CHAPTER - I

INTRODUCTION
“The cosmic religious experience is the strongest and noblest force behind scientific research”

– “EINSTEIN”

Change is the law of nature and man lives in a universe that is continuously undergoing changes from one form to another with different speeds. The speed of chemical changes varies from nanoseconds to years. The aim of chemistry is not only to determine the composition of substances and such changes which they undergo, but also to plan and control these changes and create new compounds to offer mankind a better tomorrow. It is a subject matter of chemical kinetics to find out the rate of such chemical changes and to correlate the observations in terms of simple and complex changes undergoing in a chemical system.

Kinetics is thus the study of rate of chemical reactions and molecular processes by which the reactions occur\(^1\) and is fundamentally concerned with the details whereby a system gets from the one state to another with the time required for the transition. Information regarding the rate of reaction is most valuable to chemists or engineers for developing efficient synthetic procedure for practical purposes as well as for analytical work. Kinetic study along with steriochemical studies provides the most powerful methods of determining reaction mechanism. The main use of rate data is in elucidation of the reaction mechanism. The chemical reaction is the sum of two or more steps. One of these steps is slow and is said to be rate determining step\(^2\). Thus rate measurements themselves or in combination with knowledge of appropriate thermodynamical properties of the system may be sufficient and satisfactory understanding of reaction mechanism.
Therefore chemical kinetics may be considered a powerful tool in the hands of chemists to elucidate reaction mechanism \(^3\).

The study of mechanism of redox reactions is a subject of considerable importance because it has vast application in understanding the nature of life. The mechanism of redox reactions usually involves either atom transfer or electron transfer both providing the same effect. Although it is difficult to distinguish between the two types of reactions experimentally, a considerable progress has been achieved in the field of electron transfer reactions \(^4\)–\(^6\).

1.1: SURVEY OF LITERATURE

Study of reaction rate, with all the factors which influence the rate of reaction \(^7\), is given a term as chemical kinetics which includes the explanation of rate in terms of the reaction mechanism by which chemical reaction occurs. The rate can be derived either in terms of product formation or consumption of reactant of reaction with time, i.e. \((-dc/dt)\). The rate of chemical reaction is influenced by several factors such as temperature, concentration of reactants, products, catalyst, medium (i.e. acidic or alkaline), ionic strength of the medium (in deciding the nature of reacting species of the reactants involved in the reaction), total pressure of the system (in case of gaseous reactions), viscosity of the system, the dielectric constant of reaction mixture, \(p^H\) and so on.

The main aim of every experimental kinetic investigation is to find out quantitative relationship between the rate of reaction and those factors which affect it. The manner in which the rate of a reaction varies with the concentration of reacting
species is usually denoted by stating the ‘order’ of reaction. For multi step reactions the kinetics is limited by the slowest step, which is also the rate determining step. There are many reactions in which order is not simple power function of the concentration but fractional. The elucidation of the exact kinetic law then requires carefully planned experiments in which influence of products and reactants are studied systematically.

The product concentration in a reaction varies with time and may influence the rate in a number of different ways. It is often important to establish the dependence of rate on product concentration also. A rate law can be derived for different mechanisms. Comparison of an experimentally observed rate law with the derived rate law then allows one to make correct choice among apparently reasonable mechanisms. Only that mechanism, which gives the rate law of the form determined by experiments, may be considered as plausible mechanism for the reaction. However, the proposed mechanism may no longer remain valid, if some new information is uncovered. Reaction mechanisms are derived concepts which can be changed or modified if some new concepts or new facts are observed.

All the kinetic investigations are carried out with the aim of gaining insight into mechanism by which chemical changes occur. Investigation may be solely concerned to establish the series of steps by which the reactants are converted into products. In other cases where the reaction mechanism is known, studies of kinetics of reaction may be employed to shed light on the details of the interaction among the reactant molecules. This aim demands that the experimental data be summarized in equation of the same form as those which appear in theoretical treatment of reaction kinetics. A clue to the
reality of reaction mechanism is obtained by the product identification, use of isotopic tracers\textsuperscript{9}, detection of short lived intermediates, variation of ionic strength\textsuperscript{10}, catalyst and change of solvents\textsuperscript{11}, etc. on the rate of reaction.

J.J. Berzelius\textsuperscript{12} introduced the term ‘catalyst’ for the first time in 1836 for the certain substances which were used to activate a number of chemical reactions and he assumed that catalyst exerts a special catalytic force upon reactants, which is manifestation of electrochemical affinity. In 1902, W. Ostwald\textsuperscript{13} defined catalyst as a substance which speeds up chemical reaction without affecting the equilibrium and his definition has made it the most frequently cited, of all definitions. It was reported later on that this definition was valid only for reversible reactions and does not incorporate any form of autocatalysis. P. Sabatier\textsuperscript{14} recognized the shortcomings of Ostwald’s definition and considered catalysis simply as a mechanism causing or accelerating certain chemical reactions by the substances which themselves are not irreversibly altered. This phenomenological definition is less restrictive than Ostwald but unduly stresses that catalyst must not undergo irreversible changes during reaction. Most catalysts, however, eventually become inactive due to side reactions or contaminants. The process can never the less be made ‘catalytic’ by coupling it with suitable catalyst. If this step is carried out simultaneously with the main reaction, the net effect is indistinguishable from a true catalytic process. With the development of the theories of reaction rates, it becomes clear that catalysis, in general, lowers the energy of activation of a reaction. This is useful definition, although, it is not really commensurate with the complexity and multitudinous aspects of the phenomenon. It is, further, must be specified that the lowering of activation
energy occurs through the direct interactions of the catalyst with the substrates. In more complex catalytic systems (such as enzyme) certain nonstoichiometric additives (e.g. metal ions) may cause indirect enhancements in the reaction rate. The formation of active complex in catalytic reaction makes a negative contribution to the activation entropy ($\Delta S^\#$) which is offset by larger decrease of free energy ($\Delta G^\#$). In simple reversible systems the catalyst increases the rate of attainment of equilibrium and has no effect on product distribution. By suitable modifications of catalysts or the addition of selective inhibitors, it is possible to develop catalysts which can perform only one reaction or prevent undesirable side reactions.

In modern chemical fields role of catalysts was widely recognized and therefore, it has been subjected to qualitative and quantitative studies. Heterogeneous catalysis is a well defined field for which numerous excellent examples have been observed to be of revolutionary use in industries, while survey of literature on homogeneous catalytic processes indicates that the studies in the oxidation of organic compounds involving effective and suitable homogeneous catalyst have been given little incentive to work out the kinetics and mechanism of well known homogeneously catalysed systems. Apparently the homogeneously catalysed reactions find little scope of their application in synthetic work. Yet these processes involve considerable academic interest in understanding the mechanistic paths of a reaction and also are of commercial utility in the modern applied field of chemistry.

A general mechanism for catalysed reactions$^{15}$ where single substrate is involved, is as follows$^{16}$:
There are two possibilities which can be taken into existence with regard to the stability of intermediate complex $X$. In the first possibility, when $k_{-1}$ is greater than $k_2$ then the intermediate complex $X$ will be termed as Arrhenius complex. In the second possibility, when $k_2$ is greater than $k_{-1}$ the intermediate complex $X$ will be termed as van’t Hoff complex.

The mechanism of organic/inorganic redox reactions usually involves transfer of either atom or electron, both providing the same effect. It is difficult to distinguish between these two types of reactions experimentally. A considerable progress which has been achieved in the field of electron transfer reactions due to considerable interest in the field of redox processes by a large number of workers, owing to its importance in understanding the nature, technology and analytical chemistry. The theoretical treatment of electron transfer reactions by Libby\textsuperscript{17}, Marcus, Zwolinsky and Eyring\textsuperscript{18-19}, Laidler\textsuperscript{20}, and many others have been of great help in understanding the nature of these reactions.

The application of steady state approximation is one of the most characteristic factors in deriving the rate law in which it is assumed that the rate of formation of a particular species and rate of consumption of the same species are equal. The activation parameters play an important role in deciding the nature of transition state of the reaction which supplies useful information leading to elucidation of the reaction mechanism.
Stoichiometry is also an important factor which shows the overall number of moles of one reactant consumed by one mole of the other. Product analysis is also strong evidence in predicting the reaction mechanism.

Most difficult analytical problems\(^{21}\) have found their answers through kinetic studies. Recently, kinetics has been applied to solve analytical problems by Mark and Mottola\(^{22}\). Kinetics also helps in mixture analysis\(^{23}\), enzyme analysis and use of enzyme in the determination of rate dependence on substrate concentration by the direct use of kinetic data\(^{24}\). When a desired reaction is accomplished by parasitic side reaction then a kinetic study reveals the identification of the experimental conditions under which the main reaction will be favorable (i.e. produced maximum yield with the least cost), so that selectivity of the process can be maximized. One of the important applications of kinetics is in the field of polymer chemistry to obtain greater reactivity profile and for achieving a high degree of stability/selectivity conditions\(^ {25,26}\) for better yields of desired polymer.

Among the common inorganic redox reagents which have received considerable emphasis leading to mechanistic studies are permanganate, chromic acid, Ceric(IV), Manganese(III), Vanadium(V), Cobalt(III), Lead(IV), Copper(II), Tin(II), Mercury(II), hexacyanoferrate(III), peroxy disulphate, etc. and organic redox reagents are ascorbic acid, N-chlorosuccinimide (NCS), N-bromosuccinimide (NBS), N-chlorobenzamide i.e. several N-haloimides, chloramine-T (CAT), quinines, catechol and carbonium ion etc. In a publication edited by Bomford and Tipper\(^ {27}\) a detailed account of several familiar and less familiar redox reagents have been discussed. Berka and Zyka\(^ {28}\) have also described several less familiar and newer redox titrants in another publication.
Before describing the kinetic investigations, it is necessary to present brief of literatures on kinetics and mechanism of oxidation of some reducing substrates by different oxidants (CAT and KIO₃) used here in the presence of transition metal ions as homogeneous catalyst.

1.2: CHLORAMINE-T AS AN OXIDANT: A REVIEW

K.V. Uma, S.M. Mayanna et al²⁹ have studied O₃O₄ catalysed oxidation of benzyl alcohol with chloramine-T in alkaline solution. The oxidation follows complex kinetics, being first-order each in chloramine- T, substrate and O₃O₄. The oxidation rate is also inversely proportional to [OH¯]. The kinetic results are consistent with a mechanism involving rate determining removal of H⁺ ion by a O₃O₄ – chloramine - T complex.

P.S. Radhakrishnamurti and B. Sahu³⁰ have investigated O₃(VIII) catalysed oxidation of alcohols by chloramine- T. O₃(VIII) catalysed oxidation of sec butanol, cyclopentanol cyclohexanol, cycoheptanol, 1, 3 - butanediol, 1, 4- butanediol by CAT in alkaline medium is first order with respect to CAT and O₃O₄. The dependence on [OH¯] is inverse one half. The reactions are zero order with [Substrate]. The reaction proceeds via rate determining formation of an O₃O₄- complex which undergoes a one electron transfer by the loss of a H atom. K.V. Uma, S.M. Mayanna et al³¹ have studied O₃(VIII) oxide catalysed oxidation of primary alcohols by chloramine -T. The title oxidation, studied in 10⁻⁴M - 10⁻¹M NaOH medium at 30-50⁰C, shows first order dependence each in primary alcohols, O₃O₄ and OH¯ at low concentrations. The rate is independent of chloramine-T concentration. The results suggest formation of an activated complex between substrate
and O₅O₄, which slowly decomposed into aldehyde and O₅(IV). The latter is oxidised rapidly to O₅(VIII) with chloramine -T anion.

S.L. Sharma, O.P. Bansal have studied copper catalysed oxidation of n-butanol by chloramine - T in alkaline medium. The kinetics were first order in butanol, CAT and OH⁻ and are independent of Cu²⁺. S.P. Mushran, M.C. Agrawal et al have studied O₅(VIII) catalyzed oxidation of formaldehyde and acetaldehyde in alkaline medium. The oxidation showed first order dependence to [chloramine -T] and [O₅(VIII)], inverse first order to [alkali] and zero order dependence to [aldehyde]. Variation in ionic strength did not affect reaction rate. The mechanism suggested involves the formation of an intermediate complex between chloramine - T and O₅(VIII) in the slow and rate controlling step which abstracts hydride ion from the hydrated form of aldehyde in fast step. S.P. Mushran et al have studied O₅(VIII) catalysed oxidation of isopropyl alcohol by chloramine - T. The title oxidation was 1ˢᵗ order in chloramine -T, H⁺ and O₅(VIII) was zero order in isopropyl alcohol. The ionic strength had no effect. The rate determining step involved reaction of chloramine-T with O₅(VIII), neither reactant being charged, to form an intermediate complex.

S.P. Mushran, M.C. Agrawal et al have studied osmium (VIII) catalysed oxidation of α-hydroxy acids (glycolic, lactic and mandelic acid) by chloramine-T in alkaline medium. The first order rate plots in chloramine-T were linear up to 2 half lives. Under pseudo first order conditions, the rate constants showed a slight decrease with increase in chloramine-T concentration. The rate of reaction was independent of α-hydroxy acid
concentration and directly proportional to $[\text{O}_8\text{(VIII)}]$ and the reciprocal of $\text{OH}^-$ concentration. The formation of a complex between N-chloro-p-toluene sulphonamide and $\text{O}_8\text{(VIII)}$ was rate determining and was followed by rapid transfer of a hydride ion from the substrate to this complex. Shailendra Jha et al.$^{36}$ have studied copper (II) catalysed oxidation of lactic acid with chloramine-T (CAT) in alkaline solutions. The order in CAT was unity, but the rate was independent of [lactic acid].

D.S. Mahadevappa et al.$^{37}$ have studied the oxidation of diphenyl sulphoxide by chloramine-T in acidic and alkaline medium. $\text{O}_8\text{O}_4$ was used as catalyst in latter medium. The observed rate law in acid medium is interpreted in terms of a fast interaction between diphenyl sulphoxide and $(\text{H}_2\text{OCl})^+$ formed from the hydrolysis of chloramine-T in a slow step or from the hydrolysis of $\text{Cl}_2$ formed from free acid and added $\text{Cl}^-$ ion. The results in alkaline medium was explained on the basis of a complex formation between substrate and $\text{O}_8\text{O}_4$ at lower $[\text{NaOH}]$ but formation of a cyclic complex between chloramine-T and $\text{O}_8\text{O}_4$ is the rate determining step at higher [alkali].

H.M.K. Naidu et al.$^{38}$ have studied the oxidation of $\alpha$-amino acids by chloramine-T in perchloric acid medium. The kinetics of oxidation of leucine, serine, glutamine and glutamic acid by CAT in presence of $\text{HClO}_4$ at $30^\circ\text{c}$ showed first order dependence each on CAT and amino acid and inverse first order with $[\text{H}^+]$. Ionic strength and presence of the added p-toluene sulphonamide (PTS) have no effect on rate. Chloride ions catalysed the reaction. A mechanism in which the zwitter ion interacts with protonated CAT has been proposed to account for kinetics. D.S. Mahadevappa et al.$^{39}$ have studied the
oxidation of arginine and histidine by chloramine-T in hydrochloric acid medium. The
title oxidation at 30\(^\circ\)C was catalysed simultaneously by H\(^+\) and [Cl\(^-\) ] at HCl concentration of 0.04-0.12M. The kinetics was first order for chloramine-T, H\(^+\) and arginine, but zero order for histidine and 0.7 \(^{th}\) order for [Cl\(^-\)].

S.N. Katgeri et al\(^{40}\) have studied the oxidation of hydroxylamine hydrochloride by chloramine-T in acidic medium. The reaction shows first order dependence on [CAT] and [NH\(_2\)OH] but inverse first order dependence on [H\(^+\)]. Ionic strength and added p-toluene sulphonamide (PTS) have no effect on the rate of oxidation. Chloride ions catalysed the reaction. The rate shows a positive dielectric effect. A mechanism involving interaction of unprotonated NH\(_2\)OH and N-chloro-p-toluene sulphonamide giving an intermediate complex in a slow step is suggested. S.N. Katgeri et al\(^{41}\) have studied the oxidation of \(\alpha\) amino acids by chloramine-T in hydrochloric acid medium. The kinetics of the title oxidation of leucine, serine, lysine and glutamine was first order in [CAT] and first order in [H\(^+\)], whereas the rate was independent of the concentration of amino acid. Ionic strength and the presence of the product had no effect on rate whereas [Cl\(^-\) ] catalyses the oxidation.

D.S. Mahadevappa et al\(^{42}\) have studied the oxidation of dimethyl sulphoxide by chloramine-T in aqueous solution. The title oxidation is first order each in oxidant and substrate and is accelerated by H\(^+\) in HClO\(_4\) and substrate and retarded by low [OH\(^-\) ] in NaOH – O\(_3\)O\(_4\). The proposed Mechanism in acidic medium involves electrophilic attack by chloramine-T at S atom of dimethyl sulphoxide and hydrolysis of the resulting
intermediate. In dil. NaOH – O₅O₄, the reaction involves formation of acyclic complex between CAT and O₅O₄, which reacts with DMSO in a slow step. At higher [alkali], the reaction involves direct interaction between CAT and DMSO.

Adarsh Kumar et al have studied O₅(VIII) catalysed oxidation of cyclopentanone by chloramine-T. The kinetics indicated that the title oxidation proceeded by rate determining complexation of CAT with O₅(VIII), followed by rapid oxidation of cyclopentanone enolate. The final product was 1, 2-cyclopentanedione. Munesh Chandra, O. P. Bansal have studied Cu(II) catalysed oxidation of monoethanolamine by chloramine-T in alkaline medium. The initial oxidation rates only were studied. The rate determining step involves the interaction between neutral chloramine-T and H₂N(CH₂)₂O⁻.

B.S. Yadav, S. Singh et al have studied the oxidation of lysine mono hydrochloride by alkaline chloramine-T. The oxidation is first order with respect to [Cu²⁺]. The addition of salts had a negligible effect on the reaction rate. The rate determining step involves an interaction between a neutral molecule and an ion. In the presence of Cu²⁺, there is a complex formation between lysine anions and Cu²⁺. S.P. Mushran et al have studied O₅(VIII) catalysed oxidation of acetone and ethyl methyl ketone by chloramine-T in alkali medium. The title oxidation was first order with respect [CAT], second order with respect to O₅(VIII), approximately 0.82 with respect to NaOH and 0.3 with respect to ketone. A mechanism with formation of a CAT– O₅(VIII) complex in the rate determining step and oxidation of enol anion in the fast step was discussed.
B.S. Yadav et al\textsuperscript{47} have studied the Cu\textsuperscript{2+} catalysed oxidation of 2-amino isobutyric acid by alkaline solution of chloramine-T. A first order dependence on both [CAT] and [2-amino isobutyric acid] was observed. At lower [NaOH] -1.5 order dependence on [OH\textsuperscript{-}] was found, which changed to -1 at higher [NaOH]. A zero order dependence on [Cu\textsuperscript{2+}] was observed. A negligible salt effect shows a mechanism involving a neutral molecule and a charged ion or the interaction between two neutral molecules as the rate determining step. R.S. Parihar et al\textsuperscript{48} have studied the alkaline chloramine-T oxidation of arginine monohydrochloride with and without catalytic action of Cu(II) ion. The kinetics of the title oxidation in the absence of Cu\textsuperscript{2+} was first order in chloramine-T and arginine and inverse first order in alkali.

Sushma Gupta et al\textsuperscript{49} have studied the osmium (VIII) catalysed oxidation of aliphatic amines by chloramine-T in alkaline and perchloric acid media. The order of reaction in [Chloramine-T] was always found to be unity. A zero order dependence of rate with respect to each [OH\textsuperscript{-}] and [Amine] has been observed during the osmium (VIII) catalyzed oxidation of diethylamine and triethylamine while a retarding effect of [OH\textsuperscript{-}] or [Amine] on the rate of oxidation was observed incase of osmium (VIII) catalyzed oxidation of primary aliphatic amines. The ruthenium (III) catalyzed oxidation of amines follows almost similar kinetics. The order of reactions in [Amine] or [Acid] decreases from unity at higher amine or acid concentrations. The suitable mechanism consistent with the kinetic data in each case was discussed.
Bharat Singh, Ashish et al\textsuperscript{50} have studied oxidation of crotonic acid [CA] by Chloramine-T in present of Pd(II) and O\textsubscript{8}(VIII) as homogenous catalysts. The reactions are zero order in [chloramine-T] and first order each in both [Pd(II)] and [O\textsubscript{8}(VIII)], while first order in [CA] at lower concentrations tended towards zero order at its higher concentrations. Positive effect of added [Cl\textsuperscript{−}] and zero effect of added p-toluenesulphonamide (PTS) have been observed in Pd(II) catalysed reaction, while in O\textsubscript{8}(VIII) reaction negative effect of PTS on rate of reaction has been observed. Negligible effect of change in [H\textsuperscript{+}] and ionic strength of the medium were observed and rate decrease with decrease in dielectric constant of the medium has been observed in both Pd(II) and O\textsubscript{8}(VIII) catalysed reactions. The catalytic efficiency is in the order of Pd(III)> O\textsubscript{8}(VIII). The products of oxidation in both reactions are acetaldehyde and glyoxylic acid. Activation parameters have been computed and mechanistic steps, consistent with the kinetic results, reaction stoichiometry and product analyses for both catalysed reactions have been discussed.

K.N.Vinod, Puttaswamy and K.N. Ninge Gowda\textsuperscript{51} have studied oxidative decolorization of triphenylmethane dyes by chloramine-T in alkaline medium catalyzed by Pd(II). Kinetics of Pd(II) catalyzed oxidative decolorization of p-rosaniline, crystal violet and ethyl violet dyes by chloramine-T (CAT) in NaOH medium were studied spectrophotometrically. The oxidation reaction follows the identical kinetics for all the three dyes and obeys the rate law:

\[
\text{rate} = k[\text{CAT}]^a [\text{Dye}]^b [\text{OH}^-]^c [\text{Pd(II)}]^d
\]

Where a and b are unity, and c and d are less than unity.
Addition of p-toluenesulfonamide (the reduction product of CAT) retards the rate and the order was found to be less than unity. The reaction rate increased with increasing ionic strength of the medium. Addition of chloride ions shows negligible effect on the rate of reaction. Oxidation products were characterized by GC–MS analysis. Proton-inventory studies with ethyl violet as a probe have been made in H₂O–D₂O mixtures. Puttaswamy and R. V. Jagadeesh⁵² have studied mechanistic studies of oxidation of thiols to disulfides by sodium N-Chloro-p-toluenesulfonamide in an alkaline medium. The kinetics of oxidation of five alkanethiols, viz., 1-ethanethiol, 1-propanethiol, 1-butanethiol, 1-pentanethiol, and 1-hexanethiol to symmetrical disulfides by sodium N-chloro-p-toluenesulfonamide or chloramine-T (CAT) in the presence of NaOH have been investigated at 15 °C. Reactions in all the five cases followed the identical kinetics with a first-order dependence each on [CAT]₀ and [Thiol]₀ and fractional-order dependence on [OH⁻]. Addition of p-toluenesulfonamide, a reduction product, retards the rate, and the dielectric effect is negative. Variation of ionic strength and halide ions showed no effect on the rate. The solvent isotope effect was studied using heavy water. Reaction mixture failed to induce polymerization of acrylonitrile.

Ajaya Kumar Singh, Reena Negi, Yokraj Katre and Surya Prakash Singh⁵³ have studied mechanistic study of novel oxidation of paracetamol by chloramine-T using micro-amount of chloro-complex of Ir(III) as a homogeneous catalyst in acidic medium. The reaction followed first-order kinetics with respect to [chloramine-T], [paracetamol] and [Cl⁻] in their lower concentrations range, tending to zero-order at their higher concentrations. First-order kinetics with respect to [Ir(III)] was observed for the oxidation
of paracetamol. The rate of reaction decreased with increasing $[\text{H}^+]$ and $[\text{p-toluene sulphonamid}]$ were observed for the oxidation of paracetamol. The variation of the ionic strength of the medium had no significant effect on the rate of the reaction. The first-order rate constant increased with decrease in the dielectric constant of the medium.

Alexander V. Peskin and Christine C. Winterbourn\textsuperscript{54} have studied kinetics of the reactions of hypochlorous acid and amino acid chloramines with thiols, methionine, and ascorbate. Thiol oxidation by hypochlorous acid and chloramines is a favorable reaction and may be responsible for alterations in regulatory or signaling pathways in cells exposed to neutrophil oxidants. In order to establish the mechanism for such changes, it is necessary to appreciate whether these oxidants are selective for different thiols as compared with other scavengers. We have measured rate constants for reactions of amino acid chloramines with a range of thiols, methionine, and ascorbate, using a combination of stopped-flow and competitive kinetics. For HOCl, rate constants are too fast to measure directly by our system and values relative to reduced glutathione were determined by competition with methionine. For taurine chloramine, the rate constants for reaction with 5-thio-2-nitrobenzoic acid, GSH, methionine, and ascorbate at pH 7.4 were 970, 115, 39, and 13 M\textsuperscript{-1} s\textsuperscript{-1}, respectively.

Ajaya Kumar Singh, Reena Negi, Bhawana Jain, Yokraj Katre, Surya P. Singh, Virender K. Sharma\textsuperscript{55} have studied kinetics and mechanism of Ru(III)-catalyzed oxidation of paracetamol by chloramine-T in aqueous acidic medium. The experimental result shows a first order dependence on paracetamol at its low concentrations, but tending towards zero\textsuperscript{th} order at its higher concentrations. The reactions follow a first order
rate dependence with respect to oxidant [CAT] and [Ru(III)]. The reaction showed negative fractional-order dependence on the rate for [H+] and p-toluenesulphonamide. Variation in [Cl−] and ionic strength of the medium did not bring about any significant change on the rate of reaction. The decrease in the reaction rate with decrease in the dielectric constant of the medium was observed in the oxidation of paracetamol.

Bharat Singh, R. Dubey, K. Lata Singh and Aniruddh Kumar Singh56 have studied mechanistic study of chloramine-T oxidation of crotonic acid catalysed by Rh (III) complex in alkaline medium. A 1:2 stoichiometry has been observed. The reaction exhibits pseudo-first order kinetics with respect to both [Chloramine-T] and [Crotonic acid]. The linear dependence of the reaction rate at lower [Rh (III)] tends towards zero order at its higher concentrations. Retarding effect of added para-toluene sulphonamide on the reaction rate has been observed. Positive effect of [OH−] at low concentrations is observed and after reaching a maximum the rate decreases on increasing [OH−]. Negligible effect of ionic strength variation on the reaction rate has been observed. A zero effect of added [Cl−] on the rate suggests non-replacement of chloride ion from reactive species of rhodium (III) chloride complex in alkaline medium during the course of the reaction.

Ramalingaiah, R.V. Jagadeesh and Puttaswamy57 have studied Os(VIII)-catalyzed mechanistic investigation of oxidation of some benzimidazoles by chloramine-T in alkaline medium. Under comparable experimental conditions, the oxidation reactions follow identical kinetics for all the five benzimidazoles with first order dependence each on [CAT]0 and [substrate]0 and fractional order dependence each on [OH−] and
[Os(VIII)]. The reactions were studied at different temperatures and the composite activation parameters have been computed. The calculated isokinetic temperature (b) of 380 K obtained from enthalpy-entropy relationship and Exner correlation was much higher than the experimental temperature of 303 K, indicating that the rate is under enthalpy control. Relative reactivity of oxidation of these follow the order: 2-MeBzlH > 2-HyBzlH > 2-AmBzlH > BzlH > IzlH > 2-PhBzlH. This trend may be attributed to inductive effects.

K. N. Vinod, Puttaswamy and K. N. N. Gowda\textsuperscript{58} have studied mechanistic aspects for the oxidation of sunset yellow dye by chloramine-T in presence of perchloric acid and in sodium hydroxide medium catalysed by Os(VIII). Neelu Kambo and S. K. Upadhyay\textsuperscript{59} have studied kinetics and mechanism of platinum (IV) catalysed oxidation of some hexoses by alkaline chloramine-T. The reactions are first order in oxidant, while the order of reaction in substrate and \( \text{OH}^- \) decreases from unity at higher [substrate] and [\( \text{OH}^- \)] respectively. Rate of reaction is proportional to \( \{k' + k'' \text{ [catalyst]}\} \), where \( k' \) and \( k'' \) are rate constants for uncatalysed and catalysed path, respectively.

Puttaswamy, Anu Sukhdev and J.P. Shubha\textsuperscript{60} have studied kinetics and reactivities of ruthenium (III) - and osmium (VIII)-catalyzed oxidation of ornidazole with chloramine-T in acid and alkaline media. The oxidation products and kinetic patterns were found to be different in acid and alkaline media. Under comparable experimental conditions, in Ru(III)-catalyzed oxidation the rate law is \(-d[\text{CAT}]/dt = k [\text{CAT}]_o [\text{ornidazole}]_o^x [\text{H}^+]^{-y} [\text{Ru(III)}]^{z} \) and it takes the form \(-d[\text{CAT}]/dt = k [\text{CAT}]_o [\text{ornidazole}]_o^x [\text{OH}^-]^{-y} [\text{Os(VIII)}] [\text{ArSO}_2\text{NH}_2]^{-z} \) for Os(VIII)-catalyzed reaction, where \( x, y \) and \( z \) are less than unity. In
acid medium, 1-chloro-3-(2-methyl-5-nitroimidazole-1-yl)propan-2-one and in alkaline medium, 1-hydroxy-3-(2-methyl-5-nitroimidazole-1-yl)propan-2-one were characterized as the oxidation products of ornidazole by GC–MS analysis.

1.3. POTASSIUM IODATE AS AN OXIDANT: A REVIEW

M.D. Prasad Rao and J. Padmanabha investigated the kinetics of catalysed and uncatalysed oxidation of aniline and substituted anilines by sodium iodate at constant ionic strength. They reported oxidation of aniline and substituted anilines by sodium iodate in aqueous acetic acid medium in the presence of perchloric acid. The reactions are catalysed by Ru(III). The order with respect to \( [\text{IO}_3^-] \) is unity and zero in the absence and presence of Ru(III), respectively. The order with respect to [Substrate] is two in the concentration range 0.0012 to 0.015 M for aniline and m-toluidine, while p-chloroaniline, p-toluidine and m-chloroaniline exhibit unit dependence on [substrate] in the concentration range studied. In the catalysed oxidation, the reaction follows Michaelis-Menten type kinetics. Effect of HClO\(_4\) and effect of increasing percentage of acetic acid are found to be nil both in the catalysed and uncatalysed oxidation.

P. Manikyamba, P. Raghunath Rao and E.V. Sundaram studied the kinetics and substituent effect in the oxidation of acetophenones by acid iodate in aqueous methanol medium. They reported that oxidation of acetophenone and substituted acetophenones by iodate occurs in 50% (v/v) aqueous methanol medium in presence of sulphuric acid. The reaction is first order with respect to [acetophenones] and [iodate]. The oxidation process is catalysed by sulphuric acid and increase in the proportion of methanol in the reaction
mixture enhances the rate. The order of reactivity observed among different acetophenones studied is H>P-OCH₃>P-CH₃. P-Cl>m-CH₃>m-OCH₃>P=NO₂>m-NO₂. E.V. Sundaram and Co-workers⁶³ investigated the kinetics of oxidation of benzaldehydes and substituted benzaldehydes by iodate in aqueous methanol in the presence of sulphuric acid and results showed first order dependence on [iodate] and [benzaldehyde]. There is no evidence for stable complex formation between benzaldehyde and iodate. Increase in percentage of methanol (v/v) increases the rate of oxidation. The order of reactivities is o-methoxy > H > p-methoxy > p-methyl > o-nitro > p-chloro > m.-nitro > p-nitro. A free radical mechanism, consistent with the attack of HIO₃ on protonated benzaldehyde to give an adduct in slow step followed by its oxidation to benzoic acid in the subsequent steps, is proposed.

P. Manikyamba, Vijayalaxmi and E.V. Sundaram⁶⁴ investigated the kinetics of oxidation of α- and β- naphthols by bromate and iodate ions in aqueous acetic acid medium. A first order dependence of rate on [substrate] and [oxidant] has been observed in both cases. With both the oxidants the reaction is catalysed by hydrogen ions and the order with respect to [H⁺] is fractional in the range of [H₂SO₄] studied. The rate increases with decrease in dielectric constant of the medium. P.S. Radhakrishnamurti et al⁶⁵ studied the kinetics of Osmium (VIII) and Ru(III) catalysed oxidations of styrene and stilbene by iodate in aqueous acetic acid and perchloric acid media and observed that reactions are zero order in iodate and first order each in both substrate and catalyst. O₈(VIII) catalysed oxidations are insensitive towards any change in acidity whereas in Ru(III) catalysed
oxidation, dependence on \([H^+]\) is unity. Increase in the percentage of acetic acid in the solvent medium decreases the rate of reaction in the case of \(O_3(III)\) catalysed reaction, whereas the rate is increased in the case of Ru(III) catalysed reaction.

G. K. Muthakia and S. B. Jannalagadda\(^{66}\) studied the kinetics and mechanism of uncatalysed and Ru(III) catalysed oxidation of indigo carmine (IC) (disodium-3,3-dioxobi-indolin-2,2-ylide-5,5-disulphonate) by iodate ion in aqueous sulphuric acid solution. The uncatalysed reaction order was found to be four; one each with respect to [IC] and [iodate] ion and second order in \([H^+]\) ion. The Ru(III) catalyzed reaction was of fifth order, second order with respect to \([H^+]\) and first order with respect to [reductant], [oxidant] and [catalyst]. Stoichiometric ratios of both reactions were the same with a 3:2 reductant–oxidant ratio. In both uncatalysed and catalyzed reactions isatin-5-monosulphonic acid (2, 3-dioxoindoline-5- sulphonic acid) was observed as the oxidation product. Rate constants for both the reactions are reported.

Further, a fixed time method is described for the determination of Ru(III) based on its ability to catalyze the oxidation of IC by acidic iodate. Using \([H^+]\) 2.25M, [iodate] 1.00\(\times\)10\(^{-3}\)M and [IC] 5.0\(\times\)10\(^{-3}\)M, in presence of Ru(III), the reaction followed first order kinetics with respect to IC. The interference of various cations, neutral salts, and potassium iodide in the determination of Ru(III) was studied using synthetic mixtures.

P.S. Radhakrishnamurti et al\(^{67}\) investigated the kinetic studies of the oxidation of nitrite by bromate at pH \(\approx\) 3 and Ru(III) catalysed iodate at 0.01M [HClO\(_4\)] have been studied. The reactions are acid catalyzed. Ionic strength effect and effect of added salts are found
to be marginal. P.V. Ramana and R.V. Appa Rao studied the kinetics and mechanism of oxidation of oxalic acid by iodate in aqueous sulphuric acid medium. They reported that the reaction is First order each in total initial [oxidant] and [substrate]. The reaction is acid catalysed below 1.0 mol dm$^{-3}$ of $[\text{H}_2\text{SO}_4]$, but is independent of $[\text{H}^+]$ at $[\text{H}_2\text{SO}_4] > 1.0$ mol dm$^{-3}$. The $[\text{H}^+]$ dependence of rate indicates the involvement of one or more reactive species in some prototypic equilibria.

A Brahmaiah and P. Manikyamba studied the Ru(III) catalysed oxidation of $\alpha$-hydroxy acids by iodate. They proposed that Ru(III) acts as a catalyst in the oxidation of $\alpha$-hydroxy acids by iodate. The reaction is found to be first order in [oxidant] and [Ru(III)] and fractional order in [hydroxy acid]. $\text{H}^+$ ions retard the reaction. A mechanism involves the formation of a complex (between Ru(III) and hydroxy acid) which interacts with HIO$_3$ in a slow step. Y. Sulfa and Hamid A. Elfaki investigated the kinetics of oxidation of ferrocyanide by iodate ion. In the presence of vast excess of ferrocyanide, over the pH range 1.76 – 2.65, the reaction between iodate and ferrocyanide ions follows the rate law.

$$-\frac{d[\text{IO}_3^-]}{dt} = \frac{\text{Ka}[\text{H}^+] + \text{Kb}[\text{H}^+]^2}{1 + K_1[\text{H}^+]} \left[\text{Fe(CN)}_6^{4-}\right] \left[\text{IO}_3^-\right]$$

Where, Ka and Kb have values of $1.97\times10^{-3}$M$^{-2}$ and $4.08\times10^{-5}$M$^{-3}$ min$^{-2}$, respectively, at an ionic strength $\theta$ 1.18M and at temperature of 25.0 ± 0.1°C. $K_1$ is the formation constant of monoprotonated ferrocyanide. The “overall activation energy” of the reaction was found to be 15.8 K cal/mol. Rate-determining step consistent with the observed kinetics has been proposed.
J.F. Lyun and P.O. Ukoha\textsuperscript{71} studied the kinetics and mechanism of oxidation of 1, 3-dihydroxy benzene by trioxo-iodate (V) ion in aqueous perchloric acid medium. They observed pseudo-first order conditions of an excess [benzenediol] at I = 1.10 mol dm\(^{-3}\) (NaClO\(_4\)). The reaction obeys the rate expression:

\[
-\frac{d[\text{IO}_3^-]}{dt} = \left[ K_4 + K_1 K_2 [\text{H}^+] \right] [\text{IO}_3^-] [\text{H}_2\text{O}]
\]

The reaction has been rationalized on the basis of the outer-sphere electron transfer mechanism. Kenneth Kustin et al\textsuperscript{72} investigated the kinetics and mechanism of the oxidation of thiocyanate by Iodate. A mechanistic study has been performed on the complex reaction between thiocyanate and iodate in acidic medium. A 14-steps mechanism is proposed in which the first step of the oxidation is

\[
\text{IO}_3^- + \text{SCN}^- + 2 \text{H}^+ \rightarrow \text{HOSCN} + \text{HIO}_2.
\]

The HOSCN is then rapidly oxidized by either HIO\(_2\) or I\(_2\) to give SO\(_4^{2-}\) via HO\(_3\)SCN. The transient formation of I\(_2\) in excess thiocyanate is attributed to a competition between the Dushman reaction,

\[
\text{IO}_3^- + 5\text{I}^- + 6 \text{H}^+ \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}.
\]

which is strongly catalysed by acid, and slower, acid-inhibited reactions, which consume iodine. The consumption of iodine by thiocyanate proceeds via the rapid formation of the I\(_2\)SCN\(^+\) complex, which later hydrolyzes to give HOSCN. Other observed reaction dynamic have been explained through the same proposed mechanism.

William C.E. Higginson and Mrs. Davina A. Mc Carthy\textsuperscript{73} investigated The kinetics of oxidation of aqua iron (2+) by iodate in dilute perchloric acid have been studied at 35°C
in the presence of allyl alcohol, thus avoiding catalysis by the molecular iodine normally formed in this reaction. Overall the reaction is $4 \text{Fe}^{2+} + \text{IO}_3^- \rightarrow 4 \text{Fe}^{3+} + \text{I}^-$ followed by rapid removal of $\text{I}^-$ by its reaction with, allyl alcohol. The kinetic equation is 
$$-d[\text{Fe}^{2+}]/dt = 4K_1 (K_2 + K_3[\text{Fe}^{2+}]) [\text{Fe}^{2+}] [\text{IO}_3^-] / K_1 (K_2 + K_2 + K_3[\text{Fe}^{2+}]).$$

Mihaly T. Beck and Co-workers\textsuperscript{74} suggested the oxidation of hydroxylamine with either iodate or periodate and three extrema on the iodide concentration versus time curves may be found. Perturbing the periodate oxidation with malonic acid increases the number of extrema. Gyula Rabai and Mihaly T. Beck\textsuperscript{75} observed that the oxidation of thiourea by iodate in weakly acidic solution of iodide may exhibit several extrema. The number of extrema mainly depends on the initial ratio of the concentrations of thiourea and iodate, and is at the most four. The first step of the reaction results in the formation of iodide which then reacts with iodate to give iodine. The latter oxidizes thiourea in several steps, the end products being sulphate ions, ammonium ions, and carbon dioxide. Taking into accounts the independently determined rate constants for the subsystems, the change in the concentrations of iodide and iodine with time can be calculated.

James G. Brummer and Richard J. Field\textsuperscript{76} investigated the kinetics and mechanism of the oxidation of ferrous ion by iodate ion in strong perchloric acid, aqueous media. The stoichiometry of this reaction is given by $\text{Fe(II)} + \text{IO}_3^- + 6\text{H}^+ \rightarrow 5\text{Fe(III)} + \frac{1}{2} \text{I}_2 + 3\text{H}_2\text{O}(1)$. all experiments were carried out at a temperature of $30.0 \pm 0.2^\circ\text{C}$ and at pH near zero. The ionic strength was maintained at 1.5M, and in all experiments $\text{ClO}_4^-$
was the only anion present besides \( \text{IO}_3^- \). Reaction (1) is catalyzed by \( \text{I}_2 \), one of its products. Thus experiments, falling into two general classes, were carried out. In the first class of experiments \( \text{I}_2 \) was allowed to accumulate, while in the second class of experiments \( \text{I}_2 \) was continuously removed by extraction into \( \text{CCl}_4 \). On the basis of these experiments, we propose here a complex mechanism for reaction (1) which is composed of eight steps (three reversible) and which involves seven reactive intermediates: \( \text{HIO}_3 \), \( \text{IO}_2 \), \( \text{HIO}_2 \), \( \text{IO} \), \( \text{HOI} \), \( \text{I}_2 \) and \( \text{I}^- \). Numerical simulation techniques are used to demonstrate that the proposed mechanism is able to quantitatively rationalize all experimental data obtained. This expressing indicates that there are two parallel paths by which the overall stoichiometry of reaction (1) may be achieved. The first path is a sequence of reactions initiated by the rate-determining, direct interaction of Fe(II) with \( \text{HIO}_3 \). The second path is associated with the \( \text{I}_2 \) catalysis and is initiated by hydrolysis of \( \text{I}_2 \).

Elizabeth Mambo and Reuben H. Simoji\(^7\) studied the kinetics and mechanism of the complex oxidation of aminoiminomethane sulfinic acid (AIMSA) by iodate in acidic medium. The stoichiometry of the reaction in excess of AIMSA is:

\[
2\text{IO}_3^- + 3\text{AIMSA} + 3\text{H}_2\text{O} \rightarrow 3\text{CO(NH}_2\text{)}_2 + 2\text{I}^- + 6\text{H}^+ + 3\text{SO}_4^{2-} \quad (\text{eq.1}),
\]

and the stoichiometry of the reaction in excess iodate is

\[
4\text{IO}_3^- + 5\text{AIMSA} + 3\text{H}_2\text{O} \rightarrow 5\text{SO}_4^{2-} + 5\text{CO(NH}_2\text{)}_2 + 2\text{I}_2 + 6\text{H}^+ \quad (\text{eq.2}).
\]

In excess AIMSA and high acid concentrations the reaction shows an induction period and a transient formation of iodine, while in excess iodate concentrations iodine is produced and partially consumed, leaving a finite iodine concentration at the end of the
reaction. The dynamics of the reaction is explained by a combination of three reactions: the first is the oxidation of AIMSA by iodate to give iodide, the second is the Dushman reaction, which forms iodine from the iodate-iodide reaction, and the third is the reaction of iodine and AIMSA. The relative rates of these three reactions will determine the dynamics of the reaction. The oxidation of AIMSA with I$_2$ and I$_3^-$ was also investigated. The oxidation of AIMSA by I$_2$ and I$_3^-$ was found to be inhibited by acid because the oxidation of AIMSA by HOI is faster than that with molecular I$_2$. The reaction is also auto inhibitory because I$^-$, the product of the reaction, combines with unreacted I$_2$ to forms I$_3^-$ which is relatively inert towards AIMSA.

M.D. Prasad Rao and Co-workers$^{78}$ investigated the ruthenium(III)-catalyzed oxidation of acetanilide and substituted acetanilides by potassium iodate in aqueous acetic acid medium at constant ionic strength. The title kinetics is first order in Ru$^{3+}$, zero order in HIO$_3$, and complex order in P-RC$_6$H$_4$ NHAC (I; R = H, Me, Cl, NO$_2$). The products from the reaction of I (R = H) were o- and p-benzoquinone; the products from I (R = H) are the corresponding o-benzoquinones. There is no solvent effect or [HClO$_4$] dependence in the reaction. B.T. Gowda et al$^{79}$ studied the kinetics of oxidation of thiocyanate and thiosemicarbazide (ISC) in the free and metal-bound states by potassium iodate in aqueous perchloric acid medium. Oxidation of SCN$^-$ showed first order kinetics in [KIO$_2$] and nearly first order in [NCS$^-$]. The rate was independent of [H$^+$]. Variation in either the ionic strength or dielectric constant of the medium had no effect on the rate of reaction. Oxidation of TSC in the free and metal bound states showed first order kinetics.
in [KIO₃], a title fractional order in [TSC], and inverse fractional order in [H⁺]. Variation in ionic strength of the medium and addition of \( \text{I}^- \) to the reaction mixture slightly decreased the rate. Variation in dielectric constant of the medium (by changing the solvent concentration i.e. MeOH) had no significant effect on the rate.

A Brahmaiah and P. Manikyamba⁸⁰ investigated the kinetics of oxidation of benzyl alcohols in the presence of Ru(III) in aqueous acetic acid in the temperature range of 293-318K. The reaction is first order with respect to [oxidant], and fractional order with respect to [substrate] and catalyst, [Ru(III)]. Effects of solvent and added salt on the rate of oxidation suggest a dipole - dipole type of reaction. The product of oxidation is identified to be the corresponding benzaldehyde. Electron releasing groups on the benzene ring slightly enhance the overall rate of oxidation while electron withdrawing groups retard the rate. P.S. Radhakrishnamurti et al⁸¹ has studied the kinetics of Ru(III) catalyzed oxidation of malonic acid by acid iodate in aqueous and HOAC Mixtures in the presence of perchloric acid. The reaction is first order in iodate, first order in Ru(III) and fractional order in malonic acid. It is insensitive to change in [acid]. Malonic acid is not oxidized by acid iodate without using Ru(III) as catalyst.

P.S. Radhakrishnamurti and Co-workers⁸² studied the kinetics of uncatalysed and Ru(III) catalyzed oxidation of thiocyanate in acid media by iodate. The reactions are of first order with respect to iodate and thiocyanate in both uncatalysed and Ru(III) catalyzed oxidation. The order with respect to acid is 1.75 in the case of uncatalysed oxidation, whereas it is one in case of Ru(III) catalysed oxidation. The order is fractional with respect to Ru(III) and ionic strength effect is marginal. A. Brahmaiah and P.
Manikyamba\textsuperscript{83} studied the kinetics of oxidation of cinnamic acids by iodate in aq. AcOH containing Ru(III) at 303-323 K. The reaction is first order in [oxidant] and fractional order in both [substrate] and [Ru(III)]. The oxidation products are identified as the corresponding benzaldehyde and HCHO. Electron-releasing groups retard it, compared to unsubstituted PhCH=CHCOOH. P. Manikyamba\textsuperscript{84} studied the Ru(III) catalyzed oxidation of pyruvic acid by iodate. The reaction is found to be first order with respect to [oxidant] and [catalyst] and fractional order in [pyruvic acid]. Increase in the concentration of $\text{H}_2\text{SO}_4$ and decrease in the dielectric constant of the medium retard the oxidation and product is acetic acid. A mechanism involving the formation of a complex between the substrate and the catalyst, which reacts with the oxidant in the slow step, is proposed.

Surya Prakash Singh, Ashok Kumar Singh and Ajaya Kumar Singh\textsuperscript{85} have studied kinetics of Ir (III)-catalyzed oxidation of D-glucose by potassium iodate in aqueous alkaline medium. The reaction follows first-order kinetics with respect to potassium iodate in its low concentration range but tends to zero order at its higher concentration. Zero-order kinetics with respect to [D-glucose] was observed. In the lower concentration range of Ir(III) chloride, the reaction follows first kinetics, while the order shifts from first to zero at its higher concentration range. The reaction follows first-order kinetics with respect to [$\text{OH}^-$] at its low concentration but tends towards zero order at higher concentration. Variation in [$\text{Cl}^-$] and ionic strength of the medium did not bring about any significant change in the rate of reaction. The first-order rate constant increased with a decrease in the dielectric constant of the medium.
Ashok Kumar Singh, Shalini Srivastava, Jaya Srivastava and Reena Singh\textsuperscript{86} have studied kinetics and mechanism of the Ir(III)--catalyzed oxidation of xylose and maltose by potassium iodate in aqueous alkaline medium. The reactions exhibit first-order kinetics with respect to lower \([\text{IO}_3^-]\) and \([\text{OH}^-]\) and show zero-order kinetics at their higher concentrations. Unity order at low concentrations of maltose becomes zero-order at its higher concentrations, whereas zero-order kinetics with respect to [xylose] was observed throughout its variation. The reaction rate is found to be directly proportional to [Ir(III)] in the oxidation of both reducing sugars. Negligible effect of \([\text{Cl}^-]\) and nil effect of ionic strength (\(\mu\)) on the rate of oxidation have also been noted. The species, \([\text{IrCl}_3(\text{H}_2\text{O})_2\text{OH}]^-\) was ascertained as the reactive species of Ir(III) chloride for both the redox systems. Various activation parameters have been calculated. Formic acid and arabinonic acid for maltose and formic acid and threonic acid for xylose were identified as the main oxidation products of the reactions.

Ashok Kumar Singh, Shalini Srivastava, Jaya Srivastava, Rashmi Srivastava and Priyanka Singh\textsuperscript{87} have studied kinetics and mechanism of oxidation of D-glucose (glc) and D-fructose (fru) by alkaline solution of potassium iodate in the presence of Ru(III) as homogeneous catalyst. The linear dependence of the reaction rate at lower \([\text{IO}_3^-]\) and \([\text{OH}^-]\) tends towards zero-order at their higher concentrations. Experimental results also show that the order with respect to [Ru(III)] is unity and the order with respect to [reducing sugar] is zero in the oxidation of both glc and fru. Variation in \([\text{Cl}^-]\) and ionic strength (\(\mu\)) of the medium does not affect the oxidation rate. The species, \([\text{RuCl}_2(\text{H}_2\text{O})_2(\text{OH})_2]^-\) and \(\text{IO}_3^-\), were found to be the reactive species of Ru(III) chloride
and potassium iodate in alkaline medium, respectively. A common mechanism, where the rate determining step involves the interaction between reactive species of Ru(III) chloride and reactive species of potassium iodate resulting in the formation of an activated complex,

\[
\begin{align*}
\text{RuCl}_2(\text{H}_2\text{O})(\text{OH})_2
\end{align*}
\]

has been proposed. The formation of activated complex is very well supported by the spectrophotometric evidence, observed kinetic data and also by the negative entropy of activation observed for the oxidation of both gle and fru. Arabinonic acid and formic acid were identified as the main oxidation products of the reactions.

Surya Prakash Singh, Ashok Kumar Singh and Ajaya Kumar Singh\textsuperscript{88} have studied first and novel oxidation of D-fructose by potassium iodate using \([\text{IrCl}_3(\text{H}_2\text{O})_2\text{OH}]^-\) complex as a homogeneous catalyst in alkaline medium. The experimental result shows a first order dependence on iodate and \([\text{OH}^-]\) at their low concentrations, but tending towards zero-order at their higher concentrations. Zero-order kinetics with respect to [D-fructose] was observed throughout its variation. The linear dependence of the reaction rate at lower [Ir(III)] chloride tends towards zero-order at its higher concentrations. Variation in [Cl\textsuperscript{-}] and ionic strength of the medium did not bring about any significant change on the rate of reaction. The decrease in the rate of reaction with increase in the dielectric constant of the medium was observed in the oxidation of D-fructose.
1.4: **PRESENT WORK**

The present thesis contains seven chapters.

Chapter–I deals with the fundamental definitions and classification of the chemical kinetics. Since the reactions have been performed through redox initiation, a brief account of redox systems have been given along with survey of literature.

Chapter-II contains the details of materials used, method of investigation and stoichiometry of the reaction and product analysis.

The thesis comprises of two parts: Part - A and Part - B

Part - A includes chapter-III and chapter–IV which contain the kinetic study of chloramine-T oxidation of crotonic acid using Rh(III) chloride as homogeneous catalyst in alkaline medium and kinetic study of chloramine –T oxidation of crotonic acid using osmium(VIII) as homogeneous catalyst in alkaline medium , respectively.

Part - B contains three chapters viz. chapter-V, chapter-VI and chapter-VII.

Chapter–V includes the mechanistic studies of oxidation of L-methionine by alkaline solution of chloramine-T in presence of chloro-complex of Ir(III) as homogeneous catalyst.

Chapter–VI deals with the mechanistic studies of oxidation of L-methionine by potassium iodate using micro-amount of chloro-complex of Rh (III) as a homogeneous catalyst in acidic medium.
Chapter–VII deals with the mechanistic studies of oxidation of L-methionine by potassium iodate using micro-amount of chloro-complex of Rh (III) as a homogeneous catalyst in alkaline medium.
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