The present thesis deals with the study of kinetics and mechanism of hydrolysis of iso-amyl iodide, sec-amyl iodide, n-heptyl chloride, n-heptyl iodide and n-octyl iodide in both alkaline (i.e. in presence of sodium hydroxide) and neutral (i.e. in absence of sodium hydroxide) media in alcohol-water mixture. The effect of change in the composition of medium on reaction velocity has been studied. In the reaction between n-octyl iodide and sodium hydroxide, in most of the experiments, the medium contained 70% of alcohol by volume and same composition of medium was maintained in the study of neutral hydrolysis of the halide. In case of other four halides studied, (i.e. iso-amyl iodide, sec-amyl iodide, n-heptyl chloride and n-heptyl iodide) the medium contained 60% of alcohol by volume in most of the experiments. The hydrolysis of all these halides have not been studied so far by any previous worker in any medium.

In the study of kinetics of alkaline hydrolysis of iso-amyl iodide, n-heptyl chloride, n-heptyl iodide and n-octyl iodide, it has been found that the overall process consists of three simultaneous reactions and these reactions have been shown to exhibit recognizably distinct kinetic characteristics. These three simultaneous reactions are (1) second order substitution reaction, (2) second order elimination reaction and (3) first order substitution reaction. In presence of finite concentration of hydroxyl ions the total order of reaction is two (unity with
respect to each of the reactants) while in absence of alkali, the order of the reaction is unity.

The contribution to overall velocity by first order process was found to be very small and hence the rate constant for the first order process may be neglected as compared to that of bimolecular processes in presence of even very small concentration of hydroxyl ions. In absence of sodium hydroxide, the first order process alone occurs and it has been observed that the rate of the first order process increases with the increase in the dielectric constant of the medium.

In the reaction between sec-amyl iodide and sodium hydroxide it has been found that four simultaneous reactions are occurring together. Two of these reactions are second order processes (i.e. substitution and elimination) while the other two are first order processes (i.e. substitution and elimination). Further, the study of first order processes carried out in neutral medium shows that the velocity of first order processes increase with the increase in the dielectric constant of the medium (i.e. with decrease in the concentration of alcohol).

In all cases, the reaction products have been studied and identified, the entire data obtained have been interpreted and in general it has been shown that in the second order processes, the rate determining step involves a direct attack by hydroxyl ion on the halide molecule leading to the formation of corresponding alcohol or olefin so that the overall second order process consists of two simultaneous reactions – one, the second order substitution process leading to the formation of
corresponding alcohol while the other, the second order elimination process leading to the formation of olefin. It is difficult to decide on the basis of the present data whether the reactants form identical or different activated complex in the two reactions.

The first order process alone predominates in the neutral hydrolysis of halides. The mechanism of first order process is somewhat controversial. we have, however, shown that the rate determining step in the first order processes consists of simultaneous attack by a number of water molecules on the halide molecule inside the “solvent – cage” and rate of the reaction follows first order kinetics because, for any given composition of the solvent, the concentration of the water molecules can be taken to be constant. The increase in the reaction velocity of the first order process on decreasing the concentration of alcohol (i.e. on increasing the concentration of water molecules) shows that the mechanism of the first order process postulated by us is correct.

The values of reaction constants for various first order and second order processes have been separately determined in each case. The magnitudes of various rate constants of halides studied here, under identical conditions, are as follows:

(I) Second order substitution rate constant \( (k_2) \) n- heptyl iodide > n-octyl iodide > iso-amyl iodide > sec-amyl iodide > n-heptyl chloride.
(II) Second order elimination rate constant \( k_2 \) sec-amyl iodide > iso-amyl iodide > n-heptyl iodide > n-octyl iodide > n-heptyl chloride.

(III) First order substitution rate constant \( k_{iS} \) sec-amyl iodide > iso-amyl iodide > n-heptyl iodide > n-octyl iodide > n-heptyl chloride.

(IV) First order elimination rate constant \( k_{iE} \) - First order elimination reaction occurs only in sec-amyl iodide. Since no trace of olefin was found in first order process in all halides studied here, except sec-amyl iodide, therefore, everywhere in these halides first order substitution rate constant has been written as \( k_i \), but here for comparison of first order substitution rate constants \( k_i \) in these halides with that of sec-amyl iodide, we have written \( k_i \) as \( k_{iS} \) in (III) above.

1.2 THE RATE EXPRESSION FOR THE REACTIONS STUDIED

Our study indicates that the rate expression, in general can be written in the form

\[- \frac{d[RX]}{dt} = k_2 [RX] [OH^-] + k_2^* [RX] [OH^-] + k_{iS} [RX] + k_{iE} [RX] \ldots (1.1)\]

\[= k_2 [RX] [OH^-] + k_i [RX] \ldots \ldots (1.2)\]

Where \( k_2 = (k_2 + k_2^*) \) and \( k_i = (k_{iS} + k_{iE}) \)

\( k_2 \) is the overall second order constant while \( k_i \) is the overall first order constant \( k_2 \) and \( k_2^* \) are the rate constants for the second order
substitution and second order elimination reactions respectively. Similarly \( k_{iS} \) and \( k_{iE} \) are the rate constants for the first order substitution and elimination reactions respectively.

### 1.2A STUDY OF THE HYDROLYSIS OF ISO-AMYL IODIDE, \textit{n}-HEPTYL CHLORIDE, \textit{n}-HEPTYL IODIDE AND \textit{n}-OCTYL IODIDE

#### ALKALINE HYDROLYSIS

In case of above halides the rate expression Ben (1.1) can be written in the form:

\[
- \frac{d[RX]}{dt} = k_2^' [RX] [OH^+] + k_2^" [RX] [OH^-] + k_1 [RX] \quad \ldots \quad (1.3)
\]

Further, in presence of finite concentration of sodium hydroxide, the contribution to overall velocity due to first order process is very small as compared to second order processes. Hence the last term in eq. (1.3) can also be neglected as compared to other terms and the overall velocity of the reaction will be almost entirely due to the second order processes. Hence, the rate expression in presence of sodium hydroxide can be put in the form

\[
- \frac{d[RX]}{dt} = k_2^' [RX] [OH^+] + k_2^" [RX] [OH^-] \quad \ldots \quad (1.4)
\]

\[= k_2 [RX] [OH^-] \quad \ldots \quad (1.5) \]

Where \( k_2 = (k_2^' + k_2^") \)
When the concentration of sodium hydroxide is large as compared to that of halide, the rate Eq. (1.5) can be written as

\[- \frac{d[RX]}{dt} = k_i [RX] \quad \ldots \ldots (1.6)\]

Where \( k_i = k_2 [\text{OH}^-] \quad \ldots \ldots (1.7) \)

The value of \( k_i \) can be calculated by employing the expression obtained on integrating the Eq. (1.6)

\[ k_i = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)} \quad \ldots \ldots (1.8) \]

Where ‘a’ is the initial concentration of the halide and ‘a-x’ is the concentration at time ‘t’.

Our experimental results show that the order of the reaction with respect to the halide molecule as well as hydroxyl ions is unity so that the total order of the reaction is two in presence of sodium hydroxide. According to Eq. (1.7) the value of \( k_i \) should change linearly with the initial concentration of hydroxyl ions. But actually we find that as the initial concentration of hydroxyl ions decreases, the value of \( k_2 \) increases, which is most probably due to decrease in the overall ionic strength of the medium. If the ionic strength of the medium is kept constant by adding a large quantity of a neutral electrolyte (e.g. sodium per chlorate), the value of \( k_2 \) remains constant and does not change with the change in the initial concentration of sodium hydroxide (see Tables 2.24, 4.8, 5.9 and 6.9). There is no precise commonly accepted theory to predict the effect of change of ionic strength on the velocity of the reaction which is taking place between dipolar molecule and a negative ion.
Our results are in agreement with the theory of Amis and Jaffe\(^1\). This type of behavior was also found by Hughes and Co-workers\(^2\) in the study of the reaction between iso-propyl halides and sodium hydroxide, by Hinshelwood\(^3\) in the study of the reaction between ethyl halide and potassium hydroxide and by Singh, Krishna and Behari\(^4\) in the study of reaction between bromides of n-hexyl, n-heptyl and n-octyl and sodium hydroxide. This conclusion has been further confirmed by Behari, Singh and Krishna\(^5\) in the study of alkaline hydrolysis of normal and iso-amyl bromides. The same conclusion has also been put forward by Goel, Behari and Krishna\(^17\) in the study of alkaline hydrolysis of n-amyl chloride, iso-amylchloride, n-amyl iodide and n-hexyl iodide.

**NEUTRAL HYDROLYSIS**

When the reaction is carried out in neutral medium (i.e. in absence of sodium hydroxide), the first two terms in Eq. (1.3) can be dropped and the rate can be expressed as

\[
- \frac{d[RX]}{dt} = k_i [RX] \tag{1.9}
\]

The mechanism of the first order reaction is somewhat controversial as mentioned earlier. The rate determining step in this case is ascribed due to simultaneous attack on the halide molecule by a number of water molecules present in the "solvent-cage". This is supported by the fact that the reaction velocity in neutral hydrolysis increase with the increase in the concentration of water.
In presence of finite concentration alkali, the first order processes are not entirely negligible in case of sec-amy1 iodide. Hence the first order processes have to be taken into account while studying the alkaline hydrolysis of the present halide Eq. (1.2) can be written in the form given below in the concentration of sodium hydroxide is large for any given run

\[- \frac{d[R1]}{dt} = k_1 [R1] \]  

....... (1.10)

Where \( k_1 = k_2 [OH^-] + k'_1 \)  

....... (1.11)

Therefore the value of \( k_1 \) can be calculated by the following expression for any given concentration of sodium hydroxide for any particular experiment.

\[ K_1 = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)} \]

.......(1.12)

The value of \( k'_1 \) and \( k_2 \) can be calculated from the graph plotted between \( k_1 \) and hydroxyl ion concentration. The value of \( k'_1 \) can also be determined separately by studying the reaction in neutral medium (i.e. in absence of sodium hydroxide).

The velocity of the second order processes is also influenced by the change of ionic strength of the medium, which has been discussed in detail in the experimental part (see table3.16 of section 3.4).
NEUTRAL HYDROLYSIS

In the study of neutral hydrolysis of sec-amyl iodide, the first term of Eq. (1.2) can be dropped and the velocity of the reaction can be expressed as

\[- \frac{d[R]}{dt} = k'_i [RI] \]  \hspace{1cm} \text{...... (1.13)}

Where \( k'_i = k'_{is} + k'_{ie} \)  \hspace{1cm} \text{...... (1.14)}

Our experimental data indicate that the value of \( k'_{ie} \) is small as compared to that of \( k'_{is} \) inspite of very low value of \( k'_{ie} \) it has been observed that the first order elimination process does occur and separate value of \( k'_{is} \) and \( k'_{ie} \) have been calculated (see Section 3.13).

1.2 C EFFECT OF CHANGE OF DIELECTRIC CONSTANT ON REACTION RATE

It has been observed that change in the dielectric constant of the medium (by changing the concentration of alcohol in the reaction mixture) affects the velocity of second order processes. The contribution to the overall velocity by the first order process is negligible in presence of sodium hydroxide and hence the change in the velocity observed with the change in the dielectric constant must be due to the change in the velocity of second order processes. Our results here, are in good agreement with the theory of Laidler and Eyring\(^6\) according to whom the velocity should decrease with increase in dielectric constant in a reaction between a dipolar molecule and a negative ion.
1.2 D  SEPARATION OF VARIOUS RATE CONSTANTS

It has been described earlier that in alkaline hydrolysis of halides studied here (except sec-amyl iodide where two bimolecular and two unimolecular processes simultaneously take place), two bimolecular (substitution and elimination) and unimolecular substitution reaction simultaneously take place. The various rate constants corresponding to the above described simultaneous reactions have been separated in the experimental part at appropriate places.

1.3  MECHANISM OF THE SECOND ORDER PROCESSES

On the basis of the study of the effect of various parameters on the reaction velocity, it has been concluded that the rate determining step in second order processes involves direct attack on the halide molecule by hydroxyl ion. The mechanism of the second order processes operating in reactions between halides (studied here) and hydroxyl ion can be represented as follows:

ISO-AMYL IODIDE

(1)  \[ \text{CH}_3 \text{CH}_2\text{CH}_2\text{CH}_2\text{I} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{I}^- \]  (Substitution process)

(2)  \[ \text{CH}_3 \text{CH}_2\text{CH}_2\text{CH}_2\text{I} + \text{OH}^- \rightarrow \text{CHCH} = \text{CH}_2 + \text{H}_2\text{O} + \text{I}^- \]  (Elimination process)
SEC-AMYL IODIDE

(1) \[ \text{CH}_3\text{-CH}_2\text{-CH}_2\text{CH}CH_3 + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHOHCH}_3 + \text{I}^- \]

(Substitution process)

(2) \[ \text{CH}_7\text{-CH}_6\text{-CH}_5\text{CH}CH_3 + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH} = \text{CH}_2 + \text{CH}_3\text{CH}_2\text{CH} = \text{CHCH}_3 + \text{H}_2\text{O} + \text{I}^- \]

(Elimination process)

n-HEPTYL CHLORIDE

(1) \[ \text{CH}_2\text{-} (\text{CH}_2)_3\text{-CH} - \text{Cl} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{Cl}^- \]

(Substitution process)

(2) \[ \text{CH}_2\text{-} (\text{CH}_2)_3\text{-CH} - \text{Cl} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{Cl}^- \]

(Elimination process)

n-HEPTYL IODIDE

(1) \[ \text{CH}_2\text{-} (\text{CH}_2)_3\text{-CH} - \text{I} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{I}^- \]

(Substitution)

(2) \[ \text{CH}_2\text{-} (\text{CH}_2)_3\text{-CH} - \text{I} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{I}^- \]

(Elimination)

n-OCTYL IODIDE

(1) \[ \text{CH}_2\text{-} (\text{CH}_2)_3\text{-CH} - \text{I} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{I}^- \]

(Substitution)

(2) \[ \text{CH}_2\text{-} (\text{CH}_2)_3\text{-CH} - \text{I} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{I}^- \]

(Elimination)
Our results indicate that bimolecular substitution reaction is much faster than bimolecular elimination reaction in all halides (studied here) except in sec-amyl iodide where bimolecular elimination process is much faster than bimolecular substitution.

On the basis of the present data, it is not possible to show whether both the processes pass through identical or different transition states. However, so far as the second order processes are concerned, the conclusions and mechanism put forward by us are somewhat similar to those of others in the study of the reaction between alkali and organic halides\textsuperscript{2-5, 7-17}.

1.4 **MECHANISM OF THE FIRST ORDER PROCESS**

(i.e. IN NUTRAL MEDIUM)

The mechanism of the first order process is controversial. The first order processes occurring in neutral medium has been explained in two different ways. Hughes and co-workers have emphasized in the study of hydrolysis of iso-propyl halide\textsuperscript{18}, and other alkyl halide\textsuperscript{19} that halide undergoes slow ionization followed by a rapid reaction between positive alkyl ion and a molecule of water or hydroxyl ion.

On the other hand Moelwyn Hughes and Fells\textsuperscript{20} have postulated in their study of substituted methyl halides that in the first order processes the halide molecule except carbon tetrachloride is attacked by number of solvent molecules.

\[
RX + \nu H_2O \longrightarrow ROH + (H, \nu + H_2O)^+ + (X, \nu \cdot H_2O)\]
Where RX is the organic halide molecule, $\nu$ is the order of the reaction with respect to water and $\nu^+$ and $\nu^-$ are respective coordination numbers of the cation and anion formed. Since the concentration of water molecules can be taken to be constant, the observed rate of the reaction changes according to first order law. In support of the above mechanism they have pointed out that substituted methyl halides do not react with steam at temperature where hydrolysis is extremely fast and that the rate of fall of activation energy with respect to temperature is greater than can be accounted for unless a number of water molecules participate.\textsuperscript{8}

The average activation energy over a temperature range of 25° by means of Arrhenius plots has been calculated, but it is not possible to calculate the precise value of $\frac{\delta E}{\delta T}$ from the present data as the temperature interval of measurement is quite large (at least 5°). Further evidence in support of the fact that water molecules are playing a pertinent role in the first order process is obtained when we examine the effect of change of composition of the medium on the reaction velocity of the first order process. It has been found that the velocity of the first order process is greatly enhanced on increasing the concentration of water in all cases. This increase in the velocity is not due to the change in the dielectric constant of the medium but is due to an increase in the concentration of water molecules in the medium. This has been discussed at some length in last chapter (see Discussion). It has been shown that the rate determining step in the first order process consists of simultaneous attack on the halide molecule by several water molecules present in the "solvent cage".
The work of Masimio and Giorgio\textsuperscript{21}, who studied the hydrolysis of 1-chloro – 2-nitro-ethane in water shows that the order of the reaction is multimolecular with respect to the solvent and is unity with respect to halide.

Kinetics of Uncatalysed hydrolysis of 1 – benxoyl-3-phenyl-1,2,4-triazole and p – methoxy phenyl dichloro ethanoate is studied by KERSTHOLT R.P.V etal\textsuperscript{22}. Hydrolysis of 2-(P-nitrophenoxy) tetra hydropyran: solvent and x-deuterium secondary kinetic isotope effects and relationships with the solvolysis of simple secondary alkyl arene sulfonates and the enzyme-catalysed hydrolysis of glycosides is very recently studied by Imran A. Ahmad, Saral. Birkby and coworkers\textsuperscript{23}. Kinetics of carbonyl sulfide hydrolysis. 1. catalysed and uncatalysed reactions in mixtures of water + propane by Wendy C. Andrsen and Thomas J. Bruno\textsuperscript{24}. is proved a great tool for such type of studies. The kinetics of Osmium (VIII) catalysed oxidation of aminoalcohols by chloramine – T in alkaline medium have been investigated by Sushma Gupta and Vazid Ali\textsuperscript{25}, the reactions follow a first-order rate dependence with respect to oxidant. Similar are the outcomes of uncatalysed oxidation. Uncatalysed oxidation of dimethyl sulfoxide (DMSO) by Potassium ferrate [FeVI] has been studied in alkaline medium by K. Laxmi Venkat Rao and Coworkers\textsuperscript{26} in the 9.8 -11.9 pH range, in presence of IO$_4^-$ as a stabilizing agent. The rate of oxidation decreased with increase in pH. Singh A. K., Usha Kushwaha and Coworkers \textsuperscript{27–28} have studied the kinetics of oxidation of Methacrylic acid and Maleic acid by Ce(IV) in sulphuric acid medium. Oxidation of vitamin E by sulphate radical anion in aqueous acetonitrile solution have been studied by M. Sudha Swaraga\textsuperscript{29} in pH range 7.5. A similar kinetics and mechanism
of bromination of phenols in water-acetonitrile Mixture have been done by iodometric method.

REFERENCES


3. G. H. Grant and C. N. Hinshelwood


5. K. Behari, B. Singh and B. Krishna.


7. E.A. Moelwyn-Hughes.


10. E. D. Hughes and U.G. Shapiro


    C. K. Ingold and
    S. Masterman
    and C.K. Ingold.
16. K. Behari and B. Krishna : Chimie Analytique, 51, 87-92,
    B. krishna.
    N.A. Taher.
    and I. Fells.
    636 (1955).
22. Perkin Transactins. 2 ISSN 0300-9580 CODEN JCPKBH 1993,
    in pp 49- 51(10Ref.)
23. Biological Applications of Physical organic Chemistry dedicated
    to Prof. William P. Jencks.(2006).