Kinetic study of solvolysis of iso-amyl iodide in alkaline and neutral media

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ABSTRACT

The present work pertains to kinetic behavior and mechanism of hydrolysis of Iso-amyl iodide. The base employed was NaOH. Solvent effect on the kinetics of Iso-amyl iodide has been investigated in alkaline and neutral medium in [EtOH-H$_2$O] mixtures up to 60% v/v in the temperature range of 55^{0}C-65^{0}C in alkaline and 50^{0}C-55^{0}C in neutral media respectively. The velocity in the first order process depends upon the concentration of halide molecule (i.e. Iso-amyl iodide). In presence of finite concentration of hydroxyl ions the total order of reaction is two while in absence of alkali, the order of the reaction is unity. The reaction velocity decreases with increase in the ionic strength of the medium. In the absence of sodium hydroxide the velocity of first order process is greatly increased on increasing the di-electric constant of the medium. The general form of rate expression is written as :

$$-\frac{d[RX]}{dt} = K_2[RX][OH^-] + K'_1[RX].$$ *Activation parameters were also determined.*

Key Words: Kinetics, Solvolysis, Iso-amyl iodide, mechanism, NaOH, ionic strength, dielectric constant, activation parameters.

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INTRODUCTION

Hydrolysis of an alkyl halide may proceed through SN[1] or SN[2] path depending on its structure and the set of experimental conditions used. In the study of kinetics of alkaline hydrolysis of iso-amyl 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. On the basis of the present data, it is not possible to show whether both the processes pass through identical or different transition states.

Chaurasia [1] studied the kinetics of hydrolysis of 4-bromoaniline-phosphoro mono-amidate, which is a substituted ester of orthophosphoric acid in acid concentration range 1.0-6.0M of HCl at 70^{0}C. Kallol K Ghosh [2] et. al. studied the kinetics of hydrolytic decomposition of organophosphates and thiophosphate by N-hydroxyamides in cationic micellar media. Hydrolysis of Tri-2,5-diethoxy Aniline Phosphate (An organo phosphorus pesticide) in acid medium [3], Kinetics on solvolysis of Diphenyl thiophosphorochloridate is studied by Han Joong Koh et. al. [4] Amel M Ismail [5] have reported the kinetics and mechanism of the nucleophilic ring opening of oxazolinone in mixed aqueous solvents. Previous study [6] of the hydrolysis of unsaturated oxazolinones in either acidic or alkaline medium gives the corresponding 2-acylamino acrylic acid. Computational redesign of a mononuclear zinc metalloenzyme for organophosphate hydrolysis reported [7]. G.K. Aseri et. al [8] studied the hydrolysis of organic phosphate forms by phosphatases and phytase producing fungi of arid and semi arid soils of India. Vegetables as biocatalysts in stereoselective hydrolysis of labile organic compounds reported [9].

Kinetics of Hydrolysis of Sec-Amyl Iodide in alkaline and neutral media reported [10]. Kinetically studied the oxidation of tartaric acid by potassium bromate in perchloric acid medium catalysed by Ru (III) by Usha Kushwaha

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and Co-workers [11]. Transition metal ions from complexes [12,13] and act as catalyst in oxidation and reduction reactions due to its multiple oxidation states. R. Ramchandrappa and co-workers [14] studied Ru (III) catalysed kinetics of miglitol by Bromamine-T in HCL 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 [15], and other alkyl halide [16] 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 [17] 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.

$$RX + \nu\,H_2O \longrightarrow ROH + (H, \nu + H_2O)^+ + (X, \nu^-\,H_2O)^-$$
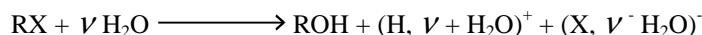
However, so far as the second order processes are concerned, the conclusions and mechanism put forward by us are somewhat similar to those of others in the study of the reaction between alkali and organic halides [18-28].

EXPERIMENTAL SECTION

Iso-amyl iodide (Fluka 99%) was distilled in a quick-fit apparatus thrice and the fraction separation between 147^0C-148^0C was used for all kinetic measurements.

G.R. (E. Merck) grade sodium hydroxide solution was prepared and restored in Jena-glass bottle. This solution was standardized with oxalic acid (A.R.B.D.H.) solution.

Silver nitrate (A.R.B.D.H.) solution was prepared by approximate weighing and standardized by titrating with a standard solution of potassium chloride. Sodium thiosulphate, starch, bromine, potassium iodide, carbon tetra chloride, sodium perchlorate, lacomide (indicator), sulphuric acid, nitric acid and hydrochloric acid were all either G.R.(E.Merck) or (A.R.B.D.H.) grade samples.

Absolute alcohol was shaken with lime and then distilled in a quick fit apparatus and the fraction boiling at 78.2^0C was retained and was used to prepare the solvent mixture which usually consisted of a mixture of alcohol and water.

Study Of The Progress Of The Reaction
Sodium hydroxide solution was taken in the requisite quantity in a conical flask containing solvent mixture consisting of alcohol and water. The conical flask was then kept in thermostat regulated by an automatic electronic relay. Another conical flask containing pure iso-amyl iodide was also kept in the thermostat. The requisite quantity of iso-amyl iodide was poured into the sodium hydroxide solution contained in the flask by means of a pipette, when the reactants had attained the temperature of the bath, when half of iso-amyl iodide had passed out of the pipette, the stop watch was started. The overall reaction mixture contained 60% of alcohol by volume.

The progress of the reaction was studied by withdrawing an aliquot of (5 ml.) reaction mixture at scheduled intervals and was immediately poured into a conical flask containing 10 ml. of sulphuric acid in order to arrest the reaction. This was vigorously shaken for a few minutes and the iodide was estimated by direct titration with silver nitrate solution using Eosin [29] as an indicator.

Measurement of Dielectric Constant and estimation of olefin [22]
The dielectric constant values were measured by a dielectrometer (Dielkometer Type TBK No. 53015) working on the principle of heterodyne beat method. Two high frequency transmitters are coupled with each other. Electromagnetic oscillations of wave length 300 m. are produced by the first transmitter. The tuning circuit of the second oscillator contains two variable condensers connected in parallel and also connecting sockets for the cell, the capacity of which is to be measured. The frequency and wave length of the second transmitter can be adapted to that of the first transmitter by shifting the variable condenser. When an unknown capacity is introduced into the connecting sockets, it becomes essential to reduce the capacity of one of variable condensers, in order to readjust the first transmitter, in such a manner so that the original value of the total capacity of the second transmitter may be obtained. Thus the decrease in the capacity of the variable condenser is measure of the unknown capacity. The null point is indicated by magic eye (Bridge Type). The dielectric constant values of absolute alcohol – water mixtures were measured with a cell of $1.68\,\mu$f capacity, which was previously calibrated with standard liquids of known dielectric constant.
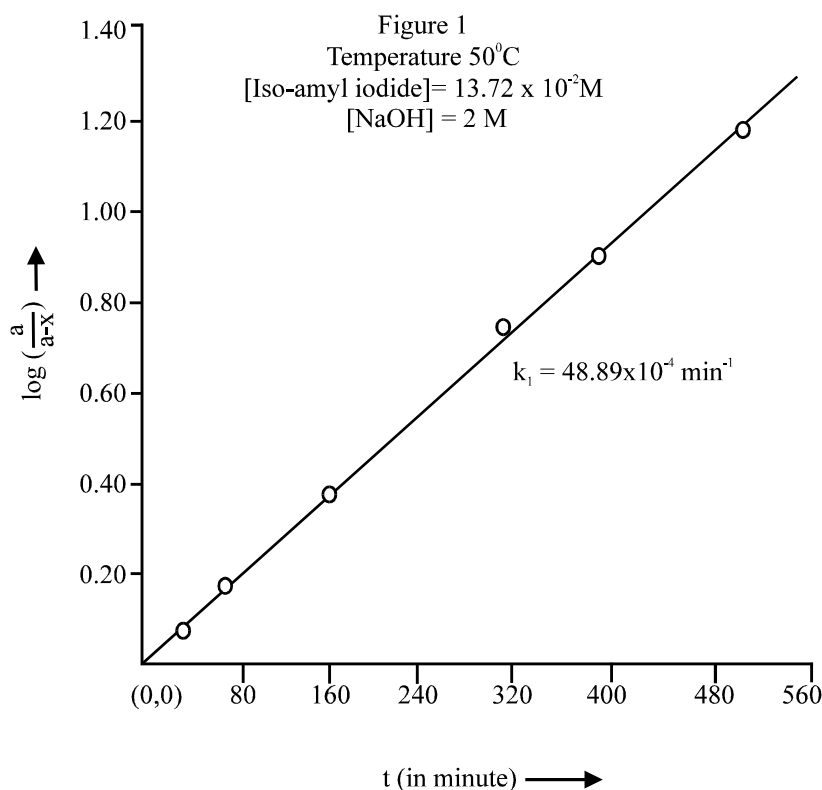
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The sealed tube containing iso-amylene produced, was broken by shaking under water, in an evacuated stoppered jar (containing sufficient sulphuric acid to neutralize the alkali present in the reaction mixture) provided with an inlet reaching to the bottom and an outlet tube. The iso-amylene was swept through a trap at 25^0C and also through two bubbling tubes containing known quantities of the standard solution of bromine in carbon tetrachloride, with the help of a slow stream of nitrogen gas (which was purified by passing it through solutions of pyrogallol, potassium permanganate and water). The second tube was kept at 0°C and a trap containing aqueous solution of potassium iodide was placed at the end of the gas train. The jar was kept at 50° – 60° and thus whole of the iso-amylene was swept over in about an hour and was estimated by titrating the remaining bromine with standard thiosulphate iodometrically.

Order of reaction with respect to iso-amyl iodide
The results obtained at 55°C for various initial concentrations of iso-amyl iodide at fixed concentration of sodium hydroxide are given in the table 1. (See Fig. 1 & 2).

Table 1
Temperature 55°C
*[NaOH] = 2M*
[EtOH – H_2O] = 60% v/v

[Iso-amyl iodide] x 10^2M	k_1 x 10^4 min^{-1}
15.24	73.95
13.72	74.79
11.43	75.13
9.14*	75.54
7.62	75.89
4.57	76.52
2.33	76.62
1.52*	76.80

Figure 1
Temperature 50^0C
[Iso-amyl iodide]= 13.72 x 10^{-2}M
[NaOH] = 2 M

k_1 = 48.89x10^{-4} min^{-1}

y-axis: $\log\left(\frac{a}{a-x}\right)$

x-axis: t (in minute)

A perusal of table-1 indicates that the first order rate constant value remains sensibly constant throughout the entire concentration range of iso-amyl iodide which further proofs that the reaction follows first order with respect to iso-amyl iodide.

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Order of reaction with respect to sodium hydroxide
Result shows in table 2 that the values in the column 5 are practically identical. They agree within 1.50% showing thereby that the order of the reaction is two, unity with respect to each reactant (Fig. 3 and 4).

Figure 2
Temperature 50^0C
[Iso-amyl iodide] = 13.72 x 10^{-2}M
[NaOH] = 2M
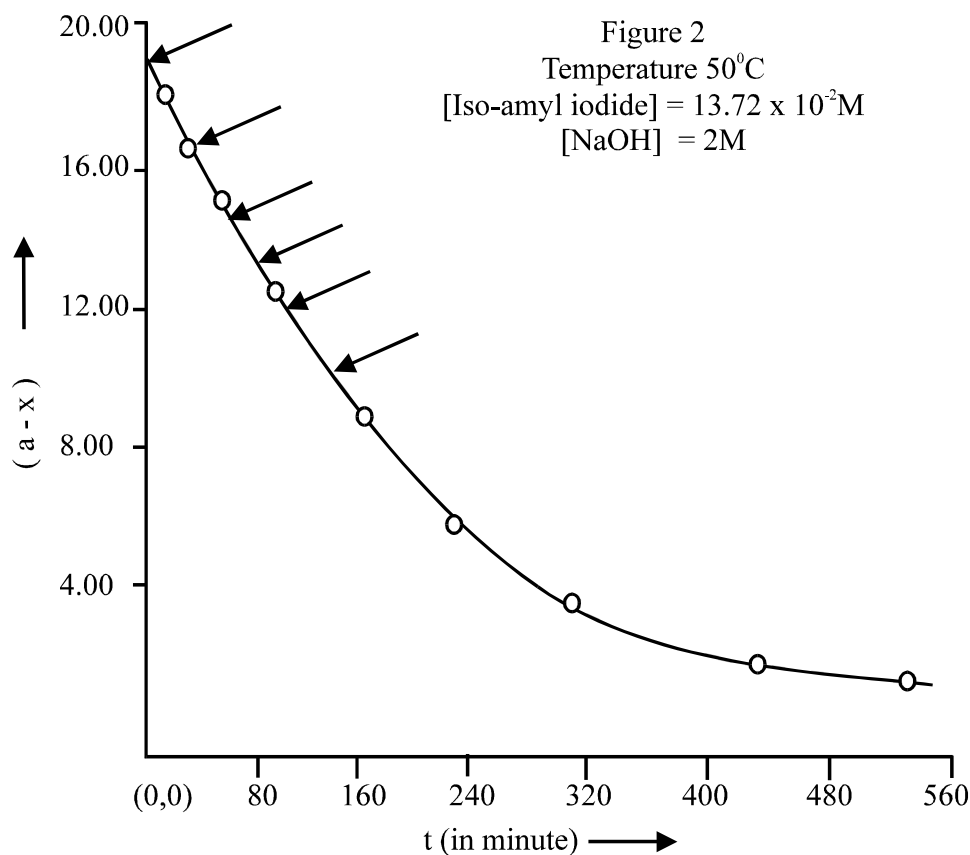
Table 2
Temperature 55°C
[Iso-amyl iodide] = 4.57 x 10^{-2} M
[EtOH – H_2O] = 60% v/v
μ = 2M

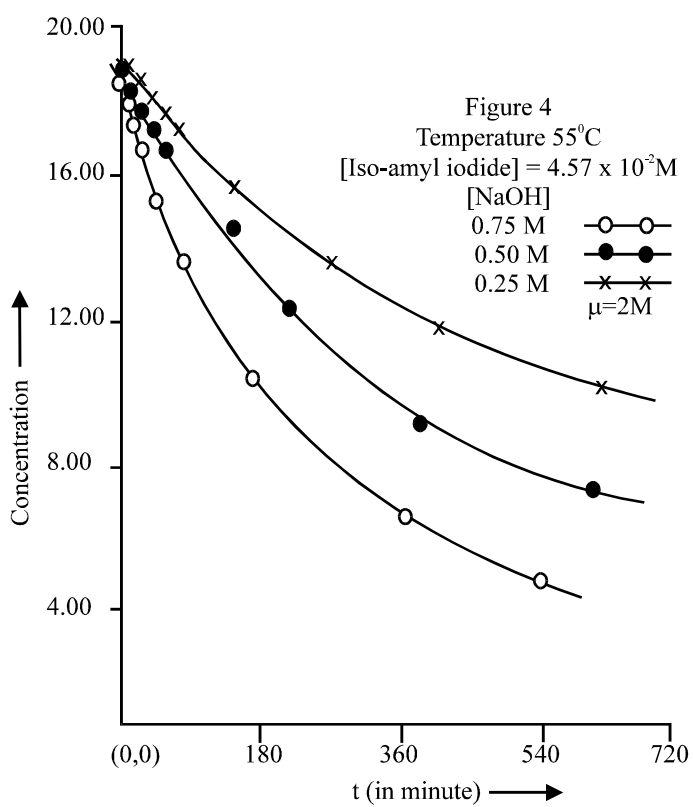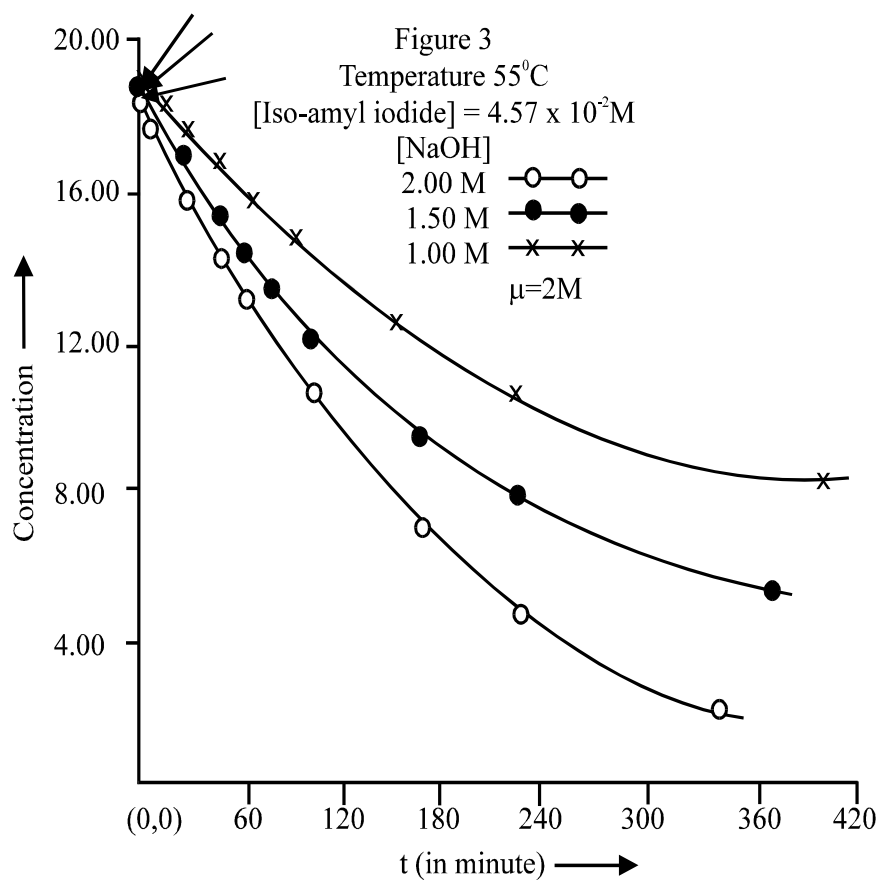| Sr. No.	$\left[OH^-\right]$ M	[Iso-amyl iodide] expressed in ml. of M/85.33 AgNO₃ per 5 ml. of reaction mixture at which $\left(-\dfrac{dc}{dt}\right)$ is measured	$\left(-\dfrac{dc}{dt}\right)$ x10² ml. min⁻¹	$\dfrac{k_2 X 10^4 \left(-\dfrac{dc}{dt}\right)}{[OH^-][Iso-amyl\,iodide]}$
1	2.00	18.00	13.79	38.31
2	1.50	18.00	10.25	37.96
3	1.00	18.00	6.67	37.06
4	0.75	18.00	5.00	37.04
5	0.50	18.00	3.27	36.33
6	0.25	18.00	1.67	37.11

*Average value = 37.39
litres mol⁻¹ min⁻¹
Average deviation = 1.5%*

The order of the reaction with respect to sodium hydroxide may be further calculated by employing the following equation

$$n = \frac{\log\left(-\dfrac{dc}{dt}\right)_1 - \log\left(-\dfrac{dc}{dt}\right)_2}{\log\dfrac{[OH^-]_1}{[OH^-]_2}}$$

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Where 'n' is the order of the reaction with respect to sodium hydroxide.

Figure 3
Temperature 55^0C
[Iso-amyl iodide] = 4.57 x 10^{-2}M

Figure 4
Temperature 55^0C
[Iso-amyl iodide] = 4.57 x 10^{-2}M

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Effect of concentration of sodium hydroxide

The value of velocity constant $\bar{k}_2$ has also been calculated and given in table 3 showed that decrease in the concentration of sodium hydroxide, increases the value of $\bar{k}_2$.

TABLE 3
[Iso-amyl iodide] = 4.57 x 10⁻² M
[EtOH – H₂O] = 60% v/v

[Sodium Hydroxide] × M	$\bar{k}_2 \times 10^4$ litres mol⁻¹ min⁻¹
2.000	38.57
1.500	41.52
1.000	46.11
0.500	60.67
0.250	70.64
0.020	77.41
0.010	94.69
0.005	115.68

Effect of solvent variation

A careful perusal of the table 4 shows that by decreasing the percentage of alcohol the velocity of the reaction decreases showing thereby that velocity decreases with increasing dielectric constant of the medium.

Table 4
Temperature 55°C
[Iso-amyl iodide] = 7.62 x 10⁻² M
[NaOH] = 2M

Percentage of alcohol	Dielectric constant (D)	$k_1 \times 10^4$ min⁻¹	$\bar{k}_2 \times 10^4$ litres mol⁻¹ min⁻¹
80	31.00	114.33	57.16
70	36.70	92.23	46.11
60	41.70	75.89	37.94
55	44.40	72.16	36.08
50	47.50	67.10	33.55
40	53.10	50.58	25.29

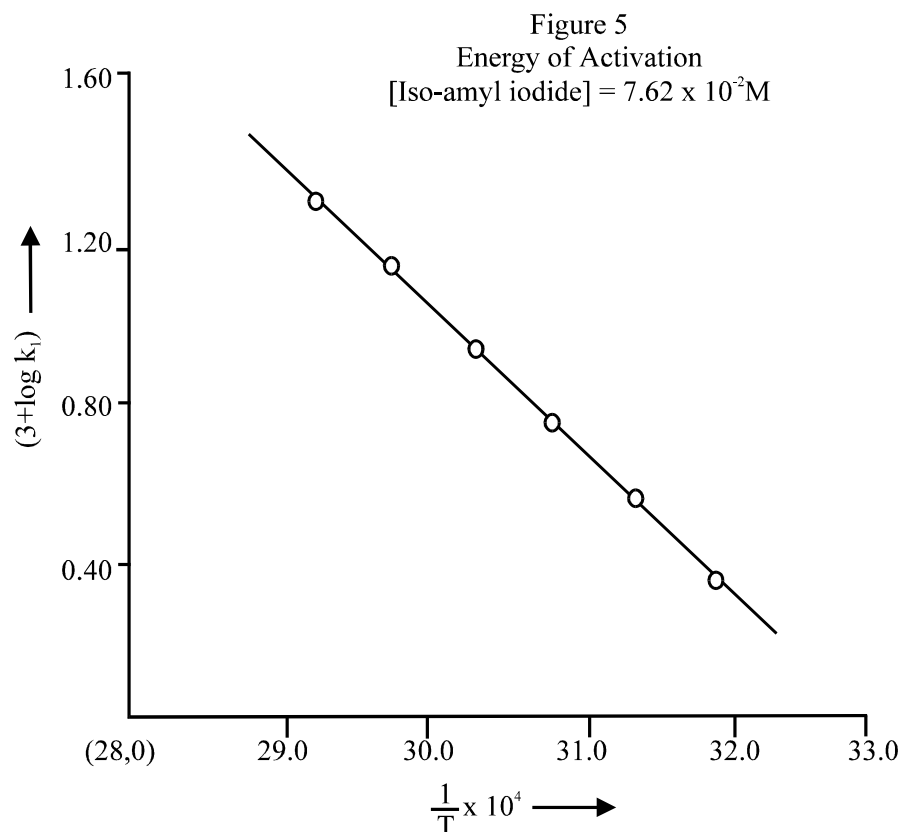*Effect of temperature on the rate of reaction and thermodynamic para meters*

The table -5 has been reproduced in the form of a graph (Fig. 5) in which log k_1 has been plotted against 1/t. The energy of activation has been found to be 17,562 Calories. The entropy of activation has been calculated by employing the formula

$$k_1 = e \frac{KT}{h} \; e^{-E\exp/RT} e^{\Delta s^{++}/R}$$

where k_1 is rate constant, K is Botmann's constant, h is Planck's constant, T is absolute temperature, R is gas constant, Eexp is energy of activation and ΔS^{++} is entropy of activation. The value of entropy of activation was found to be 27.29 e.u.

Table 5
[EtOH- H₂O] = 60% v/v
[NaOH] = 2M

Temperature	[Iso-amyl iodide] x 10² M	$k_1 \times 10^4$ min⁻¹	$k_2 \times 10^4$ litres mol⁻¹ min⁻¹	$k_2 \times 10^4$ litres mol⁻¹ min⁻¹
65°	7.62	170.12	85.06	83.72
60°	"	118.99	59.49	68.60
55°	"	75.89	37.94	87.32
50°	"	50.09	25.04	24.65
45°	"	33.10	16.55	16.29
40°	"	21.48	10.74	10.57
65°	15.24	169.98	84.99	-
60°	"	118.68	59.34	-
55°	"	73.95	36.97	-
50°	"	47.40	23.70	-
45°	"	32.86	16.43	-
40°	"	21.22	10.61	-

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Figure 5
Energy of Activation
[Iso-amyl iodide] = 7.62 x 10^{-2}M

Temperature coefficient, energy of activation and entropy of activation
A perusal of Table 6 shows that the velocity of substitution process and as well as of elimination process increases 2 to 3 times by rise of temperature by 10°. Table 6 is also reproduced in the form of graph (Fig. 6 and 7). The two straight lines are obtained by plotting log k_2' vs $\frac{1}{T}$ and log k_2'' vs $\frac{1}{T}$ respectively. The slopes of these straight lines will give the value of $-\dfrac{E}{2.303R}$ in equation.
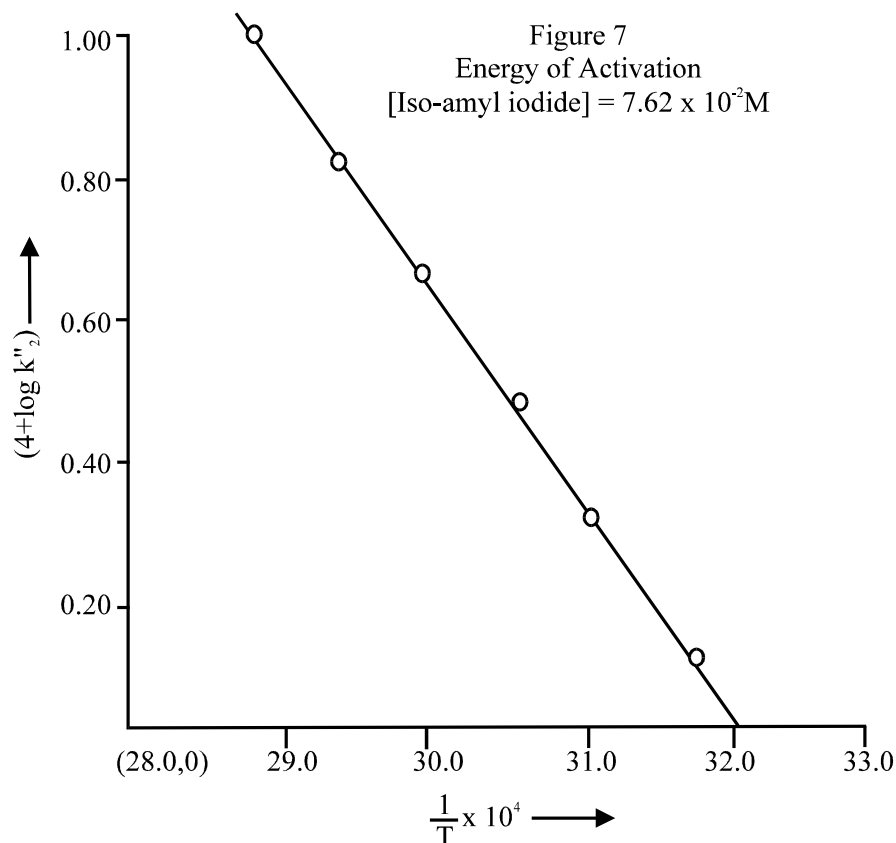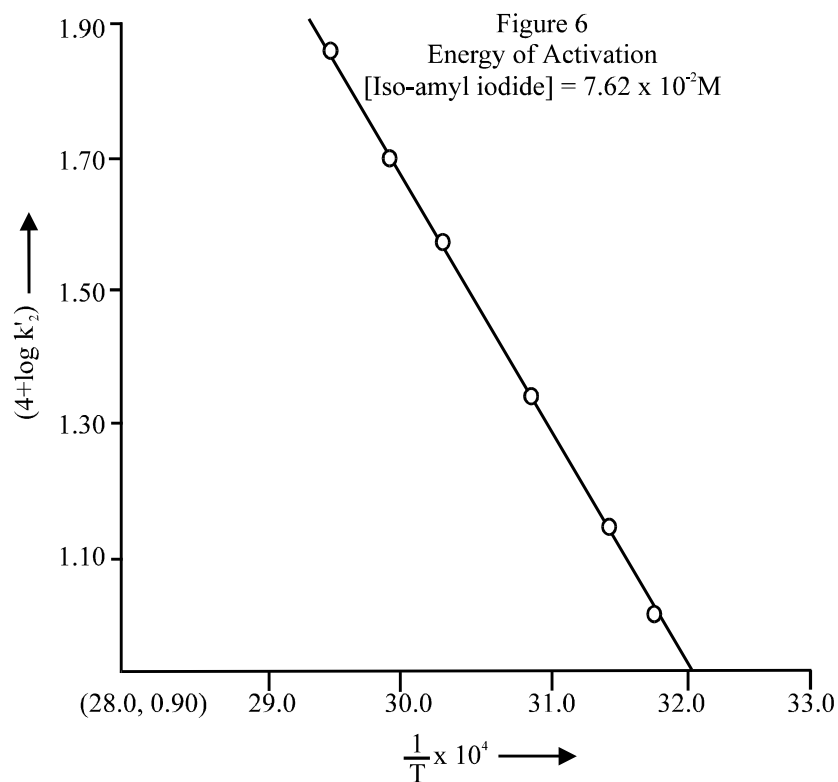
$$\log k = \log A - \dfrac{E}{2.303RT}$$

Where symbols have their usual meanings. Therefore, we can calculate the value of energy of activation (E). The value of energy of activation for substitution process comes out to be 17,369 Calories and for elimination process it is found to be 19,919 Calories. The value of entropy of activation for bimolecular substitution reaction comes out to be -27.23 e.u. and from bimolecular elimination process, it is found to be -23.36 e.u.

Table 6
[NaOH] = 2M
[EtOH – H₂O] = 60% v/v

Temperature	[Iso-amyl iodide] x 10^2M	k_2 x 10^4 litres mol⁻¹ min⁻¹	k_2' X 10^4 litres mol⁻¹ min⁻¹	k_2'' X 10^4 litres mol⁻¹ min⁻¹
65°	15.24	85.06	74.11	10.95
60°	"	59.49	51.96	7.53
55°	"	36.97	32.36	4.61
50°	"	23.70	20.79	2.91
45°	"	16.55	14.55	2.00
40°	"	10.74	9.46	1.28
65°	7.62	84.99	74.03	10.96
60°	"	59.34	51.83	7.51
55°	"	37.94	33.22	4.72
50°	"	25.04	21.97	3.07
45°	"	16.43	14.45	1.98
40°	"	10.61	9.35	1.26

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Figure 6
Energy of Activation
[Iso-amyl iodide] = 7.62 x 10^{-2}M

y-axis: $(4+\log k'_2)$ — with values 1.90, 1.70, 1.50, 1.30, 1.10

x-axis: $\frac{1}{T} \times 10^4$ — with values (28.0, 0.90), 29.0, 30.0, 31.0, 32.0, 33.0

Figure 7
Energy of Activation
[Iso-amyl iodide] = 7.62 x 10^{-2}M

y-axis: $(4+\log k''_2)$ — with values 1.00, 0.80, 0.60, 0.40, 0.20

x-axis: $\frac{1}{T} \times 10^4$ — with values (28.0,0), 29.0, 30.0, 31.0, 32.0, 33.0

Effect of solvent variation on the rate of bimolecular substitution and elimination reactions
From perusal of table 7 it is clear that by decreasing the percentage of alcohol, the velocity of bimolecular substitution and elimination reactions decreases showing thereby that the velocity decreases with increasing dielectric constant of the medium.

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Table 7
Temperature 55°
[Iso-amyl iodide] = 7.62 x 10^{-2} M
[NaOH] = 2M

Percentage of Alcohol (v/v)	Dielectric constant (D)	E_2 (%)	SN_2 (%)	$k_2 \times 10^4$ litres mol^{-1} min^{-1}	$k_2' \times 10^4$ litres mol^{-1} min$_{-1}$	$k_2'' \times 10^4$ litres mol^{-1} min^{-1}
80	31.00	13.44	86.56	57.16	49.48	7.68
70	36.70	12.98	87.02	46.11	40.12	5.99
60	41.70	12.45	87.55	37.94	33.22	4.72
55	44.40	12.10	87.90	36.08	31.71	4.37
50	47.50	11.74	88.26	33.55	29.61	3.94
40	53.10	11.52	88.48	25.29	22.38	2.91

Neutral hydrolysis of iso-amyl iodide

The reaction was also studied in neutral solution. The progress of the reaction was studied by withdrawing an aliquot of reaction mixture at schedule intervals and by pouring it into 50 ml. of absolute alcohol. The acid formed in the reaction mixture was estimated by titrating it with a very dilute solution of sodium hydroxide using locamide as an indicator. There again the reaction mixture was kept in sealed thin glass tubes at higher temperature (i.e. at 55^{0}C and onward). The reaction velocity is very slow in neutral solutions.

In the present composite reaction, so far, we have not studied its first order part since in presence of sodium hydroxide the contribution of first order reaction is negligible. In the absence of sodium hydroxide, the first order reaction alone occurs. Consequently, experiments were carried out in absence of sodium hydroxide. In such case it is observed that iso-amyl iodide is very slowly hydrolysed via first order mechanism alone. The rate constants are calculated by employing the expression.

$$K_1' = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

where K_1' is rate constant for first order substitution reaction and other terms have their usual meanings. Further, it has also been observed that in neutral hydrolysis of iso-amyl iodide, only the first order substitution reaction occurs and no olefin is formed.

A careful perusal of results of table 8 shows that the value of the first order rate constant remains practically constant throughout the entire course of reaction. We, further, find that the value of k_1' does not change from one experiment to another. Hence, we conclude that in absence of sodium hydroxide the order of reaction with respect to iso-amyl iodide is unity.

Table 8
[EtOH – H₂O] = 60% v/v

Temperature	[Iso-amyl iodide] x 10^{2}M	$k_1' \times 10^6$ min^{-1}
50°	15.24	76.30
50°	13.72	77.04
50°	11.43*	78.13
50°	9.14	77.13
50°	7.62	77.53
50°	6.10*	76.50
50°	4.57	78.33
50°	2.33	78.63
50°	1.52	76.12
55°	15.24	119.79
55°	13.72*	123.89
55°	11.43*	123.45
55°	9.14*	122.63
55°	7.62	121.06
55°	6.10*	119.88
55°	4.57*	123.45
55°	2.33	118.41
55°	1.52*	116.37

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Effect of solvent variation on the rate of unimolecular reaction
From a perusal of table (9) it is clear that as the percentage of alcohol is decreased the velocity of the reaction increases, showing thereby that the rate of reaction increase with increase in dielectric constant of the medium in the study of the first order process.

Table 9
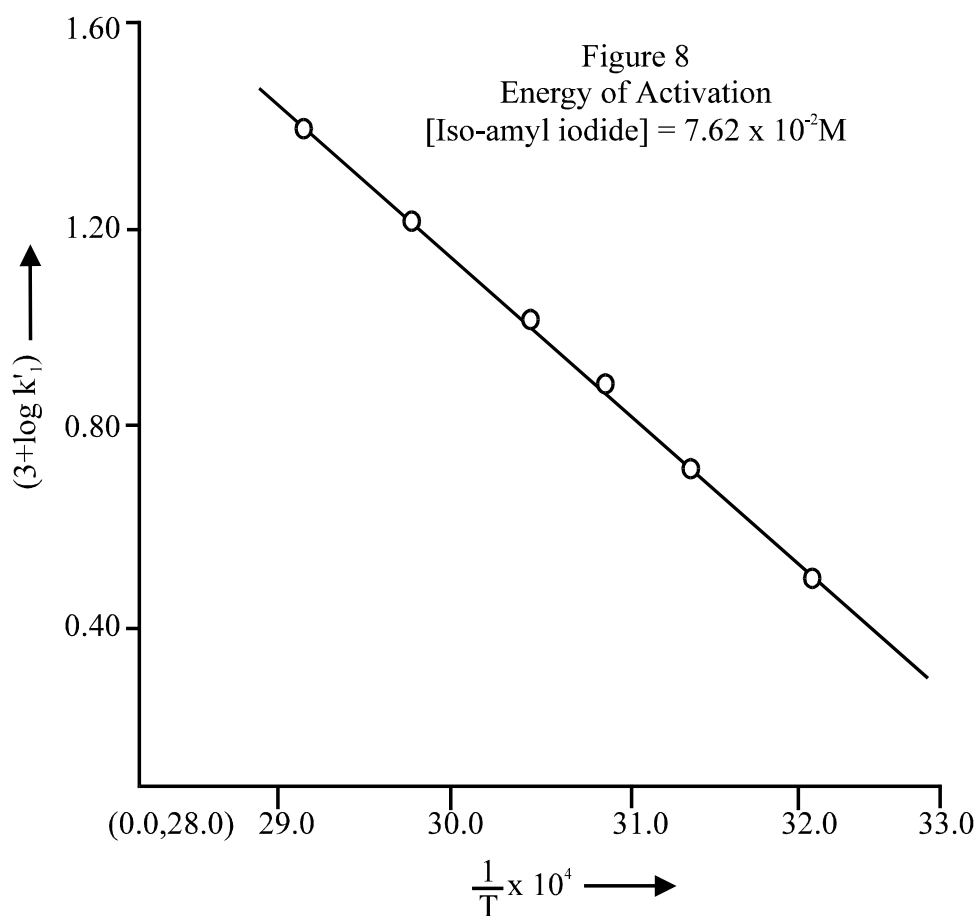*Temperature 55°C*
[Iso-amyl iodide] = 7.62 x 10⁻² M

Percentage of alcohol	Dielectric constant (D)	$k_1^{'}$ x 10⁶
80	31.00	78.39
70	36.70	105.00
60	41.70	121.05
55	44.40	156.55
50	47.50	194.62
40	53.10	246.80

Effect of addition of potassium iodide on rate of unimolecular reaction
From the table 10 it is obvious that as the concentration of potassium iodide is increased the velocity of the unimolecular reaction decreases.

Table 10
Temperature 55°
[Iso-amyl iodide] = 7.62 x 10⁻² M
[EtOH – H₂O] = 60% v/v

[K I] M	μ x M	$k_1^{'}$ x 10⁶ Min⁻¹
0.00	0.00	121.05
0.50	0.50	114.55
1.00	1.00	90.88

Figure 8
Energy of Activation
[Iso-amyl iodide] = 7.62 x 10⁻²M

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Study of temperature coefficient, energy of activation and entropy of activation of the unimolecular process

The energy of activation has been calculated by plotting graph of log $k_1^{'}$ vs $\dfrac{I}{T}$ (see Fig. 8 & Table 11). The energy

of activation comes out to be equal to 17,650 Calories and the entropy of activation thus calculated was found to be -32.98 e.u.

Table 11
[EtOH- H_2O] = 60% v/v

Temperature	[Iso-amyl iodide] x 10^2M	$k_1^{'}$ x 10^6 min^{-1}
65°	7.62	263.40
60°	"	174.14
55°	"	121.05
50°	"	77.53
45°	"	51.35
40°	"	32.91
65°	15.24*	263.76
60°	"*	175.80
55°	"	119.79
50°	"	76.80
45°	"*	50.98
40°	"*	33.54

Mechanism of the first order process
In the hydrolysis of iso-amyl halides, the halide undergoes slow ionization followed by a rapid reaction between the positive alkyl ion and hydroxyl ion or a molecule of water. Thus . . . .

$$RX \xrightarrow{\text{Slow}} \overset{+}{R} \;+\; \overset{-}{X} \tag{1}$$

$$\overset{+}{R} + O\overset{-}{H} \xrightarrow{\text{Fast}} ROH \tag{2}$$

$$\text{Or } \overset{+}{R} + H_2O \xrightarrow{\text{Fast}} ROH + \overset{+}{H} \tag{3}$$

Iso-amyl halide is soluble in alcohol but only sparingly soluble in water. Consequently, the "solvent Cage" in which solute molecule is embedded will have greater number of alcohol molecules than those of water when the concentration of water is high.

RESULTS AND DISCUSSION

The contribution to over all velocity by first order process is very small and in presence of even very small quantities of NaOH, the first order process may be neglected as compared to bimolecular processes.

The overall velocity in the first order process depends upon the concentration of halide molecules.

It has been shown that iso-amyl iodide is hydrolyzed to the extent about 1.64% at 50^0C in 2M NaOH.

The doubt, regarding the pertinent role of NaOH as a reactant in the reaction through unimolecular process appear to be valid.
It has been observed that the reaction velocity decreases with increase in the ionic strength of the medium. The change in the ionic strength of the medium affects the second order processes and our results are in good agreement with the theory of Amis and Jaffe.

Both second order processes as well as first order process are affected by a change in the dielectric constant of the medium which is affected by changing the concentration of alcohol present in reaction mixture.

In the absence of sodium hydroxide the velocity of first order process is greatly increased on increasing the dielectric constant of the medium.
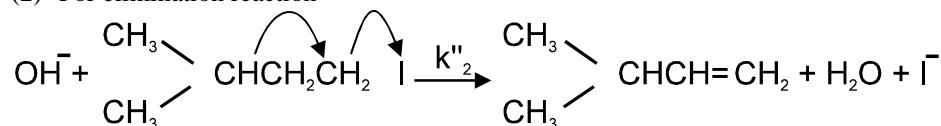
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On the basis of above findings the mechanistic path of the reactions is proposed as follows.

Scheme :
(1) For substitution reaction
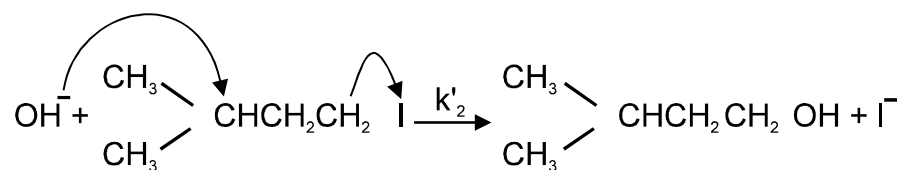
(2) For elimination reaction

CONCLUSION

On the basis of the study of previous pages it clearly indicates that the hydrolysis reactions studied are typical in nature. Hydrolysis of halides in alkaline and neutral medium has been studied for the first time.

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