# CHAPTER – I

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Chemical Kinetics deals with the rates at which or the mechanism by which different chemical reactions take place under different conditions. Some reactions take place so fast that it is almost impossible to study them. The reaction between $AgNO_3$ and $NaCl$ solutions is so fast that it looks instaneous. Certain other reactions occur very slow that no perceptible changes take place in the course of even a few years. The rusting of Iron is a slow reaction that occurs over the years. Between these two extreme stages, there are a number of reactions which proceed at measurable rates under specific conditions. These can be studied and the results obtained may be utilized to explain reactions which can not be easily studied.

When a chemical reaction takes place there is a change in concentration of the reacting substances. These concentration changes would decrease with passage of time and after a particular period of time the concentration becomes time independent. This state of the system when the properties of the system become time independent is referred to as the equilibrium state.

Chemical kinetics provides information regarding the time required by a system to reach the equilibrium state. It is a study of not only how fast reactants get converted into products but also the sequence of all physical and chemical processes which occur during the course of a reaction.

Chemical kinetics is the study of the rates of reactions and the factors that affect those rates. It offers a technique for examining the manner in which molecules, ions etc. take part in chemical reactions. It helps us to understand the mechanism of chemical reactions. It is said that, "Mechanism is to chemistry as a grammar is to a language there is no branch of chemistry which can be satisfactorily studied without a clear grasp of the principles of mechanism."

The rate or velocity of a given reaction is defined as the rate of change of concentration of the reactants or products at a given temperature.

or

$$\text{rate} = \frac{-\Delta\,[\text{reactant}]}{\Delta\,t} \text{ or } \frac{-d_x}{d_t}$$

$$\text{rate} = \frac{+\Delta\,[\text{Product}]}{\Delta_t} \text{ or } + \frac{d_x}{d_t}$$

where [reactant] and [product] refer to the concentration of reactants and products respectively.

The rate constant of a first order reaction is given by the Equation

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Where 'a' is initial concentration of the reactant in moles per litre.

'x' is moles of the reactant transferred into products after time 't'.

Thus a-x is the concentration of the reactant after time 't'.

**Importance of chemical kinetics in Reaction Mechanism –**

During the course of chemical reaction, molecules come closer, atoms change their positions, electron shift takes place and as a result new compounds are formed. A sequence of steps by which the reaction occurs is known as "reaction mechanism". The mechanism of the reaction gives a detailed picture of the activated complex.[1]

The importance of the chemical kinetics lies in the fact that its usefulness in giving the information not only about the reaction rate but also of

(i)   the factors that determine the reaction rate

(ii)  favourable conditions necessary for the production of desired product qualitatively and quantitatively.

(iii) the reactive intermediates governing the overall reaction

(iv)  extent of reaction and time.

Thus chemical kinetics plays an important role in elucidation of reaction mechanism.

For the reactions in solution, the mechanism is framed on the basis of different kinetic parameters such as order of reaction, effect of concentration, temperature, ionic strength, solvent, dielectric constant etc. Rate of reaction also provides valuable information so as to suggest the most probable mechanism of the reaction.

**Effect of concentration on the rate of a reaction :**

The credit of first significant quantitative investigation of the reaction rate goes to Ludwig Wilhelmy[2] who was working on inversion of sucrose. He showed that, the rate of reaction at any instant was proportional to the concentration of sucrose remaining at that time. On the basis of this work L. Wilhelmy deserves to be called the founder of chemical kinetics. Rate of a reaction is directly proportional to the concentration of the reactant at a given temperature.

Later on different workers studied different reactions extensively and developed the procedure to calculate the rate constant for a reaction as a function of time. In general, if the rate of reaction is proportional to the $n^{th}$ power of concentration of reactant A and to the $m^{th}$ power of the concentration of B etc. the rate law is given by an expression.

$$\frac{-d[A]}{d_t} = k \ [A]^n [B]^m$$

where k is the proportionality constant referred to as the reaction rate constant or specific rate constant.

The observed dependence of the rate on concentration of a particular reactant gives order with respect to that reactant only and the overall order of a reaction is the algebraic sum of the exponents of all the concentration terms which appear in the rate law (n+m+...). The order takes integral, zero or fractional values. The order of a reaction is determined by kinetic methods and the rate law is established on the

basis of experimental data. Order of a reaction can be determined by following methods.

(a) Integration method or Hit and Trial method.

(b) Fractional change method.

(c) Graphical method.

(d) Van't Hoff's Differential method. etc..

**Effect of Temperature on Reaction Rate :**

It is well known fact that the velocity of a chemical reaction increases with rise in temperature. In homogeneous reactions, the rate becomes doubled or tripled for each 10°C rise in temperature. This increase in the reaction velocity with temperature is some times expressed in the form of temperature coefficient, which is defined as "Temperature coefficient of a chemical reaction is defined as the ratio of rate constants of a reaction at two different temperatures separated by 10°C." The two temperatures are generally taken as 35°C and 25°C. Thus,

$$\text{Temperature coefficient} \quad = \quad \frac{k_{35^{\circ}C}}{k_{25^{\circ}C}}$$

J.J. Hood[3] was the first, who investigated the enhancement of reaction with the rise in temperature. He was Arrhenius[4] who successfully applied his ideas to the experimental data for a number of

and for various types of reactions. He suggested an Equation to show the variation of rate constant (k) of reaction with absolute temperature (T).

The Equation is $k = A e^{-E_a/RT}$ .

Where   A  - frequency factor

$E_a$  - energy of activation

R  - molar gas constant.

Thus, to account for the marked increase in reaction rate with rise in temperature, Arrhenius suggested that, molecules absorb heat energy and get activated.   According to his hypothesis,  in every system an equilibrium exists between normal reactant molecules and  activated molecules; and only activated molecules cause the chemical change. Thus molecules acquire the additional energy required for a reaction to occur, which is known as the energy of  activation. The magnitude of activation energy will depend on the nature of the  process, so that, the proportion of activated molecules will vary from reaction to reaction, and hence, they proceed with different rates.  Thus, Arrhenius attributed influence of temperature on reaction rate to the concentration of activated molecules.

**Significance of Thermodynamic Parameters**

The various thermodynamic parameters like Energy of activation ($E_a$), free energy factor (A), free energy change ($\Delta G\pm$), Entropy change ($\Delta S\pm$), change in enthalpy ($\Delta H\pm$)  are concerned with the reaction rate; hence their magnitudes give wealth of information which helps in suggesting the reaction mechanism.

The frequency factor (A) is concerned with frequency of collision in collision theory, where as it is a measure of the entropy of activation in the transition state theory.

Entropy is a measure of the randomness of a system and entropy of activation is the entropy change in going from the reactants to the activated complex. Hence its magnitude depends on the nature of reactants and the nature of activated complex. The determination of the entropy of activation and its utilization in prediction of reaction mechanism has been explained by Moelwyn[5], Frost and Pearson.[6]

Reaction is said to be normal if $\Delta S=0$ otherwise it is termed as fast or slow according to whether $\Delta S$ value is positive or negative respectively.

**Solvent effect**

When a chemical reaction takes place in solution, the effect of the solvent is one of the most useful criteria in the study of reaction rates and mechanism. It is well known that, the solvent plays an active or passive role and accordingly the rate of reaction may be dependent on or independent of solvent used.

The effect of solvent on reaction rate was studied first by Menschutkin,[7] who explained the reaction between triethyl amine and ethyl iodine at 100°C in different solvents and observed that, reactivity in various solvents was in the order – methanol > ethanol > acetone > benzene > hexane.

It was therefore, reasonable to conclude that the solvent and solute interact in some way to affect the reaction rate or cause a change in the mechanism of reaction. The pronounced effect of solvent on the reaction rate due to the solvation of reactants or activated complex has been reported by Tomila and coworkers.[8]

The solute solvent interaction decreases the potential energy of the former by an amount equal to the energy of solvation. The solvation of reactant (s) causes decrease in its potential energy which results in the increase in energy of activation and reactions become sluggish. On the other hand, decrease in potential energy of activated complex due to solvation results in equivalent decrease in activation energy, which causes increase in the rate of reaction. However, if reactant and activated complex both are solvated, the overall effect on the activation energy and reaction rate is not significant.

The solutes, particularly ions are solvated by the solvent molecules and get oriented in a definite manner. This orientation imposes a restriction on the motion; hence solvation is an important factor in determining the entropy change of system. When positively charged ions come close together in transition state the extent of solvation is greatly reduced, so that entropy of activation is positive, where as if neutral molecules are involved in the formation of transition state that carries charges, it leads to loss of freedom of motion by solvation and causes the decrease in entropy i.e. $\Delta S$ is negative.

### Effect of Dielectric Constant

The role of dielectric constant of solvent is important in reactions involving the electrostatic forces between solvent and solute molecules, Amis[9] has explained the subject systematically. To explain the effect of dielectric constant of solvent (D) on rate of reaction between two ions having valence $Z_A$ and $Z_B$, Scatchard[10] derived an expression :

$$\ln k = \ln k_o = \frac{Z_A Z_B \, e^2}{DKT_r}$$

Where $k_o$ is the specific rate constant in the hypothetical medium having indefinite dielectric constant $\mu = 0$ and e, k, T, r are the electronic charge, Boltzmann constant, absolute temperature and radius of activated complex respectively. The above equation implies that logarithm of the rate constant of ionic reaction vary linearly with the reciprocal of dielectric constant by solvent and a plot of log k versus 1/D enables one to gain the information regarding the nature of reacting ions. Aims et al.[11,12] and Lamer[13] employed such plots in prediction of nature of ionic species involved in various reactions and to explain the effect of solvent polarity on reaction rates : Where as Laidler-Eyring[14] and Bhattacharjee-Mahanti[15] have used the experimental slopes of same plots to calculate radius of activated complex (i.e. average distance of approach between the two reacting ions). The deviation of the plot from linearity has been observed in most cases, particularly in low dielectric constant region. Laidler-Eyring[14] attributed such deviation to preferential absorption of water on ions. To explain the dependence of

lnk on 1/D Amis[16] derived an expression identical with Scatchard Equation by using Coulombic energy approach.

In the study of chemical kinetics, one comes across not only ionic reactions but also reactions involving dipoles and hence dipole-dipole interactions must also be taken into account. To explain the effect of solvent polarity on rate of reaction between two neutral molecules A and B forming an activated complex AB* Kirkwood[17] suggested an expression

$$\ln k = \ln k_0 - \frac{N}{RT}\left[\frac{d^2 A}{r^3_A} + \frac{d^2 B}{r^3_B} - \frac{d^2 AB^*}{r^2 AB^*}\right]\left[\frac{D-1}{2D+1}\right]$$

Where N, R, d and r denote the Avogadros number, molar gas constant, dipole moment and radius respectively. This equation expects linear plot of log k versus $\frac{D-1}{2D+1}$ which enables one to predict the nature of transition state from the nature of experimental slope.

In addition to the ion-ion and dipole-dipole reactions ion dipole interactions are also common which cannot be ignored. The rate constant of a reaction involving an ion and neutral molecule varies with dielectric constant of the solvent according to Equation proposed by Eyring and Laidler[1].

$$\frac{d \ln k}{d\left(\frac{1}{D}\right)} = \frac{N Z^2 e^2}{2RT}\left[\frac{1}{r} - \frac{1}{r^*}\right]$$

$$\text{or } \ln k = \ln k' + \frac{N Z^2 e^2}{2RTD}\left[\frac{1}{r} - \frac{1}{r^*}\right]$$

where, k' is the value of rate constant in a medium of unit dielectric, r and r* stand for the radius of reaction ion and activated complex respectively.

## Salt Effect

The effect of added salts on the rates of chemical reactions in solution has been employed as one of the important techniques to elucidate the reaction mechanism. Due to the electrostatic interactions, the kinetics of ionic reactions differs from that of reactions between non electrolytes.

In the case of ionic reactions, the reaction rates not only depend upon the nature of the reacting ions but also on the ionic strength of the reaction medium. A very satisfactory treatment of this matter was made by Bronsted,[18] Bjerrum[19] and Christiansen[20]. The original treatments of those authors were reviewed later on by Lamer.[21] These effects of electrolytes are of two types, namely, primary salt effect and secondary salt effect. The former deals with the influence of electrolyte concentration on activity coefficients of reacting ions and transition state; where as the latter is concerned with actual changes in the concentration of the reacting ions resulting from the addition of electrolytes. Both kinds of effects are important in ionic catalysis in solution, while the primary salt is involved in non-catalytic reactions and it is subdivided into the following two categories.

(i)     Primary exponential salt effect

(ii)    Primary linear salt effect

The former primary salt effect for the reaction in dilute solutions is represented by the Bronsted-Bjerrum Equation.

$$\ln k = \ln k_o + \frac{2\,\alpha\,Z_A Z_B \sqrt{\mu}}{1 + \beta r \sqrt{\mu}}$$

and for every dilute solution, where $\mu$ is small it gets reduced to

$$\ln K \approx \ln k_o + 2\,\alpha\,Z_A\,Z_B\,\sqrt{\mu}$$

where $k_o$ is the rate constant in solution of ionic strength zero, $Z_A$ and $Z_B$ are the charges of the reacting ions with the distance of closest approach r while $\alpha$ and $\beta$ are the Debye-Huckel constants.

The second equation leads to the prediction that logarithm of the rate constant of ionic reaction should vary linearly with the square root of the ionic strength of the reaction medium. It also guides one to gain information regarding the nature of the charges on the reacting ions from a plot of log k versus $\sqrt{\mu}$.

The application of the second equation has been tested by Davies[22] for different ionic reactions. His study leads to the conclusion that, the Bronsted-Bjerrum equation is valid with high accuracy for reactions in dilute solutions : however, deviation occurs for reactions in more concentrated solution when ionic association becomes an important factor. The ionic association may result in reduction of true ionic strength of solution or change in the electrostatic interactions between reacting ions or change in mechanism which affects the reaction rate considerably.

The Bronsted-Bjerrum theory of salt effect has been criticized by Olson and Simonson[23] according to whom, the rate of reaction between ions of the same charge sign is not dependent upon the ionic strength of the solution but it is governed by the concentration and character of added ions having charge sign opposite to that of reacting ions.

**Ionic strength**

The ionic strength ($\mu$) of a solution is a measure of the electrical intensity due to the presence of ions in the solution. It is given by half of the sum of all the terms obtained by multiplying the molality of each ion by the square of its valency. Mathematically, we have

$$\mu = \frac{1}{2}(m_1 z_1^2 + m_2 z_2^2 + m_3 z_3^2 + \ldots\ldots)\,.$$

where $m_1, m_2, m_3 \ldots$ are molalities and $z_1, z_2, z_3 \ldots$ are the valencies of the various ions present in the solution.

**Identification of Intermediates and products of reaction :**

A number of organic reactions involve formation of intermediates which are transformed again in route to the products.

Reactants ⟶ Intermediate (s) ⟨ Product / by Product.

Thus, intermediates play a crucial role in the overall processes; and hence most concrete evidence about the mechanism of reaction is provided by the actual isolation or identification of one or more intermediates formed during the reaction course. This is possible only if intermediate is stable one. Sometimes the intermediate may be too labile or transient so that its isolation becomes difficult. In such cases the likely

intermediate can be trapped with some other suitable reagents which are selective enough to react only with the intermediates and not with the reactants.

Free radical is one of the important intermediates among various types of intermediates such as carbocation, carbanions, carbenes, nitrenes etc. Oxidation of certain phenols and hydrazines produces free radicals which are usually classified as oxygen or nitrogen radicals on the basis of structures of patent compounds.[24] The formation of radical cation[25] and radical anion[26] have also been reported in different reactions. The existence of transient free radicals can be established by capturing them with reagent like allyl acetate, acrylonitrile, allyl alcohol and acrylamide which act as excellent free radical scavenger.

The detection and identification of products can be carried out by isolation or directly in the reaction mixture using standard methods of qualitative analysis. The modern techniques like Infrared (IR), nuclear magnetic resonance (NMR), mass spectroscopy, chromatography, polarography etc. are used for isolation and characterization of reaction products.

**Chemistry of Thallium**

Thallium is one of the rare elements which are widely distributed in nature. It is always associated with Cu, Zn and Fe in blendes and pyrites. In the periodic table it is in IIIB group. Thallium is a soft white metal and marks paper like lead. It melts at 577 K and boils at 1730 K. Atomic weight 204.39, Atomic Number 81. Electronic configuration is

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^1$. Specific gravity 11.85. Covalent radius 1.55 A°. It is a poor conductor of electricity. It shows allotropy.

## Toxicity of Thallium[30]

Thallium compounds are toxic. Many serious and fatal diseases have resulted from accidental or therapeutic ingestion. It is a cumulative poison which may be absorbed by the skin. The human lethal dose is 1.75 gms of thallium(I) sulfate. An antidote is Prussian Blue orally administered.

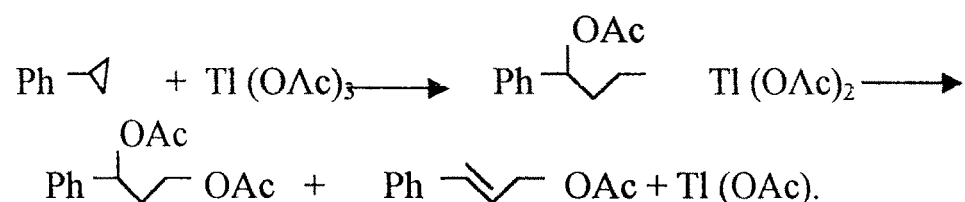## Mechanism of Thallium(III) oxidations

There has been much activity in recent years concerning thallium(III) oxidations.[30] The potentialities of this oxidant are being realised more and more especially as regards the oxidation of organic compounds.[61] Interest in the use of thallium(III) in the oxidation of organic compounds has increased only recently and research in this regard has not been extensive. The potential of this oxidant is being realised more and more as is evident from the considerable amount of work that is lately being done. Thus, the selectivity of thallium(III) is higher than its neighbours in the periodic table, mercury(II) and lead(IV) and also thallium(III) is a better oxidant than the other two.

The oxidation of olefins by thalliumj(III) involves electrophillic attack to form an oxythallation product. This step is rate-determining and is followed by solvolysis via carbo-cation ions to lead to products. The kinetics of oxidation of simple olefins was studied in detail by

Henry.[31] The reaction with ethylene was first order in ethylene and oxidant and the only primary products detectable were acetaldehyde and ethylene glycol.
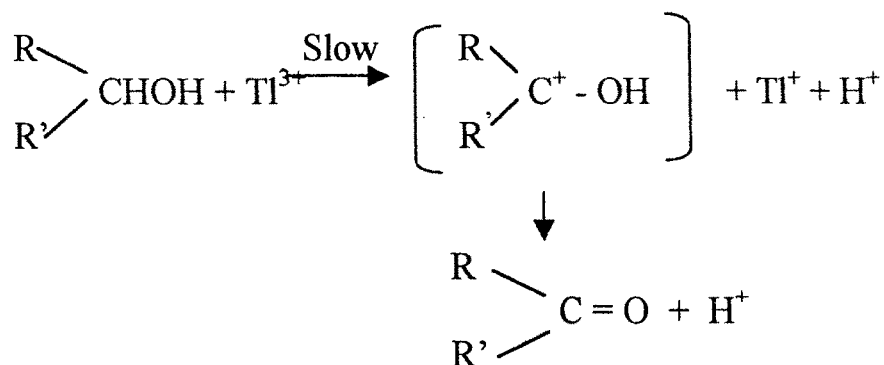
$$Tl(III) + H_2C = CH_2 \xrightarrow{\quad H_2O \quad} H_3C - CHO + \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$$
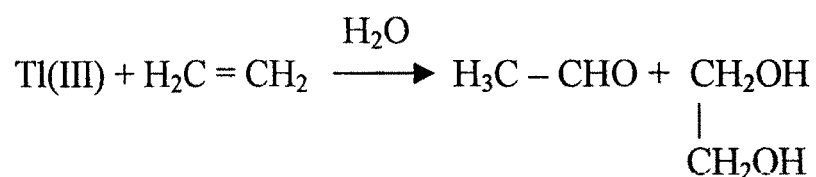
The oxidation of cyclopropanes by thallium(III) acetate in acetic acid leads to cleavage of C-H bonds.l[33] The reaction is first order in both reactants. Tl(OAc)$_3$, as compared to Tl (OAc)$^+_2$ in the case of the oxidation of olefins, is the active species. The product studies have shown that only one of the two non equivalent cyclopropane ring bonds is cleaved.

Ph $\triangleleft$ + Tl (OAc)$_3 \longrightarrow$ Ph $\overset{\displaystyle OAc}{\underset{}{\bigvee}}$ Tl (OAc)$_2 \longrightarrow$

Ph $\overset{\displaystyle OAc}{\underset{}{\bigvee}}$ OAc + Ph $\searrow\!\!\diagup$ OAc + Tl (OAc).

The oxidation of primary alcohols by Thallium(III) has not received any detailed attention and the situation with respect to secondary alcohol is not much better.

The oxidation of secondary alcohols studied include those of α-phenyl ethyl alcohol and substituted α-phenyl ethyl alcohols[34a], cyclohexanol[34b], 2-propanol[34c] and 1:3 dicyclopropane-2-ol.[34c] The reaction is first order in each reactant and the mechanism is shown by

$$\underset{R'}{\overset{R}{\diagdown}}CHOH + Tl^{3+} \xrightarrow{Slow} \left[ \underset{R'}{\overset{R}{\diagdown}}C^+\text{-}OH \right] + Tl^+ + H^+$$

$$\underset{R'}{\overset{R}{\diagdown}}C = O \ + \ H^+$$

Free radicals are not involved in such reactions. The oxidation of substituted benzyl alcohols by thallium(III) acetate in aqueous acetic acid[36] and the oxidation of cyclonols[37] has received attention.

The oxidation of oxalic acid by thallium(III) in complete darkness induces the polymerization of acrylonitrile and is also catalysed by Mn(II) ions.[38] The oxidation of $\alpha$-hydroxy acids by thallium(III) acetate in acetic acid is first order in both reactants and is acid catalysed.[39] Tl $(oAc)_2^+$ is understood to be the active species. In the case of the oxidation of (L) latic acid catalysed by Mn(II) in aqueous acetic acid, evidence of free radical intervention has been obtained.[40] The oxidation of formic acid by thallium(III) is rather complicated.[41]

$$Tl^{3+} \ + \ HCOOH \longrightarrow Tl^+ + CO_2 + H^+$$

The oxidation of cyclohexanone by thallium(III) perchlorate was zero order in oxidant which showed that enolisation was rate controlling.[43] The oxidation of benzoin by thallium(III) acetate in aqueous acetic acid is first order in both reactants and the rate decreases

with increasing acid concentration and with decreasing dielectric constant of the solvent and is suggested in [44] oxidation of acetophenone and substituted acetophenones by TTA in acetic acid has also been studied.[45] The oxidation of pinacol by thallium(III) occurs only in presence of acid, the rate is increasing with increase in acid concentration.[46] The thallium(III) oxidations of several other aliphatic, arylaliphatic and cyclic ketones have also been examined.[47]

The oxidation of methyl, ethyl, n-propyl and butyl acetates by thallium(III) in acetic acid. Sulfuric acid mixture was investigated.[48] The reaction is first order in both reactants and is acid catalysed. Chloride ions retard the reaction.

The oxidation of phenol by thallium(III) acetate in aqueous acetic acid leads to formation of dione as a major product.[49] The reaction involves a two electron transfer. The reaction of thallium(III) aquo-ions with catehol in excess giving quinone (quo) is first order in oxidant and in catechol.[50] The rate of oxidation increases with decreasing $H^+$ ion concentration.

The thallium(III) oxidation of an aldoximes leading to formation of carbonyl compounds is first order in substrate and oxidant and the mechanism is established.[51]
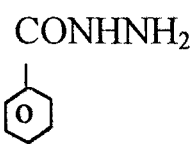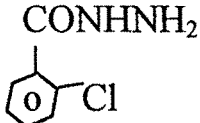
Other investigations have included those of the oxidation of captive oxalate,[53] the reaction of phenyl thallium dicarboxylate with tetramethyltin in methanol[54], oxythallation of norbornene derivatives in aqueous solution and in methanol,[55] the oxidation of aryl dialkyl

amines[56], the thallium(III) promoted hydrolysis of thiol esters,[57] and the thallium(III) oxidation of catechol in chloride containing media.[58] An interesting study of oxidation of anilines by thallium(III) acetate in aqueous acetic acid is also reported.[59]

**Present study and its aim**

The above discussion and literature survey indicate that the kinetics of oxidation of aliphatic as well as aromatic acid hydrazides by various oxidants has been studied. It is clear that little information regarding the mechanism of oxidation of hydrazides by thallium(III) ion is available. Hence, the study of kinetics and mechanism of oxidation of aryl hydrazides by acidic thallium(III) in water alcohol mixture has been undertaken iodometrically.

The hydrazides selected for the kinetic study are

A) Benzoic acid hydrazide.

$CONHNH_2$

B) 2-chloro benzoic acid hydrazide.

$CONHNH_2$, Cl

It is proposed to study the effect of substituent at ortho-position on the rate of oxidation of hydrazide by thallium(IV). The oxidant chosen for the study is a two electron transfer oxidant having the redox potential of 1.25 V in acidic medium. The oxidising capacity of thallium(III) also depends strongly on the anion present in the solution

and this property has not been explored for selective oxidation of the substrates to the desired products. The work includes the study of effect of oxidant, reductant and hydrogen ion concentration, ionic strength and dielectric constant.

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