CHAPTER-I

INTRODUCTION
SURVEY OF LITERATURE

Chemical kinetics is a very useful tool used in dealing with the study of rate of reactions with all the factors which influence the rate of reaction\(^1\). The relation between rate of the reaction and concentration of the reacting species gives the order of the reaction. The main purpose of determining the order of the reaction with respect to each reacting species is to utilize this experimental observation in elucidating the reaction mechanism through which chemical reactions occur. The rate (i.e. \(-\text{dc/dt}\)) 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.

The quantitative relationship between the rate of reaction and factors affecting it can be easily determined by kinetic investigation. The manner in which the rate of a reaction varies with the concentration of reacting species is usually expressed by the term ‘order’ of the reaction. For multi steps reactions the kinetics is limited by the slowest step, which is also called rate controlling step. There are many reactions in which orders are not simple power functions of the concentration of the reactants but even fractional. The derivation of the exact rate law then requires carefully
planned experiments in which influence of products and reactants are studied systematically.

The rate law can be derived for different mechanisms proposed on the basis of the same kinetic results. The comparison of an experimentally observed rate law with the derived rate law allows one to make some choice among apparently reasonable proposed 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 informations are uncovered or observed. Reaction mechanism is derived concept which can be changed or modified if some new concepts or new facts are observed. This makes quite evident that if one wishes to know the insight of the reaction mechanism, he should make kinetic studies.

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 kinetics. A clue to the reality of reaction mechanism is obtained by the product identification, use of isotopic tracers, detection of short lived intermediates, variation of ionic strength, catalyst and change of solvents, etc. on the rate of reaction.

The term ‘catalyst’ was introduced for the first time in 1836 by J.J. Berzelius 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\(^7\) defined catalyst as a substance which speeds up chemical reaction without affecting the equilibrium and his definition of the catalyst is most frequently cited of all the definitions. It was reported later on that this definition was valid only for reversible reactions and fails to incorporate any form of autocatalysis. P. Sabatier\(^8\) 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 became 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 non stoichiometric 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.

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

The transfer of either atoms or electrons is usually involved in the mechanism of organic/inorganic redox reactions, although both provide the same effect. It is difficult to distinguish between these two types of reactions, experimentally. A considerable progress has been achieved in the field of electron transfer reactions due to active and accelerating interest in the field of redox processes by a large number of workers owing to its importance in understanding the nature and technology used in analytical chemistry. The theoretical treatment of electron transfer
reactions by Libby\textsuperscript{9}, Marcus, Zwolinsky and Eyring\textsuperscript{10-11}, Laidler\textsuperscript{12} 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. 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. It supports the elucidated reaction mechanism and thus confirms the proposed mechanism. Stoichiometry of the reaction 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 and confirming the reaction mechanism.

Many difficult analytical problems\textsuperscript{13} have been answered by kinetic studies. 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 by the kinetic investigation. 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}. 
Chromic acid, Permanganate, 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-haloamides, chloramine-T, catechol and carbonium ion, amines and amino acids etc are among the common redox reagents which have received considerable emphasis leading to mechanistic studies. In a publication edited by Bomford and Tipper \(^{19}\) a detailed account of several familiar and less familiar redox reagents have been discussed. Berka and Zyka \(^{20}\) 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 N-haloamide and potassium iodate 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(A): N-BROMOSUCCINIMIDE AS AN ANALYTICAL REAGENT AND OXIDANT

The use of N-bromoacetamide to substitute a hydrogen in the allylic position in organic compound was first reported by Wone and Jaschinowski \(^{21}\) in 1919. However, it was not until 1942 that Ziegler and Coworkers \(^{22}\) showed that N-Bromosuccinimde (NBS) could be used successfully for allylic bromination and the reagent thus became widely used and the reaction is named now as Wone Ziegler reaction.

After the introduction of NBS as an brominating agent by Ziegler and coworkers, the preparative nature of this reaction was almost immediately employed by organic chemists, as demonstrated by the relatively large
literature, which has already accumulated on the subject during the past so many years. NBS is an ideal reagent for allylic bromination as it is (a) stable and readily available, (b) it affects allylic bromination with minimum of side reaction,(c) it is relatively low molecular weight and (d) preferably it reacts in any solvent. It has been predicted that it may not be possible to use a better reagent for allylic bromination than NBS.

Buu Hoi\textsuperscript{23} has made a detailed study of NBS reaction with a wide variety of benzene and naphthalene derivatives, notably ethers. During 1960’s, an excellent survey of the chemistry of this compound has been published\textsuperscript{24-26}. In all these reviews, reference has been made to a number of oxidation, dehydrogenation, bromination reactions. One of the earliest reports of the use of N-halogen compounds as oxidizing agents was the demonstration by Reich and Reich Stain\textsuperscript{27} that NBS in aqueous acetone smoothly oxidised secondary alcohols to ketones. Feiser and Rajgopalan\textsuperscript{28-30} described the selective oxidation of steroid alcohols by NBS.

**N. Venkatasubramanian and V. Thiagarajan**\textsuperscript{31} studied the Mechanism of oxidation of alcohols with N-bromosuccinimide. They found that electron-withdrawing substituents retard the reaction considerably and electron-releasing substituents increase the rate of oxidation. *Cis*-, and trans-4-t-butyl cyclohexanols are oxidized at nearly the same rates. There is also a good correlation between the rates of the NBS oxidations and Br, oxidations of these alcohols.

**Bharat singh, Lalji pandey, J.Sharma and S. M. Pandey**\textsuperscript{32} investigated the mechanism of oxidation of some aliphatic ketones by N-bromosuccinimide in acidic medium. They reported zero order dependence to N-bromosuccinimide and a first order dependence to both ketones and hydrogen ion concentrations. Sodium perchlorate, mercuric
acetate and succinimide additions have negligible effect while methanol addition has a positive effect on the reaction rate.

J. P. Sharma, R. N. P. Singh, A. K. Singh and Bharat Singh investigated the kinetics and mechanism of Ru(III) catalysed oxidation of some polyhydric alcohols by N-bromosuccinimide in acidic medium. They found that the reactions follow identical kinetics, being first order in each NBS, substrate and Ru(III). Zero effect of variation of [H⁺], [mercuric acetate] and ionic strength was observed. A negative effect of succinimide and acetic acid addition was observed while addition of [Cl⁻] shows the positive effect on reaction velocity. The products of the reaction were identified as the corresponding acids.

Chand Waqar, Bharat Singh and J.P. Sharma Studied the mechanism of Ru(III)-catalysed oxidation of glycollic and mandelic acids with N-bromosuccinimide in acidic medium. The reaction was carried out in the presence of mercuric acetate as a scavenger in the temperature range 30–45°C. The reactions follow identical kinetics. The rate shows a first-order dependence on [NBS], [substrate], [Ru(III)] and [Cl⁻]. Negligible effects of [H⁺], mercuric acetate and ionic strength variation have been observed. A negative effect of succinimide and acetic acid addition was observed on the reaction rate. Glyoxylic acid and benzoyl formic acid have been identified as the products.

Ashok Kumar Singh, Deepti Chopra, Shahla Rahmani and Bharat Singh investigated the kinetics of Pd(II) catalysed oxidation of D-arabinose, D-xylene and D-galactose by N-bromosuccinimide (NBS) in acidic medium using Hg(OAc)₂ as a scavenger for the Br⁻ ion. The reaction data show that first-order kinetics in each pentose and hexoses at low concentrations tend to zero-order at high concentrations. First-order
kinetics with respect to NBS and Pd(II) and inverse fractional order, i.e.,
decreasing effect of [H\(^{+}\)] and [Cl\(^{-}\)], were observed, whereas ionic
strength, Hg(OAc)\(_{2}\) and succinimide did not influence the oxidation rate.
Various activation parameters have been calculated and recorded. The
corresponding acids, arabonic, xylonic and galactonic, were identified as
the main oxidation products of the reactions.

Ashok Kumar Singh, S. Rahmani, Vinod K. Singh, V. Gupta, D.
Kesarwani & Bharat Singh\(^{36}\) Studied the kinetics of iridium (III)
catalysed oxidation of maltose and lactose by N-bromosuccinimide in
aqueous acid medium. The reaction was first order in N-
bromosuccinimide and zero order with respect to each sugar. The
reactions exhibit first order in [Ir(III)] at lower [Ir(III)], but tend towards
zero order at higher [Ir(III)]. Inverse fractional order has been observed in
[H\(^{+}\)], [Cl\(^{-}\)] and [succinimide], variation in ionic strength (I) and added
Hg(OAc)\(_{2}\) (used as Br\(^{-}\) ion scavenger) did not influenced the oxidation
rate. Activation parameters have been calculated. HOBr and [IrCl\(_{3}\)H\(_{2}\)O]\(^{2-}\)
were postulated as oxidizing and catalytic species, respectively.
Galactonic and gluconic acids have been identified as the main oxidation
products of the reactions.

K.N. Mohana and K.R. Ramya\(^{37}\) worked out on the kinetics of
ruthenium (III)-catalyzed oxidative cleavage of thiamine hydrochloride
(THM, Vitamin B\(_{1}\)) with N-bromosuccinimide (NBS) in HCl medium at
308 K. The oxidation reaction follows the rate law, 
\(-\frac{d[NBS]}{dt} = [NBS]^k [Ru(III)]^a [THM]^b [H^{+}]^c [Cl^{-}]^d\), where a, b, c and d are less than
unity. The stiochiometry of the reaction was found to be 1:1, and 2-(4-
methyl thiazol-5-yl) ethanol and 4-amino-2-methylpyrimidine-5-
carbaldehyde were identified as the oxidation products of THM. The
reaction was examined with reference to variation of ionic strength of the
medium and addition of the reduction product NBS, succinamide (RNH). The change in relative permittivity of the medium affected by changing the solvent composition with acetonitrile was studied. HOBr was postulated as the reactive oxidizing species.

Ashok Kumar Singh, Rashmi Srivastava, Shalini Srivastava, Jaya Srivastava, Shahla Rahmani and Bharat Singh\textsuperscript{38} studied the Kinetics of oxidation of maltose (mal) and d-galactose (gal) by protonated N-bromosuccinimide (N\textsuperscript{+}BSH) using chloro-complex of Rh(III) in its nano-concentration range as homogeneous catalyst at 40 °C for the first time. Almost constant values of pseudo-first-order rate constant \((k_1)\) throughout the variation of N-bromosuccinimide (NBS) in the oxidation of both the reducing sugars clearly demonstrate that order of reaction with respect to [NBS] is unity. First-order kinetics with respect to each [Rh(III)], [Sugar] and [H\textsuperscript{+}] is evident from the observed values of \(k_1\) which increase in the same proportion in which the concentration of each reactant is increased. Negligible effects of variations of [Hg(II)], [Cl\textsuperscript{−}] and [succinimide] on the rate of oxidation of each reducing sugar have been observed. Variations in ionic strength (\(\mu\)) and dielectric constant (\(D\)) of the medium have not influenced the oxidation rates. Protonated N-bromosuccinimide, N\textsuperscript{+}BSH, and chloro-complex of Rh(III) i.e. [RhCl\textsubscript{6}(H\textsubscript{2}O)]\textsuperscript{2−} have been postulated as the reactive species of NBS and Rh(III) chloride in acidic medium, respectively. The main oxidation products of the reactions were identified as arabinonic acid and formic acid in case of maltose and lyxonic acid and formic acid in case of D-galactose.

Alaa Eldin Mokhtar Abdel-Hady\textsuperscript{39} worked on Kinetics of oxidation of L-proline by N-bromosuccinimide (NBS) in aqueous acidic medium and water-alcohol solvent mixtures were performed. The reaction was first order dependent on both [proline] and [NBS]. The rate of reaction was
inversely dependent upon $[H^+]$ throughout the pH range 2.6-3.3 and varied with the cosolvent according to the order MeOH > EtOH. The conjugate base of amino acid was considered as the main reactive species. An inner-sphere mechanism, in which the conjugate base of amino acid was attacked by NBS to form the precursor intermediate complex, was proposed.

Sheila Srivastava, Anju Singh, Saumya Bajpai and Tushar Bajpai\textsuperscript{40} studied the kinetics of Ir(III) catalyzed oxidation of Mannitol in an alkaline medium by N-bromosuccinimide in the temperature range 30-45$^\circ$C. The reaction was carried out in the presence of mercuric acetate which co-catalyzes the reaction and the reaction rate follows a fractional positive order with respect to it. First order kinetics has been depicted in case of catalyst Iridium (III) chloride. The rate showed fractional positive kinetics with respect to the oxidant as well as $[OH^-]$ and $[Cl^-]$. Variation in the concentration of Mannitol showed negligible impact on the reaction rate implying zero order with respect to substrate. Various activation parameters have been calculated. A suitable mechanism in agreement with observed kinetics has been proposed.

P. Giridhar Reddy, K. Ramesh, S. Shylaja, K. C. Rajanna, and S. Kandlikar\textsuperscript{41} studied the Kinetics of Ru (III) catalyzed oxidation of aliphatic ketones such as acetone, ethyl methyl ketone, diethyl ketone, iso-butylmethyl ketone by N-bromosuccinimide in the presence of Hg(II) acetate in aqueous acid medium. The order of $[NBS]$ was found to be zero both in catalyzed as well as uncatalyzed reactions. However, the order of $[ketone]$ changed from unity to a fractional one in the presence of Ru (III). On the basis of kinetic features, the probable mechanisms were derived and individual rate parameters were evaluated.
Ashutosh Kumar and Bhanu Pratap\textsuperscript{42,43} worked out on kinetics of oxidation of ethyl amine and methyl amine by N-bromosuccinimide in the presence of alkaline solution of palladium(II) chloride as homogeneous catalyst at 30-45 °C. The reaction exhibits zero order rate dependence with respect to amines and first order at low concentration of N-bromosuccinimide tending to zero order at high concentration of N-bromosuccinimide. A positive fractional order is observed with respect to Pd(II) while addition of succinimide and mercuric acetate did not affect the rate constant of reaction in both cases. The variation of ionic strength of the medium, [OH\textsuperscript{-}] and [Cl\textsuperscript{-}] showed zero effect on the reaction rate. The activation parameters have been evaluated from the Arrhenius plot. Mechanistic steps were discussed and the rate law derived was found to confirm the observed kinetic results.

Ashutosh Kumar and Bharat Singh\textsuperscript{44} worked out on kinetics of Ru(VI) catalysis in oxidation of diethylene glycol (DG) and methyl diethylene glycol (MDG) by N-bromosuccinimide (NBS) in alkaline medium in presence of mercuric acetate as Br\textsuperscript{-} ions scavenger in the temperature range 30-45 °C. The reactions follow identical complex kinetics, being zero order in each substrates and OH\textsuperscript{-} ions and first order in [Ru(VI)]. First order kinetics with respect to NBS at its low concentrations shifts to zero order at its high concentrations. A negative effect of addition of succinimide (reduction product of NBS) is observed while variation of [Hg(OAc)\textsubscript{2}] and ionic strength has no effect on rate of both reactions. Various activation parameters were calculated and recorded. The products of the reactions were identified as corresponding acids.
1.1(B): KINETICS OF REACTIONS INVOLVING NBS AS OXIDANT

Although NBS has been extensively used as an oxidising agent, but the mechanism of the oxidation has not been clearly established. It is generally accepted that in polar solvents, a “positive bromine” is the attacking species. There is a considerable difference of opinion regarding the position of attack on the organic substrate\textsuperscript{45}. In oxidation of alcohols by NBS, it has been suggested that alcohols form a hypobromite which readily loses hydrogen bromide to form the carbonyl products\textsuperscript{46}.

The mechanism of this reaction is illustrated below:

\[
\begin{align*}
\text{H} & \quad \text{NBS} \quad \text{H} \\
- \text{C} & - \text{OH} \quad \rightarrow \quad - \text{C} & - \text{O} \text{ Br} \quad \rightarrow \quad - \text{C} = \text{O} + \text{HBr}
\end{align*}
\]

Lecomte and Gantt\textsuperscript{47} have suggested an alternative mechanism in which it is proposed that oxidation proceeds through bromine substitute of a hydrogen on the carbon atom bearing the OH group with rapid loss of hydrogen bromide.

\[
\begin{align*}
\text{H} & \quad \text{NBS} \quad \text{Br} \\
- \text{C} & - \text{OH} \quad \rightarrow \quad - \text{C} & - \text{O} \text{H} \quad \rightarrow \quad - \text{C} = \text{O} + \text{HBr}
\end{align*}
\]

There are several evidences in support of this mechanism. For example, ethyl benzyl ether which can not form a hypobromite is oxidized readily to benzaldehyde by NBS.
1.2: POTASSIUM IODATE AS AN OXIDANT: A REVIEW

M.D. Prasad Rao and J. Padmanabha\textsuperscript{48} 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 [IO\textsuperscript{3} \textsuperscript{-}] 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\textsubscript{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{49} 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-OCH\textsubscript{3}>P-CH\textsubscript{3}. P-Cl>m-CH\textsubscript{3}>m-OCH\textsubscript{3}>P=NO\textsubscript{2}> m-NO\textsubscript{2}. 

\textit{Chapter-I}
E.V. Sundaram and Co-workers\textsuperscript{50} 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\textsuperscript{51} 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\textsuperscript{52} 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$_4$(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 Os(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**\(^{53}\) 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 [OH\(^-\)] at its low concentration but tends towards zero order at higher concentration. Variation in [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**\(^{54}\) 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 [IO\(_3\)^-] and [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 [Cl\(^-\)] and nil effect of ionic strength (\(\mu\)) on the rate of oxidation have also been noted. The species,
[IrCl₃(H₂O)₂OH]⁻ 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 Singh⁵⁵ 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 [IO₃⁻] 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 (μ) of the medium does not affect the oxidation rate. The species, [RuCl₂(H₂O)₂(OH)₂]⁻ and IO₃⁻, 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, \[
\begin{array}{c}
\text{O} \\
\text{I} \\
\text{RuCl}_2(\text{H}_2\text{O})_2(\text{OH})_2 \\
\end{array}
\]²⁻, 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\textsuperscript{56} 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.

Bharat Singh, Anamika Singh and Aniruddh Kumar Singh\textsuperscript{57,58} have studied mechanistic studies of aquachlororhodium (III) catalysis in potassium iodate oxidation of 1,2-propanediol and 1,3-butanediol in acidic medium. The experimental results show a first order dependence on iodate and Zero-order kinetics with respect to [1,2-propanediol]. Variation of [HClO\textsubscript{4}] and [Cl\textsuperscript{-}] shows negative effect on rate of the reaction. The linear dependence of the reaction rate at lower [Rh(III)] chloride tends towards zero-order at its higher concentrations. Addition of sodium perchlorate was found to have positive effect on the rate of reaction.
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