps of equation (iia) to (iic).

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

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

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

Excellent support comes from the study of related reactions such as the oxidation of vanadyl ion by acid chromate ion\textsuperscript{27} (HCrO\textsubscript{4}\textsuperscript{-}) and the analytical important oxidation of ferrous ion by acid chromate\textsuperscript{28}. It is significant that in the above example the change over from chromium(IV) to chromium(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{26}. A number of studies of the catalysis by platinum metals of oxidation reactions have been made\textsuperscript{29}. The catalysis by Ag(I)\textsuperscript{30}, Cu(II)\textsuperscript{31}, Mn(III)\textsuperscript{32} and Cr(III)\textsuperscript{33, 34} 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.

The diperiodatoargentate(III) complex is diamagnetic and exhibits square planar configuration with dsp$^2$ hybrid bonds. Periodate acts as a bidentate ligand and contributes to the stabilization of Ag(III). The structure and cell dimensions of DPA compound resemble those of diperiodatocuprate(III). The Ag(III) periodate complex ion can be represented as $[\text{Ag(H}_2\text{O)}\text{(IO}_6\text{)}_2]^7^-$ and in solution it can be considered as hydroaquodiperiodatoargentate(III).

Crouthamel et al. from an extensive study of the equilibria between various periodate anionic species by UV spectrophotometry concluded that the following equilibria exists in aqueous solution of periodate at different pH ranges.

\[
\begin{align*}
\text{H}_5\text{IO}_6 & \rightleftharpoons \text{H}_4\text{IO}_6^- + \text{H}^+; \quad K_1 = 2.30 \times 10^{-2} \text{ at } 25^\circ\text{C} \\
\text{H}_4\text{IO}_6^- & \rightleftharpoons \text{H}_3\text{IO}_6^{2-} + \text{H}^+; \quad K_2 = 4.35 \times 10^{-7} \text{ at } 25^\circ\text{C} \\
\text{H}_3\text{IO}_6^{2-} & \rightleftharpoons \text{H}_2\text{IO}_6^{3+} + \text{H}^+; \quad K_3 = 2.30 \times 10^{-11} \text{ at } 25^\circ\text{C} \\
\text{H}_4\text{IO}_6^- & \rightleftharpoons \text{IO}_4^- + 2\text{H}_2\text{O}; \quad K_D = 1.05 \times 10^{-15} \text{ at } 25^\circ\text{C}
\end{align*}
\]

Periodic acid exists as H$_5$IO$_6$ in acid medium and as H$_4$IO$_6^-$ at pH 7. Thus, Buist et al., from a study of various equilibria of periodate in alkaline solutions, reported that probably H$_3$IO$_6^{2-}$ and H$_2$IO$_6^{3-}$ predominate rather than dehydrated species HIO$_5^{2-}$ and IO$_5^{3-}$. But Kirschenbaum et al., while studying the kinetics of the ligand exchange reaction between OH$^-$ ligand of the Ag(OH)$_4^-$ ion and periodate reported H$_2$IO$_6^{3-}$ to be predominant ligand species in the OH$^-$ ion concentration range 0.12 to 1.2 M.
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.

**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.

Catalyst development and synthesis have become a wide spread research field because of the increasing global demand for better systems in chemical industry. Today, the chemical industry has been blamed for producing environmentally hazardous substances, which cause acid rain, a reduction of stratospheric ozone levels and so on. Many industrial processes have become burden on the environment, and, therefore must be essentially replaced by more eco-friendly or compatible processes in addition to this, disposing of byproducts or converting them into environmentally non-hazardous substances consume much energy. The successful exploitations of a material as a catalyst will give
value-added products with improved yields and also eliminate or minimise environmental pollutants.

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 phase as a part of reactants. Homogeneous catalysts are readily amenable to kinetic and mechanistic studies, in particular using in situ spectroscopic studies. Homogeneous catalysts are uniform, reproducible and easily modified in a controlled manner. 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:\(^{40}\).

(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**

Catalysis plays a vital role in the production of fuels, commodity chemicals, fine chemicals, and pharmaceuticals, as well as providing the means
for strengthening environmental safeguards all over the world. More than 60% of all chemical products and 90% of chemical processes are based on catalysis. Catalysis is the most effective and most rational of all 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.

Osmium(VIII) is a case in point as it has been utilized 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 Upadhyaya et al.

Often, very small quantities of catalysts like Os(VIII), Pd(II), Cr(III), Ru(III), V(V) etc., causes appreciable rates accelerations of particular reactions.

**Catalytic activity**

It has been pointed out by Moelwyn- Hughes that, in the presence of the catalyst, the uncatalysed and catalysed reactions proceed simultaneously, so that

\[ k_T = k_U + K_C [\text{catalyst}] \]
Here $k_T$ is the observed pseudo first-order rate constant in the presence of ruthenium(III) catalyst, $k_U$ is the pseudo first-order rate constant for the uncatalysed reaction, $K_C$ is the catalytic constant and 'x' is the order of the reaction with respect to catalyst. Then the value of $K_C$ can be calculated using the equation

$$K_C = \frac{k_T - k_U}{[\text{catalyst}]^x} = \frac{k_C}{[\text{catalyst}]^x} \quad \text{(where, } k_T - k_U = k_C)$$

**Importance of amino acids and drugs**

Amino acids act not only as the building block in protein synthesis but they also play a significant role in metabolism and have been oxidized by a variety of oxidising agents. The oxidation of amino acids is of interest as the oxidation products differ for different oxidants. The study of amino acids becomes important because of their biological significance and selectivity towards the oxidant to yield different products. Since world war II, many important new drugs have been developed, making chemotherapy an important part of medical practice. Such drugs include the antibiotics, cardiovascular drugs, diuretics, anticoagulants, smooth-muscle relaxants, stimulants, immunologic agents, hormones, psychotherapeutics, antidepressant drugs, barbiturates, etc.

**Importance of oxidants**

Recently, the study of the highest oxidation state of transition metals has intrigued many researchers. Transition metals in a higher oxidation state generally can be stabilized by chelation with suitable polydentate ligands. Metal chelates
such as diperiodatoargentate(III), diperiodatonickelate(IV) etc. are good oxidants in a medium with an appropriate pH value. The use of complexes as good oxidizing agents in analytical chemistry has been reported. The oxidation of a number of organic compounds and metals in lower oxidation state by silver(III) has also been performed, but no further information on the kinetics is available. Because silver(III) is in the highest oxidation state and the reaction is complicated in this kind of reaction system, it is of significance to have a further study on this kind of reaction system. Investigation on them will certainly provide us with more dynamical parameters, and will provide theoretical foundation for the design of reaction route in the organic synthesis and quantitative analysis in analytical chemistry.

Study of fast reactions

The reactions, which go to equilibrium within a few seconds or less, are said to be fast reactions. The half-life range of such reactions is very small. It is of the order of 10 seconds to $10^{-10}$ second. Kinetics of such reactions cannot be studied by usual conventional methods. In recent years various methods like, flow-methods, relaxation methods, flash photolysis etc., have been developed.

The study of fast reactions is on the threshold of exciting developments, since so many of the reactions of complexes, especially of transition series and biological processes are rapid. Muscle action, self reproduction, the combustion of rocket fuel and gasoline, the action of poisons and nerve gases, appearance of
colours on addition of indicators etc. complete within a fraction of second and
would thus provide a truly formidable challenge to classical kinetics.

Five main components of a kinetic investigation are

❖ Product and intermediate detection
❖ Concentration determination of all species present
❖ Deciding on a method of following the rate
❖ The kinetic analysis
❖ Determination of the mechanism

Present work

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

1. General introduction

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

Part I: UNCATALYSED REACTIONS

2. Oxidation of paracetamol drug by a new oxidant diperiodatoargentate (III) in
aqueous alkaline medium

The kinetics of oxidation of anti-pyretic drug, paracetamol by
diperiodatoargentate(III) (DPA) in alkaline medium at a constant ionic strength of
0.01 mol dm$^{-3}$ was studied spectrophotometrically. The reaction between DPA
and paracetamol in alkaline medium exhibits 1:2 stoichiometry (paracetamol:
The reaction is of first order in [DPA] and has less than unit order in both [PAM] and [alkali]. A decrease in the dielectric constant of the medium increases the rate of the reaction. The effect of added products and ionic strength of the reaction medium have been investigated. The oxidation reaction in alkaline medium has been shown to proceed via a DPA-paracetamol complex, which decomposes slowly in a rate determining step followed by other fast step to give the products. The main products were identified by spot test, IR, NMR and GC-MS. A suitable mechanism is proposed. The reaction constants involved in the different steps of the mechanism are calculated. The activation parameters with respect to slow step of the mechanism are computed and discussed and thermodynamic quantities are also determined.

3. Mechanism of oxidation of L-alanine by a new oxidant diperiodatoargentate(III) in aqueous alkaline medium – a free radical intervention

The kinetics of oxidation of L-alanine by diperiodatoargentate(III) (DPA) in alkaline medium at a constant ionic strength of 0.90 mol dm$^{-3}$ was studied spectrophotometrically. The reaction between DPA and L-alanine in alkaline medium exhibits 1:1 stoichiometry. The reaction shows first order in [DPA] and has less than unit order dependence each in both [L-alanine] and [alkali] and retarding effect of [IO$_4^-$]. The effect of added products have been investigated. The active species of silver(III) is understood to be as monoperiodatoargentate(III) (MPA). The oxidation reaction in alkaline medium has been shown to proceed via a MPA-L-alanine complex, which decomposes in
a rate determining step to give a free radical followed by a fast step to give the products. The main products were identified by spot and spectral studies. The reaction constants involved in different steps of the mechanism were evaluated. The activation parameters with respect to slow step of the mechanism are computed and discussed. The thermodynamic quantities were also determined. The reaction follows a 1:1 stoichiometry as given below,

$$\text{CH}_3\text{CH-COO}^- + [\text{Ag(H}_2\text{IO}_6\text{(H}_2\text{O})_2\text{]} + 2 \text{OH}^- \quad \rightarrow \quad \text{CH}_3\text{-CHO}$$

$$\quad + \text{Ag(l)} + \text{NH}_3 + \text{HCO}_3^- + \text{H}_2\text{IO}_6^{3^-} + 2\text{H}_2\text{O}$$

4. Oxidation of vanillin by diperiodatocuprate(III) in aqueous alkaline medium – a kinetic and mechanistic study by stopped flow technique

The kinetics of oxidation of vanillin (VAN) by diperiodatocuprate(III) (DPC) in alkaline medium at a constant ionic strength of 0.50 mol dm$^{-3}$ was studied spectrophotometrically. The reaction between DPC and vanillin in alkaline medium exhibits 1:2 stoichiometry (vanillin: DPC). The reaction is of first order in [DPC] and has less than unit order both in [VAN] and [alkali]. Intervention of free radicals was observed in the reaction. The oxidation reaction in alkaline medium has been shown to proceed via a DPC- vanillin complex, which decomposes slowly in a rate determining step followed by other fast steps to give the products. The main products were identified by spot test, IR, MS studies. The reaction constants involved in the different steps of the mechanism are calculated. The rate law of the reaction is as follows:
Part II: CATALYSED REACTIONS

5. Osmium(VIII) catalysed oxidation of L-proline by a new oxidant diperiodatoargentate(III) in aqueous alkaline medium – a free radical intervention

The osmium(VIII) catalysed oxidation of L-proline by diperiodatoargentate (III) (DPA) in alkaline medium at a constant ionic strength of 0.90 mol dm$^{-3}$ was studied spectrophotometrically. The reaction between DPA and L-proline in alkaline medium catalysed by osmium(VIII) exhibits 1:2 stoichiometry (L-proline: DPA). The reaction shows first order in [Os(VIII)] and [DPA] and has less than unit order dependence each in both [L-proline] and [alkali]. However the order in [L-proline] and [alkali] changes from first order to zero order as the concentration change from lower to higher values. The effect of added products have been investigated. The oxidation reaction in alkaline medium has been shown to proceed via a osmium(VIII) - L-proline complex, which decomposes in presence of DPA to give a free radical in a rate determining step followed by fast steps to give the products. The main products were identified by spot test, IR and NMR studies. The reaction constants involved in the different steps of the mechanism were evaluated. The activation parameters with respect to slow step of the mechanism are computed and discussed. The thermodynamic quantities are also determined.
6. Ruthenium(III) catalysed oxidation of L-lysine by diperiodatocuprate(III) in aqueous alkaline medium – a kinetic and mechanistic approach by stopped flow technique

The kinetics of oxidation of ruthenium(III) catalysed oxidation of L-lysine (L-lys) by diperiodatocuprate(III) (DPC) in alkaline medium at a constant ionic strength of 0.15 mol dm$^{-3}$ was studied spectrophotometrically. The reaction between DPC and L-lys in alkaline medium in presence of Ru(III), exhibits 1:2 stoichiometry. The reaction is of first order in [DPC] and has less than unit order both in [L-lys] and [alkali]. Intervention of free radicals was observed in the reaction. The main products were identified by spot test, IR, GC-MS. The reaction constants involved in the different steps of the mechanism are calculated. The activation parameters with respect to slow step of the mechanism are computed and discussed and thermodynamic quantities are also determined. The active species of catalyst and oxidant have been determined. The rate law of the reaction is as follows:

$$\frac{\text{Rate}}{[\text{DPC}]} = k_\text{C} = k_T - k_U$$

$$= \frac{k K_1 K_2 K_3 [\text{L-lys}] [\text{OH}] [\text{Ru(III)}]}{[\text{H}_3\text{IO}_6^{2-}] + K_1 [\text{OH}][\text{H}_3\text{IO}_6^{2-}] + K_1 K_2 [\text{OH}] + K_1 K_2 K_3 [\text{OH}][\text{L-lys}]}$$

7. Osmium(VIII) catalysed oxidation of L-lysine by diperiodatocuprate(III) in aqueous alkaline medium – a kinetic and mechanistic approach by stopped flow technique

The kinetics of oxidation of osmium(VIII) catalysed oxidation of L-lysine (L-lys) by diperiodatocuprate(III) (DPC) in alkaline medium at a constant ionic
strength of 0.15 mol dm$^{-3}$ was studied spectrophotometrically. The reaction between DPC and L-lys in alkaline medium in presence of Os(VIII), exhibits 1:2 stoichiometry. The reaction is of first order in [DPC] and has less than unit order both in [L-lys] and [alkali]. Intervention of free radicals was observed in the reaction. The main products were identified by spot test, IR, GC-MS. The reaction constants involved in the different steps of the mechanism are calculated. The activation parameters with respect to slow step of the mechanism are computed and discussed and thermodynamic quantities are also determined. The active species of catalyst and oxidant have been determined.
REFERENCES

1  J. J. Zuckerman,

2  Sir. G. Wilkinson,

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

4  H. Taube,

5  F. Basolo and R. G. Pearson,

6  H. Taube,
    D. Banerjee,

7  W. A. Waters,
    "Mechanisms of Oxidation of Organic Compounds" Methuen and Co. Ltd.,
    London, 1964, p.35

8  E. S. Gould,
9  A. G. Sykes,  
D. Benson,  
J. Halpern,  
N. Sharma, R. Varadrajan, S. K. Mishra and P. D. Sharma,  

10  H. Taube,  

11  A. C. Harkness and J. Halpern,  
J. Am. Chem. Soc., 81, 3526 (1959)

12  K. B. Wiberg,  

13  H. A. A. Medien,  
Z. Naturforsch., 58b, 1201 (2003);  
R. G. Panari, R. B. Chougale and S. T. Nandibewoor,  

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

15  P. A. Shaffer,  
J. Am. Chem. Soc., 55, 2169 (1933);  
J. Halpern,  

16  M. Anabar and H. Taube,  
J. Am. Chem. Soc., 80, 1073 (1958);  
R. Stewart,  
Experimentia., 15, 401 (1959)
17 C. E. Johnson, Jr.,
*J. Am. Chem. Soc.*, 74, 959 (1952);
K. J. Ashurst and W. C. E. Higginson,
*J. Chem. Soc.*, 3044 (1953);
S. A. Chimatadar and J. R. Raju,

18 K. Dorfman and J. W. Gryder,
*Contribution from Hopkins University, Maryland.*, 4, 799 (1962)

19 J. Y. Marks, G. G. Welcher, R. J. Spellman,
*Appl. Spectroscopy*, 31, 9 (1977)

20 S. A. Dikshitulu and G. Gopal Rao,

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

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

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

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

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

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

27 J. H. Espenson,
*J. Am. Chem. Soc.*, 85, 5101 (1964)

28 J. H. Espenson and E. L. King,
*J. Am. Chem. Soc.*, 85, 3328 (1963)
K. T. Sirsalmath, C. V. Hiremath and S. T. Nandibewoor, 
App. Cat. A., 305, 79 (2006);

S. P. Srivastava and V. K. Gupta,

V. Sippola and O. Krause,

Y. G. Abashkin, J. R. Collins and S. K. Burt,

D. C. Bilehal, R. M. Kulkarni and S. T. Nandibewoor,

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,

G. L. Cohen and G. Atkinson,
Inorg. Chem., 3, 1741 (1964)

C. E. Crouthamel, H. V. Meek, D. S. Martin and C. V. Bakes,

C. E. Crouthamel, A. M. Hyes and D. S. Martin
J. Am. Chem. Soc., 73, 83 (1951)

G. J. Buist, W. C. P. Hipperson and J. D. Lewis,

L. J. Kirschbaum, J. H. Ambrus and G. Atkinson,
Inorg. Chem., 12, 2832 (1973)

P. Veersomaiah, K. Bal Reddy, B. Sethuram and T. Navaneeth Rao,

S. K. Upadhyaya and M. C. Agarwal,


49 M. R. Wright, "*An Introduction to Chemical Kinetics*", John Wiley and Sons, Inc., New York, 2004