CHAPTER-I

INTRODUCTION

CHAPTER - I

I N T R O D U C T I O N

Kinetics of reaction is concerned with the analysis of dynamics of chemical reactions. The importance of the study of kinetics of chemical changes is its usefulness as it furnishes information not only about the final products formed but also about the intermediates that are formed during the course of reaction. These intermediates though they are short lived, are responsible for controlling the overall reaction. Chemical kinetics is the study of systems whose properties are a function of time. The field deals with the rates of reaction with all the factors that affect them and with the explanation in terms of the reaction mechanism. The mechanism of the reaction means all the individual or other elementary processes involving atoms, molecules, radicals, ions and other reactive species that take place simultaneously or consecutively in the overall reaction. The mechanism of the reaction gives a detailed picture of the activated complex[1], not only in terms of the constituent molecules but also in terms of geometry. The mechanism is the actual process by means of which a reaction takes place. It furnishes the information regarding the types of bonds broken and in what order they are broken, the number of reaction steps involved in the process and their relative rates etc.

Thus chemical kinetics deals with the complete reaction mechanism which involves a knowledge of all molecular details of

the reaction including their energetics and stereochemistry of molecules.

Generally, in most of the reactions, especially the organic ones, the products obtained are dependant on the course of reaction adopted. Formation of products is controlled by the reaction rates of several complicating and competing reactions. The kinetic study very often is capable of predicting favourable conditions necessary for the commercial production of a desired compound. Although sometimes, it may not be possible to obtain extensive information about the path traversed by a reaction, but even then, more often, sufficient data can be had to suggest the likelihood of one mechanism over the other.

In some reactions the change occurs directly, which may be represented by an overall stoichiometric equation. However, in complex reactions, substances undergo series of stepwise changes, each consists a reaction in its own right and is much more common. The overall mechanism is then made up of contributions from all such reactions.

For example :

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

Stepwise change may take place as follows :

$$A + B \rightleftharpoons AB \quad \text{.....step I}$$

$$A + AB \rightleftharpoons A_2B \quad \text{..... Step II}$$

$$A_2B \rightleftharpoons AB + R \quad \text{..... Step III}$$

$$AB \rightleftharpoons S \quad \text{..... Step IV}$$

$$\therefore \quad 2A + B \longrightarrow R + S$$

The slowest step controls the rate of the reaction and the order is determined from experiment by using the overall rate equation. The mechanism rather than the rate equation is important to theoretical chemists.

There are two important theoretical approaches which deal with problems of reaction rates. The collision theory is largely based on kinetic theory of gases and uses a mechanical model whereas the transition state theory is based largely on the thermodynamics and uses a three dimensional surface as model, the vertical co-ordinate being energy.

The transition state theory is more generally useful of the two, particularly for organic reactions.

The collision theory is based upon the idea that if two molecules are to combine chemically, an essential first step is that they should collide with each other. Only those collisions are effective in which molecules acquire energy more than the activation energy. However, collisions between molecules having the requisite energy content do not often result in reaction. Collisions will not

be fruitful if the molecules collide in wrong way or if the excess energy in the molecules is not associated with the appropriate internal motions of the molecules. The probability of reaction occurring even in collision between activated molecules may be rather small if the stereoelectronic requirements of the reaction are stringnet. Therefore, the collision theory may be expressed as the rate of reaction equal to the number of effective collisions of activated molecules per unit time. The rate constant at unit concentration of the reactants is given by the equation,

$$k = p.z.e.^{-Ea/RT} \qquad \ldots\ldots (1.1)$$

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

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

where A is frequency or pre exponential term.

THE TRANSITION STATE THEORY :

The main assumption of this theory is that all chemical reactions proceed through transition state of potential energy higher

than the average potential energies which is in thermodynamic equilibrium with the reactants eventhough overall chemical reaction is irreversible. One of the most familiar phenomenon of reactions is the increase in the rate of reaction as the temperature is raised. The reactant molecules having average velocities generally do not undergo chemical reaction since they have insufficient energy to allow the formation of necessary transition state. The rate of reaction is then related to the number of molecules that pass from the 'reactant side' to 'the product side' in a given time. Raising the temperature, increases the concentration of molecules with sufficient energy to make the ascent and more conversions from reactants to products occur.

This theory postulates that molecules before undergoing reaction must form an activated complex in equilibrium with the reactants and that the rate of any reaction is given by the rate of decomposition of the complex to form the reaction products. Considering the reaction between A and B we may indicate the activated complex as $AB^{\neq}$ and representing the reaction as,

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

Reactants Activated complex

since the rate of reaction is proportional to the number of $AB^{\neq}$ couples passing through the transition state i.e. proportional to $AB^{\neq}$. The specific rate, $k_r = \frac{\text{rate}}{[A][B]}$ for the reaction should be

proportional to $K^{\neq}$ the equilibrium constant. Further, we can show that the constant of proportionality is very close to $\frac{kT}{h}$, where k is the Boltzmann's constant, T is the absolute temperature and h is Planck's constant. The transition state theory is analogous to corresponding-thermodynamic functions of ordinary chemical changes.

The free energy of activation

$$\Delta G^{\neq} = -RT \ln K^{\neq} = - RT \ln \left[\frac{k_r h}{kT} \right] \quad .....(1.4)$$

The enthalpy of activation $\Delta H^{\neq}$ for reactions in solutions is given by,

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

The entropy of activation, ΔS

$$\Delta S^{\neq} = \frac{\Delta H^{\neq} - \Delta G^{\neq}}{T} = R \left[T \frac{d}{dT}(\ln k) + \frac{\ln k_r h}{kT} - 1 \right]$$

$$....(1.6)$$

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$$.....(1.6)$$

ENTROPY OF ACTIVATION :

Entropy is a measure of randomness of a system. If a reaction occurs with an increase in entropy, there is more disorder, possibly more among the products than among the reactants. That is, there is more restrictions to the motion of reactant molecules

than to the motion of product molecules. The entropy of activation, which may be calculated from reaction, is a measure of freedom from restrain on motion among the reactants.[2]

The entropy of activation may be calculated by the equation,

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

It is a measure of the freedom from restraint to motion, among the reactants. Long et al.[3], amplifying a suggestion of Taft and Coworkers[4] have proposed the use of $\Delta S^{\neq}$ as a criterion of the mechanism of hydrolysis reaction. The reactions are usually classified unimolecular (A - 1,SN^1)or bimolecular (A - 2,SN^2). In the former case, a 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]

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

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

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

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

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

It seems quite reasonable that the loss of translational and rotational freedom of water molecules associated with the bimolecular process, should lead to lower the entropy of activation relative to

unimolecular process. 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 entropy of activation, and all known unimolecular acid catalysed reactions have entropy of activation nearly zero or have positive values.

SOLVENT EFFECT :

The reaction in solution state becomes much complicated due to solvent cage effect, solvation of activated complex, change in the ionic strength and dielectric constant etc. It is still important for discussing the reaction in terms of their elementary steps.

Change in solvent will affect the reaction rate much in the same way as they affect equilibria. Sometimes the solvent alters the rate without affecting the mechanism and rarely changes the mechanism without altering the rate. The most pronounced solvent effects are observed for reaction 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.[3]

The qualitative theory[6] of solvent effect, put forward by Hughes, Ingold and their collaborators, could be used as criteria for mechanism. It postulates that an increase in ionization power of solvent will favour an increase in the magnitude of charge.

IONIC STRENGTH EFFECT :

The reaction between two ionic species proceed through transition state complex which is in equilibrium with reactants. The equilibrium properties of such reactions can be greatly affected by other ionic species which are present in addition to the reactants. The ionic strength (μ) is defined by the equation,

$$\mu = \frac{1}{2}\sum C_i Z_i^2$$

where,

C_i = Molarity of the i^{th} ion

Z_i = Charge on the i^{th} ion

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

The theoretical rates can be calculated by applying second empharical equation of Debye-Huckel and can be compared with observed rates as has been done for the hydrolysis of propionamide.[6]

N -- Halogeno -- N -- Metalo -- aryl -- Sulphonamides

Oxidation and halogenation of organic compounds are two important phenomena. A lot of work has been reported in the above field. Mechanism of oxidation or halogenation follows very different pathways via different reaction intermediates under different reaction

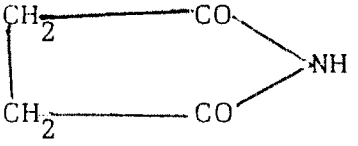
- - - - - - - - - - - - - - - - experimental conditions. Halogen derivatives of various organic substrates have played important role in industries and in laboratories, which find many applications in dyes, drugs and pesticides.

Organic haloamines are a separate class of compounds and has become the subject of interest of chemists due to their wide applications in industries and laboratories. They are strong oxidising and halogenating agents. They have been used as antiseptics, disinfectants and pest controllers.

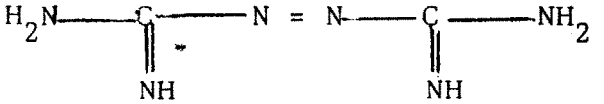
The haloamines are mainly divided into two classes, inorganic haloamines and organic haloamines. The organic haloamines are comparatively more stable than inorganic haloamines. The chloramine is the most important class of organic haloamines. These chloramines are N-chloro derivatives of following group of compounds.

i) Sulphonamide $Ph - SO_2-NH_2$

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



iii) Condensed amines from cyanamide derivatives



iv) Anilides : $C_6H_5.NH.CO.CH_3$

The diverse nature of chemistry of N-halogeno-N-metalo reagents is their ability to act as a source of

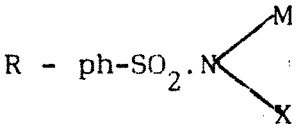
a) halonium cation

b) hypohalite species

c) N-anions

which behave as bases and nucleophiles. These metalo-haloamines react with a surprising range of functional groups resulting into an array of molecular transformations.

Several of the N-halogeno-N-metalo-aryl-sulphonamides are denoted by general formula



and

called by the trivial names. e.g.

Chloramine - T(1 X = Cl,R=Me,M = Na)

Chloramine - B(1, X= Cl,R = H, M = Na)

Bromamine - B(1, X =Br, R = Me, M = Na)

Organic chloramines are generally prepared by the reaction of hypochlorous acid with the group of compounds given above. 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 monochloramines can be represented as

$$R\text{-}Ph\text{-}SO_2N\text{-}Cl^- + 2\bar{I} + 2H^+ \longrightarrow R\text{-}Ph\text{-}SO_2\text{-}NH + I_2 + Cl^-$$

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

$$R\text{-}Ph\text{-}SO_2\text{-}NCl_2 + 4\bar{I} + 2H^+ \longrightarrow R\text{-}Ph\text{-}SO_2\text{-}NH_2 + 2I_2 + 2Cl^-$$

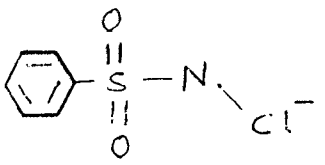
From the analytical point of view, the most important class of chloramines is perhaps the N-chloro derivatives of aromatic sulphonamides.

REACTIONS WITH CAB :

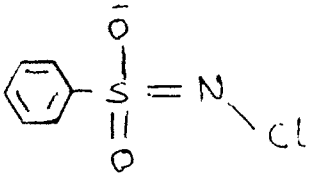
Sodium N-chlorobenzenesulphonamide or chloramine-B(CAB) has received considerable attention as a new oxidometric reagent and was first proposed by Afans'ev. CAB is a stable compound with a slightly higher active chlorine content than its analogue chloramine-T.

Chloramine-B ($phSO_2.N.Cl.Na.3H_2O$) is a stable and efficient substitute for CAT.

Chloramine-B was prepared by passing pure chlorine through benzene sulphonamide dissolved in sodium hydroxide solution(4M) over a period of 1 hr at 70^oC and recrystallized from water. The purity of compound was checked by estimating the amount of active chlorine present in the compound. The structure of CAB is generally shown as A and occasionally as B.



A



B

Oxidation and chlorination of many substrates can be carried out by CAB. CAB can liberate iodine from acidified solution of potassium iodide.

$$Ph\text{-}SO_2\text{-}NCl^-Na^+ + 2I^- + 2H^+ \longrightarrow PhSO_2NH_2 + I_2 + NaCl \qquad .....(1.1)$$

Like CAT, CAB in aqueous solution behaves as a strong electrolyte.

It dissociates as -

$$RNClNa \rightleftharpoons RNCl^- + Na^+ \qquad .....(1.2)$$

$RNCl^-$ readily picks up a proton to form free acid, RNHCl as shown below.

$$RNCl^- + H^+ \rightleftharpoons RNHCl \qquad .....(1.3)$$

The free acid cannot be isolated but can be detected. It decomposes to give benzene sulphonamide (RNH_2) and Dichloramine-B ($RNCl_2$) as-

$$2RNHCl \rightleftharpoons RNH_2 + RNCl_2 \qquad .....(1.4)$$

Dichloramine-B and free acid on hydrolysis give hypochlorous acid (HOCl)

$$RNCl_2 + H_2O \longrightarrow RNHCl + HOCl \quad .....(1.5)$$

$$RNHCl + H_2O \longrightarrow RNH_2 + HOCl \quad .....(1.6)$$

Finally HOCl ionises to H^+ and OCl^- as

$$HOCl \rightleftharpoons H^+ + OCl^- \quad .....(1.7)$$

D.N.Popov[7] showed that chloramine-B. ($Ph.SO_2.N.Cl.Na.3H_2O$) is a stable and efficient substitute for CAT with slightly higher active-Cl content. It could be efficiently used to purify drinking water.

Zilberg[8] has shown that acidic solutions of CAB give dichloramine-B and benzene sulfonamide. Mogilevski[9] et al have reported the presence of HOCl in acidic CAB solution. Chloramine-B was first prepared by Chrzaszczewska[10]. A Sing[11] introduced chloramie-B as a volumetric reagent. CAB in conjunction with KBr in presence of HCl has been used for the oxidation of alkali sulphides, thiocyanates, sulphites and bisulphites and H_2SO_3 and sodium thiosulphate and tetrathionate respectively. It has also been used with KBr as a bromometric reagent instead of $KBrO_3$ in acidic medium by Paul and Singh.[12] Higuchi[13] have studied the reaction between tertiaryamines and organic-halogenating agents. J.Veger and Perlin[14] have determined the active chlorine (28% active chlorine) and NaClO (62% active Cl) in CAB.

Direct procedure has been described for the determination of mercaptans and sodium and potassium salts of alkyl xanthates with chloramie-T and chloramine-B in presence of potassium iodide.[15] Ruff and and Kucsman[16] reported the mechanism of the reaction of sulphides with

N-chloroarenesulphonamides. They showed that $Ar.SO_2.NCl^-.Na^+$ in water transformed into $Ar.SO_2.NHCl$ and $Ar.SO_2.NCl_2$ which are reactive electrophiles which in turn react with sulphides.

CAB was introduced as an analytical reagent. Thioacetamide, thiosemicarbazides, iodide, bromide, thiourea were analysed by Shanmuganathan et al.[17] Some analytical applications of CAB have been reported by Rangaswamy et al.[18] Allyl alochol, crotyl alcohol and cinnamyl alcohol were estimated by Yathirajan et al.[19] Gowda and Murthy[20] have analysed redox indicators with CAB. Rare earth complexes of glutamic acid with CAB have been estimated.[21] Procedure for estimation of thiosemicarbazide alone and in its metal complexes[22] (with Zn, Cd, Hg, Ni, Pt and Pd) by CAB has been developed. Thiocyanate with aromatic halosulphonamides in acid and alkaline media were analysed by Gowda and Mahadevappa.[23] Cyanides in pure state and in mixtures[24] have been estimated with organic halosulphonamides.

Oxidation of KI by CAB was studied. The rate constant decreases with increasing pH was proposed.[25] The kinetics and mechanism of the oxidation of substituted benzyl alcohols and also aliphatic alcohols by CAB has been reported by Mukherjee and Banerji.[26,27] Rangaswamy and Yathirajan[28] have reported the mechanism of oxidation of dimethyl sulphoxide. Mathur and Banerji[29] reported the oxidation of glycolic, lactic and -hydroxybutyric acids by CAB and suggested the formation of $Ph.SO_2NHCl$. A mechanism involving transfer of hydride ion to oxidant is proposed.

Shah and Jain[30] have investigated the oxidation of diols by CAB in acid medium. Formation of $Ph.SO_2.NHCl$ has been postulated. Kinetics of oxidation of substituted mandelic acids by CAB in aqueous acetic acid and $HClO_4$ has been studied by Jain and Banerji.[31] Formation of $Ph.SO_2.NHCl$ has been postulated as the active oxidising species. A mechanism involving transfer of a hydride ion to the oxidant has been reported. Oxidation of methyl green by CAB has been investigated by Ramanauskas and Seskauskience.[32]

Jayaram and Mayanna[33] have studied the oxidation of caffiene by CAB. The kinetics being first order in $[CAB]$, fractional order in $[H^+]$ and $[Cl^-]$ but independent of substrate concentration and ionic strength. Whereas Mahadevappa et al[34] reported the oxidation of alanine and phenyl alanine by CAB in HCl medium and proposed reaction mechanism with ion dipole formation.

Jayaram and co-workers[35] have studied the oxidation of pyrodoxine by CAB. The mechanism involving ClO^- formation is suggested. Oxidation of methionine with CAB in aqueous solution was studied by Mahadevappa and co-workerrs.[36] Oxidation of thiocynate ions by CAB and BAB in presence of perchloric acid[37] as well as in alkaline medium[38] has been reported by Gowda and Bhat. Oxidation kinetics of E.D.T.A. by CAB in buffer medium has been investigated by Mohan, Ananda and Mahadevappa.[39] Oxidation of semicarbazides by CAB and BAB has been reported by Gowda and Bhat.[40]

The kinetics of oxidation of hydroxylamine hydro-chloride by CAB in hydrochloric acid medium has been studied by Nadig and Yathirajan.[41] The same authors have investigated the oxidation of hydroxyl amine hydrochloride[42] and cycloalkanes[43] in hydrochloric and perchloric acid media with CAB. Gowda and Bhat[44] reported the effect of metal complexation on kinetics and mechanism of oxidation of Zn (II) bound thiosemicarbazide by CAB in aqueous medium and also semiccarbazides[45] in acid medium by CAB.

CAT has been widely used as a chlorinating agent by several workers. Chlorination of cresols by CAT has been reported.[46] Balsubramanian and Thingarajan[47] have studied the kinetics and mechanism of chlorination of phenols with CAT. Chlorination of aniline, P-toluidine and P-nitroaniline with CAT has been reported by Radhakrishnamurti and Prasad Rao.[48] It is established that the reactions do not proceed through intermediate formation of hypochlorous acid. The result shows that the reactions are essentially of dipole-dipole type. A mechanism involving direct halogen transfer from CAT is proposed.

Ramanujam and Trieff[49] have reported the kinetics and mechanistic studies of reactions of aniline and substituted anilines. They have concluded that neither HOCl nor dichloro-amine-T is produced. The effective chlorinating species is N-chloro-toluene-P-sulphonamide. Kinetics of chlorination of aniline, o-chloroaniline, o-toluidine, m-chloro aniline and m-toluidine by CAT in aqueous acetic acid has been studied by Radhakrishnamurti and Prasad Rao.[50]

Kinetics and mechanism of chlorination of aliphatic amines with CAT at pH 7.4 and in 50% v/v ethanol medium has been reported by Uma and Mayanna.[51] Chlorination of aniline by dichloro-toluene sulphonamide in aqueous acetic acid medium has been studied by Gowda and Sherigara.[52]

CAB is also used as a chlorinating agent. But not much work is done in this regard. Antelo et al[53] have studied alcoholamine chlorination and the influence of pH on reaction with CAB. They showed that $ClNR.CH_2.OH$ is the intermediate precursor of the reaction products. Jayaram and Mayanna[54] have reported the chlorination of P-aminobenzoic acid by CAB in HCl medium. The reaction was first order in CAB and HCl but fractional order in P-aminobenzoic acid. Complex formation between the substrate and oxidant in equilibrium step prior to the rate determining step was suggested.

Usha and Yatiirajan and Rangaswamy[55] have studied the kinetics and mechanism of 2-methylphenol with CAB in hydrochloric acid medium. First order dependance on $[CAB]$ and zero order on $[substrate]$ and fractional order dependance on $[H^+]$ and $[Cl^-]$ was noticed. When catalysis was effected simultaneously by H^+ and Cl^- an order of 2 on gross concentration of HCl was observed. The positive ion H_2O^+Cl is considered to be the reactive chlorinating agent.

$$-\frac{d[CAB]}{dt} = k'[CAB][H^+]^{1.2} + k''[CAB][Cl^-]^{0.8}$$

was proposed.

The chlorination of aniline[56] has been reported by the same authors. Kinetics of chlorination of aniline by CAB in HCl medium obey the rate law,

$$-\frac{d[CAB]}{dt} = k\,[CAB]\,[H^+]^{1.27}\,[S]^{0.4} + k\,[CAB]\,[Cl^-]^{-0.7}\,[S]^{-0.4}$$

The active species in the oxidation is RNH_2Cl. Chloride ion catalyses the reaction. An order of 2 on gross concentration of HCl is obtained indicating mixed order kinetics with simultaneous catalysis of H^+ and Cl^-.

Recently Nadig, Yathirajan and Rangaswamy[57] have reported the chloranation of anisole by CAB in acid medium.

REACTIONS WITH AMINES :

The kinetic studies on the halogenation of labile aromatic molecules like amines have received scanty attention mainly for two reasons :

i) The reactions are too fast to permit a precise kinetic analysis and,

ii) The conventional chlorinating agents like molecular chlorine and HOCl are very active. Recently it has been reported that CAB brings about chlorination of aniline at a measurable rate: evidences were presented for direct halogen transfer from CAB but not through the formation HOCl or molcular chlorine as intermediates.

Amines find many applications in chemical industries. They have got applications as dyes, drugs, insecticides and pesticides. The halogen derivatives of amines are well known for their antifungal, antibacterial and disinfectant activities. Amines are highly reactive in nature. Aromatic amines show ortho-para directing nature due to resonance stabilisation.

Aromatic amine such as aniline being an ambident nucleophile, might be expected to react with a chlorinating agent carefully on nitrogen because this atom constitutes the most highly nucleophile site of the molecule. Ultimate carbon chlorine co-valency formation would be attributed to the instability of this N-chloroaniline intermediate.

Amines have been oxidised and halogenated by different oxidising agents. Much work has been done on oxidation and halogenation of aliphatic and aromatic amines using various oxidants such as acid bromate, chlorosuccinimide, hypohalite, chloramine-T and chloramine-B.

Generally, azocompounds, aldehydes, quinones and halogen derivatives are the oxidation products of amines. Pryde and Soper[58] have reported the formation of N-haloamines by hypohalite. A series of N-chloroanilines has been synthasized and their methanolysis has been studied in presence of silver trifluoroacetate by Gassman, Campbell and Frederick.[59] Kinetics of the bromination of some aromatic amines with aqueous bromine was studied by Bell and Ramsden.[60]

Kinetics of oxidation of aniline and substituted anilines by sodium iodate in aqueous acetic acid medium in the presence of perchloric acid has been studied by Prasada Rao and Padmanabha.[61] Free amines were the reactive species and reactions found to be of dipole-dipole type. Iodination of aniline and substituted anilines in aqueous dimethyl sulphoxide and dimethyl formamide has been reported by Radhakrishnamurti and Janaradhana.[62] The same authors studied the iodination of aniline and substituted anilines by N-iodosuccinimide[63] in aqueous acetic acid medium.

Prasad Rao and Padmanabha[64] have studied the iodination of aniline and substituted aniline by iodine monochloride. Dangat, Bonde, Gayakhe and Ghorpade[65] have carried out the iodination of aniline and anthranilic acid by iodine in aqueous medium.

The chlorination of aniline with calcium hypochlorite has been reported by Haberfield and Paul.[66] They proposed the formation of N-chloro intermediate. Gassman and Campbell[67] have studied the chlorination of anilines and related anilines; the chlorinating agents were chlorosuccinimide and calcium hypochlorite and established the intermediates of N-chloramines. They suggested that chlorination proceeds via heterocyclic cleavage of N-Cl bond to yield a nitronium ion and chloride ion.

Radhakrishnamurti and Sahu[68] have reported the kinetics and mechanism of chlorination of aniline and substituted aniline

by N-chlorosuccinimide in acetic acid and sodium acetate. A mechanism involving direct halogen transfer to the aromatic system was suggested. They have ruled out the possibility of formation of C-halogenated products. Antelo, Arce, Franco and Verla[69] have studied the chlorination of secondary amines by N-chlorosuccinimide and postulated a mechanism of direct exchange of positive chlorine between N-chlorosuccinimide and amine. Kinetics and mechanism of chlorination of aniline by trichloromelamine in aqueous perchloric acid medium has been reported by Radhakrishnamurti and Panigrahi.[70] The direct halogen transfer from active species of trichloromelamine to the aromatic system was suggested. The chlorination of reactive anilines has been reported by Neale et al[71] using N-chlorosuccinimide in hot benzene. They postulated the formation of N-chloro intermediate. Ramanujam and Trieff[49] have carried out the chlorination of aromatic amines, viz. aniline and monosubstituted anilines in 50% v/v ethanol and buffer at pH 7.4 Uma and Mayanna[51] have reported the kinetics and mechanism of chlorination of aliphatic amines in 50% v/v ethanol and buffer at pH 7.4 by CAT. Chlorination of aniline by CAB in hydrochloric acid medium has been studied by Usha, Yathirajan and Rangaswamy.[56]

SCOPE OF THE PRESENT WORK :

It is obvious from above survey that kinetics of chlorination by CAT of aniline and substituted anilines and aliphatic amines has been studied. But so far no work has been reported on

chlorination of substituted anilines by chloramine-B in HCl medium. The present work deals with the kinetics of chlorination of substituted anilines viz. ortho-toluidine (o-T) and meta-toluidine (m-T) by CAB in hydrochloric acid medium. The following parameters would be studied and suitable mechanism consistent with experimental results would be proposed.

1) Effect of concentration of chloramine-B
2) Effect of concentration of substrate
3) Effect of temperature.
4) Effect of concentration of hydrochloric acid medium.
5) Effect of hydrogen ion concentration at consttant chloride ion concentration.
6) Effect of chloride ion concentration at constant hydrogen ion concentration.
7) Effect of ionic strength.
8) Effect of change in solvent composition.