CHAPTER : I

I) Introduction

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III) Literature survey

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I. INTRODUCTION

Chemical kinetics is a fundamental science which deals with the rates at which the reactions occur and the course they adopt. In the study of chemical kinetics, time is an important variable. The rate of reaction is measured by measuring the concentration of one of the reactants or products at different intervals of time. Study of temperature dependence of the reaction rates, helps us in understanding the chemical energetics. Such rate studies provide insight into the sequence of molecular level events in a chemical reaction. Indeed it is a bold and exciting endeavour to probe how molecules come together, how they orient themselves and how the electrons shift so that new molecules are ultimately formed[1]. Kinetics is an active growing field where the applications of theory lag for behind the experiment.

The knowledge of reaction rate is of a great practical value. For all chemical processes being used on Laboratory to industrial scale, it is often necessary to know under what conditions a slow but useful reaction can be made to proceed rapidly, to give a desired product in high yield, and at the same time the reaction conditions are such that, a side reaction yielding an unwanted and undersirable product is made slow to make the process economical. Indeed, it is kinetics and not thermodynomics that enables us to guess what reaction might occur in complicated inorganic and organic systems.

Chemical kinetics covers a wide range of processes. It includes the empirical study of the effect of — concentration, temperature, catalyst, solvent, hydrostatic pressure, and ionic strength, on the reactions of various types. When a reaction has more than one elementary step, the kinetics is limited by slowest step, which is known as the rate determining step. There are different

types of reactions and wide variety of experimental techniques are used to investigate them. For reactions in solution, the most common method for investigating the rate, involves the chemical analysis for one of the products or reactants at various stages during the course of the reaction, the time corresponding to each analysis being determined accurately.

The methods devised for the determination of the reaction rate have been classified into two groups.

a) Physical methods

b) Chemical methods

Physical methods are based upon measuring a physical property of one of the species, during the course of the reaction without removing the sample or disturbing the reaction mixture. Some of the physical properties followed are -- (1) Measurement of pressure or volume (2) Electrical conductivity (3) Optical rotation (4) Dialatometry (5) Spectrophotometry (6) Potentiometry and (7) NMR Spectra.

In chemical methods the amount of reactant or product is estimated by volumetric or gravimetric methods, at different time intervals. In contrast to chemical methods, physical methods are superior, because the system is neither disturbed nor destroyed and more observations can be made in the given time. However, physical methods suffer from a limitation that they are unable to give absolute values of concentration directly and cannot be used for all types of reactions.

It is of great interest to most of the chemists in knowing the mechanism of the reactions. The mechanism of the reaction means, all individuals, or

other elementary processes involving atoms, molecules, radicals, ions and other reactive species, that take place simultaneously and consecutively in the over all reaction. The mechanism of reaction will also give a detailed picture of the activated complex[2] not only in terms of the constituent molecules but also in terms of geometry.

For the reactions in solution, the mechanism is formulated by the determination of the different kinetic parameters, the most important being the order of reaction w.r.t. the different reactants; the effect of concentration of the catalyst, if any; ionic strength, solvent, dielectric constant of the medium and temperature of the reaction rate. Determination of stoichiometry of the reaction, detection and estimation of end products, effect of substitute -nts on the rate of the reaction, are also valuable factors which throw light on the mechanism of the reaction.

The rate of reaction is determined by the mathematical expression showing the dependence of rate on the concentration of the reactants The slowest step of the reaction controls the rate of the overall reaction. The mechanism rather than the rate equation is important to theoretical chemist.

There are two main theoretical approaches which deal with problems of reaction rates.

1. The collision theory, is based largely on kinetic theory of gases and uses a mechanical model[3],
2. Transition state theory, is based largely on the thermodynomics and uses a three dimensional surface as a model[4], the vertical co-ordinate indicates energy changes.

The Collision Theory:

The collision theory is based upon the idea that, if two molecules are to combine chemically, an essential step is that, they should colloid with each other. Only those collisions are effective in which colloiding molecules have more than average energy content. However even collisions between molecules having requisite energy content, do not often result in reaction. Unfruitful collisions result, if the molecules colloid in wrong way or if the excess energy in the molecules is not associated with appropriate internal motions of the molecules. The probability of reaction occuring even in collision between activated molecules may be rather small, if the stereoelectronic requirements of the reaction are stringent. Therefore, the collision theory may be expressed as the rate of reaction equal to the number of collisions of activated molecules per unit time. The rate constant (k) at unit concentration of the reagent is given by the equation -

$$k = P.Z.e^{-Ea/RT.} \qquad (1.1)$$

where k = Rate constant

P = Probability or stearic factor

Z = Frequency of collision at unit concentration

Ea = Energy of activation

T = Absolute temperature and

R = Gas constant

The equation (1.1) is,therefore, similar to Arrhenius equation.

$$k = A\, e^{-Ea/RT} \qquad (1.2)$$

where A is frequency factor, or pre exponential factor.

Several weaknesses of the collision treatment have become appearant, because, attempts to correlate the value of 'p' with the structures and

properties of the reacting molecules have not been very successful. Secondly, it is hardly possible to interprit on this bases the abnormally high rates that are some times observed.

Therefore, transition state theory or "The theory of absolute reaction rates" is generally more useful of the two, perticularly for organic reactions.

2) The transition state theory: (Absolute rate theory)

It is a development of collision theory that requires a more exact treatment than that provided by kinetic theory. Use is made of statistical thermodynomics to derive an expression for the frequency factor, and this approach has proved to be more precise and productive than kinetic theory.

In order for any chemical change to take place, it is necessary for the atoms or molecules involved to come together to form an activated complex. This complex is regarded as being situated at the top of the energy barrier lying between the initial and final states, and the rate of reaction is controlled by the rate with which the complex travels over the top of the barrier. Thus the theory is based on an "equilibrium hypothesis". The transition state is made up of complexes that were previously either reactants or products. Equilibrium, therefore, exists between the reactants A and B and the activated complex $X^{\ddagger}$, and between the products C and D and the activated complex $X^{\ddagger}$

$$A + B \rightleftharpoons X^{\ddagger} \rightleftharpoons C + D \qquad (1.3)$$

It is proposed that, $K^{\ddagger}$ is the equilibrium constant for the equilibrium between the reactants and the activated complex, $X^{\ddagger}$, and Eyring [4] calculated the rate constant in terms of free energy change as follows :

$$K^{\pm} = e^{-\Delta G^{\pm}/RT} \qquad (1.4)$$

$$k_r = \nu K^{\pm}$$

Therefore $k_r = \nu . e^{-\Delta G^{\pm}/RT}$

$$= \frac{kT}{h} e^{-\Delta G^{\pm}/RT} \quad (\nu \simeq \frac{kT}{h}) \qquad (1.5)$$

Where $\Delta G^{\pm}$ = Free energy of activation

$K^{\pm}$ = Equilibrium constant

k_r = Rate constant

k = Boltzman's constant

h = plank's constant

T = Absolute temperature

R = Gas constant

Entropy of activation :

Entropy is the measurement of randomness of a system. If a reaction occurs with an increase in entropy, there is a disorder possible more among the products than among the reactants i.e. there are more restrictions to the motion of the reactant molecules than to the motion of the product molecules. The entropy of activation may be calculated by equation

$$\Delta S^{\pm} = \frac{\Delta H^{\pm} - \Delta G^{\pm}}{T} \qquad (1.6)$$

It is a measure of the freedom from restraint to motion among the reactants [5]. Long etal[1] amplifying a suggestion of Taft and coworkers[6] have proposed that, if the entropy of activation is negative, then the mechanism is probably bimolecular and for unimolecular reactions it is zero or positive. Empirically all known bimolecular acid catalysed reactions have negative entropy

of activation and acid catalysed unimolecular reactions have zero or positive entropy of action.

Frost and Pearson[7] pointed out that, entropy of activation of a bimolecular reaction is related to the frequency factor, A , by the equation,

$$A = \frac{kT}{h} \cdot e^{\Delta S^{\ddagger}/R}$$

or $$A = 10^{13} \cdot e^{\Delta S^{\ddagger}/R} \quad \left(\because \frac{kT}{h} \simeq 10^{13} sec^{-1} \right) \qquad (1.7)$$

or $$\Delta S^{\ddagger} = R \ln (A \times 10^{-13}).$$

According to the equation (1.7) the entropy of activation ($\Delta S^{\ddagger}$) will be negative or positive depending upon the value of "A" . If $A > 10^{13}$, $\Delta S^{\ddagger}$ will be positive and if $A < 10^{-13}$, $\Delta S^{\ddagger}$ will be negative. Reactions are classified as normal, fast and slow according to whether $\Delta S^{\ddagger}$ is equal to zero, positive and negative respectively. The magnitude of the entropy of activation gives a rough idea about the activated complex.

Temperature effect :

The rate of most reactions are very sensitive to temperature changes. Increase of temperature almost invariably increases the velocity of a chemical reaction. For reactions in a solution a rough generalisation is that, the rate is doubled by a rise in temperature of $10^{o}C$.

Arrhenius[8] first pointed out that, the variation of rate constants with temperature can be represented by an equation similar to that used for equilibrium constant, namely

$$\frac{d \ln k}{dt} = \frac{Ea}{RT^2}$$

On intigration,

$$k = A.\ e^{-Ea/RT}$$

$$\text{Log } k = \text{Log } A - \frac{Ea}{2303R}\ \frac{1}{T} \qquad (1.9)$$

Where k = Rate constant

A = Frequency factor

Ea= Energy of activation

R = Gas Constant

and T = Absolute temperature.

Arrhenius equation is tested by plotting log k verses 1/T, which should be a straight line with slope equal to $-\frac{Ea}{2.303R}$

The value of Ea, energy of activation, indicates the nature of the reaction. Ea , is also calculated by knowing the two rate constants at two different temperatures.

$$\text{Log } \frac{(k2)}{(k1)} = \frac{Ea}{2.303R} \times \frac{(T2 - T1)}{T_1 \times T_2} \qquad (1.10)$$

Ionic sgrentgh and salt effect :

Influence of ionic strength on the rates of reactions between ions were given by Brønsted Bjerrum[9], Christainsen and Scatchard. Their discussions may be considered with reference to a reaction of the general type.

$$A + B \longrightarrow X^{+} \longrightarrow \text{Product.}$$

Brønsted and Bjerrum derived an equation for the above reaction.

$$\text{Log } k_r = \text{Log } k_o + 2A\ .\ Z_A\ Z_B \qquad (1.11)$$

Where, k_r = Rate constant,

ko = Rate constant at infinite dilution.

A = Debye - Huckel constant

Z = Charge on the ion.

μ = Ionic strength.

and ionic strength= $(\mu) = \frac{1}{2} \sum m_i Z_i^2$

Where m_i = Molality of the ion.

It is seen that, the reaction rate increases for reactions between ions of like charges and decreases for reactions between ions of opposite charges.

Since the ionic strength of a solution can be changed by the addition of an inert salt, this is known as the "primary salt effect"[10]. According to the equation 1.11, a plot of log k_r against μ , is linear with slope equal to $2A$, $Z_A Z_B$. or $1.02 Z_A Z_B$. Knowing the slope value, it is very easy to predict the salt effect and also the mechanism of the reaction.

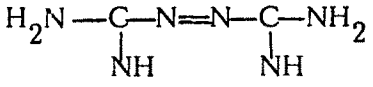
Solvent effect :

The most pronounced solvent effects are observed for reactions between ions and for those reactions in which the ions are generated from uncharged molecules. Reactions, in which charge is created, proceed most rapidly in polar solvents. The qualitative theory[11] of solvent effect put forward by Hughes, Ingold and their collaborators could be used as criteria for mechanism. It postulates that an increase in ionisation power of solvent will favour an increas in the magnitude of charge.

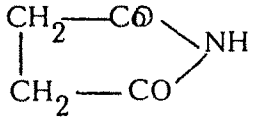
CHLORAMINE - T

Compounds, both inorganic and organic, containing one or more halogen atoms attached to a nitrogen atom are classified as haloamines. Organic chloramines are N-chloro derivatives of following group of compounds.

1. Aromatic sulfonamides, R. SO_2NH_2
2. Condensed amides from cyanamide derivatives.



3. Heterocyclic chloramines with chlorine attached to nitrogen inthe ring



4. Anilides $C_6H_5NHCOCH_3$

Organic chloramines are generally prepared by reaction of hypochlorous acid with above group of compounds. Chlorine atom bonded to nitrogen in chloramines is positive with an oxidation state +1, so all compounds containing N-Cl group liberate iodine from acidified KI solution.

$$RR'NCl + 2\ I^- + H^+ \longrightarrow RR'NH + I_2 + Cl^-$$

Fairly stable organic dichloramine-T, also reacts with acidified KI solution with evolution of iodine

$$RNCl_2 + 4\ I^- + 2H^+ \longrightarrow RNH_2 + 2I_2 + 2Cl^-$$

From analytical point of view, the most important class of chloramines is perhaps the N-chloro derivative of aromatic sulfonamides. The sodium salt of N-chloro P-toluene sulfonamide (P-CH_3- $C_6H_4NCl\,Na$) well known as, chloramine -T (CAT, RNClNa) is a very important members of this class of compounds. (R= p- CH_3-$C_6H_4SO_2$-)

It was first prepared by Chattway[12]. When toluene is allowed to react with chlorosulfonic acid, it gives ortho, and para toluene sulfonyl chlorides. The para isomer on treatment with ammonia and then with aqueous sodium hypochloride produces chloramine-T. It can be purified by recrystalisation from hot water and dried in air, 99.5% pure sample can be obtained by successive recrystallisation. It is found to be difficult to prepare anhydrous salt and preserve under laboratory conditions.[13] Hence this salt cannot be used as primary standard. Commercially available chloramine-T is about 98% pure. Contamination of dichloramine -T can be removed by repeatedly washing with carbon tetrachloride.

Solubility of chloramine-T in water is 14 gms in 100 ml at 25^{o}c, and 50 gms in 100 ml at 100^{o}c. It is soluble in alcohol and acetone. The available chlorine content in chloramine-T has been estimated which is found to be 23-26%.

Dietzel and Toufel[14] reported the decline in assay of 1.4% in twelve months in brown coloured bottle, and 5% in clear glass bottle. CAT solution exposed to sunlight is unstable. So it is protected from daylight. It is stable for nearly 4 weaks.

Nature of CAT in Aqueous solution

CAT is strong electrolyte[13] and it dissociates in aqueous solution as

$$R\text{-}NClNa \rightleftharpoons R\,NCl^{-} + Na^{+}$$

The anion then picks up a proton to form a free acid RNCHCl[15]

$$RNCl^{-} + H^{+} \rightleftharpoons RN\,HCl \qquad Ka = 2.82 \times 10^{-5}\ ,\ \text{at } 25^{o}c$$

The free acid has not been isolated but the evidence for existance has been reported[17,18]. The free acid then undergoes disproportionation, giving rise to p - toluene sulfonamide and dichloramine -T[16]

$$2R\text{-}NHCl \underset{}{\overset{Kd}{\rightleftharpoons}} R\text{-}NH_2 + RNCl_2\ .\quad Kd = 5.8 \times 10^{-2} \text{ at } 25^{o}c.$$

The dichloramine -T and free acid hydrolyse to give hypochlorous acid[19]

$$R\text{-}NCl_2 + H_2O \underset{}{\overset{Kh}{\rightleftharpoons}} R\text{-}NHCl + HOCl \qquad Kh = 8.0 \times 10^{-7} \text{ at } 25^oc.$$

$$R\text{-}NHCl + H_2O \overset{Kh}{\rightleftharpoons} R\text{-}NH_2 + HOCl \qquad Kh = 4.88 \times 10^{-8} \text{ at } 25^oc.$$

Finally HOCl ionises as

$$H_2O + HOCl \overset{Ka}{\rightleftharpoons} H_3O^+ + OCl^- \qquad Ka = 3.3 \times 10^{-8} \text{ at } 25^oc$$

CAT liberates iodine with acidified KI solution.

$$R\text{-}NClNa + 2I^- + 2H^+ \longrightarrow R\text{-}NH_2 + I_2 + Nacl.$$

Soper[19] has determined the composition of CAT solution acidified with acids other than HCl. He observed that (HOCl) is very small and is independent of (CAT). The predominant species is R-NHCl. Recently evidences for further protonation of R-NHCl have been found [20].

$$R\text{-}NHCl + H_3O^+ \rightleftharpoons R\ NH_2Cl + H_2O. \qquad K=103$$

Between pH 3 and 11 the main reactive species are R-NHCl and HOCl and in more alkaline solution [21] the dominant oxidising species are $R\text{-}NCl^-$ and OCl^-.

Chloramine -T is widely used as an oxidising agent in both acidic and alkaline media, and well reviewed by many authors [22-25].

In general CAT undergoes a two electron change in its reactions, the products being p- toluene sulfonamide ($R-NH_2$) and Na Cl The reduction potential of CAT / $R\ NH_2$ is pH dependent[26] and decreases with an increase in the pH of the medium having values of 1.14 V, 0.778 V, 0.614 V, and 0.5 V, at pH 0.65,7.0, 9.7 and 12.0 respectively. Depending on the pH of the medium, CAT furnishes different types of reaction species in solution, such as N-chloro - p - toluene sulfonamide (R-NHCl), Dichloramine-T ($R-NCl_2$),

HOCl and possibly H_2OCl^+ in acid solutions and $R-NCl^-$ and OCl^- ions in alkaline medium. Free chlorine has also been detected in acid medium in the presence of chloride ions.

Commercial chloramines (CAT) are more stable than hypochloride and they have been used as disinfectants and antiseptics in preference to hypochlorites. The germicidal action has been attributed to the labile N-Cl bond.

✻ LITERATURE SURVEY

The kinetics and mechanism of reactions of CAT have been investigated by many authors. Coull and coworkers[27], were the first to investigate the kinetics and mechanism of decomposition of H_2O_2 by CAT in presence of HCl. Then Pryde and Soper[28] investigated the chlorination of p-cresol by CAT. The kinetics of some reaction i.e. chlorination of p-cresol was investigated by Higachi and Hussain[29].

In recent years extensive study in kinetics and mechanism of oxidation of different types of compounds with CAT have been reported. It is briefly reviewed here.

I. Oxidation of Organic Compounds :

i) Hydroxy Compounds :

The oxidation of some primary alcohols and cycloalkanols have been studied by Mushran et al[30,32], with CAT in acidic medium. The mechanism proposed involves the hydrolysis of RNHCl giving rise to HOCl in slow step, which further reacts with substrate to form aldehyde. The rate law is given as

$$-\frac{d(CAT)}{dt} = k\,[CAT]\,[H^+]$$

The reactions of secondary alcohols, viz. propan-2-ol, Butan-2-ol, Pentan 2-ol, Octan-2-ol, 1,3 dichloro propan-2-ol with CAT in acetic acid medium

have been studied by Natarajan and Thiagarajan[33] in presence of strong mineral acid in aqueous medium. The rate law is suggested as

$$-\frac{d[CAT]}{dt} = k\,[CAT]\,[Alcohol]$$

The oxidation of benzyl alcohol and ethanol by CAT, CAB, and BAB, was investigated by Banerji and coworkers[34,39] . The reaction exhibits substantial primary kinetic isotope effect, thereby confirming the cleavage of C-H bond in the rate determining step. The kinetic feutures are best explained by assuming a hydride ion transfer from the alcohol to the protonated N-halogen sulfonamide

$$R-\underset{\underset{OH}{|}}{\overset{H}{\overset{|}{C}}}-H+X-\overset{+}{N}H_2--R \xrightarrow{slow} \overset{+}{R}CHOH + HX + RNH_2$$

$$\overset{+}{R}CHOH \xrightarrow{fast} R-CHO + H^+$$

The oxidation of unsaturated alcoholslike - allyl alchohol, crotyl alcohol and phenyl allyl alcohcl by CAT in HCl medium was investigated by Mahadevappa et al[40,41]. The reactions are zero order dependence in [alcohol] and first order dependence in [oxidant] and [acidity]. The reactions are shown to be catalysed by Cl^- ions also. Herlihy [42] reinvestigated the oxidation of allyl alcohol by CAT in HCl medium and obtained the rate law.

$$-\frac{d[CAT]}{dt} = K\,[H^+]\,[Cl^-]\,[CAT]\,[Alcohol]^0$$

Herlihy further reported that, the major reaction involved addition of chlorine across the olefinic bond to yield 2,3, dichloro propan-1-ol. This is contrary to the reports of Mahadevappa et al, who obtained the corresponding unsaturated aldehyde as the major product.

2.Oxidation of Phenols :

The oxidation of phenol and substituted phenols by CAT in aqueous alkaline medium have been reported by Radhakrishnmurti[43]. The reaction is found to follow first order kinetics w.r.t. both [substrate] and [CAT] and fractional order in[alkali] . The reactivity order showed that, electron releasing groups accelerate the reaction. Kinetics of oxidation of anisole and substituted anisole by CAT in aqueous acetic acid medium has been reported by Murti and Sasmal[44].

3. Oxidation of Carbohydrates

The oxidation of xylose, arabinose, mannose and galactose with CAT in highly alkaline medium have been investigated by Mushran et al[45]. The oxidation rates were found to follow the order.

Xylose > Arabinose > Galactose > Mannose and rate determining step involves interaction of three charged ions OCl^-, OH^- and anion derived from aldoses. Identical mechanism was proposed by Gupta and coworkers [46]. The oxidation of fructose and dulcitol by CAT was studied by Mandawat et al[47] in alkaline medium, which is a first order dependence in [alkali].

4. Oxidation of carbonyl compounds -

The oxidation of aliphatic aldehydes by CAT in alkaline medium was reported by Mushran et al[48]. It is first order in [CAT] [Aldehyde] and [alkali]. The reactive species are the enolate and hypochlorite ions. The oxidation at acetaldehyde by CAT in HCl, H_2SO_4 and $HClO_4$ media was studied by Mahadevappa et al[49]. It is first order in [CAT], [aldehyde] and $[H^+]$, but at higher [aldehyde] and $[H^+]$, the rate is independent of [substrate] and $[H^+]$. A mechanism involving a slow interaction between CAT and the aldehyde has been proposed.

The kinetics and mechanism of oxidation of ketones have been extensively studied by Mushran etal[50]. They have reported the oxidation of acetone, methyl ethyl ketone in alkaline medium in presence of osmium (viii) catalyst. Some authors[51] have studied the kinetics of ethyl methyl ketone and methyl isobutyl ketone by CAT in alkaline medium. Balasubramanium and Thiagarajan[52] have investigated the kinetics and mechanism of chlorination of ketones by CAT in aqueous acid medium in presence of acetic acid and N,N'- diethyl formamide. It has been observed that at high concentration of CAT and in aqueous acetic acid in presence of sodium acetate, rate law is independent of [Ketone]. Sharma and coworkers[53], have reported the kinetics and mechanism of oxidation of methyl-n-propyl, methyl isopropyl and ethyl isopropyl ketones by CAT in alkaline medium. Naidu and Mahadevappa[54] have studied the oxidation of some aliphatic ketones by CAT in HCl medium. A rate expression of the form

$$-\frac{d[CAT]}{dt} = k\,[CAT]\,[S]\,[H^+]$$

has been suggested.

Uma and Mayana[55] reported the oxidation of 4- hydroxy - 4 - methyl - 2-pentanone by CAT. It is first order in [CAT], second order in $[H^+]$ and zero order in [substrate]. The proposed oxidising species is $(H_2OCl)^+$.

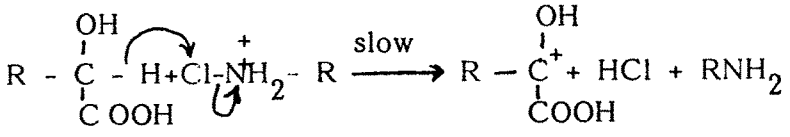
Singh and Saxena[56] studied the oxidation of 2 - keto and 3 - keto pentadioic acids by CAT in perchloric acid medium and showed that it is first order in [CAT] and [substrate], and independent of $[H^+]$

Oxidation of cyclohexanone and cyclopentatone by CAT in alkaline medium have been reported by Mushran and coworkers[57]. Singh et al[58],

investigated the oxidation of acetophenone by CAT in aqueous acetic acid medium. In this case the enol form of the ketone was supposed to interact with HOCl in the slow and rate determining step.

5. Oxidation of Hydroxy acids -

The oxidation of hydroxy acids like glycollic, lactic, 1-hydroxy butanoic and substituted mandalic acids by CAT have been studied,[59,60] in perchloric acid solution. The main product of the oxidation is the corresponding keto acid. The reactions exchibit first order dependence each of [CAT] and [hydroxy acid] and are catalysed by H^+ ions. The kinetic data can be explained on the basis of the mechanism shown below -



$$RC^+(OH)COOH \xrightarrow{Fast} R(CO)COOH + H^+$$

kinetics and oxidation of lactic acid by CAT, catalysed by Cu (II) ion has been reported by Gupta and coworkers.[61] Formation of complex between Cu(II) and p-toluensulfonamide has been suggested.

6. Oxidation of Amino acids -

The kinetics and oxidation of a number of amino acids with CAT in both acid and alkaline medium have been reported.

i) In acid medium - Only recently some generalisations have been drawn about the mechanistic aspects by Gowda and coworkers.[62] Variable stoichiometries of 2,4, & 6 electron changes have been noted with the formation of aldehydes, nitriles or cyanates as products of oxidation. In general, a first order dependence of the rate in [CAT] is noticeable, the orders are

found to be different in [substrate] and $[H^+]$.

The oxidation of alanine, phenyl alanine, leucine, serine, lysine, glutamine and histidine by CAT in HCl medium has been reported by Mahadevappa et all.[63-65] They proposed the rate law as -

$$- d\frac{[CAT]}{dt} = k\,[CAT]\,[H^+]$$

But Gowda and coworkers[66] proposed that, a first order dependence in [amino acid] is found in the oxidation of arginine, valine and glycine in presence of HCl, and leucine, serine, glutamine and glutamic acid in perchloric acid. In the case of threonine an identical rate law is obtained in 3 acid media viz. HCl, $HClO_4$ and H_2SO_4.

$$\text{Rate} = \frac{k\,[CAT]\,[S]^x}{[H^+]}$$

where x is a fraction (~ 0.60)

The kinetics of oxidation of alanine and phenyl alanine in HCl medium by CAT are found to obey identical kinetics by Mahadevappa[67]. At low acid concentrations the rate is first order in [oxidant], but fractional order in $[H^+]$ and $[Cl^-]$. At $[H^+] > 0.2 \times 10^{-3}$, the rate is first order in [CAT] and fractional in [substrate].

Ramchandran et al[68] have recently reinvestigated the oxidation of threonine by CAT in perchloric acid solution, both in the presence and absence of chloride ions. The rate law observed by Ramchandran et al is completely different from the earlier work of Mahadevappa[69]

$$\frac{- d\,[CAT]}{dt} = \frac{k_1\,[\text{Threonine}]\,[CAT]^2}{[H^+]\,[TSA]} + k_2\,[Cl^-][CAT]$$

The authors have pointed out that assumption of neutral amino acid ($RCH(NH_2)COOH$) of the reactive species is an error. In solution of $PH<1+pK_1$ the existance of neutral amino acid is not plausible. The more probable reactive species is the zwitter ionic form of the amino acid. The second order dependence in [CAT] leads to the postulation of $RNCl_2$ as the reactive oxidising species.

Kinetics of oxidation of (Gly), (Val), (Ser), (Thr), (Arg), (Hist), and (Gln), amino acids by CAT has been investigated in low acid medium (pH 2.5) by Timme Gowda and Sherigar.[70] The rate follows first order kinetics in [CAT] and zero order each in [amino acid] and $[H^+]$. Addition of p. tolune sulfonamide has no effect on the rate and $RNCl^-$ is the predominant and reactive species.

The kinetics of oxidative decarboxylation of glycine and L-aspartic acid by CAT has been investigated by Timme Gowda and Vijayalkshmi,[71] both in the absence and presence of Cl^- ion in perchloric acid medium. In the absence of Cl^-ion, the rate followed second order kinetics in [CAT], first order in [substrate], inverse first order in $[H^+]$ with both the amino acids. Chloride ion is found to enhance the rate of oxidation and affect the kinetics. In the presence of chloride, the rate followed first order in [CAT], in both cases. But the rate was fractional and zero order in [substrate], with glycine and aspartic acid, respectively. The kinetic order in $[H^+]$, was inverse fractional order with glycine and fractional order with aspartic acid. The effect of chloride was more pronounced with aspartic acid.

II) In alkaline medium:-

The work of Mushran etal,[72,73] and Mahadevappa & coworkers[62,74]

has shown some common features for the oxidation of - glycine, valine, leucine alanine, phenyl alanine, serine, proline, arginine, histidine,and threonine. A four electron stoichiometry was noticed with a commen rate law

$$\text{Rate} = k\,[CAT]\,[S]\,[OH^-]^x$$

where x varies from 0.67 to unity. Only in the case of threonine, the rate is found to independent of $[OH^-]$. Addition of TSA and Cl^- ion has no effict on the rate.

In alkaline solutions of CAT, the possible species are $RNCl^-$ and OCl^- which would be transformed into more reactive oxidising species, RNHCl and HOCl through reactions (1),(2), and (3).

$$RNCl^- + H_2O \rightleftharpoons RNHCl + OH^- \qquad 1$$

$$RNCl^- + H_2O \rightleftharpoons RNH_2 + OCl^- \qquad 2$$

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^- \qquad 3$$

$$RNHCl + S^- \longrightarrow RNH_2 + S'' \qquad 4 \text{ (slow)}$$

$$S'' + RNHCl \longrightarrow \text{Products} \qquad 5 \text{ (slow)}$$

Kinetics of oxidation of arginine monohydrochloride by CAT in alkaline medium has been investigated by Parihar and coworkers.[75] The kinetics are found to be first order in both [CAT] and [arginine]. The rate is inversely dependent in $[OH^-]$ and has negligible salt effect. The oxidation of aspartic acid and glutamic acid by CAT in alkaline medium has been reported by Mushran et al.[76] Kinetics of oxidation of L-histidine by CAT in alkaline medium is reported by Gupta.[77] The rate of reaction is found to be decreasing with increase in pH. Change in ionic strength has no effect on rate of reaction. The suggested mechanism involves dipole - dipole interaction between histidine and CAT.

The oxidation of glutamic acid by CAT in alkaline medium with or without catalytic action of Cu (II) ion have been reported by Varma and Yadav[78]. The order w.r.t. [substrate] and [CAT] is one in each case. The rate is independent of $[OH^-]$, when $[NaOH] > 4.8 \times 10^{-2}$ M. Yadav and co-workers[79] have reported the kinetics of oxidation of aspartic acid both uncatalysed and Hg (II) catalysed by CAT in alkaline medium. The order w.r.t. [CAT] and [substrate] is one each, but inverse first order in $[OH^-]$.

7. Oxidation of Oximes, hydrazines and other compounds-

The oxidation of cyclohexanone oxime by CAT in H_2SO_4 resulted in the formation of cyclohexanone.[80] The reaction is zero order in [CAT] and first order in [substrate]. An increase in $|H^+|$, increases the rate but a limiting rate is obtained at $[H^+] \simeq 0.02$ M. RNHCl has been proposed as the reactive oxidising species.

The oxidation of substituted benzoyl hydrazines[81] by CAT in the pH range of 8.9 to 11.5 exhibits reaction constant = + 0.80. The reaction is first order in [CAT] and [substrate]. It is independent of pH. The kinetics of oxidation of acetic, propionic buteric and isobuteric acid hydrazides by CAT in alkaline medium has been carried out by Swami[108]. The reaction is first order, each in [CAT] and [Hydrazide] and is independent of |alkali|. Similarly the kinetics of oxidation of "valeric acid" and "isovaleric acid hydrazides" by CAT in alkaline medium was reported by Telwekar.[109] Mali[110] studied the kinetics of oxidation of salicylic acid and o-chloro benzoic acid hydrazides by CAT at pH 7.4 using buffer solution. Both proposed the same mechanism. of Swami.

The oxidation of substituted anilines[82] by CAT in buffered 1:1 (v/v) ethanol-water medium at pH 7.4 leads to the formation of N-chloroanilines. The reaction is first order in [CAT] and Michaelis-- Menten type kinetics have been observed w.r.t. [substrate].

Antelo etal[84] have studied the effect of pH in the reaction of diethanolamine with CAT. The oxidation rate of diethanol amine with CAT was studied at pH range 8 to 13. It reaches maximum at pH 10.8 and decreases to a constant rate.

Kinetics of chlorination of toluene and some substituted toluenes by CAT, in aqueous acetic acid, in presence of perchloric acid have been reported by Murti and coworkers.[85] Nuclear halogenation has observed with m - xylene, while nuclear and side chain halogenation for p - xylene and o - xylene, and sice chain halogenation for toluene and m - chlorotoluene. Added acetate ion inhibits the reaction.

8. Oxidation of sulphur compounds -

The oxidation of sulfide group, generally involves formation of a halosulfonium ion in the rate determining step. The main products of the oxidation are corresponding to sulfoxide and / or sulfimides, depending on the reaction conditions and nature of the reactants. In certain cases, the sulfoxides are further oxidised to the corresponding sulfones. A reaction constant of - 0.94 supports the formation of a chlorosulfonium ion in the oxidation of aryl methyl sulfides by CAT in acetic acid solution.[86]

The oxidation of arylthio–acetic acid by CAT has been reported by Shrinivasan and coworkers.[87] In moderately alkaline solution, the reactive species were found to be both RNHCl and hypochlorite ion. Formation of

halosulfonium ion in the rate determining step has been proposed.

The oxidation of methionine, is best considered along with the other sulfur containing compounds as it behaves like a sulphide and the oxidation product is the corresponding sulphone.[88,89] The oxidation of methi-onine by CAT in acid solution is independent of [substrate] and is first order each in [oxidant] and $[H^+]$. Methionine racts with $(H_2OCl)^+$ in the fast step to yield a Cl^+ ion which ultimately yields the corresponding sulfone.

The oxidation of methionine by CAT[89] in alkaline medium was first order in [CAT] and [methionine] and inverse fractional order in [alkali].

The oxidation of dimethyl sulfoxide (DMSO) by CAT has been studied in HCl and perchloric acid mediums by Mahadevappa and coworkers.[90,91] Dimethyl sulfone has been identified as the main product in all these reactions The oxidation in HCl media is first order in [CAT] and $[H^+]$, fractional order in [DMSO] and reactions are catalysed in Cl^- ions. The oxidation of DMSO by CAT in perchloric acid solution is first order each in [DMSO],[CAT] and $[H^+]$. The reactive oxidising species is $(RNH_2Cl)^+$.

The oxidation of diphenyl sulfoxide[92] by CAT in HCl and $HClO_4$ solutions is first order in [CAT], and $[H^+]$ and is independent of [substrate]. Cl^- ions catalyse the reaction. The oxidation of alkyl aryl sulfoxides by CAT has been studied by Ganapathi and Jayagandhi.[93] In HCl medium the rate is independent of [substrate], first order in [CAT] and fractional order in $[H^+]$, and $[\ Cl^-\ ]$. (HOCl) and $(H_2OCl)^+$ has been postulated as the reactive species which react with sulfoxide in a fast step to give the corresponding sulfone. In the oxidation of some o-substituted phenyl methyl sulfoxides by CAT[93] in neutral medium, both RNHCl and $RNCl_2$ are the reactive species.

9. Osmium (VIII) catalysed oxidations by CAT in alkaline solutions of α-hydroxy acids[94], aldehydes[95], ketones,[96,97] 1,2, diols[98] benzaldehydes[99], cycloalkanol, butan- 1,3 and 1,4 diols[100] are governed by the rate law

$$-\frac{d[CAT]}{dt} = \frac{k[CAT][Os\ (VIII)]}{[OH^+]}$$

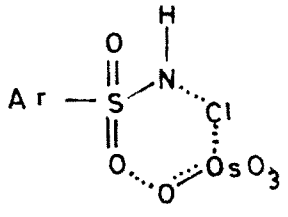
The following scheme accounts for the mechanism proposed

$$RNCl^- + H_2O \rightleftharpoons RNHCl + OH^-$$

$$RNHCl + Os\ (VIII) \rightleftharpoons \underset{(A)}{Complex}$$

$$A + Substrate \longrightarrow RNH_2 + Products.$$

The complex (A) has been assigned the following structure [94-97]



Complex A

II) Oxidation of Inorganic compounds.

1) Hypophosphorus acid -

The kinetics of oxidation of H_3PO_2 acid by CAT in H_3PO_4 acid medium follows the rate law,[101]

$$-\frac{d[CAT]}{dt} = \frac{k[CAT][H_3PO_2][H^+]}{[H^+] + k}$$

where k is the dissociation constant of H_3PO_2. The reaction is catalysed by Cl^- ion. The reactive species are RNHCl and H_3PO_2

2) Arsenic (III): The rate law for the oxidation of As (III) by CAT in alkaline solution[102] was given by

$$-\frac{d[CAT]}{dt} = k\,[CAT]\,[As\ (III)]\,[OH^-]$$

3) Tellurium (IV) The oxidation of tellurium (IV) by CAT[103] occurs only in the presence of Cl^- ions. The reaction shows a first order dependence in [Te(IV)], [CAT], $[H^+]$ and $[Cl^-]$ ions.

4) Thio cyanate ion - The oxidation of thiocyanate ions[104] by CAT in alkaline medium shows first order dependence in [CAT], fractional order in [Substrate] and is independent of [alkali]. The products are sulfate and cyanide ions. The reaction is first order in [CAT] and [thiocyanate ions] but zero order in $[H^+]$ in perchloric acid solution.

5) Hydroxyl amine - The oxidation of $NH_2OH.HCl$ by CAT[83] in HCl and $HClO_4$ media is first order in [CAT] and [substrate] and inverse order in $[H^+]$. Chloride ion catalyses the reaction.

6) Selenium (IV) - The oxidation of Se(IV) by CAT[105] is extreemly slow in H_2SO_4 and $HClO_4$ media but is quite rapid in HCl medium. The reaction is first order in [CAT]. The order in [Se(IV)] varies between one and two. The rate decreases with increase in $[H^+]$ but to a limiting value. Further increase in acidity has no effect.

7) Cyanide ion - The oxidation of cyanide ion by CAT[106] in alkaline solution was inhibited by the addition of alkali between 0.01 and 0.035 M, but at higher alkali concentration, the rate is independent of $[OH^-]$. The reaction is first order in [CAT] and $[CN^-]$. The effect of ionic strength is positive.

8. Permanganate ion :- An interesting reaction between acid permanganate and CAT in aqueous H_2SO_4 solution has been reported by Vivekanandan et al.[107] When $KMnO_4$ is in excess, the products obtained are PTS,N_2 and Cl_2. Mn (VII) is reduced to Mn(V). The reaction proceeds by an induction period. The reaction is first order in [CAT], [MnO_4] and [H^+].

Thus CAT is a versatile oxidising agent which reacts with diverse functional groups under different reaction conditions.

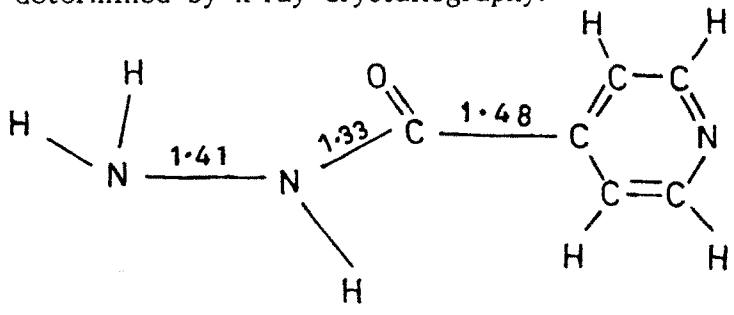
PRESENT STUDY AND ITS OBJECT.

The chemistry of hydrazides is very important and interesting branch of organic chemistry due to the fact that many hydrazides are found to have physiological activities. They have been extensively studied, since, the discovery of 'isonicotinic acid hydrazide' as a strong anti-tuberculostatic agent.[111] Many derivatives of this compound have been synthesised and tested for antibacterial activity[112,113] Diacyl hydrazine group in certain derivatives of hydrazides has been supposed to be biologically active.[114] Carboxylic acid 1,2 diaryl hydrazides have been reported to possess antiinflamatory properties.[115] Isoxazole carboxylic acid hydrazides[116] are active against leprosy and phenothiazine carboxylic acid hydrazide[117] has been reported to have anticonvulsive action. Dihydrazides have recently been introduced as antihelminties.[118] Maleic acid hydrazide is used to regulate and inhibit the growth of the plants.[119] Apart from physiological activity of hydrazides, some of them are important starting materials and intermediates in the synthesis of certain amines, aldehydes and heterocylic compounds.

The hydrazides are used in heat and corrosive stabilisation of cellulose and its derivatives.[120] These are also used as antioxidants for polyolefins and polyurethanes, which are otherwise oxidised in presence of copper. An incorporation of hydrazides[121] has improved the applicability in plastics and cable insulations. The small amount of hydrazides is useful in sensitising electrophotographic layers made up of polyvinyl carbazole.[122] Dihydrazides can be used in cigarette filters for the selective removal of aldehydes from tobacco smoke.

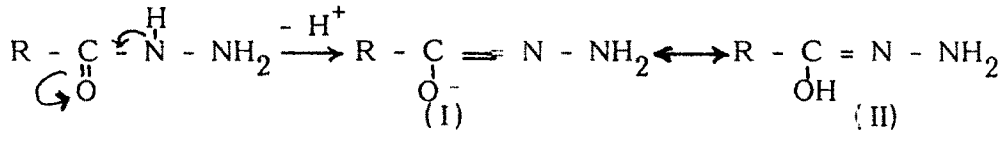
The hydrazides are the derivatives of carboxylic acids as well as hydrazine. The preffered nomenclature is to describe any hydrazide as

carboxylic acid hydrazide. This nomenclature is also used in chemical abstract. The nitrogen atoms of the hydrazides are designated as 1 and 2 or α & β or N &N^1. The first nitrogen of each pair denotes the nitrogen, where the acyl group is inserted.[123] The structure of isonicotinic acid hydrazide has been determined by x-ray crystallography.[124]



The N-N bond length is always between 1.39 and 1.42A^o, which is shorter than, in hydrazine which is in between 1.46 and 1.47A^o. This is due to the formal charge effect and the electron attracting acyl group, which reduces the repusion between the loan pair of nitrogen atoms. The C-N bond length is 1. 33 A^o, this bond, therefore, must aquire roughly 50 % double bond charecter. The two hydrogen atoms are in the same plane.

The hydrazide group is stabilised due to the resonance between amide form (I) and the tautomeric enol form (II), by the shift of a hydrogen atom from nitrogen to the oxygen.



The kinetics of oxidation of hydrazides has been investigated by many workers. Krishna Rao and his coworkers[125] reported the kinetics of oxidation of nicotinoyl and isonicotinoyl hydrazines by iodine in aqeous HCl medium. Further they[126] investigated the oxidation of same hydrazides by hexacyanoferrate (III) in pH 7.0 - 8.0. The second order rate dependence

on hexacyanoferrate (III) was explained by the following rate law.

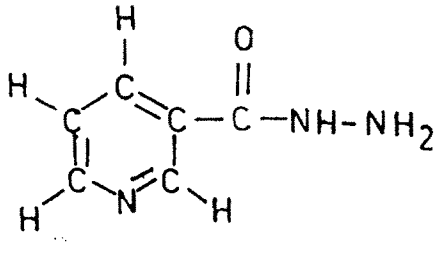
$$\frac{d\,[Fe\,(CN)_6]^{3-}}{dt} = \frac{2k\,k_2\,[Fe\,(CN)_6^{3-}]^2\,[substrate]}{2 + k_1\,[Fe\,(CN)_6^{4-}] - k_1[substrate]}$$

Hogale et al[127] reported the Ag(I) catalysed oxidation of nicotinic and isonicotinic acid hydrazides by peroxydisulfate. The rate was first order in $[S_2O_8^{2-}]$ and [Ag(I)], and independent of [substrate]. The oxidation products of hydrazides were found to be corresponding acids and nitrogen.

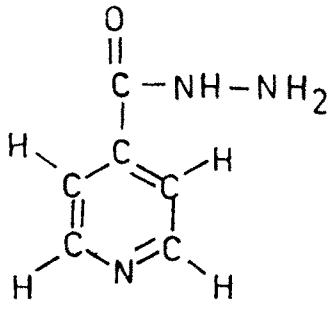
In the light of the above discussion and previous survey, the kinetics of oxidation of nicotinic and isonicotinic acid hydrazides by chloramine-T in alkaline medium has been undertaken. It is desired to study the effect of structure on the rate of oxidation of these hydrazides, as one of them is meta - isomer and other is para - isomer. They are -

1) Nicotinic acid hydrazide and

2) Isonicotinic acid hydrazide



(1)



(2)