CHAPTER-I

INTRODUCTION
SURVEY OF LITERATURE

Chemical kinetics is one of important topics of physical chemistry which deals with the study of rate of reactions with all the factors which influence the rate of reaction\(^1\) and with explanation of rate in terms of the reaction mechanism through which chemical reactions occur. The rate (i.e. \(-dc/dt\)) can be derived either in terms of product formation or consumption of reactant of reaction with time. The rate of chemical reaction is influenced by several factors such as temperature, concentration of reactants and products, catalyst, medium (i.e. H\(^+\) or OH\(^-\)), ionic strength of the medium (used for 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, pH and so on.

Kinetic investigation gives an idea about the 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 the term ‘order’ of the reaction. For multi steps reactions the kinetics is limited by the slowest step, which is also called rate determining step. There are many reactions in which orders are not simple power functions of the concentration of the reactant but fractional. The elucidation of the exact rate law then requires carefully planned experiments in which influence of products and reactants are studied systematically.

It is often important to establish the dependence of rates on product concentration because the concentration of products of reaction varies
with time. A rate law can be derived for different mechanisms. Comparison of an experimentally observed rate law with the derived rate law allows one to make some 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. Experimental observations are variant with time. However, the proposed mechanism may no longer remain valid, if some new information's are uncovered. Reaction mechanism is derived concept which can be changed or modified if some new concepts or new facts are observed².

In order to know the insight of the reaction mechanism by which chemical changes occur, one should go for kinetic investigation. Kinetic investigation is 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 objective demands that the experimental data be summarized in equations of the same form as those which appear in theoretical treatment of reaction kinetics¹. A clue to the reality of reaction mechanism is obtained by the product identification, use of isotopic tracers³, detection of short lived intermediates, variation of ionic strength⁴, catalyst and change of solvents⁵, etc. on the rate of reaction.

J.J. Berzelius⁶ 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 exert a special catalytic force upon reactants, which is manifestation of electrochemical affinity.
In 1902, W. Ostwald defined catalyst as a substance which speeds up chemical reaction without affecting the equilibrium and his definition has made it most frequently cited of all the 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 recognized the shortcoming 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. Certain reactions can, in fact, only be carried out stoichiometrically as the catalyst is chemically changed into an inactive form. The process can nevertheless be made ‘catalytic’ by coupling it with suitable catalyst regeneration step. 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 catalyst, 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. Further, it 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 catalyst which is 'instructed' for performing only one reaction or to prevent undesirable side reactions.

The qualitative and quantitative studies of the role of catalysts were widely recognized in modern chemical field. Heterogeneous catalysis is a well defined field for which numerous excellent examples have been observed to be of revolutionary use in industries. The 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 for 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.

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 achieved in the field of electron transfer reactions due to a large number of workers attracted interest in the field of redox processes owing to its importance in understanding the nature and technology used in analytical chemistry. The theoretical treatment of electron transfer reactions by Libby, Marcus, Zwolinsky and Eyring, Laidler and many others have been of great help in understanding the nature of these reactions.
One of the most characteristic factors in deriving the rate law is the application of steady state approximation under which it is assumed that the rate of formation and rate of consumption of a particular species are equal. The activation parameters play an important role in deciding the nature of transition state of the reaction which supplies useful informations leading to elucidation of the reaction mechanism.

Stoichiometry is an important factor which shows the overall number of molecules of one reactant consumed by one molecule of another. Product analysis is also strong evidence in predicting the reaction mechanism.

Kinetics has answers to many difficult analytical problems\textsuperscript{13}. Earlier, kinetics has been applied to solve analytical problems by Mark and Mottola\textsuperscript{14}. Kinetics also helps in mixture analysis\textsuperscript{15}, enzyme analysis and use of enzyme in the determination of rate dependence on substrate concentration by the direct use of kinetic data\textsuperscript{16}. 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 favourable (i.e. producing maximum yield with the least cost). So 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 for better yields of desired polymer\textsuperscript{17-18}.

Permanganate, chromic acid, Ceric(IV), Managanese(III), Vanadium(V), Cobalt(III), Lead(IV), Copper(II), Tin(II), Mercury(II), hexacynoferrate(III), peroxydisulphate, etc. and organic redox reagents such as ascorbic acid, N-Chlorosuccinimide, N-Bromosuccinimide (NBS), N-Chlorobenzamide and several N-haloimides, chloramine-T, catechol and carbonium ion etc are among the common redox reagents
which have received considerable emphasis leading to mechanistic studies. In a publication edited by Bomford and Tipper\textsuperscript{19} a detailed account of several familiar and less familiar redox reagents have been discussed. Berka and Zyka\textsuperscript{20} have also described several less familiar and newer redox titrants in another publication.

Before describing the kinetic investigations in the present thesis, it is necessary to present brief literatures on oxidations involving chloramine-T and potassium bromate which have been used as oxidants in the present thesis. A survey of literature is also presented on substrates and catalysts used in the present studies.

1.1: CHLORAMINE – T AS AN OXIDANT : A REVIEW

K.V. Uma, S.M. Mayanna et al\textsuperscript{21} have studied OsO\textsubscript{4} catalysed oxidation of benzyl alcohol with chloramine –T in alkaline solution. The oxidation follows complex kinetics, being 1\textsuperscript{st} order each in chloramine – T, substrate and OsO\textsubscript{4}. The oxidation rate is also inversely proportional to [OH\textsuperscript{−}] . The kinetic results are consistent with a mechanism involving rate determining removal of H\textsuperscript{+} ion by a (OsO\textsubscript{4} – chloramine – T) complex.

P.S. Radhakrishnamurti and B. Sahu\textsuperscript{22} have investigated Os (VIII) catalysed oxidation of alcohols by chloramine-T. The Os (VIII) catalysed oxidation of sec- butanol, cyclopentanol cyclohexanol, cycloheptanol, 1,3–butanediol,1,4 butanediol by CAT in alkaline medium is first order with respect to both CAT and OsO\textsubscript{4}. The dependence on [OH \textsuperscript{−}] is inverse one half. The reactions are zero order in [Substrate]. The reaction proceeds via rate determining formation of an osmium (VIII) complex which undergoes one electron transfer by the loss of a hydrogen atom.
K.V. Uma, S.M. Mayanna et al\textsuperscript{23} have studied Os(VIII) catalysed oxidation of primary alcohols by chloramine–T. The title oxidation studied in 10^{-4}M–10^{-1}M [NaOH] at 30-50°C shows first order dependence on each of primary alcohols, O_{2}O_{4} and [OH\textsuperscript{-}] at low concentrations. The rate is independent of chloramine–T concentration. The results suggest formation of an activated complex between substrate and O_{2}O_{4}, which slowly decomposes into aldehyde and Os(VI). The latter is oxidised rapidly to Os(VIII) with chloramine - T anion.

S.L. Sharma and O.P. Bansal\textsuperscript{24} have investigated copper(II) catalysed oxidation of n – butanol by chloramine – T in alkaline medium. The kinetics observed were first order in each of [n-butanol], [CAT ] and [OH\textsuperscript{-}] and are independent of Cu\textsuperscript{2+}.

S.P. Mushran, M.C. Agrawal et al\textsuperscript{25} have studied Os(VIII) catalyzed oxidation of formaldehyde and acetaldehyde in alkaline medium. The oxidation showed first order dependence to [chloramine – T] and [Os(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 Os(VIII) in the slow and rate controlling step which abstracts hydride ion from the hydrated form of aldehyde in a fast step.

S.P. Mushran et al\textsuperscript{26} have studied Os(VIII) catalysed oxidation of isopropyl alcohol by chloramine – T. The title oxidation was 1\textsuperscript{st} order in chloramine –T, H\textsuperscript{+} and Os(VIII) and it was zero order in isopropyl alcohol. The ionic strength had no effect. The rate determining step involved reaction of chloramine-T with Os(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 two half lives. Under pseudo - first order conditions, the rate constant 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 [Os(VIII)] and the reciprocal of [OH⁻]. The formation of a complex between N-chloro-p-toluene sulphonamide and Os(VIII) was rate determining step which was followed by rapid transfer of a hydride ion from the substrate to this complex.

Shailendra Jha et al. 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. have studied the oxidation of diphenyl sulphoxide by chloramine-T in acidic and alkaline medium. OsO₄ 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 (H₂OCl)⁺ formed from the hydrolysis of chloramine-T in a slow step or from the hydrolysis of Cl₂ formed from free acid and added chloride ion. The results in alkaline medium was explained on the basis of a complex formation between substrate and OsO₄ at lower [NaOH] but formation of a cyclic complex between chloramine-T and OsO₄ is the rate determining step at higher [alkali].

H.M.K. Naidu et al. have studied the oxidation of α-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
HClO₄ at 30°C showed 1ˢᵗ order dependence each on CAT and amino acid and inverse 1ˢᵗ order with H⁺ ion. Ionic strength and presence of the added p-toluene sulphonamide (PTS) have no effect on rate. Chloride ion catalyses the reaction. A mechanism in which the zwitter ion interacts with protonated CAT has been proposed to account for kinetics.

D.S. Mahadevappa et al³¹ have studied the oxidation of arginine and histidine by chloramine-T in hydrochloric acid medium. The title oxidation at 30°C was catalysed simultaneously by H⁺ and Cl⁻ at HCl concentration of 0.04-0.12M. The kinetics was 1ˢᵗ order for chloramine-T, H⁺ and arginine, but zero order for histidine and 0.70 order for chloride ion.

S.N. Katgeri et al³² have studied the oxidation of hydroxylamine hydrochloride by chloramine-T in acidic medium. The reaction shows 1ˢᵗ order dependence on [CAT] and [NH₄OH] but inverse 1ˢᵗ order dependence on [H⁺]. Ionic strength and added p-toluene sulphonamide (PTS) have no effect on the rate of oxidation. Chloride ion catalyses the reaction. The rate shows a positive dielectric effect. A mechanism involving interaction of unprotonated NH₄OH and N-chloro-p-toluene sulphonamide giving an intermediate complex in a slow step is suggested.

K.V. Uma, S.M. Mayanna et al³³ have studied O₅(VIII) catalysed oxidation of benzyl alcohol by chloramine-T. in alkaline medium. The oxidation follows complex kinetics, being 1ˢᵗ order each in chloramine-T, substrate and O₅O₄. The oxidation rate is also inversely proportional to [OH⁻]. The kinetic results are consistent with a mechanism involving rate determining deprotonation of O₅O₄ -chloramine-T complex.
S.N. Katgeri et al\textsuperscript{34} 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 1\textsuperscript{st} order in [CAT] and 1\textsuperscript{st} order in [H\textsuperscript{+}] whereas the rate was independent of the concentration of amino acids. Ionic strength and the presence of the product had no effect on rate whereas Cl\textsuperscript{-} ion catalysed the oxidation.

D.S. Mahadevappa et al\textsuperscript{35} have studied the oxidation of dimethyl sulfoxide by chloramine-T in aqueous solution. The title oxidation is first order each in oxidant and substrate and is accelerated by H\textsuperscript{+} in HClO\textsubscript{4} and retarded by low [OH\textsuperscript{-}] in NaOH and O\textsubscript{2}O\textsubscript{4}. The proposed mechanism in acidic medium involves electrophilic attack by chloramine-T at S atom of dimethyl sulfoxide and hydrolysis of the resulting intermediate. In dilute NaOH-O\textsubscript{2}O\textsubscript{4}, the reaction involves formation of a cyclic complex between CAT and O\textsubscript{2}O\textsubscript{4} which reacts with DMSO in a slow step. At higher [alkali] the reaction involves direct interaction between CAT and DMSO.

Adarsh Kumar et al\textsuperscript{36} have studied O\textsubscript{2}(VIII) catalysed oxidation of cyclopentanone by chloramine-T. The kinetics indicated that the title oxidation proceeded by rate determining complexation of CAT with O\textsubscript{2}(VIII), followed by rapid oxidation of cyclopentanone enolate. The final product was 1,2-cyclopentanedione.

Munesh Chandra and O.P. Bansal\textsuperscript{37} 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 H\textsubscript{2}N(CH\textsubscript{2})\textsubscript{2}O\textsuperscript{-}. 

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B.S. Yadav, S. Singh et al\textsuperscript{38} have studied the oxidation of lysine mono hydrochloride by alkaline chloramine-T. The oxidation is first order with respect $[\text{Cu}^{2+}]$. The addition of salts had negligible effect on the reaction rate. The rate determining step involves an interaction between a neutral molecule and an ion. In the presence of $\text{Cu}^{2+}$, there is a complex formation step between lysine anion and $\text{Cu}^{2+}$.

S.P. Mushran et al\textsuperscript{39} have studied Os(VIII) catalysed oxidation of acetone and ethyl methyl ketone by chloramine-T in alkali medium. The title oxidation was first order with respect $[\text{CAT}]$, 2\textsuperscript{nd} order with respect to Os(VIII), about 0.82 with respect to NaOH and 0.3 with respect to ketone. A mechanism with formation of a CAT- Os(VIII) complex in the rate determining step and oxidation of enol anion in the fast step was discussed.

B.S. Yadav et al\textsuperscript{40} have studied the Cu\textsuperscript{2+} catalysed oxidation of 2-amino isobutyric acid by alkaline chloramine-T. A first order dependence on both $[\text{CAT}]$ and $[2$-amino isobutyric acid$]$ was observed. At lower $[\text{NaOH}]$, -1.5 order dependence on $[\text{OH}^-]$ was found, which changed to -1 at higher $[\text{NaOH}]$. A zero order dependence on $[\text{Cu}^{2+}]$ 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{41} 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$^{2+}$ was 1\textsuperscript{st} order in chloramine-T and arginine and inverse 1\textsuperscript{st} order in alkali, whereas the kinetics of the Cu$^{2+}$ catalysed oxidation exhibited a linear dependence in the concentration of Cu$^{2+}$ when $[\text{Cu}^{2+}]$ was
Sushma Gupta et al\textsuperscript{42} 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] is 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 diethyl amine and triethylamine while a retarding effect of [OH\textsuperscript{-}] or [Amine] on the rate of oxidation is observed in case of osmium (VIII) catalyzed oxidation of primary aliphatic amines. The ruthenium (III) catalyzed oxidation of all amines follow 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 is proposed in each case and discussed.

Bharat Singh, Ashish et al\textsuperscript{43} have studied oxidation of crotonic acid (CA) by chloramine-T in presence of Pd(II) and O\textsubscript{s}(VIII) as homogenous catalysts. The reactions are zero order in [chloramine-T] and first order each in both [Pd(II)] and [O\textsubscript{s}(VIII)] while first order in [CA] at lower concentrations tending towards zero order at its higher concentrations has been observed. 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{s}(VIII) catalysed 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 and decrease in rate with decrease in dielectric constant of the medium have been observed in both Pd(II) and O\textsubscript{s}(VIII) catalysed reactions. The catalytic efficiency is in the order of Pd(III) > O\textsubscript{s}(VIII). The products of oxidation in both reactions are

\(\langle 2 \times 10^{-5} \text{ M At[Cu}^2\text{+}] \rangle \) 2 \times 10^{-5} \text{ M} a fixed rate constant was observed for all catalytic concentrations.
acetaldehyde and glyoxylic acid. Activation parameters have been computed and mechanistic steps consistent with the kinetic results, reaction stoichiometry and product analysis for both catalysed reactions have been discussed.

1.2: POTASSIUM BROMATE AS AN OXIDANT: A REVIEW

Reddy and Kumar\textsuperscript{44} have studied kinetics and mechanism of oxovandium (IV) catalysed and uncatalysed bromate oxidation of lactic acid in acidic medium. The uncatalysed and vanadium(IV) catalysed lactic acid-bromate reactions were reported by them to follow first order kinetics in each of bromate and lactic acid respectively, but in catalysed reaction rate constant increases non linearly with increase in lactic acid and reaches to a limiting value at higher [lactic acid] and definite intercept in the Michaelis-Menten's plot was observed. They have reported HBrO\textsubscript{3} and H\textsubscript{2}Br\textsuperscript{+}O\textsubscript{3} to be oxidizing species in acidic medium and acetaldehyde and CO\textsubscript{2} were found as products.

K.K. Sengupta et at\textsuperscript{45} have studied the kinetics of oxidation of some $\alpha$-hydroxy acids by potassium bromate in dilute hydrochloric acid medium. The reactions were reported to follow first order kinetics with respect to each of bromate ion, $\alpha$ - hydroxy acid and hydrogen ion concentrations. The reaction rate was reported to be governed by two factors: (i) the ease with which the protonated hydroxyl acid is produced and (ii) the stability of the intermediate (1:1) bromate ester. The reactivity of $\alpha$ - hydroxy acid towards bromate ion was found to be as follows: 9- hydroxy - 9- carboxy fluorine\textsuperscript{> atrolactic acid > mandelic acid > benzilic acid > $\alpha$ - hydroxy- isobutyric acid\textsuperscript{> lactic acid > glycolic acid.}
R. Natarajan and N. Venkatasubramanian\textsuperscript{46} have studied the kinetics of oxidation of secondary alcohols by potassium bromate. The kinetic data revealed overall second order kinetics, being first order with respect to both the bromate and alcohols. The most surprising aspect of the kinetic data is that alcohols (R-CHOH-R') with varying substituents in the R and R' groups (propan-2-ol, butan-2-ol, pentan-2-ol, heptan-2-ol, octan-2-ol, $\alpha$-phenyl ethyl alcohol and benzhydrol) give very neatly the same second order rate constant. It was only when the alcohol was of a totally different structures (such as fluren-9-ol) or had strongly electron withdrawing substituents as the -Cl or -NO$_2$ group the reaction exhibited any variation in rate.

R. Natarajan et al\textsuperscript{47} have studied oxidation of few secondary alcohols by potassium bromate and they have reported that the reaction rate does not depend on the nature and structure of alcohol.

B.T. Gowda and V. Pardhasaradhi\textsuperscript{48} have reported that kinetics and mechanism of oxidation of thiosemicarbazide by potassium bromate in aqueous sulphuric acid and water-acetic acid media. They observed that rate of reaction followed first order kinetics in [oxidant] but showed fractional order kinetics in the thiosemicarbazide and 1.5 order in hydrogen ion in aqueous medium compared to first order dependence in thiosemicarbazide and fractional order in hydrogen ion in water-acetic acid. Addition of KBr did not affect the rate while ionic strength variation showed decreasing effect. Hydrazine was reported to be main oxidation product. The kinetics of Ru(III) catalysed oxidation of primary and secondary alcohols by bromate have been studied by P.S. Radhakrishnamurthy and L.D. Sarngi\textsuperscript{49}. They have suggested hydride ion abstraction by Ru(III) from alcohol as the slow and rate
determining step. The carbocation thus formed was deprotonated in fast step to yield the corresponding aldehyde as final product. \([\text{Ru(H)}]^2+\) produced in slow step reacts with Br(V) rapidly to regenerate Ru(III) catalyst. They have showed that three moles alcohols required one mole of bromate.

**Vijaylakshmi and E.V.Sundaram**\(^{50}\) have studied the kinetics of oxidation of primary alcohols by acid bromate and had observed first order kinetics with respect to oxidant and fractional order with respect to substrate.

**S.N.Shukla and C.D.Bajpai**\(^{51}\) have studied the kinetics of oxidation of D(+) glucose by potassium bromate in acid medium and have observed first order kinetics in bromate as well as glucose but second order kinetics with respect to hydrogen ion.

**K.K.Sengupta et al**\(^{52}\) have studied the kinetics and mechanism of oxidation of aromatic aldehyde by acid bromate. They have examined the effects of various functional groups on the ring at the ortho, meta and para positions of benzaldehyde. The reaction is first order with respect to bromate concentration whereas the order with respect to substrate is less than 1.

**Ch. Sanjeeva Readdy and T.V.Kumar**\(^{53}\) have studied the kinetics and mechanistic study of Br(V) oxidation of glycolic acid catalysed by aquochlororuthenium(III) complex at different acid strengths. They have suggested that HBrO\(_3\) and Ru(III) form a complex which on protonation yields Ru(V) which attacks glycolic acid to form another complex. This gives products by its slow and rate determining decomposition.
P.N.Char, S.Sondu, B.Sethuram and T.N.Rao\textsuperscript{54} have studied the kinetics and mechanism of oxidation of some aliphatic esters by bromate in acid medium. They have observed first order kinetics in both Br(V) and ester, but second order in hydrogen ion. A mechanism involving direct oxidation of ester before hydrolysis by bromate has been proposed.

K.K.Sengupta et al\textsuperscript{55} have studied kinetics and mechanism of oxidation of some aryl alcohols by acid bromate. The results indicated that the reaction takes place by way of intermediate ester formation. Methoxy compounds react at much faster rates than the corresponding nitro substituted derivatives.

K.R.Sankaran and V.K.Srinivas\textsuperscript{56} have reported the kinetics of potassium bromate oxidation of Cobalt (III) bound and unbound α-hydroxy acids. The reaction shows total second order kinetics, being first order in each reactants. A suitable mechanism involving formation of a radical intermediate in a slow step from the bromate ester is suggested.

T.Veeraiah and S.Sondu\textsuperscript{57} have studied the kinetics and mechanism of oxidation of heterocyclic aldehydes by acid bromate. They have observed that the reaction is first order each in bromate ion concentration and substrate concentration and second order in hydrogen ion concentration. HBrO\textsubscript{3} and protonated hetero aldehyde have been established as the reactive species. The products of oxidation are the corresponding carboxylic acids.

P.N.Char et al\textsuperscript{58} have studied the kinetics of Ru(III) oxidation of chalcones by acid bromate in H\textsubscript{2}SO\textsubscript{4}- CH\textsubscript{3}COOH medium. They have reported that the reaction follows first order kinetics each in chalcone
concentration and Ru(III) concentration and zero order each in hydrogen ion concentration and bromate ion concentration.

N. Krishnamurthy et al\textsuperscript{59} have reported kinetics and mechanism of acid bromate oxidation of aliphatic and alicyclic ketoses. They have observed that the reaction is first order in both bromate and ketene. The rate increases with increase of acid concentration of the medium. The mechanism proposed involves the attack of acid bromate on the enol-form of the ketone in the rate determining step which is the formation of an intermediate followed by its fast decomposition to products.

Bharat Singh and Sheila Srivastava\textsuperscript{60-61} have studied the mechanism of ruthenium tetroxide catalysed oxidation of cyclic alcohols by bromate in alkaline medium. They have observed first order dependence in each bromate and cyclic alcohols. The reaction was found to be zero order in [OH\textsuperscript{-}] and first order in RuO\textsubscript{4}.

K.K. Sengupta et al\textsuperscript{62} have studied the reactivity of some aldoses and aldosamines towards potassium bromate in hydrochloric acid medium. They have observed that the reactions appear to proceed through the intermediate formation of bromate ester followed by the decomposition of the esters to give products. Hydrogen ion accelerates the rate of each reaction. The order of reaction with respect to bromate ion was unity. An increase in concentration enhances the rate of oxidation.

A. K. Singh et al\textsuperscript{63} have studied Ru(III) catalysed oxidation of diethanolamine (DEA) and triethanolamine (TEA) by potassium bromate in presence of perchloric acid. First order kinetics with respect to each of [KBrO\textsubscript{3}] and [Ru(III) chloride] was observed in oxidation of both DEA and TEA. With about eight- fold variation in [DEA] and ten - fold
variation in [TEA] first order kinetics in [substrate] was observed upto nearly 3-fold variation in [DEA] and 5-fold variation in [TEA]. Kinetics with negative effect of [substrate] became more complex in both cases when a significant decrease in pseudo first order rate constant was observed at their higher concentrations. Inverse fractional order in [H\(^+\)] was noted throughout its 10-fold variation. Variation in [Hg(OAc)\(_2\)], [Cl\(^-\)] and ionic strength (\(\mu\)) of the medium did not bring about any significant change on the rate of reaction. The values of rate constants observed at four different temperatures were utilized to calculate the activation parameters. Acetic acid and ammonia have been identified as main oxidation products of the reactions. A suitable mechanism involving the formation of a complex between [Rh(III)-amino alcohol] complex and bromate ion prior to the rate-determining step is proposed.

**Bharat Singh, Ashish et al\(^{64}\)** have studied osmium (VIII) promoted oxidation of crotonic acid (CA) by aqueous alkaline solution of potassium bromate. Zero order dependence in [KBrO\(_3\)] was observed while first order with respect to CA in its lower concentration range tends to zero order at its higher concentration range. The order in [O\(_3\)(VIII)] was found to be unity and a positive effect of [OH\(^-\)] was observed. Variation of the ionic strength (\(\mu\)), dielectric constant of the medium and addition of Hg(OAc)\(_2\) (used as Br\(^-\) scavenger) had insignificant effect on the rate of reaction. Thermodynamic parameters have also been calculated and reported. A suitable mechanism consistent with the observed kinetic results has been suggested and the related rate law deduced.
1.3: POTASSIUM IODATE AS AN OXIDANT: A REVIEW

M.D. Prasad Rao and J. Padmanabha\textsuperscript{65} 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\textsuperscript{66} 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$>\text{P-OCH}_3$$>\text{P-CH}_3$. P-Cl$>\text{m-CH}_3$$>\text{m-OCH}_3$$>\text{P}=\text{NO}_2$$>\text{m-NO}_2$.

E.V. Sundaram and Co-workers\textsuperscript{67} 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. The plot of log $k_{obs}$ versus Hammett’s
substituent constant gives a curve, suggesting a continuous change in the
transition state. A free radical mechanism, consistent with the attack of
HIO$_3$ 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. Sundaram$^{68}$ investigated the
kinetics of oxidation of $\alpha$- and $\beta$- 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 [H$_2$SO$_4$] studied. The rate
increases with decrease in dielectric constant of the medium. P.S.
Radhakrishnamurti et al$^{69}$ 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. O$_8$(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$_8$(III) catalysed reaction, whereas the
rate is increased in the case of Ru(III) catalysed reaction.
Surya Prakash Singh, Ashok Kumar Singh and Ajaya Kumar Singh 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 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 \([\text{Ir(III)}]\) 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** have studied kinetics and mechanism of oxidation of D-glucose and D-fructose by alkaline solution of potassium iodate in the presence of Ru(III) as homogeneous catalyst. The linear dependence of the reaction rate at lower [IO$_3^-$] and [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 their oxidation. Variation in [Cl$^-$] and ionic strength ($\mu$) of the medium does not affect the oxidation rate. The species, [RuCl$_2$(H$_2$O)$_2$(OH)$_2$]$^-$ and 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, 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 glucose and fructose. 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** have studied first and novel oxidation of D-fructose by potassium iodate using [IrCl$_3$(H$_2$O)$_2$OH]$^-$ complex as a homogeneous catalyst in alkaline medium. The experimental result shows a first order dependence
on iodate and [OH\textsuperscript{-}] 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.
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