1.1: GENERAL

Any attempt to understand the mechanism of a chemical process requires knowledge of elementary processes involving atoms, molecules and ions that participate simultaneously or consecutively in producing the observed overall reaction. Kinetics, a branch of physical chemistry, is an important and effective tool to deal with the role of all factors which may influence the velocity of a chemical reaction under investigation. The observed effect in the rate of the reaction is explained in terms of reaction steps, called reaction mechanism.

Chemical reactions of wider application have attracted the attention of several scientists since long period for showing their interest in evolving or suggesting the mechanism of such reactions. The scientists engaged in such endeavour have employed the kinetic observations gathered in their studies to achieve their aims to large extent. Their interest in such studies is based on the vast applications of such reactions in several fields such as industries, agricultural problems and medicinal zones. For a chemist the importance of a kinetic study lies in the fact that by understanding the dependence of the various reactions on different reaction variables such as concentrations of various species involved in the chemical process, temperature, solvent dielectric constants, ionic strength of the medium, solvent isotope etc., one can
control the course of formation of products of a chemical reaction with such parameters. Thus a researcher in this field can find out the conditions required for favouring a desired product. A knowledge of the mechanism by which the reactants are converted into products is of great value and the study of kinetics of the reaction coupled with other techniques offers one of the most satisfactory and successful ways for obtaining information about the pathways involved in a particular reaction. The present interest of chemists in kinetics is due to precise and careful interpretation of kinetic data collected under different conditions. The numerous scientific publications of difficult and complicated reactions have helped in acquiring further developing confidence in researchers. The scientists with such an amount of confidence have been able to solve many difficult reactions mechanism.

The most thoroughly probed reactions in solutions from kinetic points of view have been redox systems. It is customary to represent generally the redox reactions as electron transfer reactions in inorganic chemistry while transfer of atoms or ions is involved in most of the organic redox systems. The presence of a considerable solvation barrier formed by the surrounding water molecules around the ions has ruled out the direct electron jump from the reactant to oxidant molecules in solution, while during oxidation-reduction process the transfer of atoms or ions between the species involved is supported by experimental
facts. The mechanism based on such transfer of atoms or ions seems to be quite reasonable.

The studies of radioactive exchange between two species in different oxidation states involving no net chemical reactions also support the mechanism of transfer atoms or ions.

Thus oxidation process is accompanied by transfer of hydrogen species such as hydrogen atom or hydride ion but not the proton, while the transfer of oxygen species such as oxygen atom but not oxide or hydroxide ion and transfer of chlorine species such as chlorine atom or chlorinium ion but not chloride ion brings about reduction. Although in many inorganic redox systems electron transfer alone has been reported to cause a change in the oxidation state of donor and recipient, but recent reports indicate that electron transfer is by no waves the only favored route used by such powerful oxidants as permanganate ion and chromic acid. Thus kinetics provides a very interesting tool to identify the routes or paths of reactions and is time dependent.

In order to elucidate the satisfactory mechanism of reactions in solution, considerable informations are required. These informations can be collected by studying the effect of several factors that may or may not influence the rate of the reactions. If kinetics is taken as basic tool for the study of mechanism of such reactions, then one important factor is the order of the reactions with respect
to all possible species involved in the chemical reactions. The studies of effect of ionic strength of the medium, effect of solvent, and effect of variation of dielectric constant of the medium and temperature variation effect on the rate of the reactions are also important information which guide in evolving a suitable and convincing mechanism of the reactions. The structures and identifications of intermediates and other informations about them and use of isotopic method immensely help in establishing the real reactions routes followed in a chemical reaction. Finally, on the basis of such above mentioned informations, the rate law is derived with the help of suitable possible assumptions and thus better and clear insight of the mechanism of the chemical reaction is exposed.

Bomford and Trapper have discussed a detailed account of a large number of familiar and less familiar redox reagents in a recent publications. In another publications, Berke and Zyka have also discussed several less familiar and newer redox titrants. The authenticity of the proposed mechanism on the basis of aforesaid informations is, further, strengthened by isolation, characterisation and identification of the final reaction products it is thus possible to visualise many intermediate products which are although very reactive but at the same time short lived. The existence of such valuable short lived intermediates or free radicals can be demonstrated by the addition of radical traps or scavengers such as allyl acetate, vinyl
monomers which readily combine with the free radicals. These free radicals can also be identified by informations obtained from electron paramagnetic resonance (EPR) studies.

The oxidising and reducing capacity of a compound is often determined by its redox potential from which the knowledge of free energy available for a redox reaction can be obtained. However, this knowledge is not ultimate as there are several other factors which affect the rate of a reaction. In recent studies it is reported that an increase in electronegativity causes reduction while an increase in electropositivity brings about oxidation. Thus oxidation and reduction processes are complimentary to each other and these processes take place simultaneously.

Recently, systematic reports on kinetics and mechanism of several redox processes involving newer redox titrants have been made. The detailed investigations on a number of reactions catalysed by silver (I), copper (II), Osmium (VIII) and colloidal silver have been reported. A recent study has been reported on the kinetics of oxidation of some α-hydroxy acids by chloramine-T using osmium tetroxide as catalyst. Several aliphatic aldehydes and reducing sugars have been used as substrates for chloramine-T oxidation kinetics in alkaline media. Agrawal and Mushran have also discussed the oxidation of Hexacyanoferrate (II) by chloramine-T in acidic media. Recently Mehrota and Mushran have investigated the
mechanistic steps in the oxidation of monohydric primary and secondary alcohols by chloramine-T in acidic media with and without the use of osmium tetroxide as catalyst.
Chloramine-T is known as sodium salt of N-chloro-p-toluenesulphonamide. It is less familiar but a very potent oxidising agent both in alkaline and acidic media. A close survey of literature reveals that chloramine-T has been employed for the determination of numerous inorganic and organic substances. Although much work has been quoted in literature on this compound used as oxidant but still there is much scope to study the kinetics and mechanism of oxidation of various reducing substances using different kinds of catalyst with this oxidant both in alkaline and acidic media. Keeping this aim in mind, the present work envisages the investigation on the kinetics and mechanism of oxidation of a few cycloalcohols with chloramine-T using osmium tetroxide as catalyst in alkaline media and further, an attempt has been made to establish the mechanism and spell out the various intermediate steps involved in such reactions.

The aqueous solutions of chloramine-T if stored in dark, do not change their strength for several months and hence are stable. It has been observed that solutions become cloudy due to slow decomposition with the formation of chlorinated sulphonic acids in the presence of sunlight. This precipitate is not the same as the dichloramine-T thrown down in acid solution and pH falls to 5.6 from initial value of 7.7 over a year giving support to the
contention of dietzel and taufel that the photochemical self oxidation decomposition product of acidic in nature.

According to Carlsen, the photochemical deterioration of chloramine-T solution is not detectable beyond 450 mµ. The hydrolysis of chloramine-T in water is often incompletely described so that chloramine-T and hypochlorite solutions are regarded as completely similar in properties. It follows that chloramine-T may be substituted directly for hypochlorite, or for bromate in the presence of bromide, iodate in the presence of iodine monochloride or iodine in the presence of iodide.

It has been reported that chloramine-T hydrolysis in water according to the following equation.

\[ \text{CH}_2\text{C}_6\text{H}_4\text{SO}_2 \text{N} \text{NaCl} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2\text{C}_6\text{H}_5\text{SO}_2\text{NH}_2 + \text{Na}^+ + \text{ClO}^- \]  \( (1) \)

The species in the right side of above equation (1) will ionise and except in alkaline medium, the hypochlorite ion will hydrolyse to hypochlorous acid which is assumed to be oxidising species as described above. Most of the publications on chloramine-T deal with qualitative properties and pharmaceutical use of the reagent and its stability. However recent publications on chloramine-T have discussed mostly the kinetic behaviour of the reactions. In the present investigation an attempt has been made to reveal the kinetic observations on which basis the reaction routes have been proposed.

The structure of chloramine-T is generally described as (A) and occasionally as (B)
In addition to above, other reactions would take place as given below:

\[
\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N} \cdot \text{NaCl} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHCl} + \text{NaOH} \quad \ldots \text{(2)}
\]

\[
2\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N} \cdot \text{NHCl} \rightleftharpoons \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NC}_{12} + \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2 \quad \ldots \text{(3)}
\]

\[
\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NC}_{12} + \text{NaOH} \rightleftharpoons \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHCl} + \text{NaClO} \quad \ldots \text{(4)}
\]

\[
\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N} \cdot \text{NHCl} + \text{NaOH} \rightleftharpoons \text{NaClO} + \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2 \quad \ldots \text{(5)}
\]

Hypochlorous acid is formed as a result of hydrolysis of sodium hypochlorite in an acidic or neutral media.

\[
\text{NaClO} + \text{H}_2\text{O} \rightleftharpoons \text{NaOH} + \text{HClO} \quad \ldots \text{(6)}
\]

Some of researches such as Bishop and Jennings 54 48 55 Soper, Dietzel et al and Morris et al have reported that quite different equilibria exist in the hydrolysis of chloramine-T. Accordingly, Chloramine-T has been described as strong electrolyte which first dissociates.

\[
\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N} \cdot \text{NaCl} \rightleftharpoons \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NC}_{12}^- + \text{Na}^+ \quad \ldots \text{(7)}
\]

The anion thus formed takes up hydrogen ion to form the free acid which disproportionates to give p-toluene sulphonamide and sparingly soluble dichloramine-T.

\[
\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NC}_{12}^- + \text{H}^+ \rightleftharpoons \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHC}_{12} \quad \ldots \text{(8)}
\]

\[
2\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHC}_{12} \rightleftharpoons \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NC}_{12} + \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2 \quad \ldots \text{(9)}
\]

The dichloramine-T and free acid hydrolysis as

\[
\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NC}_{12} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHCl} + \text{HOC}_{12} \quad \ldots \text{(10)}
\]

\[
\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHCl} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2 + \text{HOC}_{12} \quad \ldots \text{(11)}
\]

The hydrolysis constant for these two reactions (10) and (11) are \(8 \times 10^{-7}\) and \(4.88 \times 10^{-8}\). It appears that hydrolysis is therefore slight. Finally the hypochlorous acid ionises \((\text{Ka} = 3.30 \times 10^{-8})\). The concentration of
various species present in 0.05 M chloramine-T solution over a range of pH value are given by Bishop and Jennings, thus the nature of the main oxidising species of chloramine-T depends upon the pH of solution.

The solutions of chloramine-T can be standardised easily by the addition of potassium iodide and starch and titrating the liberated iodide by standard sodium thiosulphate solutions. Chloramine-T has also been employed for the direct titration of sodium arsenite using potassium iodide and starch.

In the estimation of halides, chloramine-T has also been used as a substitute for chlorine water. The redox potential of chloramine-T & p-toluene sulphchloramide system was reported by Afanas'ev as 0.90 Volt in the neutral solution and 1.52 Volts in 1N-H₂SO₄. Murthy and Rao have reported that redox potential for this system varies from 1.139 to 0.499 Volts for the variation of pH from 0.65 to 1.20. Noll has used chloramine-T as substitute for iodine in analytical chemistry.

Mahadevappa and coworkers have estimated rongalite thioglycollic acid, cysteine, they have also estimated unsaturated alcohols such as allelic alcohols, crotyl alcohol and cymnmyl alcohol by chloramine-T.
1.3: KINETICS AND MECHANISM OF CHLORAMINE-T OXIDATION

Much work thus appears to have been done on exploring the importance of chloraminometric oxidation of a large number of compounds but literature on step by step oxidation with this oxidant under a variety of conditions is scanty.

Coul and coworkers for the first time studied the kinetics and mechanism of hydrogen peroxide by chloramine-T in presence of hydrochloric acid. Logistic function was used for the determination of the reaction rates. The rate law showed a first order dependence to hydrogen peroxides and chloramine-T and an inverse first-order in p-toluenesulphonamide concentration. They suggested a mechanism involving formation of chlorine as a result of interaction between chloramine-T and hydrochloric acid.

Kocsman and coworkers studied the kinetics and mechanism of reaction of substituted methyl aryl sulphides and diaryl sulphides with chloramine-T and proposed the mechanism of sulphilimine synthesis. Further, Modena and coworkers obtained similar results for the oxidation of same thioanisoles. Kinetics and mechanism of oxidation of glycerol by chloramine-T has been made by Weker and Valic in neutral and alkaline media. The rate of the reaction was found to be independent of glycerol concentration and the reaction was autocatalytic in nature.

Higuchi and Hussain have studied the kinetics of
chlorination of p-cresol by chloramine-T.

The kinetics of chloramine-T oxidation of secondary alcohols has recently been studied. Mushran and Coworkers have recently reported oxidation of amino acids. They have also studied the kinetics of oxidation of EDTA by chloramine-T. Banerjee has studied the oxidation kinetics of primary alcohols-chloramine-T redox system in acidic media. Recently Santappa and Coworkers have investigated decarboxylation chlorination of cinnamic and crotomic acids by chloramine-T in acidic buffered media. Radhakrishnamurti and Sahu have studied the kinetics and mechanism of halogenation of benzaldehyde by chloramine-T in acidic media of pH 4.5. Carboxylic acids are the products at PH 4.5 in aqueous media where as halogenated benzaldehydes are formed in aqueous acetic acid sodium acetate buffer medium.
1.1: PRESENT WORK

In the present thesis, an attempt has been made to study the kinetics and mechanism of oxidation of cyclopentanol, cyclohexanol, and 2-methyl cyclohexanol by alkaline solution of chloramine-T in the presence of osmium tetroxide as homogeneous catalyst. The main aim of the present investigation is to explore the catalytic species of osmium tetroxide in alkaline medium in chloramine-T-cycloalcohols redox systems and to interpret its catalytic role in elucidation of reaction mechanism of the reaction undertaken here.
1.5: A SUMMARY OF KINETIC RESULTS AND RATE LAW DERIVED ON THE BASIS OF PROPOSED MECHANISM

The following kinetic observations have been recorded in osmium tetroxide catalysed oxidation of a few cycloalcohols by alkaline solution of chloramine-T.

(i) Oxidation of cyclopentanol, cyclohexanol and 2-methyl cyclohexanol shows first order dependence on oxidant which is chloramine-T.

(ii) First order dependence of all reactions on each of cycloalcohols was observed.

(iii) First-order kinetics with respect to sodium hydroxide was exhibited.

(iv) All reactions showed first-order with respect to osmium tetroxide.

(v) Negligible effect of change in ionic strength of reaction mixture on rate of oxidation of all cycloalcohols was observed.

(vi) Zero effect of addition of P-toluenesulphonamide (a reduction product of chloramine-T) on rate of reactions was observed.

(vii) Marked effect of rise in temperature on reaction velocity was observed.

On the basis of kinetic data, a suitable mechanism of proposed, which yielded the following rate law in agreement with kinetic observations:

\[-d[\text{CAT}]/dT = k [\text{CAT}][\text{OH}^-][\text{OsO}_4][S]\]
where $S = \text{cycloalcohols}$

$\text{CAT} = \text{Chloramine-T}$ &

$k = k_2 k_3 k_1 / k_- [\text{H}_2\text{O}]$
42. A. Berka, Chemic, 10, 121 (1958).
47. T. Carlsen, Denk. Tidersks, Farm, 30, 29 (1956).