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Study of the Solvolysis of N-Heptyl Chloride 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 n-heptyl chloride. The base employed was NaOH. Solvent effect on the kinetics of n-heptyl chloride has been investigated in alkaline and neutral medium in [EtOH-H₂O] mixtures up to 60% v/v in the temperature range of 50^oC-75^oC. The overall velocity in the first order process depends upon the concentration of halide molecule (i.e. n-heptyl chloride). 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 first order reaction alone occurs in absence of sodium hydroxide. It has been found that rate of the first order process and the velocity of first order process increase with increase in the dielectric constant of the medium. The rate expression can be written as:

$$-\frac{d[RX]}{dt} = K_2 [RX] [OH^-] + K_1 [RX].$$
 Activation parameters were also determined.

Keywords: Kinetics, Solvolysis, n-heptyl chloride, mechanism, NaOH, ionic Strength, dielectric constant, activation parameters.

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INTRODUCTION

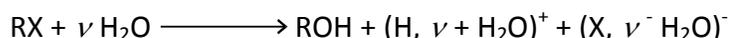
Hydrolysis of an alkyl halide may proceed through SN^1 or SN^2 path depending on its structure and the set of experimental conditions used. In the study of kinetics of alkaline hydrolysis of n-heptyl chloride, it has been found that the overall process consists of three simultaneous reactions and these 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.

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°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]. Study of the hydrolysis of sec-amyl iodide in alkaline and neutral media is done kinetically to by Usha Kushwaha et al. [10].

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 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 [11], and other alkyl halide [12] 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 [13] 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.



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 [14-24].

MATERIALS AND METHODS

Experimental

Materials employed

Normal heptyle chloride (Fluka 99%) was distilled in a quick-fit apparatus and the fraction separation between 158⁰C-159⁰C was employed for the study of kinetic measurements.

Ammonium thiocyanate, nitrobenzene, carbon tetrachloride, ferric alum were all either (A.R.B.D.H.) or G.R. (E. Merck) grade samples.

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, lacamide (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 78.2⁰C was retained and was used to prepare the solvent mixture which usually consisted of a mixture of alcohol and water.

Methods

Study of the Progress of the Reaction

The requisite quantity of sodium hydroxide solution was added to the solvent-mixture consisting of water and alcohol contained in a conical flask. The conical flask containing the solvent mixture along with another conical flask containing pure n-heptyl chloride was kept in a thermostat regulated by an automatic electronic relay. When the reactants had attained the temperature of the bath, the requisite quantity of n-heptyl chloride was poured into the flask containing sodium hydroxide solution by means of a pipette. The stop watch was started as soon as half of the halide has passed out of the pipette. The overall reaction mixture contained 60% of the alcohol by volume unless mentioned otherwise. The progress of the reaction was studied by withdrawing an aliquot of (5 ml.) reaction mixture at scheduled intervals. This was immediately poured into a mixture consisting of 10 ml. of 2N sulphuric acid and 25 ml. of nitrobenzene in order to arrest the reaction. This was vigorously shaken for a few minutes after

adding a known quantity of silver nitrate solution with some nitric acid (10 ml. of 2N nitric acid). The excess of silver ion was estimated by titrating against a standard solution of ammonium thiocyanate using ferric alum as an indicator. Here nitrobenzene plays dual role, it extracts the unreacted halide and thus minimises further hydrolysis and the possible reaction with the silver nitrate. It also improves the end point by coagulating silver chloride formed.

The reaction was studied at all temperatures (i.e. except 50°) by keeping the reaction mixture in a number of thin glass tubes which were sealed and kept in the thermostat. These were taken out at scheduled intervals and broken in a beaker. The contents were then estimated as described above.

Study of hydrolysis of n-heptyl chloride in neutral medium

The reaction was also studied in neutral solutions (in absence of sodium hydroxide). The progress of the reaction was studied by withdrawing an aliquot of reaction mixture at scheduled 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 lacomide¹⁴ as an indicator. There again the reaction mixture was kept in sealed thin glass tubes at higher temperatures (i.e. at 55°C and onward). The reaction velocity is very slow in neutral solutions.

Measurement of Dielectric Constant and estimation of olefin

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 μ f capacity, which was previously calibrated with standard liquids of known dielectric constant.

In order to estimate olefin produced as a result of hydrolysis of the halide, the sealed tubes were broken under ice cold carbon tetrachloride (50 ml.) and the organic layer was washed with sulphuric acid and water. To this, 10ml. of a solution of bromine in carbon tetrachloride was added. The mixture was allowed to stand for 30 minutes, during which the olefin reacts with bromine. The remaining bromine was titrated iodometrically by adding potassium iodide and titrating the iodine liberated against a standard solution of sodium thiosulphate with

starch as an indicator. A blank experiment was run in the same way with 10ml. of the medium and results of this experiment were taken as the bromine equivalent when no olefin was present.

RESULTS AND DISCUSSION

Order of reaction with respect to n-heptyl chloride

In order to find out the order of reaction with respect to halide in all experiments the concentration of sodium hydroxide was kept large as compared to that of halide. For any given run, therefore the reaction velocity will depend upon the concentration of halide. The order of the reaction with respect to n-heptyl chloride is found to be unity and the value of the first order rate constant is calculated by employing the following expression.

$$k_1 = \frac{2.303}{t} \log \frac{a}{(a-x)} \quad (i)$$

Where 'a' is initial concentration of n-heptyl chloride and 'n' the decrease in concentration in time 't'.

The value of k_1 will depend upon the concentration and order of reaction with respect to sodium-hydroxide in addition for all velocity is also found to be dependent to some extent on ionic strength and dielectric constant of the medium. However, Eq. (i) will hold good for constant, dielectric constant and ionic strength of the medium. In this section it is intended to show that the order of the reaction is unity.

A careful perusal of table 1 shows that the first order rate constants are sensibly constant. We may, therefore, conclude that the reaction follows first order with respect to n-heptyl chloride. The order of the reaction with respect to halide has been further confirmed by graphical method. A straight line is obtained when a graph is plotted between $\log \frac{a}{(a-x)}$ and t

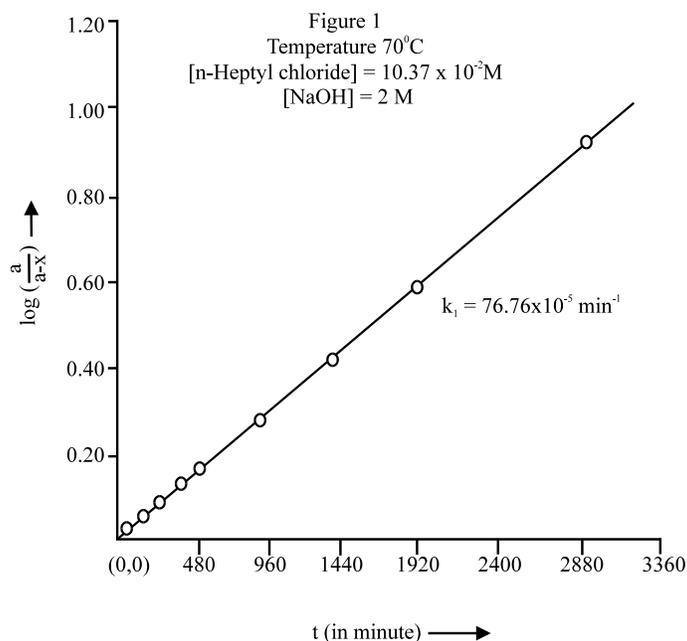
(Fig. 1) the slope of which is equal to $\frac{k_1}{2.303}$. The value of k_1 thus obtained i.e., $76.76 \times 10^{-5} \text{ min}^{-1}$

is not much different from the value obtained by integral method (Table 1). Hence we can assume that the order of reaction is unity with respect to n-heptyl chloride.

TABLE 1
 Temperature 70°C; [n-Heptyl chloride] = $10.37 \times 10^{-2} \text{ M}$; [EtOH – H₂O] = 60% v/v; [NaOH] = 2M
 [n-Heptyl chloride] expressed in ml. of M/25.79 NH₄SCN per 5 ml. of reaction mixture

Time in minute	[n-Heptyl Chloride]	$k_1 \times 10^5$	$k_2 \times 10^5$	$k_1' \times 10^5$	$k_2 \times 10^5$
				(b-x)	
0	13.38				
60	12.78	76.38	38.19	0.14	38.05
120	12.18	78.49	39.24	0.14	39.10
240	11.08	78.77	39.38	0.14	39.24

360	10.14	77.08	38.54	0.14	38.40
480	9.24	77.15	38.57	0.14	38.43
960	6.42	76.52	38.26	0.14	38.12
1440	4.38	77.56	38.78	0.14	38.64
1920	3.06	76.86	38.43	0.14	38.29
2880	1.50	75.99	37.99	0.14	37.85
T_{∞}	0.00				
Average value =		77.20 min^{-1}	$38.60 \text{ Litres mol}^{-1} \text{ min}^{-1}$		$38.46 \text{ litres mol}^{-1} \text{ min}^{-1}$
Average deviation =		0.90%			



Order of reaction with respect to sodium hydroxide

In order to determine the order of the reaction with respect to sodium hydroxide the velocity expression can be written as

$$\left(-\frac{dc}{dt}\right) = k_2 [\text{Sodium hydroxide}]^n [\text{n-Heptyl Chloride}] \quad (\text{ii})$$

$$\text{or } \left(-\frac{dc}{dt}\right) = k_1 [\text{n-Heptyl Chloride}] \quad (\text{iii})$$

Where k_1 will be given by expression

$$k_1 = k_2 [\text{sodium hydroxide}]^n \quad (\text{iv})$$

Where k_2 is the true velocity constant of the reaction. Since the concentration of sodium hydroxide was kept large as compared to n-heptyl chloride the former can be assumed to be constant and hence the equation (iii) is valid. Now if the value of n is unity the value of k_1 will be directly proportional to the concentration of sodium hydroxide. This direct proportionality of the reaction velocity with the concentration of sodium hydroxide, however, marked to several

factors, the most important of which is ionic strength of the medium. Our results show that an increase in the ionic strength of the medium leads to a retardation in velocity,

The effect of variation of the concentration of sodium hydroxide on the value of k_1 has been studied at constant ionic strength by adding requisite amount of sodium perchlorate in the reaction mixture. However, it is found that in presence of sodium perchlorate the value of k_1 slightly decreases towards the end of the reaction. We have, therefore, determined the value of k_2 in Eqn. (ii) by measuring the value of $\left(-\frac{dc}{dt}\right)$ (Figs 2 and 3) near the initial region and by dividing it by the product of concentration of sodium hydroxide and that of the halide. The procedure shows that the value of k_2 so obtained remains practically constant (see the last column of Table 2). The value of $\left(-\frac{dc}{dt}\right)$ is calculated in terms of ml. min^{-1} but the final value of k_2 is given in $\text{litres mol}^{-1} \text{min}^{-1}$.

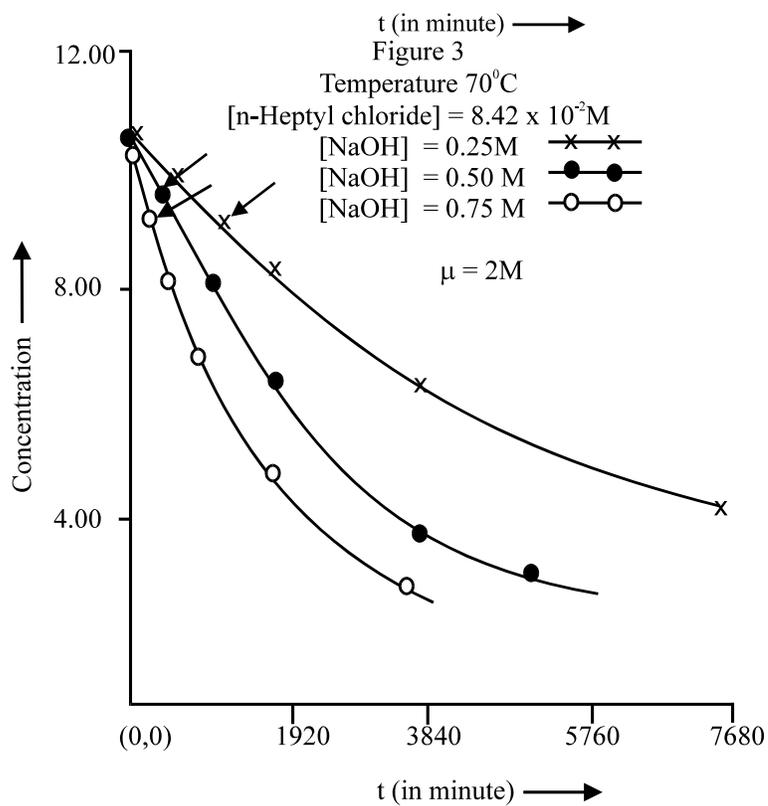
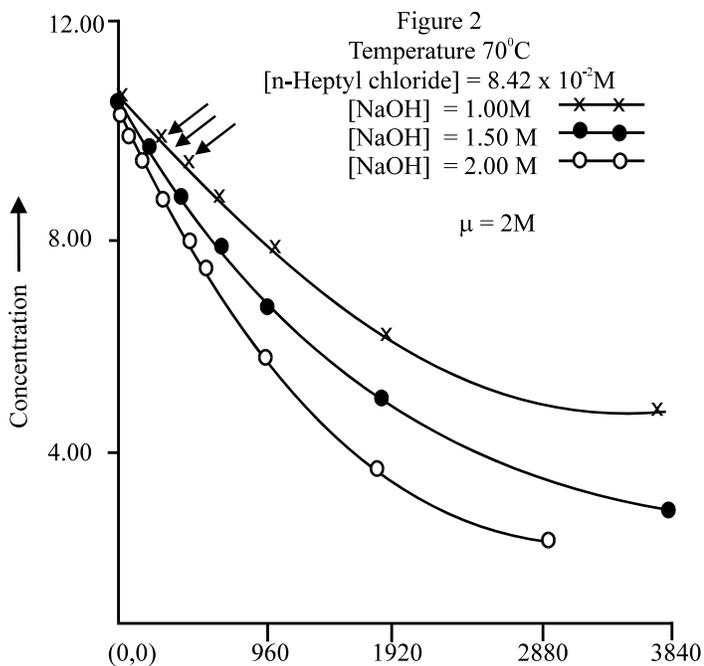
A careful perusal of the table 2 shows that the values in the last column are sensibly constant. They agree within 2.47% showing thereby that the total order of the reaction is unity with respect to each reactants.

From the calculation, it is obvious that the order of the reaction with respect to sodium hydroxide is unity. Hence, the total order of the reaction is two.

Table 2
 Temperature 70°C; [n-Heptyl Chloride] = 8.42×10^{-2} M; [EtOH – H₂O] = 60% v/v; $\mu = 2\text{M}$

S.No.	[OH] M	[n-Heptyl chloride] expressed in ml. of M/25.80 NH ₄ SCN per 5ml. of reaction mixture at which $\left(-\frac{dc}{dt}\right)$ is measured.	$\left(-\frac{dc}{dt}\right) \times 10^4 \text{ ml. min}^{-1}$	$k_2 \times 10^5 =$
				$\left(-\frac{dc}{dt}\right)$ [OH] [n-Heptyl Chloride]
1	2.00	10.00	75.75	37.87
2	1.50	10.00	55.55	37.03
3	1.00	10.00	37.50	37.50
4	0.75	10.00	29.76	39.68
5	0.50	10.00	19.84	39.68
6	0.25	10.00	9.69	38.76

Average value = 38.42 litres mol⁻¹ min⁻¹
 Average deviation = 2.47 %



Dependence of reaction rate on the initial concentration of sodium hydroxide and the electrolyte effect associated with change in the concentration of sodium hydroxide

The results of the experiments at different concentration of sodium hydroxide are summarized in the table 3 for the sake of completeness and have only a qualitative significance. The values of the rate constant of first order with respect to n-heptyl chloride obtained in experiments 1, 2 and 3 and the values of first order rate constant with respect to sodium hydroxide obtained in experiment Nos. 6, 7 and 8 are given in third column of table 3 respectively. The value of \bar{k}_2 have been obtained by dividing the values of k_1 by the corresponding concentration of sodium hydroxide in experiments 1, 2 and 3 while the \bar{k}_2 values were obtained by dividing the values of k_1 (obtained with respect to sodium hydroxide) by concentration of halide in experiments 6, 7 and 8. The values of \bar{k}_2 in experiments 4 and 5 have been calculated by employing the following formula

$$\bar{k}_2 = \frac{2.303}{t(b-a)} \log \frac{a(b-x)}{b(a-x)}$$

Table 3

Temperature 70°C; [n-Heptyl Chloride] = 8.42×10^{-2} M; [EtOH – H₂O] = 60% v/v

Experiment No.	[Sodium Hydroxide] x M	$k_1 \times 10^5 \text{ min}^{-1}$	$\bar{k}_2 \times 10^5 \text{ litres mol}^{-1} \text{ min}^{-1}$
1	2.00	77.34	38.67
2	1.50	61.56	41.04
3	1.00	46.38	46.38
4	0.50	-	49.48
5	0.25	-	57.07
6	0.02	5.52	65.56
7	0.01	6.29	74.70
8	0.005	6.72	79.98

The total order of the reaction is two, unity with respect to both, n-heptyl chloride and sodium hydroxide.

Solvent variation effect on reaction velocity

In the reaction between a dipolar molecule and a negative ion, there is no commonly agreed precise theory regarding the exact role of dielectric constant. Our results are in conformity with the theory of Laidler and Eyring. The results in the table 4 have only a qualitative significance as no attempt has been made to calculate $\mu = 0$ $k_D = \infty$ in the present reaction. Here our main attempt has been to show the composite nature of the reaction and to separate the values of various reaction constants.

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

Table 4

Temperature 60°C; [n-Heptyl Chloride] = 4.54×10^{-2} M; [NaOH] = 2M

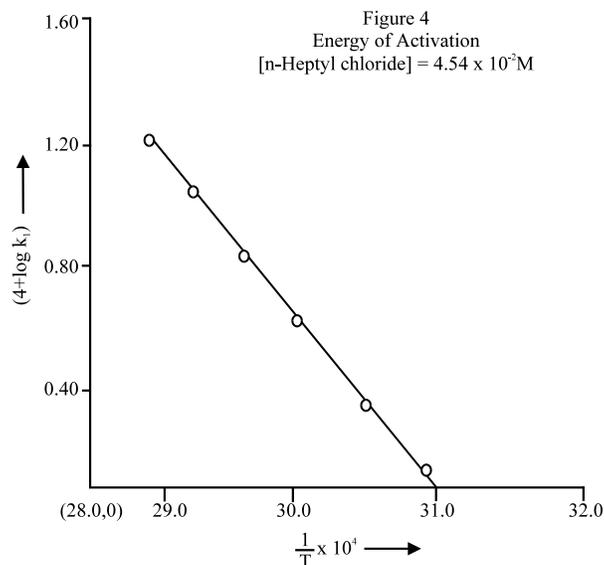
Percentage of alcohol	Dielectric constant (D)	$k_1 \times 10^5 \text{ min}^{-1}$	$k_2 \times 10^5 \text{ litres mol}^{-1} \text{ min}^{-1}$
80	31.00	35.73	17.86
70	36.70	33.16	16.58
60	41.70	31.01	15.50
50	47.50	27.97	13.98

Effect of temperature variation on reaction velocity

The table 5 has also been reproduced in the form of a graph (Fig. 4) in which $\log k_1$ has been plotted against $1/T$. The energy of activation has been found to be 21,694 Calories. The entropy of activation has also been calculated by using the value of energy of activation in the usual equation and has been found to be 21.20 e.u.

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

Temperature	[n-Heptyl chloride] x 10 ² M	$k_1 \times 10^5 \text{ min}^{-1}$	$k_2 \times 10^6 \text{ litres mol}^{-1} \text{ min}^{-1}$
75°	4.54	124.55	62.27
70°	"	78.19	39.09
65°	"	49.55	24.77
60°	"	31.01	15.50
55°	"	19.05	9.52
50°	"	11.23	5.61
75°	12.96	123.32	61.66
70°	"	77.52	38.76
65°	"	49.73	24.86
60°	"	30.72	15.36
55°	"	18.65	9.32
50°	"	11.60	5.80



Estimation of olefin and separation of bimolecular rate constants

The overall reaction velocity may be represented by

$$\frac{-d[R-Cl]}{dt} = k_1'[R-Cl] + k_2'[R-Cl][OH^-] + k_2''[R-Cl][OH^-] \quad (v)$$

In presence of finite concentration of sodium hydroxide this equation can be rewritten as

$$\begin{aligned} \frac{-d[R-Cl]}{dt} &= (k_2' + k_2'')[R-Cl][OH^-] \\ &= k_2[R-Cl][OH^-] \end{aligned} \quad (vi)$$

The olefin produced at various times during a run is a constant fraction of the total second order reaction which indicates that the olefin is formed by second order process.

The percentage of olefin formed at different intervals of time has been shown in the second column of table 6. It is clear from column VI of the table 6 that olefin formation is a constant fraction of total second order reaction.

Table 6
Temperature 70°C; [EtOH - H₂O] = 60% v/v; [NaOH] = 2M

Time in minute	[n-Heptyl chloride] x 10 ² M	E ₂ (%)	SN ₂ (%)	$\frac{SN_2}{SN_2 + E_2}$	$\frac{E_2}{SN_2 + E_2}$
120	4.54	0.88	99.12	0.9912	0.0088
360	"	0.90	99.10	0.9910	0.0090
480	"	0.93	99.07	0.9907	0.0093
1150	"	0.92	99.08	0.9908	0.0092
1890	"	0.94	99.06	0.9906	0.0094

T_{∞}	"	0.93	99.07	0.9907	0.0093
120	12.96	0.90	99.10	0.9910	0.0090
240	"	0.88	99.12	0.9912	0.0088
480	"	0.92	99.08	0.9908	0.0092
960	"	0.92	99.08	0.9908	0.0092
1920	"	0.91	99.09	0.9909	0.0091
T_{∞}	"	0.91	99.09	0.9909	0.0091

It is quite clear from table 6 that it is not necessary to estimate olefin at various times in order to obtain the ratios shown in the table. The experiments have been carried out at other temperatures and compositions of the reaction mixtures also and percentage of olefin formed has been found out after completion of reactions. These percentages are the average of atleast three observations. The results obtained are summarized in table 7.

Table 7
[NaOH] = 2M

Temperature	[n-Heptyl chloride] x 10^2 M	Solvent [EtOH-H ₂ O] % v/v	E_2 (%)	SN_2 (%)	$\frac{SN_2}{SN_2 + E_2}$	$\frac{E_2}{SN_2 + E_2}$
75°	4.54	60	1.13	98.87	0.9887	0.0113
70°	"	"	0.93	99.07	0.9907	0.0093
65°	"	"	0.74	99.26	0.9926	0.0071
60°	"	"	0.56	99.44	0.9944	0.0056
60°	"	80	0.84	99.16	0.9916	0.0084
60°	"	70	0.69	99.31	0.9931	0.0069
60°	"	50	0.42	99.58	0.9958	0.0042
55°	"	60	0.37	99.63	0.9963	0.0037
50°	"	"	0.27	99.73	0.9973	0.0027
75°	12.96	"	1.14	98.86	0.9886	0.0114
70°	"	"	0.91	99.09	0.9909	0.0091
65°	"	"	0.72	99.28	0.9928	0.0072
60°	"	"	0.57	99.43	0.9943	0.0057
55°	"	"	0.36	99.64	0.9964	0.0036
50°	"	"	0.28	99.72	0.9972	0.0028

Temperature coefficient, energy of activation and entropy of activation

A perusal of Table 8 shows that the velocity of both, bimolecular substitution and bimolecular elimination processes increases 2 to 3 times by rise of 10°C of temperature. Table 8 has also been reproduced in the form of graph (Figs. 5 and 6). The two straight lines are obtained by plotting $\log k_2'$ vs. $1/T$ and $\log k_2''$ vs. $1/T$ respectively. From the slopes of these straight lines the values of energy of activation for the two processes are calculated. The values of energy of activation for both bimolecular substitution and elimination processes have been found out to be 21,050 Calories and 28,901 Calories. These values of energy of activation were utilized to calculate the values of entropy of activation for these reactions and the values of

entropy of activation were found to be -23.14 e.u. and -9.73 e.u. for bimolecular substitution and elimination reactions respectively.

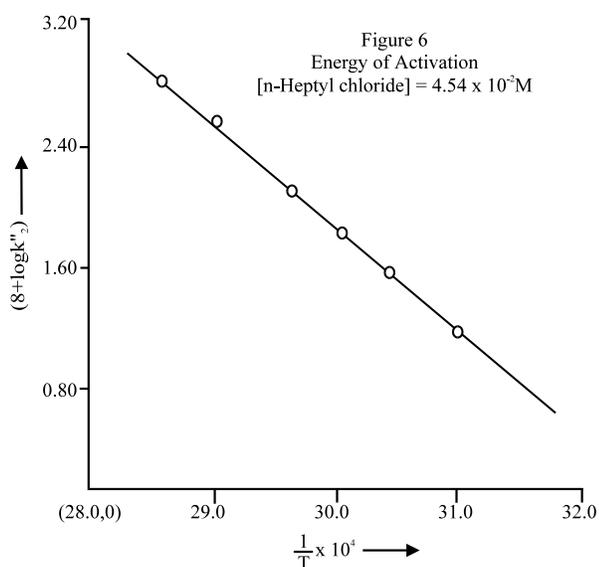
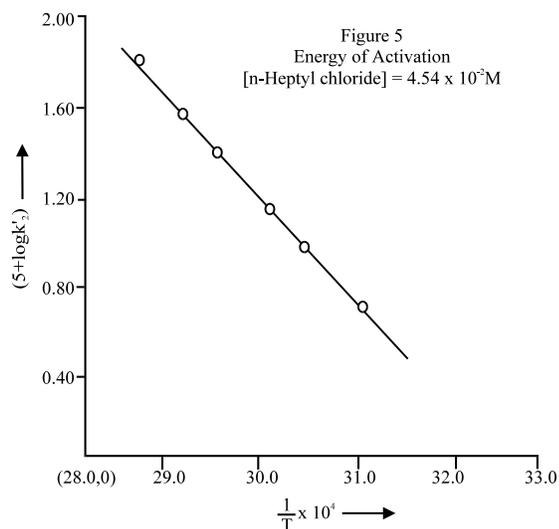


Table 8
[NaOH] = 2M

Temperature	[n-Heptyl chloride] x 10 ² M	Solvent [EtOH-H ₂ O] % v/v	k ₂ x 10 ⁵ litres mol ⁻¹ min ⁻¹	k' ₂ X 10 ⁵ litres mol ⁻¹ min ⁻¹	k'' ₂ X 10 ⁵ litres mol ⁻¹ min ⁻¹
75°	4.54	60	62.27	61.57	0.70
70°	"	"	39.09	38.73	0.36
65°	"	"	24.77	24.59	0.18
60°	"	"	15.50	15.41	0.09
60°	"	80	18.63	18.47	0.16
60°	"	70	17.39	17.27	0.12

60°	"	50	13.72	13.66	0.06
55°	"	60	9.52	9.48	0.04
50°	"	"	5.61	5.59	0.02
75°	12.96	"	61.66	60.96	0.70
70°	"	"	38.76	33.41	0.35
65°	"	"	24.86	24.68	0.18
60°	"	"	15.36	15.27	0.09
55°	"	"	9.32	9.29	0.03
50°	"	"	5.80	5.78	0.02

Neutral hydrolysis of n-heptyl chloride

The first order part of the composite reaction has, so far, not been studied since the contribution of the first order reaction is negligible in presence of sodium hydroxide. The first order reaction alone occurs in absence of sodium hydroxide, consequently experiments were carried out in absence of sodium hydroxide. It has been observed that n-heptyl chloride is very slowly hydrolysed via first order mechanism alone. The rate constants are calculated by the following expression.

$$k_1' = \frac{2.303}{t} \log \frac{a}{(a-x)} \quad \text{(vii)}$$

Where k_1' is rate constant for first order substitution reaction.

From a careful perusal of the results of different experiments we find that the value of the first order rate constant remains practically constant throughout the entries course of the reaction. We also, further, find that the value of k_1' does not change from one experiment to another. Hence, we conclude that order of reaction with respect to n-heptyl chloride is unity in absence of sodium hydroxide.

Effect of solvent variation on reaction velocity

In the table 9, the results of various experiments carried out in different compositions (Ethyl alcohol water) of the reaction mixture are summarized. It has been found that rate of reaction increases as the dielectric constant of the medium is increased and the velocity of the reaction increases with the decrease in the percentage of alcohol in the reaction mixture.

Effect of addition of potassium chloride on the reaction velocity

From a close look at the table 10 it becomes evident that as the concentration of potassium chloride is increased the velocity of the reaction decreases.

Table 9
 Temperature 60°C; [n-Heptyl Chloride] = 4.54×10^{-2} M

Percentage of alcohol	Dielectric constant (D)	$k_1' \times 10^7 \text{ min}^{-1}$
80	31.00	6.02
70	36.70	8.58
60	41.70	10.41
55	44.40	18.16
50	47.50	24.05

Table 10
 Temperature 65°C; [n-Heptyl Chloride] = 4.54×10^{-2} M; [EtOH – H₂O] = 60% v/v

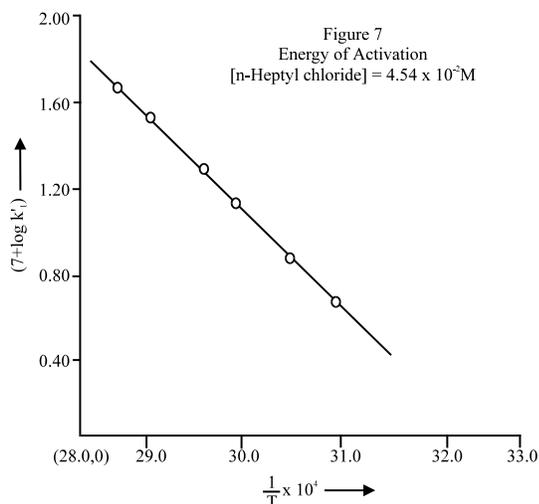
[KCl] x M	$\mu \times \text{M}$	$k_1' \times 10^7 \text{ min}^{-1}$
0.00	0.00	16.98
0.25	0.25	15.92
0.50	0.50	14.80
0.75	0.75	13.64

Study of the temperature coefficient, energy of activation and entropy of activation of the first order process

The table 11 has also been reproduced in the form of a graph (Fig. 7) which shows the velocity increases as the temperature is increased. The energy of activation has been calculated by plotting graph of $\log k_1'$ vs. $1/T$ (Fig. 7). The energy of activation comes out to be equal to 21,965 Calories. The entropy of activation has been calculated by utilising the value of energy of activation in the usual formula and the value of entropy of activation was found to be 30.32 e.u.

Table 11
 [EtOH – H₂O] = 60% v/v

Temperature	[n-Heptyl Chloride] x 10^2 M	$k_1' \times 10^7 \text{ min}^{-1}$
75°	4.54	46.02
70°	"	27.26
65°	"	16.98
60°	"	10.41
55°	"	6.05
50°	"	3.26
75°	12.96	46.33
70°	"	27.52
65°	"	16.60
60°	"	10.26
55°	"	6.37
50°	"	2.99



CONCLUSION

The contribution to overall 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 n-heptyl chloride is hydrolyzed to the extent about 0.43% at 50°C 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 [25].

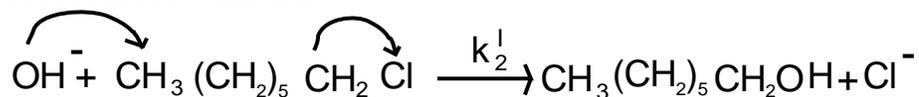
Both second order processes as well as first order process are affected by a change in the dielectric constant of the medium which is affected by changing the concentration of alcohol present in reaction mixture.

In the absence of sodium hydroxide the velocity of first order process is greatly increased on increasing the dielectric constant of the medium.

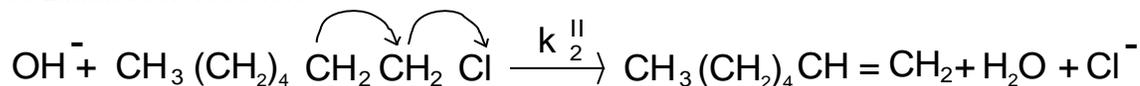
On the basis of above findings the mechanistic path of the reactions is proposed as follows.

Scheme:

(1) For substitution reaction



(2) For Elimination reaction



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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