CHAPTER-I

GENERAL INTRODUCTION

AND

LITERATURE SURVEY

(A) INTRODUCTION

Chemical kinetics is concerned with the quantitative study of the rates of chemical reactions and of the factors upon which they depend.[1] At present the study of reaction rate is a very widely practical speciality in organic chemistry, since, it is a most powerful tool for investigation of reaction mechanism.[2] The study of chemical kinetics is of great practical interest in both laboratory and industry. In practice it was found that the time required to complete a particular reaction depends on the reaction conditions used. Some reactions require years for their completion, but there are some reactions that are completed within a fractions of second like hazardus explosions. Therefore it is necessary to understand the factors that control the reactions before the reaction becomes useful on any scale.

The chemistry of carbonium ions, carbanions, carbenes and free radicals constitutes a major part of organic chemistry. Among these unstable intermediates, only a minute fractions have been isolated, observed and characterised and such isolations were made possible by mechanistic studies.[3]

The conversion of starting material to products, constitutes an organic reaction. One of the things that particularly should be known is 'how far the reaction go over towards the products ?' For this purpose mechanism of the reaction is studied. The mechanism of the reaction is the step by step description of the path of each atom from start to end. In ideal case mechanism of the reaction can be considered as a hypothetical motion picture of the behaviour of the participating atoms. Such a

picture would presumably begin at sometime before the reacting species approach each other, then go on to record the continuous paths of the atoms during the reaction, and come to an end after the products have emerged.[4]

To measure the rates of reactions a wide variety of experimental techniques can be used. They involve (1) ELECTRICAL CONDUCTIVITY : in which concentration of the substrate is measured at certain fixed time intervals because it has a property known as conductivity, (2) OPTICAL ROTATION : in which optical rotation of an optically active compound is measured at certain fixed time intervals, (3) MEASUREMENT OF PRESSURE OR VOLUME OF GAS : in which reaction is followed either by measuring the volume of gas formed at constant pressure or the pressure produced by the gas at constant volume, (4) REFRACTOMETRY : in which refractive index is measured, (5) DILATOMETRY : here the change in volume produced by reaction is measured as a function of time, (6) SPECTROPHOTOMETRY : here the measurement of intensity of light transmitted by a solution at various wave length is counted and (7) IODO-MEKTRY : In which iodometric titration is used to follow the rate of reaction.[59] This iodometric technique is chosen for the practical purpose to follow the rate of oxidation of dihydrazides by chloramamine-T.

The rate of reaction which may also be called as its velocity or speed may be expressed in terms of the concentration of the reactant or the product of the reaction. The rate of reaction will change as the structures of one or more of the reactants are subjected to a given change. The products of the reaction depend upon the course of the

reaction adopted, which in turn is controlled by the reaction rates. Therefore kinetic study is quite helpful in predicting the conditions that are favourable and necessary for commercial production of a desired compound. The least stable high energy species through which the reactants have to pass during the course of reaction is generally referred to as activated complex or transition state.[5b]

The activated complex is regarded as being situated at the top of an energy barrier lying between the initial and final states. The rate of reaction is controlled by the rate with which the complex travels over the top of the energy barrier.

Experimentally, the measurement of the reaction rates consists of the investigation of the rate at which starting material disappear and/or products appear at a particular (constant) reaction conditions and seeking to relate this to the concentration of one, or all, of the reactants. It is a well established fact that a chemical reaction takes place at a certain rate under a particular set of conditions such as temperature, pressure, concentration and presence or absence of catalyst.[1] All the reactions under similar conditions do not proceed at same rate. The study of reaction rates, which form the field of chemical kinetics, with the help of which one can increase or decrease the rate of reaction by changing the conditions that are used.

The rate of a reaction is determined from the mathematical expression showing the dependance of the rate on the concentration of the reactants. In some reactions the change occurs directly, which may be represented by an overall stoichiometric equation. However, in complex

substances undergo a series of stepwise changes. Then the overall mechanism is made up of contributions from all such reactions and the overall mechanism is visualised as follows :

$$2A + B \longrightarrow C + D$$

This may takes place as follows :

$A + B$	$\rightleftharpoons$	AB	Step-I
$A + AB$	$\rightleftharpoons$	A_2B	Step-II
A_2B	$\rightleftharpoons$	$AB + C$	Step-III
AB	$\rightleftharpoons$	D	Step-IV
$2A + B$	$\rightleftharpoons$	$C + D$	

The slowest step amongst these, controls the rate of overall reaction and it may be determined from the rate equation. The mechanisms of the reaction as well as the rate equation is important to theorotical chemists.

In kinetics the major effort is devoted to explain why certain reactions occur faster than others on the basis of the rate of reaction. An empirical expression for the rate constant was developed by Arrhenius[6] and the relation between the properties of the molecule and the magnitude of the rate constant was given by 'collision' and 'transition state' theories.

Collision Theory :

This theory is based on the fact that if two molecules are to combine chemically, an essential step is that they should colloid with each other.

Rate of reaction is directly proportional to the number of colliding molecules per litre per sec. The number of collisions is proportional to the product of the concentrations of the reacting molecules. A simple collision between

two molecules, does not necessarily result in a product formation. Only those collisions are effective in which colliding molecules have more than average energy content.[7] Therefore, a minimum energy called the activation energy (Ea) is needed for the reaction to occur. There will be no reaction if the energy of the molecules in a collision is less than energy of activation. The rate constant according to collision theory can be expressed by equation (1.1).

$$k = Ze^{-Ea/RT} \qquad \ldots (1.1)$$

where, k is the rate constant, T is the absolute temperature, R is the gas constant, Ea is the energy of activation and Z is the number of collisions per unit time. However, some molecules with the required amount of energy could not result in fruitful collisions. Therefore equation (1.1) requirs some modification. The molecules collide in a certain manner in relation to each other to result in product formation. To account this the probability factor 'P' was introduced. The overall equation for the rate constant becomes,

$$k = PZe^{-Ea/RT} \qquad \ldots (1.2)$$

This theory postulates only fruitful collisions that results in reactions. It offers no information about the orientation of molecules since for the reaction to take place orientation of the molecules in collision may be necessary. These shortcomings observed in this Arrhenius theory further leads to the development of the 'transition state theory which is more useful in predicting the rates and mechanism of reactions.

Transition State Theory :

According to this theory, molecules undergoing reaction must form an activated complex in equillibrium with the reactants and then pass into

the products.[8] Considering the reaction between the species A and B, we may designate the activated complex as $[AB^{++}]$ and represent the reaction as,

$$A + B \rightleftharpoons [\ AB^{++}\ ] \longrightarrow \text{Products} \qquad \text{... (1.3)}$$

Activated Complex

$$k_r = \frac{\text{rate}}{[A]\ [B]} \qquad \text{... (1.4)}$$

should be proportional to K^{++} (equilibrium constant). Furthermore, using the principles of statistical mechanism it is possible to show that constant of proportionality[9] is close to kT/h where, k is the Boltzmann's constant, T is the absolute temperature and h is the Plank's constant.

The transition state theory further defines the following quantities, analogous to the corresponding thermodynamic functions.

The free energy of activation, $\triangle F^{++}$

$$\triangle F^{++} = - RT \ln K^{++} = - RT \ln [\ krh/kT\ ] \qquad \text{... (1.5)}$$

The enthalpy of activation, ΔH^{++}

$$\Delta H^{++} = -R \frac{d(\ln K^{++})}{d(1/T)} = -R \left[\frac{d(\ln kr)}{d(1/T)} + T \right] \qquad \text{... (1.6)}$$

The entropy of activation, ΔS^{++}

$$\Delta S^{++} = \frac{\Delta H^{++} - \Delta F^{++}}{T} = R \left| \frac{d(\ln kr)}{dT} + \ln \frac{krh}{kT} - 1 \right| \qquad \text{... (1.7)}$$

Entropy of Activation :

Entropy is a measure of the randomness of a system. Since all systems tend to attain a state of randomness or chaos the increase in entropy i.e. a positive value for entropy, means much disorder and negative

value of entropy will imply loss of freedom and a constrained system. Processes which accompany the loss of freedom of atoms in the transition state are less favourable. The entropy of activation is calculated by equation (1.7).

Long et.al.[10] amplifying a suggestion of Taft[11] have proposed the use of ΔS^{++} as a criteria to understand the mechanism of hydrolysis reactions. The reactions are classified as a unimolecular (A-1,SN') or bimolecular (A-2,SN^2). A-1 type of mechanism accounts for positive value of ΔS^{++} and does not involve participation of water molecule in rate determining step. A-2 type mechanism accounts for negative value of ΔS^{++} with the participation of water molecule in the transition state[11]. Both A-1 and A-2 processes involve specific hydronium ion catalysis and may be represented as follows.[12]

$$S + H^+ \overset{\text{fast}}{\rightleftharpoons} SH^+$$

$$SH^+ \xrightarrow{\text{slow}} \text{Products (A-1)} \qquad \ldots(1.8)$$

$$S + H^+ \overset{\text{fast}}{\rightleftharpoons} SH^+$$

$$SH^+ \xrightarrow[H_2O]{\text{slow}} [\, X^+ \,] \overset{\text{fast}}{\rightleftharpoons} \text{Products (A-2)} \qquad \ldots (1.9)$$

Activated complex

It seems quite reasonable that the loss of transitional and rotational freedom of water molecule associated with the bimolecular process, should lead to lower the entropy of activation relative to unimolecular processes. It can be said that if the entropy of activation is negative then the mechanism is probably bimolecular. Empirically all known bimolecular, specifically acid catalysed reactions have negative entropies of activation and all known

unimolecular acid catalysed reactions have entropies of activation near zero or have positive values.[1,13]

Solvent Effect[14]

When a chemical reaction takes place in the solution the solvent used is generally in great excess so that, its concentration cannot change appreciably, during the course of reaction and rate expression does not involve it. In some cases the stoichiometric equation for the reaction does not involve the solvent and it just provides the physical environment for the reaction. But in some cases it is believed that the solvent enters into the chemical change and cannot be regarded at the end. Thus it gets involved in the rate expression.[1] Thus the solvent can affect both the rates and mechanisms of reactions. Sometimes the solvent alters the rate without influencing the mechanism, but it would be a co-incidence if the solvent changed the mechanism without changing the rate. A solvent can change a rate without changing the mechanism by changing the force between reacting particles and hence altering the randomness with which they approach each other. Such a phenomenon is illustrated by the effect of dielectric constant on electrostatic forces among reacting particles.

A qualitative theory of solvent effects on reactivity represented by Hughes and Ingold[13,15]. This theory accounts the changes in magnitude of charge and in distribution of charge that occur between reactant and transition state. The rules are as follows (a)solvation will increase with the magnitude of the charge, (b) solvation will decrease with increasing dispersal of a given charge, (c) the decrease in solvation due to the dispersal of a charge will be less than that due to its destruction.

Ionic Strength Effect

The reaction between two ionic species proceeds through transition state complex which is in equillibrium with reactants. The equillibrium properties of such reactions can be greatly affected by the other ionic species which are present in addition to the reactants. The variables that determine the effect of ion on the equillibrium is the ionic strength (μ) defined by equation

$$\mu = 1/2 \sum m_i Z_i^2 \qquad \ldots (1.10)$$

where, m_i = molarity and Z_i = charge

The effect of electrostatic interaction of ionic species can be successfully treated by activity rate theory which was developed by Bronsted, Bjerrum and Debye-Huckel[16].

The theoritical rates can be calculated by applying second empirical equation of Debye-Huckel and can be compared with observed rates as has been done for the hydrolysis of propionamide.[17]

The Salt Effect

Bronsted,[18] Bjerrum[19] and Christiansen have applied the Debye-Huckel theory to the influence of neutral salts upon the velocity of reactions in solution. Salt effects are of two kinds. In the first case the activities of the reactants, whether ion or polar molecules, may be altered by added electrolyte. This is primary salt effect. In the second case the effective concentration of a reactant ion coming from a weak electrolyte may be decreased by the decreased ionisation of the electrolyte due to added salt. This is the secondary salt effect. The catalytic effect of acetic acid upon the inversion of cane sugar is decreased in presence of alkali acetates. In this

case the activity of the hydrogen ion, reactant is increased by the added salt, but the effective concentration of ion is so reduced by the common ion effect that the inversion rate constant may be decreased as much as 40 to 50% at ordinary concentrations of acid and added salt.

SUBSTITUTION EFFECT : This effect was studied by Hughes and Ingold[13] on the hydrolysis of alkyl halides who found changes in reaction rate as the structure of compound undergoing substitution is changed by introduction of groups of known polar characters, as a criteria of mechanism. By successive introduction of alkyl groups in place of hydrogen atoms of methyl bromide, the electron density on the carbon atom can be increased. The three methyl groups attached to α -carbon atom in tertiary butyl bromide make the hydrolysis of tertiary carbon to bromide bond feasible without the help of nucleophilic reagent. This conversion of bimolecular to unimolecular mechanism involves difference in the mechanism of hydrolysis of methyl bromide and tertiary butyl bromide.

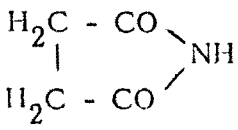
EFFECT OF CATALYSIS : It is of two types. One is acid-base catalysis and other lynonium-ion catalysis. Acid base catalysis is generally seen in reactions of type hydrolysis, saponification, oxidation, synthesis of esters, amides etc. Sometimes strongest acid that can exist in large concentration in a given solvent i.e. the 'Lyonium ion'. This is the most effective acid catalyst for the reactions that are carried out in solvents. Thus almost half the organic reactions are devoted to reactions that are catalysed by acids, bases or by both.

(B) CHLORAMINE-T (A REAGENT)

Chloramines are compounds in which one or more chlorine atoms are attached to nitrogen atom of sulfonamides, Organic chloramines are N-chloro derivatives of following group of compounds.

1) Suphonamides RSO_2NH_2

2) Heterocyclic chloramines in which chlorine is attached to the nitrogen in the ring



3) Condensed amines forms cynamide derivatives

$H_2NC(NH)N : NC(NH)NH_2$

4) Anilides $C_6H_5NHCOCH_3$

Generally organic chloramines are prepared by reaction of hypochlorus acid with above group of compounds. Commercial chloramines such as chloramine-T and chloramine-B are used as antiseptics and disinfectant reagents in tooth paste, mouth washes soaps and in treatment of infected wounds.[20]

Chlorine atom bounded to nitrogen in chloramines is positive[21] with an oxidation state + 1. So all compounds containing N-Cl group liberate iodine in acidified potassium iodide solution. The overall reaction for monochloramines can be written as :

$$RR'N\text{-}Cl + 2\,I^- + H^+ \longrightarrow RR'NH + I_2 + Cl^-$$

Fairly stable organic dichloramine-T (DCAT) also react with acidified potassium iodide solution with evolution of iodine.

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

From the analytical point of view, the most important class of chloramines are perhaps the N-chloro derivatives of aromatic sulphonamides.

Chloramine-T [$p\text{-}CH_3C_6H_4SO_2NClNa.3H_2O$]

The sodium salt of N-chloro p-toluene sulphonamide known as chloramine-T was first prepared by Chattway.[22] When toluene is allwed to react with chloro-sulphonic acid it gives ortho and para-toluene sulphonyl chloride. The para isomer on treatment with ammonia and then with aqueous sodium hypcchlorite solution produces chloramine-T. It can be purified by recrystalisation from hot water and dried in air. Chloramine-T sample with maximum purity of 99.5% can be obtained by successive recrystallization. The 0.5% impurity is due to moisture. It is found to be difficult to prepare anhydrus salt and preserve this under laboratory conditions.[23] Hence this salt cannot be used as a primary standard. Commercially available chloramine-T has about 98% purity. By successive washing with carbon tetrachloride contamination of dichloramine-T can be removed from it.

Solubility of chloramine-T in water is 14 gms in 100 ml at 25^o and 50 gms in 100 ml at 100^o. It is soluble in alcohol and acetone but it decomposes on standing. The available chlorine content in commercial chloramine-T has been estimated to be 23 to 26%.

There are conflicting reports on the stability of chloramine-T in solid state and in solution[24]. Dietzel and Toufel[25] reported the decline in assay of 1.4% in 12 moths in brown coloured bottle and 5% in clear glass bottle. Solution of chloramine-T exposed to direct sunlight is unstable and if it is protected from day light it is stable for nearly four weeks.

Chloramine-T is a strong electrolyte and it dissociates in aqueous solution as

$$RNClNa \rightleftharpoons RNCl^- + Na^+$$

where R = p-$CH_3C_6H_4SO_2^-$. The anion then picks up a proton to form the free acid, RNHCl.

$$RNCl^- + H^+ \rightleftharpoons RNHCl$$

The free acid has not been isolated but the evidence for existance has been reported.[23,24] The free acid then gives rise to p-toluene sulphonamide and dichloramine-T, $RNCl_2$.[26]

$$2\ RNHCl \rightleftharpoons RNH_2 + RNCl_2$$

The dichloramine-T and the free acid then hydrolyse to give hypochlorus acid.

$$RNCl_2 + H_2O \rightleftharpoons RNHCl + HOCl$$

$$RNHCl + H_2O \rightleftharpoons RNH_2 + HOCl$$

Finally HOCl ionises as

$$HOCl \rightleftharpoons H^+ + OCl^-$$

Chloramine-T liberates iodine with acidified potassium iodide solution.

$$RNClNa + 2\ I^- + 2\ H^+ \longrightarrow RNH_2 + I_2 + NaCl$$

Oxidising properties of chloramine-T are well reviewed by many authors.[27,31] It was introduced as an analytical reagent by Null[32] and then several workers attracted towards the use of chloramine-T in analytical chemistry. The behaviour of chloramine-T as titrimetric reagent have been critically examined by Bishop and Jennings.[23,33]

Chloramine-T has been widely used as an oxidising agent in acid medium as well as in alkaline medium. Chloramine-T solution can be standardised by adding potassium iodide in presence of 2N-sulphuric acid solution and titrating the liberated iodine against the standard sodium-thiosulphate solution. A large number of organic and inorganic reducing agents have been estimated using chloramine-T as an oxidant by volumetric, potentiometric and amperometric methods. The redox potential of 0.1 M chloramine-T solution saturated with p-toluene sulphonamide at different pH have been reported by Murthy and Rao.[34] The values were found to be 1.139, 0.778 and 0.614 V at pH 0.65, 7.00 and 9.70 respectively.

Taking into consideration these different properties of chloramine-T many workers get attracted towards it. They studied this reagent in detail by using variety of compounds. It was observed that no information was given towards the oxidation of dihydrazides. Therefore to rectify this situation study of oxidation of dihydrazides have been done by using chloramine-T.

(C) LITERUATURE SURVEY

The kinetics and mechanism of reactions of chloramine-T have been investigated by several authors. Coull[35] and coworkers were the first to investigate the kinetics and mechanism of decomposition of hydrogen peroxides by chloramine-T in presence of hydrochloric acid. Then Pryde and Soper[36] investigated the chlorination of p-cresol by chloramine-T. The kinetics of same reaction i.e. chlorination of p-cresol was investigated by Higuchi and Hussain.[37]

In recent years extensive study in kinetics and mechanism of oxidation of different types of compounds with chloramine-T have been reported. It is briefly reviewed below.

Alcohols :

Oxidation of primary alcohols have been studied by Mushran[38,39] et.al (n-butanol, iso-butanol and iso-propanol) with chloramine-T in acid medium. The mechanism proposed involves protonation of CAT to form $p\text{-}MeC_6H_4SO_2NHCl$, followed by rate determining hydrolysis to form HOCl which oxidises alcohol to aldehyde. The rate law is given as

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

Reaction is first order in [CAT] , $[H^+]$ and zero order in alcohol. Uma and Mayanna[40] studied OsO_4 catalysed oxidation of primary alcohols by CAT in NaOH medium. Results suggest formation of an activated complex between the substrate and OsO_4 which slowly decomposes into aldehyde.

The reactions of secondary alcohols (propan-2-ol, butan-2-ol, pentan-2-ol, octan-2-ol and 1,3 dichloropropan-2-ol) with chloramine-T in

aqueous acetic acid medium have been studied by Natrajan and Thigarajan[41]. The rate law is suggested as follows.

$$-\frac{d[CAT]}{dt} = k[CAT][Alcohol][H^+]^2$$

Oxidation of some allyl alcohol have been reported by Mahadevappa and Naidu[42,43] in higher acid concentration. The rate law suggested is

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

The kinetics of oxidation of benzyl alcohol and substituted benzyl alcohol p-R-$C_6H_4CH_2OH$ (R = H, OCH_3, CH_3, Cl, NO_2) by CAT have been studied by Uma and Mayanna[44]. The reaction is first order with respect to oxidant, alcohol and shows fractional order dependance on the concentrations of H^+ and Cl^-. This suggests a complex formation between $RNCl^-$ and HCl.

Carbohydrates :

Kinetics of the oxidation of xylose, arabinose, mannose and galactose in alkaline medium with CAT have been investigated by Agrawal and Mushran.[45] The oxidation rates follow the order

Xylose > arabinose > galactose > mannose

A mechanism involving a termolecular rate determining reaction among hypochlorite ion (OCl^-), hydroxide ion and the anion derived from ß-anomer of the aldose is suggested. Identical mechanism for oxidation of D(-) ribose,[46] D(+) sorbose[47] and fructose[48] by chloramine-T in alkaline medium is suggested.

Aldehydes

Osmium catalysed oxidation of formaldehyde and acetaldehyde by chloramine-T have been studied by Sanehi et.al.[49] The mechanism involves formation of an intermediate complex between N-chloro p-toluene sulphonamide and OsO_4 in slow step which abstracts hydride ion from the hydrated form of aldehyde in fast step . Mahadevappa and coworkers[50] studied oxidation of acetaldehyde in acid medium. A mechanism in terms of slow intraction between N-chloro p-toluene sulphonamide and aldehyde molecule is suggested.

Ketones

The kinetics and mechanism of oxidation of ketones have been extensively studied by Mushran et al.[51,52] They have reported oxidation of acetone and ethyl methyl ketone by chloramine-T catalysed by osmium (VIII) in alkaline medium. In oxidation of ethyl methyl ketone, diethyl ketone and methyl iso-butyl ketone[52] by chloramine-T in alkaline medium reaction product 1,2 diketone have been reported. Sharma and coworkers[53] have reported the kinetics and mechanism of oxidation of methyl isopropyl, methyl n-propyl and ethyl isopropyl ketones by CAT in alkaline medium.

An oxidation of cyclohexanone and cyclopentanone by chloramine-T in alkaline medium have been studied by Mushran and coworkers.[54,55] Singh et.al.[56] have reported the oxidation of acetophenone by chloramine-T in aqueous acetic acid medium.

Balsubramanian and Thiagarajan[57] have investigated the kinetics and mechanism of chlorination of acetone in aqueous acidic medium in presence of acetic acid and N.N'diethyl formamide by CAT. It has been

observed that at high concentration of chloramine-T in aqueous acetic acid medium in presence of sodium acetate; rate law is independent of concentration of ketone. Singh and coworkers[58] have reported the mechanism of chloramine-T oxidation of methyl vinyl ketone and isopropyl methyl ketone in aqueous alkaline medium. A mechanism proposed involves reaction of enolate anion with CAT in rate determining step.

Amino Acids

The kinetics and mechanism of the oxidation of amino acids by chloramine-T have been extensively investigated. Mushran et.al.[59-61] have studied the kinetics of oxidation of α-amino acids by chloramine-T in alkaline medium. The kinetic study of oxidation of glycine and valine by chloramine-T in hydrochloric acid medium have been reported by Gowda and Mahadevappa[62]. Naidu and coworkers[63] have reported the kinetics of oxidation of leucine, serine, glutamine and glutamic acid by chloramine-T in perchloric acid medium. First order dependence of rate in each, CAT, amino acid and inverse $[H^+]$ ion have been reported chloride ion is found to catalyse the reaction.

Oxidation of arginine and histidine by chloramine-T in acid and alkaline medium have been reported by Mahadevappa et.al.[64-66] Kinetics was found to be first order in arginine and zero order in histidine. The rate expression that suggested is as follows.

$$-\frac{d[CAT]}{dt} = k_1 [CAT][H^+][\text{Amino acid}] + k_2[CAT][\text{amino acid}][Cl]^{0.6}$$

Addition of methanol decreases the rate. Effect of the chloride ion on the kinetics of decarboxylation and deamination of histidine and arginine

by CAT in H_2SO_4 medium have been reprted by Gowda et.al.[67,68] The catalytic effect is more pronounced at high acid concentration. The rate is enhanced by H^+. The kinetics of chloride ion catalysed reactions are different from uncatalysed reactions due to formation of reactive species from Cl^+ of oxidant and participation of these species in slow step.

Gowda and Mahadevappa[69] studied available data on oxidation of amino acids by CAT in both acid and alkaline medium and have generalised the mechanism for both medium. Oxidation in acid medium proceeds via two paths. The first path involves direct interaction of R.NHCl (R=p-CH_3 $C_6H_4SO_2$) with neutral amino acid in slow step leading to formation of monochloro amino acid which subsequently interacts with another moelcule of R.NHCl in a fast step to give N.N.dichloro amino acid which further undergoes molecular rearrangement and elimination to give the products. The second path way involves H_2OCl^+ or Cl_2 produced from disproportiona tion of R-NHCl in presence or absence of Cl^- with substrate to give the products. In alkaline medium the mechanism involving the interaction of R-NHCl, HOCl, R-NCl^- and OCl^- are proposed. Sharma et.al.[70] reported similar path way in the oxidation of proline by chloramine-T.

Gupta and Gupta[71] studied oxidation of α-amino acids L(-) arginine, L(-)histidine, L(+)ornithine, L(-)tryptophan and L(-)threonine by chloramine-T in alkaline medium. The reaction was first order in each amino acid and CAT and inverse fractional order in $[OH^-]$. A general mechanism for oxidation is suggested considering anionic species of amino acid and p-toluene sulphonamide. Fractional order in $[OH^-]$ is due to the fact, fraction of overall reaction proceed via an alternative OH^- indepen-

dent path. Mahadevappa and coworkers[72] reported oxidation of DL methionine in alkaline and acid medium. The reaction follows identical kinetics. Isotope effect study using D_2O shows retardation in the rate in both medium.

Kinetics of oxidation of L(-) histidine by chloramine-T in alkaline medium have been studied by Gupta and Gupta.[73] Reaction showed the first order dependance in CAT and histidine. The rate decreases with increase in pH. A mechanism suggested involves dipole-dipole intraction between p-$MeC_6H_4SO_2NH_2$ and histidine.

Kageri et.al.[74] have reported kinetics of oxidation of glutamic acid by chloramine-T. In acid medium reaction is first order with respect to CAT, glutamic acid and H^+. A mechanism involving Zwitter ionic intraction with protonated CAT have been proposed. In alkaline medium Mushran and coworkers[75] studied same reaction and reported inverse first order dependance in OH^-. Verma and Yadav[76] also studied same kinetics of oxidation of glutamic acid by chloramine-T with and without catalytic action of Cu(II). The order with respect to [substrate] and [CAT] is one in each. Above 4.8 x 10^{-2}M NaOH reaction is independent of $[OH^-]$.Cu(II) ion catalyse the reaction and catalytic action is correlated with complex formation with glutamic acid.

Mushran and coworkers[77] have investigated the oxidation of α-hydroxy acids (glycolic, lactic, mandelic) by chloramine-T in alkaline medium in presence of Os(VIII) as catalyst. Hingorani et al.[78] studied same reaction for glycolic and lactic acid. Kinetics follow the first order dependance on CAT ; zero order with respect to glycolic acid and the reaction rate was found to be independent of lactic acid.

Kinetic studies on the oxidation of EDTA by chloramine-T in acid medium has been investigated by Sanehi et.al.[79] The protonated form of EDTA is assumed to react with R.NHCl in slow step forming an intermediate which then interact with six molecules of RNHCl in fast step giving end products. Shrinivasan and coworkers[80] investigated kinetics and mechanism of oxidation of (substituted phenyl thio) acetic acids by chloramine-T at pH 10.06 in alkaline medium. The rate of oxidation decreased with increasing pH.

Saxena et.al.[81,82] reported kinetics of the oxidation of ketoglutaric acids by chloramine-T in both acid and alkaline medium. For α and ß-ketoglutaric acid positive ionic strength and dielectric constant effects are observed. A mechanism involving formation of an intermediate in termolecular rate determining step among the hypochlorite, hydroxide ion and enolate ion of keto acids followed by a fast step leading to the formation of formaldehyde and formic acid have been identified as an end products.

Amines, Hydroximes etc. :

Radhakrisna Murthi et al.[83] investigated kinetics of oxidation of aniline and substituted aniline by chloramine-T in aqueous ethanol. The reaction is first order each in [Substrate] , [CAT] and independent of [alkali]. Oxidation of cyclohexanone oxime by chloramine-T have been studied by Shanmuganathan and coworkers.[84]

Kinetics of oxidation of hydroxyl amine hydrochloride in hydrochloric acid and perchloric acid medium have been investigated by Mahadevappa and coworkers.[85] Chloride ion catalyse the reaction. A mechanism

involving interaction of unprotonated hydroxyl amine and p-$MeC_6H_4SO_2NH_2$ giving an intermediate complex is suggested.

Kinetics and mechanism of oxidation of dulcitol by chloramine-T have been investigated by Mandnwat et.al.[86] in alkaline medium. A mecha nism similar to galactose formation is suggested. Jayaram and Mayanna[87] reported oxidation of caffeine by chloramine-T. Reaction is zero order with respect to caffeine and first order with respect to chloramine-T.

Mahadevappa and coworkers[88-91] have oxidised dimethyl sulphoxides[88,89] and diphenyl sulphoxides[90,91] in perchloric acid, hydrochloric acid and sodium hydroxide medium by chloramine-T. The mechanism in acid medium is assumed to involve an electrophillic attack by free acid (RNHCl) at the sulphur site of dimethyl sulphoxide forming a reaction intermediate in slow step, which subsequently decomposes to dimethyl sulphone in fast step. In alkaline medium OsO_4 catalyst is supposed to interact with RNHCl forming cyclic complex which in turn reacts with substrate in slow and rate determining step.

Ganapathy and Jaygandhi[92] have reported kinetics of oxidation of some m - and p - substituted phenyl methyl sulphoxides by chloramine-T in buffered ethanol/water medium (1:1; v/v) at pH = 7.0. The reaction was followed no simple order kinetics. The following possible mechanism is suggested involving three rate controlling steps (i) The reaction between R-NHCl (R = p-$MeC_6H_4SO_2$)) and the sulphoxide (ii) the disproportionation of RNHCl and (iii) the reaction between $RNCl_2$ and sulphoxide.

Krishnrao and coworkers[93] have reported the oxidation of benzoyl hydrazins by chloramine-T in alkaline medium. The order with respect to each [substrate] and [CAT] is found to be one. The rate is found to be

to be indepndent of pH and the reaction is accelerated by electron withdrawing groups. The mechanism involves the attack of chloramine-T on benzoyl hycrazine molecule in rate determining step.

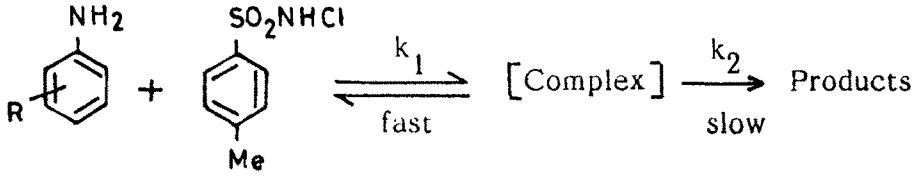
Kinetics and mechanism of oxidation of hydrazine with chloraminet-T have been reported by Jha et.al.[94]. The reaction is carried out in ethanol/perchloric acid mixture and is first order in [CAT] and $[H^+]$ and the rate increased with increasing concentration of substrate.

Kinetics of oxidation of thiosemicarbazide (TSC) and its hydrazone (benzaldehyde thiosemicarbazone) by chloramine-T in aqueous methanol medium in presence of perchloric acid have been studied by Gowda and Sherigaca.[95] Oxidation showed first order dependance in oxidant fractional order in [TSC] and inverse first order in $[H^+]$. Increasing ionic strength of the medium slightly decreased the rate. Addition of p-toluene sulphonamide had no effect on the rate.

Chloramine-T is not only a well known oxidant but also a well known chlorinating reagent. Chlorination of phenol and substituted phenols by chloramine-T in aqueous alkaline medium have been carried out by Murthi et.al.[96]. The reaction is found to follow first order kinetics with respect to both substrate , chloramine-T and fractional order with respect to alkali . Kinetics of oxidation of anisole and substituted anisols have been reported by Murthi and coworkers.[97]

Ramanujam and Trief[98] have reported kinetics and mechanistic studies of chlorination reactions of aniline and substituted anilines with chloramine-T. The reaction involves (i) 1:1 stoichiometry (amine : CAT) (ii) Fractional order dependance on amine indicating formation of an inter-

mediate complex and (iii) a decrease in rate with decrease in dielectric constant of the medium suggesting dipole-dipole interaction and a general mechanism is proposed as follows



Antelo et.al.[99] have studied the effect of pH on the reaction of diethanolamine with chloramine-T. The oxidation rate of diethanolamine with CAT have studied at pH range 8 to 13, it reaches maximum at pH 10.8 and further rate constant decreases.

Nimbalkar and coworkers[100] reported kinetic investigations of oxidation of salicylic acid hydrazide and o-chlorobenzoic acid hydrazide in presence of methanol at pH 8.88 by chloramine-T. The end products of the oxidation are bishydrazides, p-toluene sulphonamide and nitrogen. The mechanism in which chloramine-T reacts with hydrazide giving acyl-imide as an intermediate in slow and rate determining step is suggested.

(D) OBJECT AND SCOPE OF THE PROPOSED WORK

The chemistry of hydrazides is very important and interesting branch of organic chemistry due to its physiological activity and other applications. They have been extensively studied since it is found that isonicotinic acid hydrazide is found to be a best drug against tuberculosis.[101] Many derivatives of this compound have been synthesised and tested for antibacterial properties.[101-103] High activity of certain derivatives is assumed to be due to the presence of diacyl hydrazine group as the biological active center.[104] Carboxylic acid 1,2 diaryl hydrazides have been reported to possess antiinflammatory properties[105] and diuretic[106] action has been ascribed to benzoic acid hydrazide derivatives. Isoxazole carboxilic acid hydrazides are active against leprosy.[107] Dihydrazides have recently been introduced as an anthelmintics.[108] Maleic acid hydrazide is used to regulate and inhibit the growth of plants.[109] Succinic acid dihydrazide is used in determination of organophosphorus pesticide derivative in plants.[110]

Hydrazides are important starting materials in the synthesis of certain amines, aldehydes and heterocyclic compounds which are otherwise difficult to prepared. The hydrazides are used for heat and corrosion[112] stabilization of cellulose and its derivatives. Succinic acid dihydrazide is used as corrosion inhibitor in sulphuric acid.[111] It can also be used as antioxidants for polyolefins and polyurethanes which are oxidised otherwise in presence of copper. Incorporation of hydrazides have improved the applicability of plastics and cable insulations.[113] The small amount of hydrazide is useful in sensitizing electrographic layers made up of polyvinyl carbazole.[114]

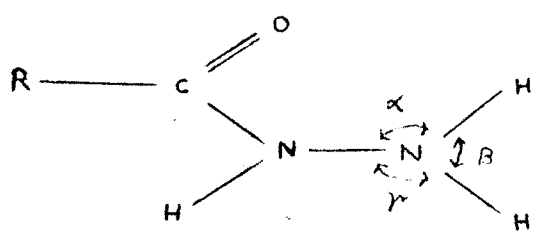
Dihydrazides can be used in ciggarete filters for the selective removal of aldehyde from tobacco smoke.[115] Ion exchange resin for the separation of Cu, Ni, Co, Mg and transition metal ions have been prepared from co-polymers of 2-methyl-5-vinyl pyridine and hydrazides of 1,2 ethylene dicarboxylic acid.[116]

Ninteen hydrazides and meldrums acid derivative were tested for antifungal activities. Malonic acid dihydrazide showed highest antifungal activity.[117] Aspergillus and penicillum are succeptible to malonic acid dihydrazide.

The hydrazides are derivatives of carboxylic acids and hydrazine. The preferred nomenclature is to describe any hydrazide as carboxylic acid hydrazide. This nomenclature is used in chemical abstract. The nitrogen atoms of hydrazides are designated as 1 and 2 or α and β or N and N'. The first member of each pair denote the nitrogen where the acyl group is inserted.[118]

The structure of hydrazide is determined by modern techniques of the structure determination. The structure of isonicotinic acid hydrazide has been determined by x-ray crystallography.[119]

The N-N bond length is in between 1.39 and 1.42 A^{O}. Hydrazine bond length is in between 1.46-1.47 A^{O}. This is due to formal charge



$\alpha = 101^{O}$

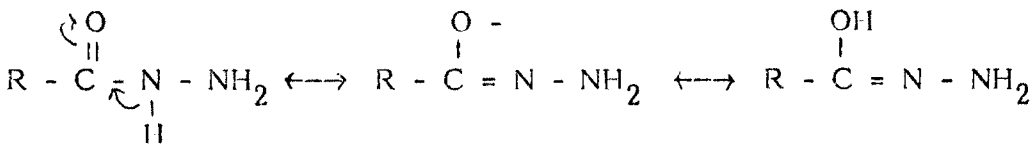
$\beta = 98^{O}$

$\gamma = 109^{O}$

effect and to the fact that the electron attracting acyl group reduce the repulsion between the loan pair ~~of electrons~~ of electrons of nitrogen atoms

The C-N bond length is 1.33 A^{o} which is same as in pyridine ring which is supposed to be aromatic. This bond must have therefore roughly a 50% double bond character. The two hydrogen atoms present almost exactly in the same plane.

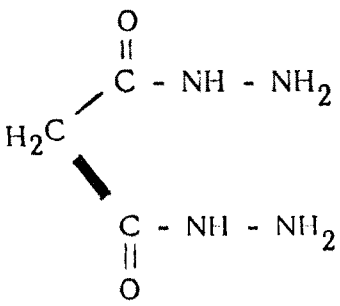
The hydrazide group is stabilized due to the resonance between amide form [Keto] (I) to tautomeric enol form (II) by a shieft of a hydrogen from nitrogen to oxygen.



(I) keto form (II) enol form

Due to resonance stabilization of hydrazide group, its basicity is drastically reduced.

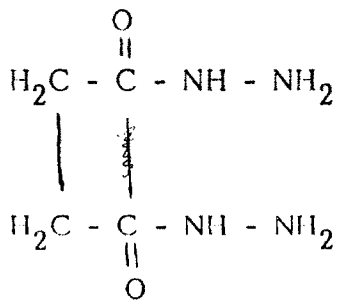
From this discussion it is clear that hydrazides are useful in agriculture, medicine and industry and day by day their applications are increasing in different fields. But detailed pathways of these all reactions are not clear. If we are able to understand the mechanism of all such useful reactions of hydrazides it is possible to understand the exact role of the hydrazide in various reactions. Oxidation is one of these reactions. Therefore it is necessary to make a detail study of oxidation of hydrazides. Oxidation of hydrazides by chloramine-T is one branch of such a study. Therefore we have undertaken the study of 'Oxidation of Aliphatic Carboxylic Acid Dihydrazides by Chloramine-T' in aqueous buffered medium. Following two dihydrazides are selected for the study.



I

Malonic Acid Dihydrazide

(MAD)



II

Succinic Acid Dihydrazide

(SAD)

These two dihydrazides are selected because the distance of two hydrazide groups in these reactions are not similar. This difference in the distance between the two hydrazide groups might be related with the rates of these reactions. Therefore, it is essential to take an account of such study. Hence, we have selected two dihydrazides for our study.

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