CHAPTER I

INTRODUCTION
Unchanging systems are easier to understand and describe than changing ones because we have time to observe the given state of the system. If the system changes, the time has to be incorporated into our description of it. Attention in kinetics is, after all, focussed on the concept "reaction rate" which is a time dependent property\(^1\). Of prime importance is the measurement of the rate and its quantitative dependence on any factors that are found to affect it. Chemists use these experimental data to increase their understanding of how chemical reactions occur\(^2\).

Kinetics is an important and indispensable subject. Real chemical systems, such as those which occur in nature or are involved in industrial processes, are often exceedingly complex. In his effort to understand these systems, the chemist studies selected components of the system, and attempts to fuse knowledge thus gained into a comprehensive picture of the whole phenomena. Chemical kinetics provides one of the tools for this synthesis.

Mass action chemical kinetics and its application to
the elucidation of chemical reaction mechanisms understandingly followed its historical development. Mass action principles were first used to empirically relate observed rates to concentrations in those comparatively few cases where the laws seemed to be strictly obeyed. Somewhat later the appearance of the Arrhenius rate law made it possible to account for the behaviour as well. For the many processes which did not fit the simple relation, more complex mechanisms were proposed such as simultaneous or consecutive reactions. While the chemists came to consider kinetics as a valuable tool for the investigation of reaction mechanism which must be taken as a detailed stepwise process involving molecules, atoms, radicals or ions that occur simultaneously or consecutively and culminated in the observed over all reaction, the engineer seized upon it as a convenient way to correlate process rate information, without too much regard for the details of the underlying reaction.

An ultimate goal for the study of chemical kinetics is to relate specific rate constants to molecular properties. The use of this study in the interpretation of the structure of organic compounds has received greater attention only in the last two decades. Studies of the mechanism of a variety of chemical reactions, vigorously pursued over a
wide front by physical chemists of many countries, are steadily adding to the number of reactions whose mechanism is understood. How useful kinetics is for the reaction mechanism, is more than proved by the fact that Professor Henry Taube of Stanford University has been awarded Nobel Prize in Chemistry for 1983 for his pioneering work in the Mechanism of Electron Transfer Reactions with kinetics as the main tool. However, we are still at relatively early stage, and a large number of reaction mechanisms still remain to be investigated and more precise.

Most of the reactions encountered in practice take place in solution of one kind or other. The reaction in homogeneous gaseous phase are simple to deal with kinetically but in condensed media present many inherent difficulties due to many factors and uncertainty of species taking part in the chemical reaction at various steps. Solvation, activities, dielectric constant, etc. has a great influence on the kinetics of the reaction. The most thoroughly investigated type of reactions in solution are the electron transfer reaction between an oxidant and reductant. The study of such reactions is of great significance and interest because of its vast implication in understanding the nature of the chemical processes involved.

However, the study of the kinetics of oxidation of
different organic compounds occurring in aqueous solution is likely to be complicated, yet such a study presents one of the interesting problems of chemistry. The probable reason is that reaction mechanism is a mental model to explain facts obtained by the kinetic study and in several cases it very successfully predicts the optimum conditions for running the chemical reaction.

**Oxidation reduction reactions:**

The oxidation – reduction (or redox) concept is currently widespread use in chemistry (1) as an organising structure for chemical knowledge (2) as a guide to the prediction of reactants, and (3) as a mathematical device to enable the balancing of certain complex reactions.

To the inorganic chemist the statement that the oxidation is a process in which one or more electrons are lost by an atom, ion or a molecule and reduction as the reverse of this, eg.

\[
\text{Fe}^{2+} \overset{\text{oxidation}}{\rightarrow} \text{Fe}^{3+} + e^{-} \overset{\text{reduction}}{\leftarrow}
\]

is adequate for describing reactions of ionisable substances. Thus, reactions involving the change of electric charges on a reacting species are called redox reactions. By developing
this concept, oxidising capacity of different compounds can be compared utilizing oxidation potential. But this approach is of little practical importance for organic reactions as most of these are not thermodynamically reversible.

In the past three decades, new theoretical ideas and usages have developed in reaction mechanisms, complex ion formation, and electronegativity which are of significance to the redox concept. A more consistent definition of oxidation and reduction is provided in terms of "oxidation state concept". According to a study made by Yalman, electronegativity was employed in the definition of oxidation state. The key elements to current utilization of the redox concept lie within the definition of the oxidation number. "The oxidation number of a given atom equals the sum of the electrons linked by the given atom to atoms of higher electronegativity, less the sum of the electrons linked to the given atom by atoms of lesser electronegativity". Goodstein proposed that an oxidation reduction be defined as a reaction in which "a change in the relative order of atomic electronegativities takes place between a given atom and the atoms to which it is bonded prior and subsequent to reaction; concurrently an opposite change in order of electronegativities takes place elsewhere among the reactants. The difference in relative electronegativities of the atoms undergoing oxidation state change is..."
factor in causing the changes to occur.

In terms of making and breaking of bonds redox reactions may be classified as homolytic and heterolytic. Homolytic fission takes place in a way that each fragment carries one unpaired electron as shown below:

\[
X-Y \xrightarrow{\text{homolysis}} X^* + Y^*
\]

Free radicals

In heterolytic fission, the covalent bond joining the atoms \(X\) and \(Y\) breaks in such a way that the pair of electron stays on any one of the atoms and may be shown as

\[
X-Y \xrightarrow{\text{heterolysis}} X^+ + Y^-
\]

or

\[
X-Y \xrightarrow{\text{heterolysis}} X^- + Y^+
\]

such reaction takes place because an attacking ion or fragment of the reagent has an inherent affinity for either an electron pair or an atomic nucleus. Since homolytic fission leads to the formation of an active atom or highly reactive free radical, all homolytic electron transfer reactions require very much less activation energy. Homolytic oxidation are, therefore, very rapid. Heterolytic
oxidation occurs when an electrophilic reagent attacks
the exposed electron pair of an atom such as O, N, S or
the loosely held π (π) electrons of reductant. Hetero-
lytic reactions yield stable molecules or ionic products
in one or almost two consecutive stages and very rarely
lead on to chain mechanism.

In recent years the kinetics and mechanism of redox
reactions has been studied in considerable detail8,9.
Among many kinds of redox reactions in which changes of
oxidation state take place are -

1. Inorganic reactions in which net transfer of
electrons occur.

2. Electrochemical reactions.

3. Free radical reactions in which transfers of the
electrons take place.

4. Free radical autoxidations

5. Many organic reactions of which a partial loosing
would include all of those reactions in which carbon
progresses through the oxidation stages from the
alkanes to carboxylic acids and then to CO₂, reactions
in which peroxy compounds undergo oxidation and
reduction, oxidation by permanganate, Ce(IV), Cr(III)
and other inorganic oxidations and reactions where
hydride transfer takes place.
The chemistry involved in the oxidation reduction reactions are very interesting and quite rich. The understanding of such types of reaction is of great significance for other areas of science, among them reactions involving oxygen, hydrogen peroxide, metabolic reactions and other catalytic processes.

**Hydrogen peroxide as an oxidant**:

For almost a century, hydrogen peroxide is considered to be one of the most important oxidising agent used in volumetric analysis and degradative chemistry. Inspite of this, knowledge of their reaction is still very fragmentary. Baxendale\(^{10}\) in his extensive review article writes "it is a measure of the complexity and variety of the chemical reactions in which hydrogen peroxide participates that they have attracted the attention of chemical kineticians for almost a hundred years, and that many of the earliest reactions to be investigated still provide matter for further investigation".

Hydrogen peroxide has played a leading role in the oxidation reduction catalytic reactions. It has been used as an oxidising agent in organic synthesis. To illustrate, reactions such as epoxidation, hydroxylation halogenation which find a wide applications for many industrial processes
use hydrogen peroxide as an oxidant. The chief advantage of this over other oxidising agents is that its only by product is water and so, in organic preparative work, the recovery of a product of high purity is facilitated.

Hydrogen peroxide molecule is dihedral, that is the two O-H bonds are not in the same plane. The geometry and the most probable structure\textsuperscript{11} is given below:

![Hydrogen peroxide molecule](image)

- Oxygen
- Hydrogen

This is the most stable configuration because the repulsion between the lone pairs on the two oxygen atoms is a minimum. In the neutral molecule of $H_2O_2$, the peroxide ion $O_2^{2-}$ does not exist as such. This means that H atoms are not attracted to any appreciable degree by the peroxo group via electrostatic force\textsuperscript{12}.

The redox chemistry of hydrogen peroxide in aqueous solutions may be indicated by the oxidising and reducing power of an oxidising agent in terms of the oxidation potential\textsuperscript{13}. Thus the oxidising intensity of hydrogen peroxide in the
conversion to water is defined by the potentials of the half reaction in acid and alkaline solution.

\[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2e \rightleftharpoons \text{H}_2\text{O} \quad \text{E}^0 = 1.78 \text{ e.v.} \]

\[ \text{HO}_2^- + \text{H}_2\text{O} + 2e \rightleftharpoons 3\text{OH}^- \quad \text{E}^0 = 0.87 \text{ e.v.} \]

On the other hand, the reducing intensity of hydrogen peroxide in the formation of free oxygen will be determined by the following potential level.

\[ \text{O}_2 + 2\text{H}^+ + 2e \rightleftharpoons \text{H}_2\text{O}_2 \quad \text{E}^0 = 0.69 \text{ e.v.} \]

In dilute aqueous solutions it has more acidic character than water

\[ \text{H}^+ + \text{HO}_2^- \rightleftharpoons \text{H}_2\text{O}_2 \]

In acid solutions, oxidations with \( \text{H}_2\text{O}_2 \) are said to be slow whereas in basic solutions, they are reported to be fast. In basic solution, however, the decomposition of the reagent occurs most rapidly even at low temperature.

Contradictory reports appear in the volume of literature regarding the mechanism of oxidations with hydrogen peroxide. Kirk and Browne\textsuperscript{14} suggested that \( \text{H}_2\text{O}_2 \), as an oxidant, accepts two electrons in one step. Higgins, Sutton and Wright\textsuperscript{15}
are of the opinion that the oxidation proceeds with one electron step, in which the first step involves the formation of one of the entities, CH⁺, HO₂⁻, OCH or HO₂ as more or less independent intermediates. Weiss⁶⁶-⁶⁸ has postulated an additional radical ion, O₂⁻, in the mechanism. Evans, Hush and Uri⁶⁹ report the presence of HO₂ and O₂⁻ in acidic solutions of H₂O₂. Edwards⁷⁰ has shown that in reactions of H₂O₂, both H₂O₂ and H₃O⁺ contribute appreciably to the total reaction.

Reactions of hydrogen peroxide:

During the last three decades, reactions of hydrogen peroxide with various chemical species have been extensively studied²¹.²². Recently there has been a growing interest in the studies of redox reactions of hydrogen peroxide. The successful application of catalytic methods in analytical chemistry²³,²⁴ is connected with investigations on the kinetics and mechanism of the oxidation of various reducing agents by hydrogen peroxide. These reactions are rather easily carried out and pure reactants can usually be obtained. Usually the reaction rate can easily be controlled if suitable reducing agents are used.
Reactions involving metallic complexes:

There has been a good deal of interest in the study of mechanism of formation, decomposition and substrate reactions of peroxo compounds of biologically important metal chelates such as catalase and peroxidase. Present trends in this area are towards identifying the role of complexes in the catalyzed decomposition of hydrogen peroxide. Siegel et al. have shown a mechanism that decomposition of hydrogen peroxide proceeds through the intermediate involving hydrogen peroxide in the inner sphere. However, little attention has been drawn to the processes of coordination of hydrogen peroxide to metal complexes preceding the decomposition of hydrogen peroxide.

The kinetics of the reaction of N-methylimino-diacetato-dioxovanadate with hydrogen peroxide was investigated by Funahashi, Yoshiakito and Tanaka. The rate of the mixed ligand complex formation is of the first order each with respect to N-methyliminodiacetatodioxovanadate and hydrogen peroxide. They have also studied reaction of hydrogen peroxide with nitrilotriacetatodioxovanadate(V) and dioxo(2,6-pyridine carboxylato) vanadate(V).

Bowers, Kovacs and Shepherd studied the oxidation of imidazolepentacyanoiron(II) by hydrogen peroxide and showed
that loss of imidazole from \((\text{CN})_5\text{Fe(ims)}\)\(^{3-}\) and substitution of \(\text{H}_2\text{O}_2\) into the inner coordination sphere of \((\text{CN})_5\text{FeH}_2\text{O}_3\)\(^-\) are rate determining. The reaction of tetramine platinum(II) cation with \(\text{H}_2\text{O}_2\) has been reported to produce trans-\(\text{Pt}\) \((\text{NH}_3)_4\) \(\text{CH}_2\)\(^2+\). Harrigan and Johnson\(^{34}\) studied this system using high ion exchange chromatography and provided a one step two electron oxidation mechanism. Oxidation of Ti(IV) complexes with \(\text{H}_2\text{O}_2\)\(^{35}\) in perchloric acid media indicated that at \(\text{pH} > 2\) a tetrameric titanium(IV) complex is the reaction species. The observed law at constant \(\text{pH}\) is

\[
\text{rate} = k_1 [\text{H}_2\text{O}_2] [\text{Ti}_4\text{O}_4(\text{NTA})_4]
\]

The kinetics of oxidation of cobalt(II) aminocarboxylates with \(\text{H}_2\text{O}_2\) is reported by Fujari and Banerjee\(^{36}\). The cyclohexyl ring in cydta produces significant steric compression. A highly oriented transition state has been inferred on the basis of large negative entropy of activation. An analogous reaction\(^{37, 38}\) of \(\text{Co(EDTA)}^{2-}\) and \(\text{Co(HEDTA)}\) has shown that the second order rate constants for the oxidation of two \(\text{Co(II)}\)-aminocarboxylates are dominated by the contribution from \(\text{HO}_2\)^\(-\)

\[
(\frac{k_{\text{HO}_2}}{k_{\text{H}_2\text{O}_2}} \approx 10^7)
\]

under comparable conditions. The oxidation of dimethylenetriaminedipentaceta-co- cobalt(II)\(^{39}\) can be well interpreted on the basis of the following mechanism.
consistent with the pH dependence.

\[
\begin{align*}
    \text{H}_2\text{O}_2 & \rightleftharpoons \text{HO}_2^- + \text{H}^+ \quad (Y_a) \\
    \text{Co(DTPA)}^{3-} + \text{H}_2\text{O}_2 & \xrightarrow{K_{\text{H}_2\text{C}}} \text{Co(III)-DTPA} + \text{OH}^- + \text{OH}^- \\
    \text{Co(DTPA)}^{3-} + \text{OH}^- & \xrightarrow{\text{fast}} \text{Co(III)-DTPA} + \text{OH}^- \\
    \text{Co(DTPA)}^{3-} + \text{HO}_2^- & \xrightarrow{K_{\text{H}_2\text{C}}} \text{products}
\end{align*}
\]

A series of cobalt(II) complexes of tetradentate^{40} 14 membered macrocyclic ligands with nitrogen donor atoms is oxidised by hydrogen peroxide. Only one of the cobalt(II) complexes, Co^{II}(\text{[14]aneN}_4)^{2+}, reacts with \text{H}_2\text{O}_2 producing a hydroxyl radical intermediate. The other peroxide reaction apparently do not produce \text{HO}_2^-.

Reaction such as this are termed non-complementary, in that the oxidation state changes do not match.

Peroxide oxidation of a variety of other metal complexes have also been carried out^{41-48}.

(ii) Oxidation of inorganic compounds:

Hydrogen peroxide is known to react with variety of inorganic species. Oxidations of sulphite with hydrogen peroxide have been a subject of investigation by earlier
workers. Halpern and Taube\textsuperscript{49} have suggested a perhydroxyl mechanism in the oxidation of sulfite to sulfate by $\text{H}_2\text{O}_2$, $\text{SO}_2$ acting as the accepter intermediate. The reaction is rapid and in acidic solutions one atom of oxygen of sulphite is reported to be related to the solvent per mole of hydrogen peroxide\textsuperscript{50,51}. The oxidation of sulphite by $\text{H}_2\text{O}_2$ has also been studied by Ojha\textsuperscript{52}. In a recent kinetic study, the oxidation of sulphite by hydrogen peroxide was investigated by stopped flow spectrophotometry\textsuperscript{53} over the pH range 4-8.

The most thoroughly investigated reaction in acidic medium is the oxidation of iodide by hydrogen peroxide. The reaction $2\text{I}^- + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{I}_2 + 2\text{H}_2\text{O}$ has been studied in detail\textsuperscript{54,55}. They have found that the rate of evolution of iodine is expressed by the equation

$$\frac{d[\text{I}_2]}{dt} = k [\text{H}_2\text{O}_2] [\text{I}^-]$$

The effect of various catalysts such as compounds of molybdenum, tungsten, tantalum and iron has also been studied\textsuperscript{56}. This reaction is still under investigation\textsuperscript{57,58}.

Recently, a new induced reactions were observed in the $\text{Tl}^{\text{III}} - \text{H}_2\text{O}_2$ system\textsuperscript{59-61}. Csanyi et al. studied the reaction between $\text{Tl}(\text{III})$ and $\text{H}_2\text{O}_2$ in detail\textsuperscript{62} and assumed that $\text{HO}_2$
radicals are formed in successive one electron step as given below:

\[
\begin{align*}
\left[ \text{Tl} \left( \text{O}_2\text{H} \right) \right]^{2+} & \quad \xrightarrow{+} \quad \left[ \text{Tl}^{3+} \right] \quad \xrightarrow{\text{H}_2\text{O}_2} \quad \left[ \text{Tl}^{2+} \right] \\
\text{H}_2\text{O}_2 & \quad \rightarrow \quad \text{H}_2\text{O}_2
\end{align*}
\]

The HO₂ radicals being in favourable positions may disproportionate before diffusing out of the solvent cage, and end products are formed. Ce(IV) induced reduction of Thallium(III) by H₂O₂ has also been investigated.

The kinetics and mechanism of the reaction between nitrous acid and hydrogen peroxide has been carried out in perchloric acid medium by Bhattacharya and Veeraghavan. The results are interpreted on the basis of the following mechanism.

\[
\text{HNO}_2 + \text{H}^+ \xrightarrow{K_{\text{eq}}} \text{H}_2\text{NO}_2^+.
\]
\[ \text{H}_2\text{NO}_2^+ + \text{H}_2\text{O}_2 \xrightarrow{K} \text{HOONO} + \text{H}_3\text{O}^+ \]

\[ \text{HOONO} \xrightarrow{K_2 \text{fast}} \text{NO}_3^- + \text{H}^+ \]

The kinetics of the reaction

\[ \text{U(IV)} + \text{H}_2\text{O}_2 \longrightarrow \text{UO}_2^{2+} + 2\text{H}^+ \]

is also reported\(^6\). A detailed mechanism has been proposed where the hydrolytic reaction

\[ \text{U(SO}_4\text{)}^{2+} + \text{H}_2\text{O} \xrightarrow{K_4} \text{U(SO}_4\text{)(OH)}^+ + \text{H}^+ \]

followed by the rate controlling reaction

\[ \text{U(SO}_4\text{)(OH)}^+ + \text{H}_2\text{O}_2 \longrightarrow \text{U(SO}_4\text{)(OH)}_2^+ + \text{OH} \]

and subsequent fast reactions of \text{U(V)} and \text{OH radicals} are involved.

Among other notable contributions on the oxidation by hydrogen peroxide are the study of the oxidation of antimony(III) in NaOH solution\(^6\) aquated sulphur dioxide at low pH, \text{N}_p(\text{IV})\(^6\), \text{Cr(II)}\(^7\). Giridhar\(^7\) suggested that the conversion of ferrocyanide to ferricyanide in the presence of \text{H}_2\text{O}_2 follows a compensating oxidation reduction.
mechanism involving free radical.

(iii) Oxidation of organic compounds:

The oxidation of several organic substances by hydrogen peroxide has been carried out largely. Bunton\textsuperscript{72} investigated the oxidation of $\alpha$-diketones and $\alpha$-keto acids with hydrogen peroxide. The oxidation of $\alpha,\beta$-unsaturated ketones\textsuperscript{73}, fatty acids\textsuperscript{74}, fructose\textsuperscript{75} has also been carried out. Ross\textsuperscript{76} attempted to investigate the mechanism in the reaction between thiodiglycol and hydrogen peroxide and between triethylamine and hydrogen peroxide. Thiodialiphatic acid\textsuperscript{77} and simple aldehydes\textsuperscript{78} have also been put under study.

Several studies have been reported in recent years on the oxidation of organic compounds in acidic medium catalysed by metallic species. The oxidation of ascorbic acid by H$_2$O$_2$ in presence of Fe(III) salts follows quite a complex mechanism\textsuperscript{79-81}. During the Fe(III) chelate catalysed reduction of hydrogen peroxide, the formation of mixed ligand chelates and the radicals was proposed.

Recently, Shatamm and Skulatov\textsuperscript{82,83} investigated the mechanism of Cu(II) catalysed oxidation of ascorbic acid by hydrogen peroxide. The experimental rate law was obtained
As

\[- \frac{d}{dt} [AH_2] = \frac{[Cu^{2+}] [AH_2]^{1/2} [H_2O_2]^{1/2}}{[H^+]}\]

Taking Cu(I) as the chain transfer agent, it was possible to propose a chain mechanism leading to the above mentioned rate law. Mechanism of the copper(II) catalysed peroxide oxidation of m-amino benzoic acid and 1,3,5-trihydroxybenzene has also been studied\(^8\). The results have been interpreted on the basis of a mixed ligand catalyst-substrate oxidant complex and through a radical mechanism with the formation of free radicals in the substrate oxidation. Other reactions involving catalytic amounts of Cu(II) and H\(_2\)O\(_2\) include decomposition of hydrogen peroxide activated by pyridine\(^8\), oxidation of tartaric acid\(^8\) and oxidation of ethylenediamine\(^8\).

It is well known that osmic, tungstic, molybdic, tantalic, titanic and selenious acids are converted to per oxyacids on treatment with aqueous hydrogen peroxide. Metal peroxo acids react with olefins to form an intermediate adduct which then hydrolyzes to diol. For example pertungstic acid, formed by the reaction of H\(_2\)O\(_2\) and WO\(_3\) catalyses hydroxylation of olefins in aqueous or mixed solvents to form diols\(^8\). Such hydroxylation is sterospecific, with trans addition of \(\text{OH}\) groups to the olefine.
The ionic mechanism has been proposed, involving the participation of an intermediate hydroperoxide species, HWO₃-C-OH.

\[
R_2C = CR_2 + HWO_3OH \rightarrow R_2C - CR_2
\]

\[
OH
\]

\[
R_2C-CR_2 + H_2O \rightarrow R_2C-CR_2 + HWO_3OH
\]

\[
OH
\]

HWO₃OH + H₂O₂ \rightarrow HWO₃OCH + H₂O.

The participation of free radicals has been ruled out on the basis that the free radical scavenger does not react with the intermediate free radicals. Similar addition of H₂O₂ across olefins double bonds is catalysed by other metal peroxo acids. These reactions are generally stereospecific and produce high yields of the glycol.

Thus the hydrogen peroxide becomes very effective epoxidising agents of allylic alcohols and compound having strong withdrawing substituents close to the double bond. Several studies have been reported in recent years on the oxidation of organic compounds with hydrogen peroxide catalysed by sodium tungstate, sodium molybdate and sodium orthovanadate. Among the notable ones the mechanism of
the oxidation of allyl alcohol\textsuperscript{91}, fumaric acid\textsuperscript{92}, maleic acid\textsuperscript{93}, amines\textsuperscript{94-96}, dimethylsulphide\textsuperscript{97}, Allylchloride\textsuperscript{98} and acrylic acid\textsuperscript{99} has been investigated in presence of sodium tungstate and sodium molybdate as a catalyst. All the reaction studied except that of amines were found to be pH dependent and follows a first order kinetics in the substrate and catalyst concentration but independent of the hydrogen peroxide concentration. It is assumed that the peroxyacids is the epoxidising species in a rate determining step. The oxidation of amines follows a different mechanism. Kinetics and mechanism of the epoxidation of maleic and fumaric acids\textsuperscript{100}, crotonic acid\textsuperscript{101} and diphenylsulphide with hydrogen peroxide in the presence of sodium vanadate as a catalyst has also been carried out. Ogata and Tanaka\textsuperscript{102} suggested the following mechanism for the oxidation in neutral 96% methanol at very low concentrations of sodium metavanadate with negligible concentration of polyperoxy vanadates.

\[
\begin{align*}
\text{VO}_3^+ + \text{H}_2\text{O}_2 & \rightleftharpoons \text{VO}_5^- + 2\text{H}^+ \\
\text{VO}_5^- + n\text{H}_2\text{O}_2 + (\text{VO}_3^-)(\text{H}_2\text{O}_2)_n & \overset{\text{fast}}{\longrightarrow} (\text{VO}_5^- - \text{Ph}_2\text{S})^-(\text{H}_2\text{O}_2)_n \\
(\text{VO}_5^-)(\text{H}_2\text{O}_2)_n + \text{Ph}_2\text{S} & \overset{\text{fast}}{\longrightarrow} (\text{VO}_5^- - \text{Ph}_2\text{S})^-(\text{H}_2\text{O}_2)_n \\
(\text{VO}_5^- - \text{Ph}_2\text{S})^-(\text{H}_2\text{O}_2)_n + \text{Ph}_2\text{S} & \overset{\text{slow}}{\longrightarrow} \text{Ph}_2\text{SO}+(\text{VO}_4^- - \text{Ph}_2\text{S})^-(\text{H}_2\text{O}_2)_n
\end{align*}
\]
Here the equation (1) shows the hydrogen bonded association of $H_2O_2$ with $VO^-$. In view of the rate equation, this aggregated complex seems to form 1:1 coordination complex with diphenyl sulphide and this complex seems to react with another molecule of diphenyl sulphide to give diphenyl sulfoxide.

**Role of Fe(II) as a catalyst in the reactions of hydrogen peroxide:**

The usefulness of iron(II) as a catalyst for peroxide oxidations in acid solution was discovered by H.J.H. Fenton in 1894. The iron(II)-hydrogen peroxide reagent termed as Fenton's reagent possesses potent oxidising properties not present in the separate reagents. One of the systems in which redox reactions involving atoms and radicals have been extensively studied is that between $Fe^{++}$ and $H_2O_2$.

The oxidation of iron(II) by $H_2O_2$ was first studied by Haber and Weiss. They measured the consumption ratio under various conditions and put forward their mechanism on the concept of one electron transfer as shown below:

$$Fe^{2+} + H_2O_2 \overset{k_1}{\rightarrow} Fe^{3+} + OH^- + OH^- \quad (1)$$

$$Fe^{2+} + OH^- \overset{k_2}{\rightarrow} Fe^{3+} + OH^- \quad (2)$$
\[
\text{OH}^\cdot + \text{H}_2\text{O}_2 \xrightleftharpoons{k_3} \text{HO}_2^\cdot + \text{H}_2\text{O} \\
\text{HO}_2^\cdot + \text{H}_2\text{O}_2 \xrightleftharpoons{k_4} \text{O}_2 + \text{H}_2\text{O} + \text{OH}^\cdot
\]

This combination of radical reactions leads to the equation

\[
n = 0.5 + k_3 \left[\text{H}_2\text{O}_2\right]/k_2\left[\text{Fe}^{2+}\right]
\]

The idea of one electron transfer has been successful in explaining a variety of photochemical and photosensitized reactions\textsuperscript{106,107}. The driving force for one electron transfer in these reactions is the entropy gain in the formulation of a free radical complex in the process. For a two electron transfer, very strong interaction is needed between the donor and acceptor since the electrons have to be paired before transfer. Bray and Gorin\textsuperscript{108} have proposed a two electron oxidation of Fe(II) to Fe(IV) in the reaction of iron(II) and \text{H}_2\text{O}_2 and proposed the

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \longrightarrow \text{FeO}^{2+} + \text{H}_2\text{O} \tag{5}
\]

\[
\text{FeO}^{2+} + \text{H}_2\text{O}_2 \longrightarrow \text{Fe}^{2+} + \text{H}_2\text{O} + \text{O}_2 \tag{6}
\]

\[
\text{Fe}^{3+} + \text{OH}^\cdot \longrightarrow \text{FeO}^{2+} + \text{H}^+ \longrightarrow \text{Fe(OH)}^{3+} \tag{7}
\]

\[
\text{Fe(OH)}^{3+} + \text{Fe}^{2+} \longrightarrow 2\text{Fe}^{3+} + \text{OH}^-
\]

\tag{8}
The oxidation of iron(II) to iron(IV) by a two-electron reduction of $H_2O_2$ has also been proposed by Cahil and Taube\textsuperscript{109} based on $H_2^{18}O_2$ studies.

Kolthoff and Medalia\textsuperscript{110} and Barb \textit{et al.}\textsuperscript{111,112} studied the reaction of iron(II) with hydrogen peroxide in the presence of an added organic substrate and suggested the following mechanism:

\begin{align*}
Fe^{2+} + H_2O_2 & \longrightarrow Fe^{3+} + OH^- + OH^- \quad \text{..(9)} \\
Fe^{2+} + OH^- & \longrightarrow Fe^{3+} + OH^- \quad \text{..(10)} \\
H_2A + OH^- & \longrightarrow HA^- + H_2O \quad \text{..(11)} \\
HA^- + Fe^{3+} & \longrightarrow HA^+ + Fe^{2+} \quad \text{..(12)} \\
HA^+ + OH^- & \longrightarrow H_2O + HA^- \quad \text{(primary product)} \quad \text{..(13)} \\
HAOH + OH^- & \longrightarrow HOA^- + H_2O \quad \text{..(14)} \\
HOA^- + Fe^{3+} & \longrightarrow Fe^{2+} + H^+ + AO \quad \text{(secondary product)} \quad \text{..(15)}
\end{align*}

Cleavage of the HO-OH bond by iron(II) produces HO$^-$ and OH$^-$. The hydroxyl radical then react either with iron(II) or the substrate in steps to yield iron(III) or the
substrate radical, HA⁺, respectively. The substrate radical then undergoes a series of oxidation in subsequent steps to form the primary product HA⁺OH. Continuation of free radical reactions results in dehydrogenation to form A⁺ or in the formation of higher hydroxylation products.

An alternative attack for radical reaction on peroxide is

\[ \text{CH}_3\text{CHOH} + \text{HOOH} \rightarrow \text{CH}_3\text{CH(OH)}_2 + \text{OH}^- \]

Typical examples are the oxidation of ethanol and benzene\textsuperscript{113}. The oxidation of ethanol is a chain reaction requiring only a small quantity of iron(II). The mechanism is represented as follows:

\[ \text{Fe(II)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(OH)}^{2+} + \cdot\text{OH}^- \]
\[ \cdot\text{OH} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{CHOH} \]
\[ \text{Fe(OH)}^{2+} + \text{CH}_3\cdot\text{CHOH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} + \text{Fe(II)}^- \]

The oxidation of benzene may lead to phenol or biphenyl

\[ \text{Fe(II)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(OH)}^{2+} + \cdot\text{OH}^- \]

\[ \text{OH}^- + \text{Fe(II)} + \text{H}^+ \rightarrow \text{Dimerisation} \]

\[ + 2\text{H}_2\text{O} \]
The Fe(II)-EDTA complex has been found to catalyse hydroxylation in the course of the reduction of peroxide to water. The reactions of these systems are considered models for peroxidase action. Hydroxylation of the substrate takes place by a free radical addition of $\text{OH}^-$. The mechanism proposed by Braslow and L.N. Lukens$^{114}$ and Grinstead$^{79}$ for the hydroxylation of salicylic acid is given below:

$$\text{Fe(III)} - \text{EDTA} + \text{OH}^- + H_2A \rightarrow \text{HA}^* + \text{Fe(II)} - \text{EDTA} + H_2O$$

$$\text{Fe(III)} - \text{EDTA} + \text{OH}^- + \text{HA}^* \rightarrow \text{A} + \text{Fe(II)} - \text{EDTA} + H_2O$$

The first step is the cleavage of the HO-OH bond by one electron reduction of $H_2O_2$. This is followed by the reaction of the hydroxyl radical with the substrate to give an organic radical similar to that proposed by Barb et al. for
hydroxylation by Fenton's reagent. A second attack of the substrate by the hydroxyl radical yields the hydroxylated product. In the last two steps, one electron reduction of Fe(III)-EDTA to the original catalyst, Fe(II)-EDTA, is accomplished by the oxidation of ascorbic acid or some other suitable two electron donor.

α-hydroxy pyridine and nicotine was oxidised using Fenton's reagent. The oxidation of indigocarmine(I) by H₂O₂ in the presence of Fe(ClO₄)₂ and o-phenanthroline(II) is a first order in Fe²⁺ concentration and maximum rate occurs at 1:1 molar ratio. The study relates to the effect of o-phenanthroline on oxidation with Fenton's reagent. A Fe²⁺ - diethylene-triamine pentaacetic (DTPA) complex oxidised to a Fe³⁺ - DTPA complex and CH is produced when H₂O₂ is added to a solution of Fe²⁺-DTPA in a phosphate buffer at neutral pH.

Oxidation of amino acids:

Amino acids date back to the beginning of human race, but they escaped human attention owing to less developed scientific innovations. They are of highest importance since they form the fundamental building blocks of proteins which like the nucleic acids take part in all living processes. In addition to the protein bound amino acids, the
cellular tissue are fluid of living organisms contain a permanent reservoir of free amino acid. These free amino acids take part in numerous metabolic reactions. The amino acids distribution patterns of blood plasma and urine are of great diagnostic significance in medicine. Specific metabolic roles of amino acids include the biosynthesis of polypeptides and proteins and the synthesis of phosphatides, prophyrrins and nucleotides.

Besides being incorporated into proteins, amino-acids also serve as source of carbon and nitrogen when required. The first stage in their catabolism is the removal of $-\text{NH}_2$ group and formation of corresponding keto acid.

Due to their large practical applications in the field of biological sciences, pharmacy and medicine, the oxidation reactions of amino acids have been the subject of intensive kinetic studies. There has been a keen interest of researchers in the mechanism of biochemical processes in which individual amino acids has a vital role.

The chemical oxidation of amino acids has received considerable attention in recent years. In general, amino acids on oxidation by different oxidants leads to loss of the amino group and the formation of carbonyl compounds.
The reaction proceeds with decarboxylation and leads to the aldehyde having one carbon atom less than the starting amino acids.

\[
R-CH(\text{NH}_2)-\text{COOH} \xrightarrow{-2\text{H},-\text{CO}_2} R-\text{CH}=\text{NH} \xrightarrow{\text{H}_2\text{O}} R-\text{CHO} + \text{NH}_3
\]

Clamp and Hough\textsuperscript{121} suggested that the oxidation of glycine and N-substituted glycine by periodate proceed by an electrophillic attack of the oxidant on nitrogen giving an intermediate complex which decomposes to products via the imino compound. Oxidation of some \(\alpha\)-amino acids by periodate has also been investigated\textsuperscript{122}. They propose that the intermediate in a slow rate determining step cyclizes and undergoes C-C bond fission giving rise to products via the imino compound. Oxidation of glycine by \(\text{KBrO}_3\) has also been examined\textsuperscript{123}.

Recently the kinetics of oxidation of some \(\alpha\)-amino acids by alkaline ferricyanide in presence of osmium(VIII) has been investigated\textsuperscript{124-125} and a strong catalytic influence of ferricyanide has been observed. On the other hand, the oxidation of histidine in absence of osmium(VIII) showed a retarding influence of ferricyanide ion\textsuperscript{126}.

Adinarayana, Sethuram and Navaneeth Rao\textsuperscript{127} examined the Ce\textsuperscript{4+} oxidation of a series of amino acids in presence
and absence of Ag⁺. The observed rate law has been explained by assuming the formation of an adduct between amino acid and Ag⁺ in a fast step.

Navaneeth Rao *et al.* 128-130 kinetically performed the oxidation of amino acids by peroxysulphate catalysed by Ag⁺ or Cu²⁺ or (Ag⁺ - Cu²⁺) mixture in aqueous solution. They observed that the rate constant in the presence of mixed catalyst is far higher than even the sum of the rate constants in the presence of Ag⁺ or Cu²⁺. The rate law was examined by assuming the formation of Ag²⁺, SO₄⁻, which later react with the substrate to give radicals and are trapped and oxidised by Cu²⁺. Some what identical observations were reported as in the case of Glutamic acid 131. Oxidation of benzyl glycine by peroxysulphate has been reported recently 132. Mixed catalyst system such as [Ir(III)-Mn(II)] has also been used for the oxidative decarboxylation and deamination of amino acid and [Ir(III)-Mn(II)] catalysed reaction is found to be greater as compared to that of Ir(III) or Mn(II) employed separately 133. kinetics and mechanism of the oxidation of amino acids by peroxysulphate has been recently investigated 134.

Chloraminometric oxidation of bio-organic compounds has been reported in the literature. A few of these reactions in alkaline medium have been kinetically
investigated\textsuperscript{135-136}. The kinetics and mechanism of oxidation of amino acids by chloramine-T were studied in acid medium by Mahadevappa et al.\textsuperscript{139-142}. The reactions follow identical kinetics for all the amino acids. The rate shows a first order dependence on [oxidant] but is independent of substrate. The oxidation occurs via complex intermediate formed by the electrophillic attack of $\text{Cl}_2$ or $\text{H}_2\text{O Cl}^+$ on the nitrogen atom of the amino acid which disproportionate to give the mono-$N$-chloroderivative of the amino acid, which in turn interacts with a second molecule of the oxidant to form the $N,N$-dichloroderivative. The latter undergoes molecular rearrangement and elimination processes to give the reaction products.

The oxidation of amino acids by permanganate has been investigated by Verma and co-workers\textsuperscript{143,144} and a mechanism based on the direct reaction between the substrate and oxidant has been proposed. Bromine ion catalysed oxidation of glycine was studied for its mechanistic details by kinetic method in 3 M $\text{H}_2\text{SO}_4$\textsuperscript{145}. The results conform to the rate law

$$-\frac{d[MnO_4^-]}{dt} = \frac{k_1[H^+]}{1+k_2[H^+]} [MnO_4^-] + k_3[G] + (k_2+3)[Br^-]$$

The first term corresponds to the uncatalysed reaction and second and third terms are for catalysed paths. Bromide
catalysis were considered to operate through two paths: (i) ion-pair formation between bromide and glycine; and (ii) Br⁻/Br₂ cycle. An ion-pair or complex formation between glycine and bromide has been confirmed by spectrophotometric measurements. They also compared their results with earlier studies of uncatalyzed oxidation.\textsuperscript{146}

Kamaluddin\textsuperscript{147,148} studied the oxidation of some \(\alpha\)-amino acids with Mn(III) sulphate. He noticed the increase in initial Mn(III) from first to second, the latter case being accompanied by an inhibitory effect. He also demonstrated that the reaction follows a path through deamination accompanied by decarboxylation. The oxidation of higher amino acids\textsuperscript{149} was also performed to generalise the reaction pathway. Oxidation of glycine with Mn(III) has been reinvestigated\textsuperscript{150}.

The data on the oxidation of Serine, Methionine and cysteine by chromic acid\textsuperscript{151}, can be well interpreted on the basis of rate determining of hydride ion loss with consequent product of an electron deficient transition state leading to a ready decarboxylation. In the case of methionine and cysteine oxidation, chromic acid attacks the sulphur group as sulphur is more nucleophilic than nitrogen. Stiochiometry, kinetics and mechanism of Cr(VI) oxidation of L-cysteine at neutral pH has been
recently reported\textsuperscript{152}. The results of studies on the kinetics of anation of hexaaquochromium(III) ion by serine in aqueous acidic medium show that the rates are insensitive towards the change in ionic strength of the medium\textsuperscript{153}. The overall reaction is best accounted for by an ion-pair equilibrium involving zwitterion followed by slow interchange of the bound water and the entering ligand in the ion pair.

Kinetics and mechanistic aspects of oxidative decarboxylation and deamination of glycine and DL-\(\alpha\)-Phenyl glycine by lead tetraacetate with and without pyridine as a catalyst\textsuperscript{154,155} led to the conclusion that the interaction of zwitterion of the amino acid with \(\text{Pb(OAC)}_4\) takes place in the rate determining step which gives ammonia and intermediate mono ester. This mechanism envisages a cyclic intermediate which would facilitate the release of ammonia in a fast step. Cyclic intermediates are also known in lead tetraacetate\textsuperscript{156}. The mono ester may later form carbonium ion intermediate. The carbonium ion could react in a fast step with water molecule to give a proton. Disproportionation of the monoeaster derivative could involve the heterolytic cleavage of Pb-O bond and a rupture of C-C bond, giving the products.

Diperiodatocupriate(III) has also been used as an oxidant for the oxidation of amino acids\textsuperscript{157}. The rate of
oxidation increased with decrease in $pK_d$ values of amino acids. The presence of electron withdrawing groups at $\alpha$-carbon increased the rate, whereas electron releasing groups decreased the rate. The decrease in the rate of oxidation with increasing chain length among the amino acids has been explained on the basis of the difficulty in the formation of adduct due to the decrease of positive charge on the N atom caused by $+I$ effect of alkyl groups and also steric effect.

Object and scope of the proposed investigation:

The oxidation of amino acids is of utmost importance, both from a purely chemical point of view and from the point of view of its bearing on the mechanism of amino acid metabolism. Biochemical reactions taking place in various physiological processes of human body are estimated to have resemblance with the simple chemical reactions. It was a probable consideration that the study of the mechanism of oxidation of amino acids in presence of Fe(II) might expose the possible correlation among biological and non-biological pathways which frequently have striking similarities, but sometimes differ in some fundamental way. Truly speaking kinetic studies of the reactions of biological significance is first normal trend in interpreting the complex biological reactions. A good amount of
work in exploring the kinetics of many of interesting oxidation of amino acids that are catalysed by metal ions has been performed in the last twenty years, and since the reactions frequently occur under mild conditions, there has been considerable success in interpreting the reaction mechanism in terms of the nature of reactive intermediates and the properties of metal catalysts.

Despite the biological significance of catalytic functions of Fe(II) and its formation of complex during amino acid metabolism there is scant information about the kinetics and mechanistic aspects of these reactions. The aim of the present investigation is to study the mechanistic aspects of the oxidation of amino acids by hydrogen peroxide in presence of Fe(II) as catalysts in acid media. The present study includes specific aims of investigating the dependence on –

(i) Variation of substrate, oxidant and catalyst concentration,
(ii) Variation of ionic strength
(iii) Temperature variation and the thermodynamic parameters.
The range of investigation extends from fixation of order with respect to oxidant, substrate and catalyst to stoichiometry, and product study and evaluation of thermodynamic parameters.

To a good extent the present work has contributed in confirming the free radical mechanism as is reported and discussed in subsequent chapters. It may be concluded that there is a necessity for further kinetic investigation of oxidation of some higher amino acids to generalise the reaction paths. More information on different amino acids, along with their systematic account will help broaden the existing knowledge.