CHAPTER – I

INTRODUCTION

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The subject of chemical kinetics is mainly concerned with the quantitative study of the rates of chemical reactions, and of the factors upon which they depend. Such studies may be prime importance in connection with technical processes, they may throw light on the general principles of the reactivity or may be useful in arriving at a reaction mechanism.

Thermodynamics is concerned only in the initial and final states of a system. Time is not one of the thermodynamic variables; that means thermodynamics is more powerful tool for investigating conditions at equilibrium. Time is the most important factor while considering the kinetics of reactions. Kinetics gives details of process whereby system gets from one state to another and the time required for transition. Equilibrium can also be treated in principle on the basis of kinetics as that situation in which the rates of forward and reverse reactions are equal. The converse is not true; or reaction rate cannot be understood on the basis of thermodynamics alone. Therefore, chemical kinetics may be considered a more fundamental science than thermodynamics. Unfortunately chemical kinetics is difficult to apply with accuracy.

Chemical kinetics provides most powerful method of investigating the mechanism of the process. The mechanism of the reaction will give a detailed picture of the activated complex,[1] not only in terms of the constituent molecule but also in terms of geometry.

Ideally, a complete reaction mechanism would involve a knowledge of all the molecular details of the reaction including energetics and stereochemistry. The rate of reaction is determined by the mathematical expression showing the dependence of rate on the concentration of the reactants. In complex reactions substance undergoes a series of stepwise changes. Out of these steps the slowest step of the reaction controls the rate of the overall reaction. The mechanism is important rather than rate to the theoretical chemist. Investigation of the mechanism of the reactions has, therefore, been undertaken since the beginning of modern Chemistry.

While considering the problems of reaction rates there are two main theoretical approaches. The collision theory, and transition state theory. The first is based on the kinetic theory of gases and uses of mechanical model while second one is largely based on the thermodynamics and uses of three dimensional surface as a model.

Out of these two, transition state theory is generally more useful particularly for organic reactions.

The collision theory may be expressed as the rate of reaction equal to number of collision of activated molecules per unit time. The rate constant (k) at unit concentration of the reagent is given by the equation.

$$k = p.\ z.\ e.^{-Ea/RT} \qquad \ldots(1,1)$$

where k = Rate constant

p = Probability factor

z = Frequency of collision at unit concentration

Ea = Energy of activation

T = Absolute temperature

R = Gas constant

The above theory is based upon the idea that if two molecules are to combine chemically, an essential first step is that they should colloid with each other. Only those collisions are effective in which colloiding molecules have more than average energy content.

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

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

Where A is frequency factor.

In the transition state theory the rate of the reaction increases as the temperature is raised. The rate of reaction is related to the number of molecules that pass from the 'reactant side' to 'product side'. in a given time. The concentration of molecule increases as the temperature increases and more conversions from reactants to products then occur.

'Activated complex' is nothing but molecule or group of molecules passing through the transition state. Considering the reaction between species A and B, we may indicate the activated complex as AB^{++} and represented the reaction as

$$A + B \longrightarrow \underset{\text{Activated complex.}}{AB^{++}} \longrightarrow \text{products} \qquad \ldots(1.3)$$

The transition state theory is analogous to corresponding thermodynamic functions of ordinary chemical changes.

The free energy of activation $\Delta G^{\neq}$

$$\Delta G^{\neq} = -RT \ln K^{\neq} = -RT \ln \left[\frac{krh}{kT} \right] \qquad \ldots(1.4)$$

The heat of activation $\Delta H^{\neq}$

$$\Delta H^{\neq} = - R \frac{d (\ln K^{\neq})}{d(1/T)} = - R \left[\frac{d(\ln kr)}{d(1/T)} + T \right] \ldots(1.5)$$

The entropy of activation, $\Delta S^{\neq}$

$$\Delta S^{\neq} = \frac{\Delta H^{\neq} - \Delta G^{\neq}}{T} = R \left[T \cdot \frac{d(\ln kr)}{dT} + \frac{\ln Krh}{kT} - 1 \right] \quad ..(1.6)$$

In the above expressions k is Boltzman's constant, T is the absolute temperature and h is the Planck's constant.

Mechanism of redox reactions is important not only in the field of inorganic and organic chemistry but has vast implications in biochemistry to understand the nature of life. The dramatic effect of temperature on rate of reactions is illustrated by the fact that a $10^{o}C$ rise in temperature of the human body invariably leads to death.

Entropy of Activation :

The entropy of activation may be calculated by equation :

$$\Delta S^{\neq} = \frac{\Delta H^{\neq} - \Delta G^{\neq}}{T} \quad ..(1.7)$$

It is the measurement of randamness of a system. If the reaction occurs with an increase in entropy, there is a disorder possible more among the products than among the reactants.

The reactions are usually classified as unimolecular (A-1, SN_1) or bimolecular (A-2, SN_2). Thus entropy is a measure of the freedom from restrain to motion among the

reactants.[2] Long et. al.[4], amplifying a suggestion of Traft and co-workers,[5] have proposed the use of hydrolysis reaction.

In unimolecular reactions, water molecule does not participate in the rate determining step. The A-1 and A-2 processes involve specific hydronium ion catalysis and may be represented as follows.[5]

$$S + H^+ \rightleftharpoons SH^+$$

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

$$S + H^+ \rightleftharpoons SH^+$$

$$SH^+ \xrightarrow[H_2O]{\text{slow}} [\, X^{\neq} \,] \longrightarrow \text{products (A-2)} \qquad ..(1.9)$$

$X^{\neq}$ is an activated complex.

Emphirically all known bimolecular, specifically acid catalysed reactions have negative entropy of activation, and all Unimolecular acid catalysed reactions have entropy of activation nearly zero or have positive value. Thus it can be said that lower entropy of activation relatively to unimolecular process and if the entropy of activation is negative then the mechanism is probably bimolecular.

In the relation of organic reactions, oxidation reaction occupies an important place. In oxidation reactions, the common oxidising agents used are nitric acid, potassium dichromate, potassium permanganate, chlorine, bromine,

ceric sulphate, potassium periodate and V^{+5}, These oxidising agents are sufficiently strong and oxidation is rather fast. It is easy to show experimentally that the rates of chemical reactions vary with time but careful experiments are needed to show that this variation is regular and can be described by mathematical equation.

Different effects on the rates of reactions are explained as follows :

Ionic-Strength Effect :

The ionic strength (μ) is defined by the equation

$$\mu = 1/2 \sum mi \cdot zi^2$$

where mi = molality of ion and
zi = charge on ion

The reaction between two ionic species proceeds through transition state which is in equilibrium with reactants and the equilibrium properties of such reactants can be greatly affected by the other ionic species which are present in addition to the reactants. Bronsted, Bjerrum and Debye-Huckel successfully explained, the effect of electrostatic interaction of ionic species, with the help of activated complex rate theory.

Solvent Effect :

The rate of the reaction can also be affected by change in solvent. Some times solvent alters the rate without affecting the mechanism and rarely changes the mechanism without altering the rate. Those reactions in which ions are generated from uncharged molecules, are mostly affected by solvent. Reactions in which charge is created proceed most rapidly in polar solvents.[3]

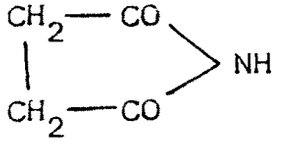
Hughes, Ingold and their Collaborators put forward the qualitative theory[6] of solvent effect. This theory could be used as criteria for mechanism. According to postulates an increase in ionization power of solvent will favour an increase in the magnitude of charge. Thus it affects the rate of reaction.

Chloramine-T [p - CH_3- C_6H_4-SO_2NCl Na]

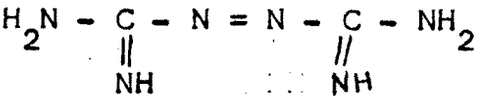
Organic chloramines are N-chloro derivatives of following group of compounds

i) Sulphonamides $R\text{-}SO_2\text{-}NH_2$

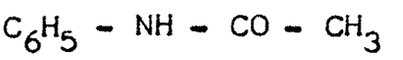
ii) Heterocyclic chloramines with chlorine attached to nitrogen in the ring



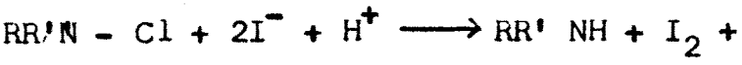
iii) Condensed amines from cyanamide derivatives



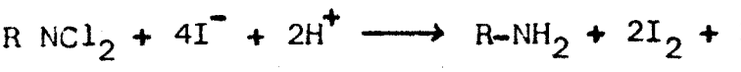
iv) Anilides



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 potassium iodide solution. The overall reaction for monochloroamines can be presented as



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



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

The sodium salt of N-chloro-p-toluene sulphonamide known as chloramine-T [CAT] was first prepared by Chattway.[7] When toluene is allowed to react with chloro-sulphonic acid, it gives ortho and para-toluene sulphonyl chlorides. The para isomer on treatment with ammonia and then with aqueous sodium hypochloride produces Chloramine-T. It can be purified by recrystallisation from hot water and dried in air. 99.5 % pure sample can be obtained by successive recrystallisations. It is found to be difficult to prepare anhydrous salt and preserve under laboratory conditions.[8] Hence, this salt cannot be used as primary standard. Commercially available Chloramine-T is about 98 % pure. Contaminations 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°C and 50 gms in 100 ml at 100°C. It is soluble in alcohol and acetone. The available chlorine content in Chloramine-T has been estimated which is found to be 23 to 26%. There are conflicting reports on the solubility of chloramine-T in solid state and in solutions.[8]

Dietzel and Toufel[9] reported the decline in assay of 1.4 % in 12 months in brown coloured bottle and 5 % in clear glass bottle. Chloramine-T solution exposed to sun-light is unstable. So it is protected from day light. It is stable for nearly four weeks.

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

$$R - N\,Cl\,Na \rightleftharpoons R - NCl^- + Na^+ \qquad ..(1.10)$$

Where R is the p-toluene sulphonyl group i.e. R = $[p- H_3C - C_6H_4 - SO_2 -]$. The anion then picks up a proton to form a free acid RNHCl

$$R - N\,Cl^- + H^+ \rightleftharpoons R - N\,HCl \qquad ..(1.11)$$

The free acid has not been isolated but the evidence for existance has been reported.[8] The free acid then gives rise to p-toluene Sulphonamide and dichloramine-T.[10]

$$2R\,NHCl \rightleftharpoons R\text{-}NH_2 + R.NCl_2 \qquad ..(1.12)$$

The dichloramine-T and free acid hydrolyse to give hypochlorous acid.[11]

$$RNCl_2 + H_2O \rightleftharpoons R.\,NHCl + HOCl \qquad ..(1.13)$$

$$R.NHCl + H_2O \rightleftharpoons R.\,NH_2 + H\,OCl \qquad ..(1.14)$$

Finally HOCl ionizes as

$$HOCl \rightleftharpoons H^+ + OCl^- \qquad ..(1.15)$$

Chloramine-T liberates iodine with acidified potassium iodide solution.

$$R - NCl^-Na^+ + 2\,I^- + 2\,H^+ \longrightarrow R\,NH_2 + I_2 + NaCl \qquad ..(1.16)$$

Chloramine-T as an oxidising agent has been well reviewed by many authors.[12-15] It is introduced as an analytical reagent by Null[16] and then many workers used chloramine-T as an analytical reagent. Bishop et al.[8] and Jennings[17] have cirtically examined Chloramine-T as titrametric reagent.

Chloramine-T is widely used as an oxidising agent in acid medium. A large number of organic and inorganic reducing agents have been estimated by using Chloramine-T as an oxidant by volumetric, potentiometric and amperometric methods.

Chloramine-T solution can be standardized by adding potassium iodide solution in the presence of (2N) H_2SO_4 and titrating the liberated iodine against standard solution of sodium thiosulphate. The redox potential of 0.1 M Chloramine-T solution saturated with p-Toluene sulphonamide at different pH values has been reported by Murthy and Rao.[18] The values are 1.139, 0.778 and 0.614 at pH 0.65, 7.00 and 9.70 respectively.

Literature Survey :

The study of kinetics and mechanism of oxidation by chloramine-T has been undertaken by many authors. Goull and co-workers[19] were the first to report the kinetics and mechanism of decomposition of Hydrogen peroxide by Chloramine-T in the presence of Hydrochloric acid. Bernanose and Simons[20]

have investigated the oxidation of luminol by Chloramine-T in acid medium. The chlorination of p-cresol by chloramine-T has been investigated by Pryde and Soper,[21] HOCl formed in the hydrolysis of chloramine-T is supposed to be used in the Chlorination of the p-cresol.

The oxidation of different types of alcohols by Chloramine-T has been throughly investigated e.g. Mushran et. al.[22] have studied the oxidation of n-butanol, iso-butanol and iso-pentanol in acid medium. The mechanism proposed involves the hydrolysis of RNHCl giving rise to HOCl in a slow step, which then interacts with the substrate in the fast step giving rise to the corresponding aldehydes. The rate law is given by

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

The oxidation of secondary alcohols, like Propan-2-ol, butan-2-Ol, pentan-2-Ol, octan-2-Ol and 1,3-dichloropropan-2-Ol, by Chloramine-T in acid medium has been studied by Natrajan and Thiagarajan.[23] Mahadevappa and Naidu[24] studied the kinetics of oxidation of some unsaturated alcohols by chloramine-T in hydrochloric acid medium. At low acid concentration the rate law was shown to be

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

and at higher acid concentration[25] the rate law was

$$-\frac{dc}{dt} = k\,[CAT]\,[H^+]^2.$$

Oxidation of phenol and substituted phenols by Chloramine-T in aqueous alkaline medium has been reported by Radhakrishnmurthi.[26] The reaction was found to be first order with respect to substrate and Chloramine-T. It was also observed that the electron releasing groups accelerate the rate of the reaction. Kinetics of oxidation of anisole and substituted anisoles by Chloramine-T in aqueous acetic acid medium has been reported by Murti and Sasmal.[27] Below 0.003 M concentration, a fractional order dependence on [Anisole] was observed, which then changed to first order at high concentration.

Aldoses oxidation by Chloramine-T in highly alkaline medium has been studied by Agarwal and Mushram.[28] The oxidation rates were of the following order.

Xylose > arabinose > galactose > mannose.

The oxidation of D-Ribose[29] and Fructose[30] by Chloramine-T in alkaline medium have been reported.

The kinetics and mechanism of oxidation of ketones by chloramine-T has been extensively studied. Mushran et. al.[31] have reported the oxidation of acetone and methyl ethyl ketone by Chloramine-T in alkaline medium in the presence of Os (VIII) catalyst. Sanehi and

and co-workers[32] have reported the kinetic investigation of reactions between methyl ethyl ketone, diethyl ketone, methyl iso-butyl ketone and chloramine-T in alkaline medium. In these cases the corresponding 1,2-diketones were formed. Sharma and co-workers[33] studied the kinetics and mechanism of oxidation of methyl isopropyl, methyl n-propyl, ethyl iso-propyl ketones by chloramine-T in alkaline medium.

Oxidation of cyclohexanone[34], cyclopentanone[35] by chloramine-T in alkaline medium has been reported. Oxidation of acetophenone by chloramine-T in aqueous acetic acid medium has been reported by Singh et. al.[36] In this case the enol form of the ketone was supposed to interact with HOCl in the slow and rate determining step.

OsO_4 catalysed oxidation of formaldehyde in alkaline medium has been studied by Sanehi et. al.[37] The complex formation between Chloramine-T and Os(VIII) in a slow step has been assumed. The complex was then supposed to abstract a hydrazide ion from the hydrated form of the substrate in a fast step. The following rate law was suggested

$$-\frac{d[CAT]}{dt} = k \frac{[CAT]\,[OsO_4]}{[OH^-]}$$

This rate law is in agreement with the experimental results and the mechanism was investigated.

The observation of kinetic study of Chlorination of anilines have been reported by Ramanujam and Trieff[38]

Chlorination of p-toludine and p-nitroaniline have been reported by Murti et. al.[39] The mechanism of chlorination is shown to be dipole dipole type involving direct transfer of chloride from Chloramine-T to the substrate.

The kinetics and mechanism of oxidation of amino acids by Chloramine-T has been extensively investigated. Mushran and co-workers[40-42] have investigated the kinetics of oxidation of α-amino acids by Chloramine-T in alkaline medium. The proposed mechanism was supposed to involve two paths. The first path was followed by major fraction of the reaction and proceeded through the interaction between amino acids molecule and RNHCl in a slow rate determining step, resulting in the formation of an intermediate. The intermediate subsequently attacks another molecules of RNHCl in a fast step, yielding the products. The second path involves the minor fraction of the reaction in which hypochloride ion replaces RNHCl in the above step.

The oxidation of glycine and valine by Chloromine-T in hydrochloric acid medium has been reported by Cowda and Mahadevappa.[43] Naidu and Co-workers[44] studied the kinetics of oxidation of leucine, serine, glutamine and glutamic acid by chloramine-T in perchloric acid medium. Kinetics of oxidation of α-histidine by chloramine-T in

alkaline medium has been investigated by Gupta.[45] The rate of reaction decreased with an increase in pH. Change in ionic strength has no effect on reaction rate. Kinetics of oxidation of α-amino-iso-butryic acid by Chloramine-T in alkaline medium has been reported.[46] A mechanism involving an interaction between neutral molecule and a charged ion or between two neutral molecules in a rate determining step has been reported.

Banerji[47] has reported kinetics of oxidation of substituted mandelic acid by chloramine-T in $HClO_4$ medium. $[ClOH_2]^+$ is assumed to be the reactive species. Singh and co-workers[48] have studied the kinetics of oxidation of α- and β- ketoglutaric acids by chloramine-T in acidic medium. A mechanism involves the interaction of enol form of the substrate with Chloramine-T in the rate determining step.

Srinivasan and co-workers[49] have reported the kinetics and mechanism of oxidation of phenyl thio substituted acetic acids by chloramine-T, in alkaline medium at pH 10.06. The oxidation proceeds via two paths, the major one involving RNHCl as the main oxidising species and the other involving ClO^- ions. Kinetics and mechanism of oxidation of lactic acid by chloramine-T catalysed by Cu(II) ion has been reported by Gupta and co-workers.[50]

Mahadevappa and co-workers[51] have reported the detailed investigation of the kinetics of oxidation of thiocyanate ion by Chloramine-T in alkaline medium.

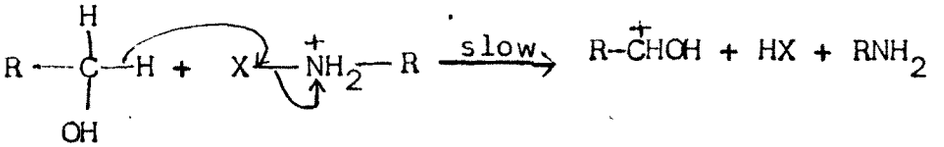
At low substrate concentration, the rate law was shown to be

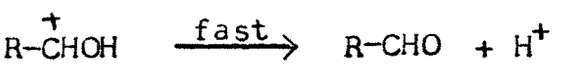
$$-\frac{d[CAT]}{dt} = k \frac{[CAT]\,[NCS]}{[NaOH]^2}$$

which was simplified to

$$-\frac{d[CAT]}{dt} = k\,[CAT]\,[NaOH]^{-1}$$

The oxidation of benzyl alcohol and ethanol by CAT, CAB, and BAB, was investigated by Banerji and co-workers.[52-53] The reaction exhibits substantial primary kinetic isotope effect, thereby confirming the cleavage of C-H bond in the rate determining step. The kinetic features are best explained by assuming a hydride ion transfer from the alcohol to the protonated N-halogen sulfonamide.





The oxidation of unsaturated alcohols like - allyl alcohol, crotyl alcohol and phenyl allyl alcohol

by CAT in HCl medium was investigated by Mahadevappa et al.[54-55] 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[56] reinvestigated the oxidation of allyl alcohol by CAT in HCl medium and obtained the rate law.

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

Kinetics of oxidation of anisole and substituted anisole by CAT in aqueous acetic acid medium has been reported by Murti and Sasmal.[57]

Kinetics of oxidation of lactic acid by CAT, Catalysed by Cu(II) ion has been reported by Gupta and Co-workers.[58] Formation of complex between Cu(II) and p-toluensulfonamide has been suggested.

The kinetics of oxidation of number of amino acids with CAT in both acid medium and alkaline medium have been reported. Recently some generalisations have been drawn about the mechanistic aspects by Gowda and co-workers[59] 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. al.[60,61] They proposed the rate law

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

The kinetics of oxidation of alanine and phenyl alanine in HCl medium by CAT is found to obey identical kinetics by reported Mahadevappa.[62] At low acid concentration 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[63] 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.[64]

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

The work of Mushran et. al.[65,66] and Mahadevappa and coworkers[59] 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 common 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 be independent of $[OH^-]$. Addition of TSA and Cl ion has no effect on the rate.

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 sulfoxide 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.[67].

The oxidation of arylthio-acetic acid by CAT has been reported by Shrinivasan and co-workers.[68] 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.[69,70] The oxidation of methi-onine

by CAT in acid solution is independent of [Substrate] and is first order each in [oxidant] and $[H^+]$. Methionine reacts with $(H_2OCl)^+$ in the fast step to yield a Cl^+ ion which ultimately yields the corresponding sulfone.

Osmium(VIII) catalysed oxidations by CAT in alkaline solutions of α - hydroxy acids,[71] aldehydes,[72] ketones,[73,74], 1,2 diols,[75] benzaldehydes,[76] Cycloalkanol, butan-1,3 and 1,4 diols[77] are governed by the rate law

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

The kinetics of oxidation of H_3PO_2 acid by CAT in H_3PO_4 acid medium follows the rate law[78]

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

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

Arsenic (III) the rate law for the oxidation of Ar(III) by CAT in alkaline solution[79] was given by

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

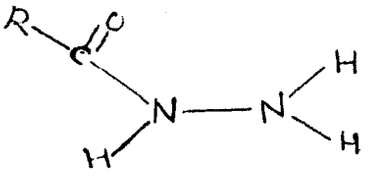
Tellurium (IV). The oxidation of tellurium (IV) by CAT[80] occurs only in the presence of Cl^- ions. The reaction shows a first order dependence in [Tr(IV)], [CAT], $[H^+]$ and $[Cl^-]$ ions.

Present study and its object :

The Chemistry of hydrazides is very important and interesting branch of Organic Chemistry. Due to physiological activity of many hydrazides, they have been extensively studied. Since, the discovery of isonicotinic acid hydrazide as a strong anti-tuberculotic agent,[81] many derivatives of this compound have been synthesised and tested for anti-bacterial activity.[82,83] Apart from physiological activity of hydrazides, some of them are important starting materials and intermediates in the synthesis of certain amines, aldehydes and heterocyclic compounds.

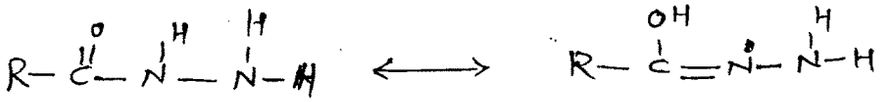
The hydrazides are the derivatives of carboxylic acids and hydrazines. The preferred nomenclature is to describe any hydrazide as the carboxylic acid hydrazide. This nomenclature is used in chemical abstract. The nitrogen atoms of the hydrazide are designated as 1 and 2 or α and β or N and N^1, first number is the one, to whom acyl group is attached. The structure of hydrazide is

determined carefully by using modern techniques of structure determination. The structure of isonicotinic acid hydrazide has been determined by X-ray crystallography.[84]



The N-N bond length is always between 1.39 - 1.42 A^{o}, which is shorter than tnat in hydrazine molecule which is always between 1.46 - 1.47 A^{o}. This is due to the formal charge effect and the electron attracting acyl group, which reduces the repulsion between the lone pair of electron on nitrogen atoms. The C - N bond length is 1.33A^{o}, this bond, therefore, must acquire roughly 50 % double bond character. The two hydrogen atoms are in the same plane.

The hydrazide group can be resonance stabilized between amide form (I) and the tautometric enol form(II), by the shift of hydrogen atom from hitrogen to the oxygen.



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

The kinetics of oxidation of hydrazides has been investigated by some workers. The oxidation of hydrazides by lead tetraacetate leads to the formation of corresponding acids and nitrogen.

The oxidation of Benzhydrazides[85] by MnO_2 proceeds via formation of azo compounds, which are solvalysed to corresponding acids. The oxidation of salicylic and substituted salicylic acid hydrazides have been studied by Hasker and co-workers.[86] Silver catalysed oxidation of some hydrazides by peroxydisulphate has been studied by Hogale[87] and Patil.[88]

The kinetics of oxidation of acetic, propionic, butyric and iso-butyric acid hydrazides by Chloramine-T has been carried out by Swami.[89] Telwekar[90] also studied oxidation of n-valeric and iso-valeric acid hydrazides by Chloramine-T. In the light of above discussion and previous survey the kinetics of oxidation of n-caproic and n-Heptanoic acid hydrazides by Chloramine-T in alkaline medium has been undertaken. It is desired to study the effect of increase in the length of carbon chain on the rate of oxidation of these hydrazides as both of them are straight chain hydrazides. They are :

1) CH_3- CH_2- CH_2- CH_2- CH_2- CO $NHNH_2$

n - Caproic acid hydrazide [n-CAH]

2) CH_3- CH_2- CH_2- CH_2- CH_2- CH_2- CO N HNH_2

n - Heptanoic acid hydrazide [n-HAH].

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