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Study of the Hydrolysis of Sec-Amyl Iodide in Alkaline and Neutral Media: A Kinetic and Mechanistic Approach

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ABSTRACT

The present work pertains to kinetic behavior and mechanism of hydrolysis of sec-amyl iodide. In the kinetic study of alkaline hydrolysis of sec-amyl iodide, it has been observed that four simultaneous, recognizably distinct reactions are occurring together. Two of these reactions are second order processes, while other two of them are first order processes, each with respect to halide. The base employed was NaOH. Solvent effect on the kinetics of sec-amyl iodide has been investigated in alkaline and neutral medium in[EtOH-H_2O] mixture up to 60% v/v in the temperature range of 40^0C-75^0C in alkaline and 50^0C in neutral media respectively. The velocity in the first order process depends upon the concentration of halide molecule (i.e. sec-amyl iodide). In absence of NaOH the first order process alone occurs and it has been observed that the rate of the first order process and the velocity of first order processes increase with the increase in the dielectric constant of the medium. The rate expression can be written as : $-\dfrac{d[RX]}{dt}=K_2[RX][OH^-]+K'_1[RX]$. *Activation parameters were also determined.*

Key Words : Kinetics, Hydrolysis, sec-amyl iodide, mechanism, NaOH, dielectric constant, activation parameters.

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 sec-amyl iodide, it has been observed that four simultaneous, recognizably distinct reactions are occurring together. Two of these reactions are second order processes while other two of them are first order processes (i.e. substitution and elimination) each with respect to halide.

Hydrolysis of Tri-2,5-diethoxy Aniline Phosphate (An organo phosphorus pesticide) in acid medium[1], Kinetics on Solvolysis of Diphenyl Thiophosphorochloridate is studied by Han Joong Koh et. al.[2] Amel M Ismail[3] have reported the kinetics and mechanism of the nucleophilic ring opening of oxazolinone in mixed aqueous solvents. Previously studied [4] 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 [5]. Chaurasia [6] 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 70^0C. Kallol K Ghosh [7] et. al. studied the kinetics of hydrolytic decomposition of organophosphates and thiophosphate by N-hydroxyamides in cationic micellar media. 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].

Kinetically studied the oxidation of tartaric acid by potassium bromate in perchloric acid medium catalysed by Ru (III) by Usha Kushwaha and Co-workers [10]. Transition metal ions from complexes [11,12] and act as catalyst in oxidation and reduction reactions due to its multiple oxidation states. R. Ramchandrappa and co-workers [13] studied Ru (III) catalysed kinetics of miglitol by Bromamine-T in HCl medium. By using few transition metal ions as homogenous catalyst, kinetics of oxidation of some molecules have been studied [14,15].

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[16], and other alkyl halide[17] 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[18] 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[19-29].

EXPERIMENTAL SECTION

Sec-amyl iodide (99% Fluka) was distilled thrice in a quick-fit apparatus and the fraction separating between 144^0C-145^0C was employed for the study of 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 sec-amyl iodide was also kept in the thermostat. The requisite quantity of sec-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 sec-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 [30] as an indicator.

Measurement of Dielectric Constant and estimation of olefin [23]

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 1.68μf capacity, which was previously calibrated with standard liquids of known dielectric constant.

The sealed tube containing sec-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 sec-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 sec-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 sec-amyl iodide

The overall reaction between sec-amyl iodide and sodium hydroxide is composite one and the velocity expression for this reaction can be represented as

$$-\frac{d[RI]}{dt} = k'_2[RI]\left[OH^-\right] + k''_2[RI]\left[OH^-\right] + k'_{1S}[RI] + k'_{1E}[RI] \qquad \text{(i)}$$

$$= \left(k'_2 + k''_2\right)[RI]\left[OH^-\right] + \left[k'_{1S} + k'_{1E}\right][RI]$$

$$= k_2[RI]\left[OH^-\right] + k'_1[RI] \qquad \text{(ii)}$$

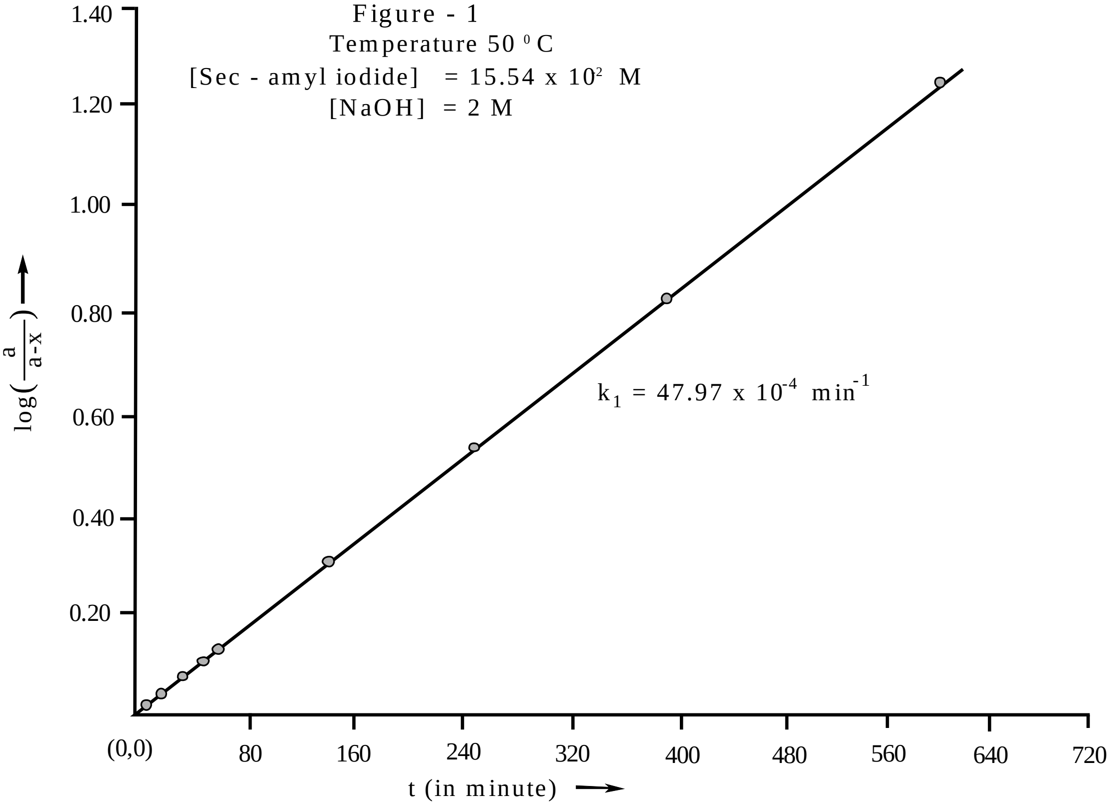
Where k'_2, k''_2 and k_2 are rate constants for bimolecular substitution, bimolecular elimination and total bimolecular reactions respectively while k'_{1s}, k'_{1E} and k'_1 are the rate constants for unimolecular substitution, unimolecular elimination and total unimolecular reactions respectively.

A perusal of table (1) shows that first order rate constants are sensibly constant. We may, therefore, conclude that the order of the reaction with respect to sec-amyl iodide is unity. The first order of reaction with respect to halide has been, further, confirmed by graphical method by plotting a graph between the values of t and log $\frac{a}{(a-x)}$ (Fig. 1). A straight line is obtained, the slope of which is equal to $\frac{k_1}{2.303}$.

TABLE 1

Temperature 50°C
[Sec-amyl iodide] = 15.54 x 10^{-2} M
[EtOH – H_2O] = 60% v/v
[NaOH] = 2M
[Sec-amyl iodide] expressed in ml. of M/25.60 $AgNO_3$ per 5 ml. of reaction mixture

Time in minute	[Sec-amyl iodide]	k_1 x 10^4	$\bar{k}_2$ X 10^4	k'_1 X10^4	k_2 x 10^4
				(b-x)	
0	19.88				
10	18.92	49.50	24.75	1.10	23.65
20	18.08	47.55	23.77	1.10	22.67
40	16.52	46.34	23.17	1.11	22.06
60	15.02	46.75	23.37	1.12	22.25
80	13.58	47.67	23.83	1.12	22.71
160	9.26	47.77	23.88	1.14	22.74
240	6.42	47.10	23.55	1.15	22.40
380	3.30	47.27	23.63	1.17	22.46
590	1.18	47.90	23.95	1.18	22.77
T_∞	0.00				
Average value		47.54 min^{-1}	23.77 Litres mol^{-1} min^{-1}		22.63 litres mol^{-1} min^{-1}
Average deviation =1.14 %					



The value of $\left(-\frac{dc}{dt}\right)$ are calculated by measuring the slope of curve (obtained by plotting concentration vs. time) at various concentrations (Fig. 2 and Table 2).

Table 2

Temperature 50°C
[Sec-amyl iodide] = 15.54 x 10^{-2} M
[EtOH – H_2O] = 60% v/v
[NaOH] = 2M
[Sec-amyl iodide] expressed in ml. of M/25.60 $AgNO_3$ per 5ml. of reaction mixture

[Sec-amyl iodide]	**Value of $\left(-\frac{dc}{dt}\right)$ ml. min^{-1} at the points indicated in the figure**	**$\left(-\frac{dc}{dt}\right)$/[C] x 10^4**
19.50	0.0952	48.82
19.00	0.0909	47.84
18.50	0.0869	46.97
18.00	0.0833	46.27
17.00	0.0769	45.23
16.00	0.0747	46.68

Average Value = 46.97
Average deviation = 2.29%

Further, the value of log $\left(-\frac{dc}{dt}\right)$ are plotted against those of log C. (Fig. 3). A straight line is obtained, the slope of which is equal to unity. Also the value of $\left(-\frac{dc}{dt}\right)$/[C] recorded in column 3 of table 2 are fairly constant which further shows that velocity of reaction is directly proportional to the concentration of sec-amyl iodide confirming that the order of the reaction with respect to sec-amyl iodide is unity. In order to further confirm that the reaction follows first order kinetics with respect to sec-amyl iodide (Table 3).

Figure - 2

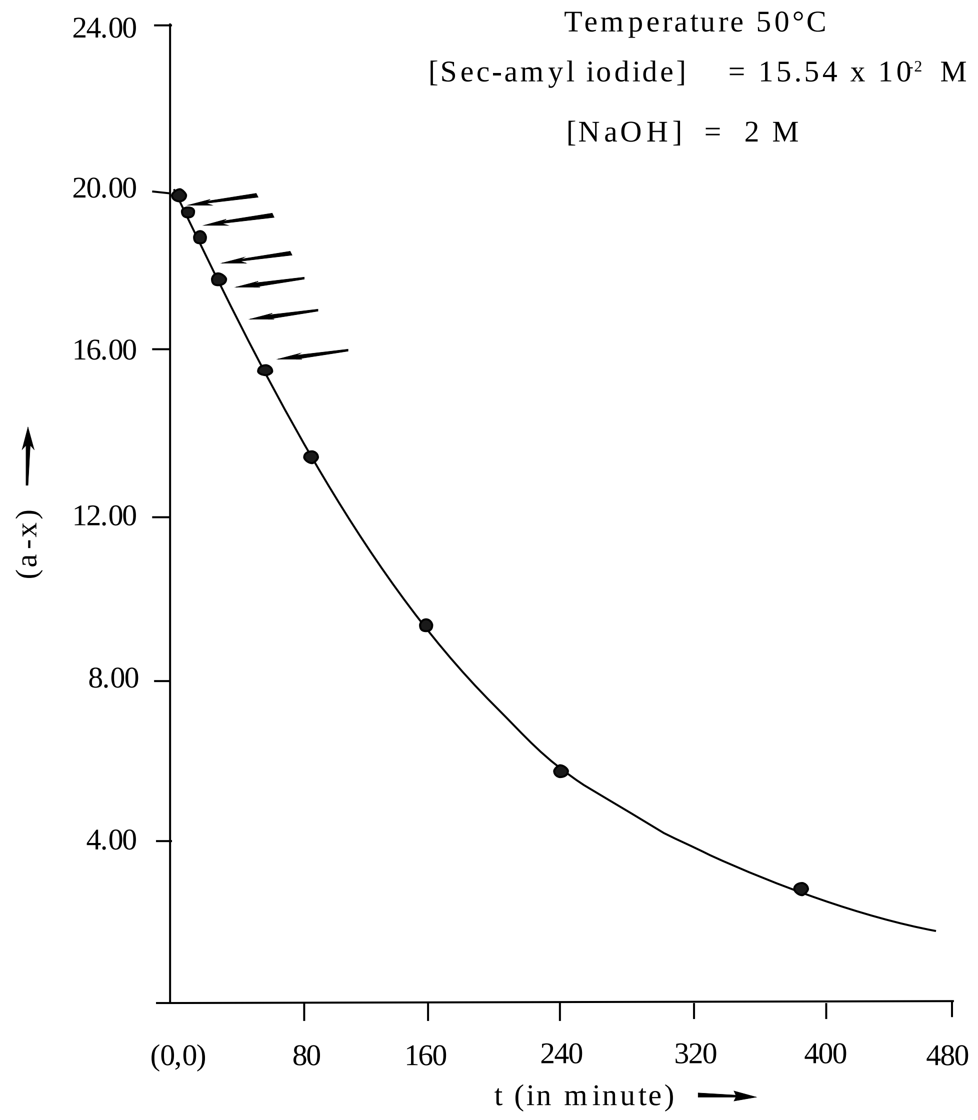


TABLE 3

[Na OH] = 2M

[EtOH – H_2O] = 60% v/v

[Sec-amyl iodide] x 10^2M	k_1 x 10^4 min^{-1}	k_2 x 10^4 litres mol-1 min-1	k_2 x10^4 litres mol^{-1} min^{-1}
1.55*	49.30	24.65	23.50
3.11	48.92	24.46	23.30
5.44	48.56	24.28	23.13
7.77	47.06	23.53	22.44
9.32	47.16	23.58	22.48
12.43	47.34	23.67	22.55
15.54	47.54	23.77	22.63

Order of reaction with respect to sodium hydroxide

A perusal of a number of experiments containing different concentration of hydroxide ions (Table 4), a graph is plotted between k_1 vs $\left[OH^-\right]$ (Fig. 4) a straight line is obtained, the slope of which will give the value k_2 while the intercept on the y-axis will give the value of k'_1. The value of k_2 thus calculated comes out to be equal to 30.50x10^4 liters mol^{-1} min^{-1}.

Figure - 3

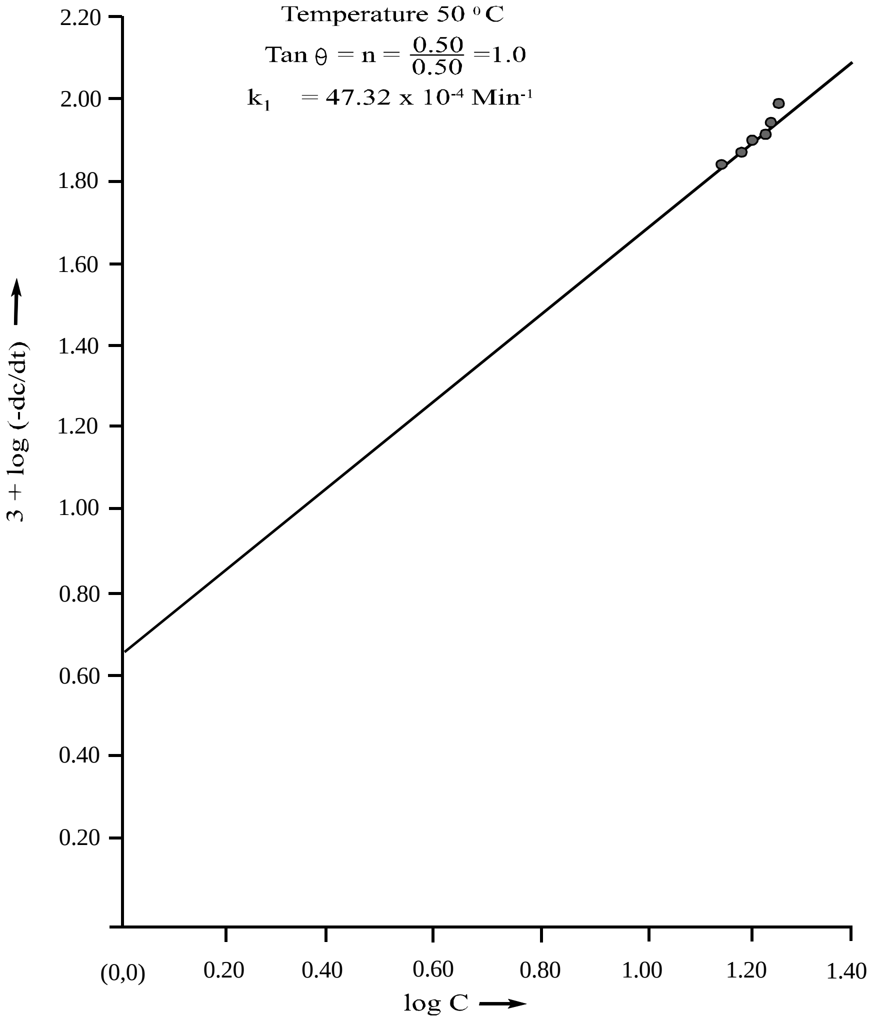


Table 4

Temperature 55°C

[Sec-amyl iodide] = 7.77 x 10^{-2} M

[EtOH – H_2O] = 60% v/v

μ = 2 M

[Sec-amyl iodide] expressed in ml. of M/40.43 $AgNO_3$ per 5ml. of reaction mixture = 15.00, at which $\left(-\frac{dc}{dt}\right)$ *is measured.*

S.No.	[OH^-]M	$\left(-\frac{dc}{dt}\right)\times10^2$ ml. min^{-1}	$k_1x10^4\ min^{-1} = \frac{\left(-\frac{dc}{dt}\right)}{[Sec-amyl\ iodide]}$	$\bar{k}_2$ x 10^4 litres mol^{-1} min^{-1} = $\frac{\left(-\frac{dc}{dt}\right)}{[OH^-][Sec-amyl\ iodide]}$
1	2.00	9.75	65.00	32.50
2	1.50	7.40	49.33	32.88
3	1.00	4.88	32.53	32.53
4	0.75	3.92	26.13	34.84
5	0.50	2.56	17.06	34.12
6	0.25	1.23	8.20	32.80

Average value = 33.23 litres mol^{-1} min^{-1}

Average deviation = 2.25%

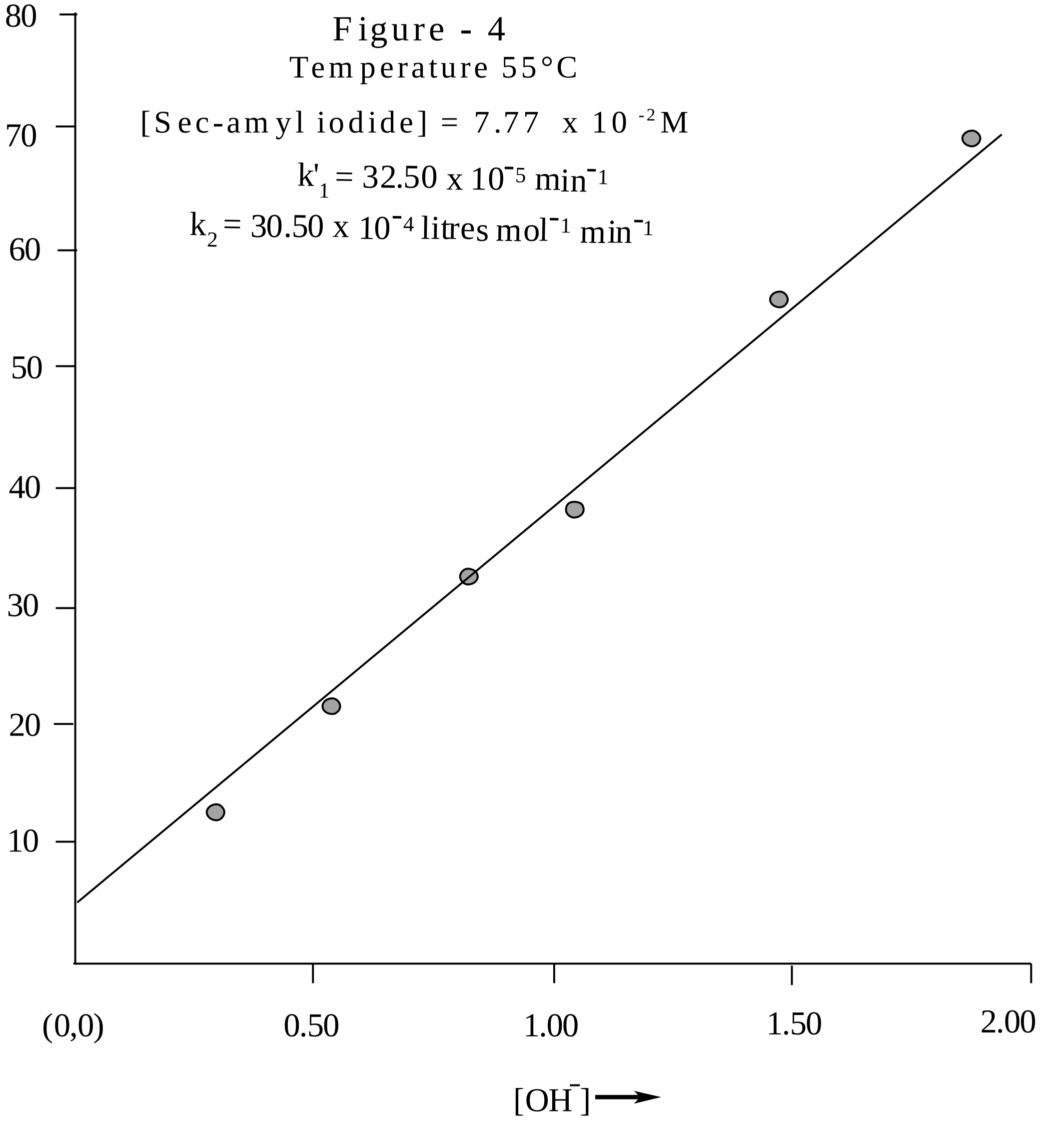


Figure - 4

Temperature 55°C

[Sec-amyl iodide] = 7.77 x 10^{-2}M

$k'_1 = 32.50 \times 10^{-5}$ min^{-1}

$k_2 = 30.50 \times 10^{-4}$ litres mol^{-1} min^{-1}

Effect of concentration of sodium hydroxide

From a careful perusal of Table (5) it is clear that value of both $\bar{k}_2$ (experimental bimolecular rate constant) and k_2 (true bimolecular rate constant) increases with the decrease in the ionic strength of the medium.

TABLE 5
Temperature 55°C
[Sec-amyl iodide] = 7.77x 10^{-2} M
[EtOH – H_2O] = 60% v/v

[Na OH] x M	**μ x M**	**$\bar{k}_2$ x10^4 litres mol^{-1} min^{-1}**	**k_2 x10^4 litres mol^{-1} min^{-1}**
2.00	2.00	33.80	32.11
1.50	1.50	37.71	35.47
1.00	1.00	46.58	43.20
0.50	0.50	57.43	50.60
0.25	0.25	67.51	52.88

Effect of solvent variation

A careful perusal of the table 6 shows that the velocity of the reaction decreases with the decrease in the percentage of alcohol showing thereby that by increasing dielectric constant of the medium velocity of the reaction decreases.

Table 6
Temperature 55°C
[Sec-amyl iodide] = 9.32 x 10^{-2} M
[NaOH] = 2 M

Percentage of alcohol	Dielectric constant (D)	k_1 x 10^4 min^{-1}	K'_1 x 10^6 min^{-1}
80	31.00	74.41	91.98
70	36.70	71.68	244.50
60	41.70	69.94	336.50
55	44.40	68.95	444.50
50	47.50	66.54	670.00

Study of the reaction in neutral medium

It has been found that in absence of sodium hydroxide, the contribution by bimolecular reaction to overall velocity constant is practically negligible. The value of first order rate constant is determined by estimating the acid produced at various intervals of time and the value of $k_1^{'}$ (the first order rate constant) is calculated by employing the usual integrated formula.

A careful perusal of the tables 7 shows that the value of first order rate constant remains practically constant throughout the entire course of the reaction. Further, we find that the value of $k_1^{'}$ remains sensibly constant from one experiment to another. Hence, we conclude that the order of reaction with respect to sec-amyl iodide is unity.

Table 7
Temperature 50°C
[Sec-amyl iodide] = 3.11 x 10^{-2} M
[EtOH – H_2O] = 60% v/v
[Sec-amyl iodide] expressed in ml. of M/218.39 NaOH per 5ml. of reaction mixture

Time in minute	[Sec-amyl iodide]	$k_1^{'}$ x 10^5
0	33.96	
30	33.74	22.26
60	33.50	23.03
120	33.04	23.03
180	32.56	23.41
241	32.14	22.93
360	31.14	24.09
480	30.42	22.93
960	27.22	23.05

Average value = 23.09 min^{-1}
Average deviation = 1.38%

Effect of addition of potassium iodide on the unimolecular reaction rate

A perusal of table 8 shows that the rate of the reaction decreases on increasing the concentration of potassium iodide (on increasing ionic strength).

Table 8
Temperature 55°C
[Sec-amyl iodide] = 9.32 x 10^{-2} M
[EtOH – H_2O] = 60% v/v

[KI] x M	μ x M	$k_1^{'}$ x 10^5 min^{-1}
0.00	0.00	33.65
0.50	0.50	31.02
0.75*	0.75	29.86
1.00	1.00	28.27

Temperature coefficient, energy of activation and entropy

It is quite clear from table 9 that the velocity of total unimolecular process, unimolecular substitution as well as for unimolecular elimination process increase by 2 to 3 times due to rise of temperature by 10°C. The straight lines are obtained by plotting log $k_1^{'}$ vs. $\frac{1}{T}$, log $(k_{1S}^{'})$ vs. $\frac{1}{T}$ and log $(k_{1E}^{'})$ vs. $\frac{1}{T}$ respectively (Fig. 5). The slopes of these straight lines will give the value of –E/2.303R. Thus the value of energy of activation for three processes can be calculated and the value of energy of activation for these reactions comes out to be 17,822 calories. (Total unimolecular), 17,732 Calories (unimolecular substitution) and 19,176 Calories (unimolecular elimination). The value of entropy of activation was found to be -30.48 e.u., -30.86 e.u. and -32.38 e.u. for total unimolecular, unimolecular substitution and unimolecular elimination processes respectively.

A perusal of table 10 has also been reproduced in the form of graph (Fig. 6). Straight lines are obtained when values of log $k_2^{'}$ and log $k_2^{''}$ are plotted against I/T separately. The slopes of these straight lines will give the value of –E/2.303R from which the energy of activation for the two reactions, bimolecular substitution and bimolecular elimination is calculated. The value of energy of activation from bimolecular substitution and bimolecular elimination was found to be 17,541 Calories and 20,816 Calories respectively. The value of entropy of activation for bimolecular substitution was found to be -29.04 e.u. and that for bimolecular elimination comes out to be -17.64 e.u.

Figure - 5

[Sec-amyl iodide] = 9.32 x 10^{-2} M

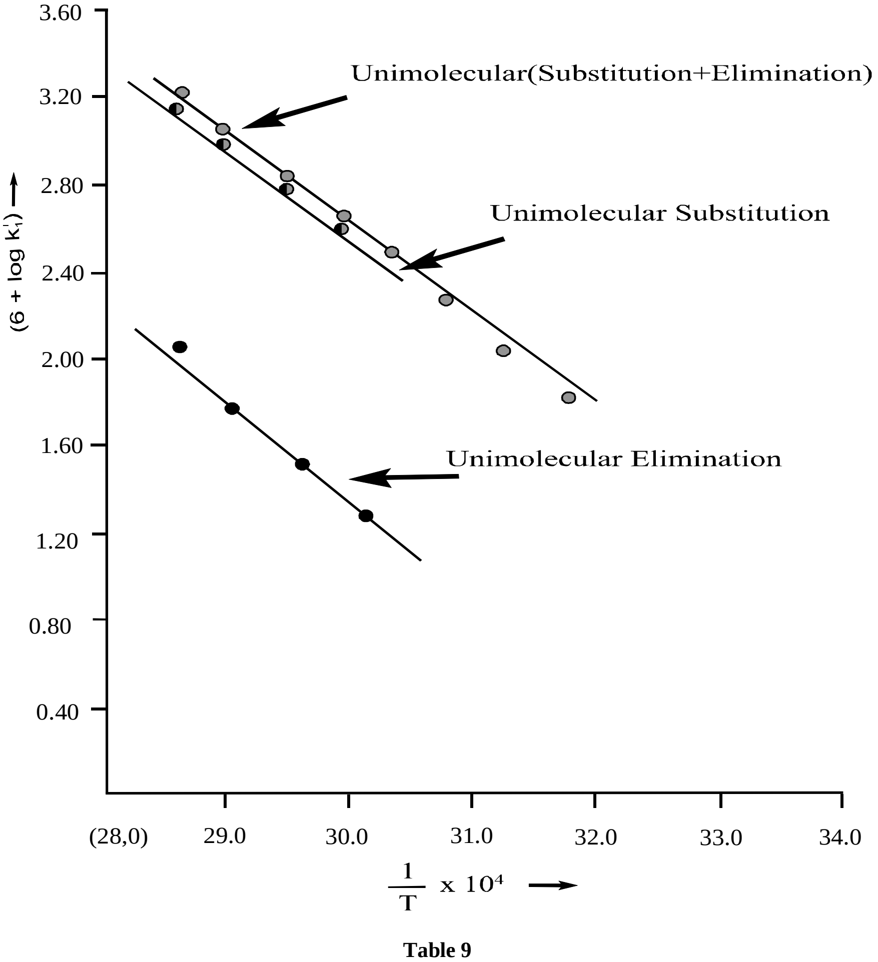


Table 9

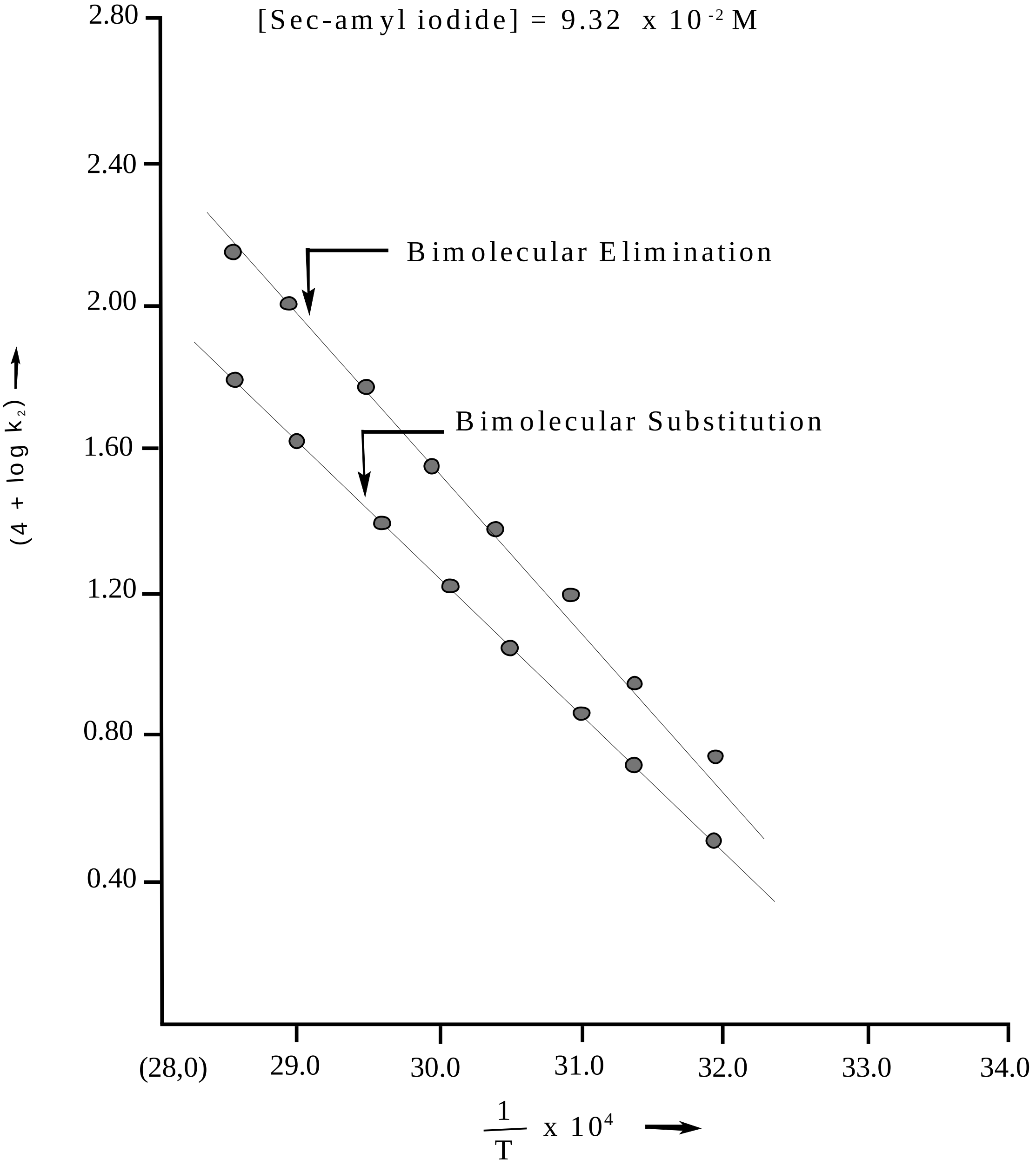
[EtOH- H_2O] = 60% v/v

Temperature	[Sec-amyl iodide] x 10^2M	$k_1^{'}$ x 10^5	$k_{1S}^{'}$ x 10^5	$k_{1E}^{'}$ x 10^5
75°	9.32	172.24	162.80	9.44
70°	"	114.98	108.89	6.09
65°	"	72.59	68.84	3.75
60°	"	48.31	45.87	2.44
75°	15.54	172.42	162.94	9.48
70°	"	115.06	108.90	6.16
65°	"	72.74	68.96	3.78
60°	"	48.57	46.11	2.46

Figure - 6

Energy of Activation

[Sec-amyl iodide] = 9.32 x 10^{-2} M



On the basis of our study of the salt effect as well as the effect of change of dielectric constant of the medium, it can be visualised that in the second order processes, the hydroxyl ion directly reacts with sec-amyl iodide. The mechanism of the second order processes is simple and can be represented as follows:

Scheme

1. For substitution reaction

$$CH_3\,CH_2\,CH_2\,CHI\,CH_3 + OH^- \xrightarrow{k_2'} CH_3\,CH_2\,CH_2\,CHOHCH_3 + I^-$$

2. For elimination reaction

$$CH_3\,CH_2\,CH_2\,CHICH_3 + OH^- \xrightarrow{k_2''} CH_3\,CH_2\,CH_2\,CH = CH_2 + CH_3CH_2CH{=}CHCH_3 + H_2O + I^-$$

Table 10

[EtOH – H_2O] = 60% v/v

Temperature	**[NaOH] M**	**[Sec-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}**
75°	2.00	9.32	158.04	47.19	110.85
70°	"	"	107.91	32.92	74.99
65°	"	"	70.51	21.91	48.00
60°	"	"	47.51	15.09	32.42
55°	"	"	33.25	10.74	22.51
50°	"	"	22.48	7.39	15.09
45°	"	"	12.60	4.23	8.37
40°	"	"	8.00	2.73	5.27
75°	"	15.54	157.61	46.84	110.77
70°	"	"	107.42	32.68	74.74
65°	"	"	70.48	21.84	48.64
60°	"	"	48.66	15.45	33.21
55°	"	"	33.85	10.94	22.91
50°	"	"	22.63	7.42	15.21
45°	"	"	12.57	4.21	8.36
40°	"	"	8.00	2.73	5.27
55°	"	7.77	32.11	10.41	21.70
55°	1.50	"	35.47	11.42	24.05
55°	1.00	"	43.20	13.88	29.32
55°	0.50	"	50.60	14.98	35.62
55°	0.25	"	52.88	16.10	36.78

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 sec-amyl iodide is hydrolyzed to the extent about 4.81% at 50^0C in 2M NaOH. 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. The doubt, regarding the pertinent role of NaOH as a reactant in the reaction through unimolecular process appear to be valid.

In the absence of sodium hydroxide the velocity of first order process is greatly increased on increasing the di-electric constant of the medium. 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. On the basis of the data obtained the reaction between sec-amyl iodide and NaOH shows most general feature out of all the halides studied. The rate expression can be written in general form.

$$-\frac{d[RX]}{dt} = K_2^{'}\ [RX\ \left[OH^-\right] + K_2^{''}[RX]\left[OH^-\right] + K_{1s}^{'}[RX] + \left[K_{1E}^{'}\right][RX] \qquad (1)$$

or

$$-\frac{d[RX]}{dt} = K_2\ [RX\ \left[OH^-\right] + K_1^{'}[RX] \qquad (2)$$

Where $K_2 = \left(K_2^{'} + K_2^{''}\right)$ and $K_1^{'} = \left(K_{1S}^{'} + K_{1E}^{'}\right)$ (3)

Where K_2 is the total second order rate constant for bimolecular process. $K_2^{'}$ and $K_2^{''}$ are the rate constants for bimolecular substitution and elimination reactions respectively. $K_1^{'}$ is total unimolecular rate constant while $K_{1S}^{'}$ and $K_{1E}^{'}$ are rate constants for substitution and elimination respectively in first order process.

CONCLUSION

The study of previous pages 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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