

KINETICS AND MECHANISTIC STUDIES ON THE ALKALINE HYDROLYSIS OF ETHYL PYRIDINE-3-CARBOXYLATE IN SULPHOXIDE – WATER MEDIUM

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Abstract – The kinetics of alkaline hydrolysis of ethyl pyridine -3- carboxylate in aqueous dimethyl sulphoxide(DMSO) medium. The ethyl pyridine -3- carboxylate is a safe substance. Dimethyl sulphoxide is a dipolar, aprotic and protophilic solvent. The kinetics of the reaction was studied by mixing 10 ml of reaction mixture (Ethyl pyridine -3- carboxylate and NaOH) with 10 ml of 0.1N HCl and excess of alkali was titrated by means of 0.05N baryta solution. The rates of kinetics were followed by changing the ionic strength of the solution, DMSO percentage composition, temperature and dielectric constant of the medium. The order of reaction is found to be second. The values of rate constant remain constant by increasing the ionic strength of the KCl solution. However the rate, extent and mechanism also remains same. The value of rate constant decreases with increase in the percentage of DMSO (30.0-80.0) solution and increases with increase in temperature (293K-313K). The increase of dielectric constant of medium from 62.5-75.0 increases. The value of rate constant and it is found to optimum at 313K. The thermodynamic parameter of activated state ΔG^\ddagger , ΔH^\ddagger and ΔS^\ddagger are not much favourable of the hydrolysis of ethyl pyridine -3- carboxylate. The negative value of entropy of activated indicates that transition state is more solvated than reactants.

Key words: Aprotic, Dimethyl sulphoxide, Ethyl pyridine -3- carboxylate, Hydrolysis, Kinetics, Protophilic,

INTRODUCTION - The mechanism of hydrolysis of esters is just reverse of the mechanism of esterification. Usually the hydrolysis of esters is carried out either in presence of acids or in presence of alkali. Alkaline hydrolysis is irreversible process. A carboxylic ester is hydrolysed to a carboxylic acid and alcohol or phenol is formed. Under alkaline condition reaction involves first attack on ester by hydroxide ion and it displaces catalysed by acids and bases. In alkaline hydrolysis of ester in nucleophilic substitution of hydroxyl ion (OH⁻) take place at the alkyl carbon atom during the alkyl – oxygen bond cleavage by cleavage of bond between oxygen and acyl group. Kamlet et.al. established that the effect of solvent on the reaction rate depends on the dielectric values which facilitate the separation of opposite charges on the transition state. In solution reactants, products and activated state are solvated. The strength of the solute solvent interaction depends on some solvation parameter like polarisability, hydrogen bond acceptor basicity. Kamlet et.al. reported that the effect of solvent on the reaction rate should depend on (1) The behaviour of the solvent as a dielectric (2) Ability of a solvent to donate a proton to a solute and thus stabilises the anion of the transition state. (3) The ability of a solvent to donate an electron pair. However Exner and Swain reported that the major contribution of a solvent is its polarity. On the other hand Hummett observe that rate of hydrolysis of ester increases with increase of the acidity of a solvent. Taft, Charton and others considered the acidic and steric factor as important parameter. Different point of view have been put forward by different group of workers for the hydrolysis of esters and primary controversial observations are related to the activity of its intermediates, complex formation of the substrate with reactant and on the concentration. Solvents are usually of three types: 1. protic solvents 2. Aprotic solvents and 3. Polar and weakly polar solvents. The four types of solvent solute interactions are present in solution. Normally (1) dipole – dipole type, (2) ion – dipole type (3) ion – ion type, and (4) vanderwaal attraction. Ethyl pyridine is generally recognised as a safe substance and it contains heterocyclic ring. DMSO is dipolar, aprotic, moderate dielectric constant and has high dipole moment. The choice of the solvent is purely solubility of the ester. The present work represents the study of the kinetics of alkaline hydrolysis of ethyl pyridine-3- carboxylate in aqueous dimethyl sulphoxide (DMSO) medium. The effect of various compositions of DMSO, ionic strength, dielectric constants, and temperature are also some of the parameter of the present study. Mechanistic steps of the kinetic processes are also discussed..

EXPERIMENTAL- Ethyl pyridine -3- carboxylate (Flake AG make, 99% pure) was used as ester, Dimethyl sulphoxide of Merck grade were used as solvents. Barium hydroxide [Ba(OH)₂·8H₂O] of BDH grade was used for the preparation of Baryta solution and was standardise against 0.05 succinic acid solution using phenolphthalein as an indicator. BDH make hydrochloric acid (AR grade) was standardised against 0.05N sodium carbonate (BDH grade) using methyl orange as an indicator, Sodium hydroxide (E. Merck grade) after standardised by 0.05 succinic acid using phenolphthalein as an indicator was used for the alkaline hydrolysis of ethyl pyridine -3- carboxylate. All the experiments were performed in free double distilled carbon dioxide.

PROCEDURE - In order to study the kinetics of alkaline hydrolysis of ethyl pyridine -3- carboxylate appropriate quantities of DMSO and NaOH solutions were taken in a 250ml stopper glass conical flask. The total volume of the solution was made to 100ml and its base strength become 0.1M. Furthermore 0.70ml of ethyl pyridine -3- carboxylate was added to 100 ml reaction mixture. Immediately after shaking 10ml of the solution was withdrawn with the help of pipette and taken in 10ml of ice cold HCl (0.1N) solution. The remaining alkali of solution as titrated against 0.05N baryta solution using phenolphthalein as indicator. These experiments were repeated at various intervals of time. After twenty four hours the remaining reaction mixture was heated in water bath for about half an hour and infinity reading was taken. The specific rate constants were determined using second order kinetics. By varying the composition of organic solvents, ionic solvents, dielectrically constant and temperature all the experiments were repeated.

RESULTS AND DISCUSSIONS - The influence of ionic strength on the kinetics of hydrolysis of ethyl pyridine -3- carboxylate the different compositions of potassium chloride were studied at 303K is 0.43 dm³mol⁻³DMSO solution. It is evident from the data recorded in Table-2 that the values of rate constants remains almost unchanged. Generally a reaction between an ion and a neutral molecule or between two neutral molecules should not be affected by the ionic strength of the solutions. The results of the kinetics of alkaline hydrolysis of ethyl pyridine -3- carboxylate is varying the percentage composition of DMSO solution from 30.0-80.0 are recorded in Table -3 at different temperatures (293K-313K) keeping ionic strength of the solution constant. It is evident that value of rate constant decreases with increases of percentage composition of DMSO (V/v) and it increases with the rise of temperatures. Furthermore the order of reaction is found to obey second order kinetics. Similar results were also reported by Hummett, Zucker- Hummett and Bummert, Bummert-Olsen and Arrhenious. Furthermore as a result of hydrolysis a carboxylic acid is formed. Alkali promotes hydrolysis by the strongly nucleophilic reagent OH⁻. This is essentially an irreversible reaction. Hydroxyl ions attacks at carbonyl carbon and involve cleavage of the bond between oxygen and acyl groups. However it is two step process with the formation of a tetrahedral intermediate followed by displacement of alkoxide. The possibility of exchange of oxygen with that of the solvent can not ruled out. Aprotic solvents make more nucleophilic to hydroxyl ion due to increase in composition of DMSO may decrease the dielectric constant of the medium which reduces the rate of reaction. The effect of dielectric constants on the rate of hydrolysis are studied at different temperatures (293K-313K) of DMSO solution at fixed ionic strength and the results are shown in Table-4. It may be seen from this table that the values of rate constants increases by increase of both dielectric constant of the medium (62.5-75.0) and temperatures (293-313K). This increases of rate may be due to change in solvent polarity, hydrogen bond acceptor basicity and hydrogen bond donor acidity. The thermodynamic parameters of activated state are recorded in Table-5. It is evident from that the value

of free energy of activation G^* increases from $8.21 \times 10^5 \text{ J mol}^{-1}$ to $8.69 \times 10^5 \text{ mol}^{-1}$ with increases of percentage of DMSO (V/v) solution from 30.0-80.0. The observe negative value of entropy of activation supports that as the charge separation takes place in the transition state the charge ends become highly solvated. This results in immobilization at the large number of solvent molecule at the transition state. And it become more compact and ordered. On the other hand, the value of both enthalpy of activation and entropy of activation decreases with the increases in concentration of DMSO solutions. The increase in value of G^* may be due to change in salvation of reactants, activation state and product and change in dielectric constants of the solvents are due to complexation effect. However, one cannot explain the complexation effect is the only factors. Detailed consideration of solvents- solute interaction, hydrostatic pressure, pre exponential factor, ion- dipole, dipole-dipole, internal pressure are some of the parameters that may be affect the rate and mechanism of hydrolysis. The hydrolysis of the ester the base first forms a covalent bond with the ester to make a tetrahedral intermediate which has a negative charge and is more crowded.¹¹

CONCLUSION - The kinetics of alkaline hydrolysis of ethyl nicotinate follows a second order reaction mechanism. The rate constant of the reaction is unchanged with the change in ionic strength of the medium. It decreases with the increase in organic solvents composition. However there are increases with decrease in aqueous to organic ratio of the solution. Rate constant of the reaction increases with the increase of dielectric constants and temperature.

Table-1

Influence of KCl concentration on the kinetics of alkaline hydrolysis of ethyl nicotinate in aqueous DMSO and DMF solution at 303k. Organic solvent composition: 30% V/v

Conc. KCl (M)	Rate constant(k)x10 ³ dm ⁻³ mol ⁻¹ s ⁻¹	
	DMSO	DMF
0.00	4.47	3.37
0.20	4.37	3.36
0.40	4.38	3.37
0.60	4.37	3.37
0.80	4.37	3.37

Table-2

Influence of organic solvents composition on the rate constant for alkali hydrolysis of ethyl nicotinate at 303 K.

Organic solvent composition (%) in V/v	Rate constant (k) x 10 ³ dm ³ mol ⁻¹ s ⁻¹	
	DMSO	DMF
40.0	3.01	2.93
50.0	2.09	2.34
60.0	1.31	1.89
80.0	0.62	1.33

Table-3

Influence of water composition on the kinetics of hydrolysis of ethyl nicotinate at 303K.

Aqueous to organic ratio (V/v)	Rate constant (k) x 10 ³	
	DMSO	DMF
2.33	0.83	1.66
1.50	1.31	1.89
1.00	2.09	2.34
0.43	4.37	3.37

Table-4

Influence of dielectric constant value on the rate constants for the alkali hydrolysis of ethyl nicotinate at 303 K organic solvent composition: 30% V/v

Dielectric constants	Rate constant (k) 10 ³ dm ³ mol ⁻¹ s ⁻¹	Dielectric constant		Rate constant(k) x10 ³ Dm ³ mol ⁻¹ s ⁻¹
		DMSO	DMF	
78.98	4.37	70.54	3.37	
76.40	2.09	64.96	2.34	
70.98	0.84	56.80	1.66	
65.25	0.62	51.86	1.33	

Table-5

Variation of rate constants with temperatures of alkali catalysed hydrolysis of ethyl nicotinate in DMSO and DMF solutions. Organic solvent composition: 30% V/v

Temperature (K)	Rate constant (k)x 10 ³ dm ³ mol ⁻¹ s ⁻¹	
	DMSO	DMF
293	0.86	0.99
298	2.01	1.94
308	8.37	6.79
313	18.71	11.38

REFERECES

1. J. N. Bronsted 2. Phys., Chem. 102 169(1922)
2. P.J.W. Debye & E.Hucker, Phys., 24, 185 (1923)
3. G.Scatchard, chem. Rev. 10, 229(1932)
4. D. Hughes and C.K. Ingold J. Chem. Soc. 244(1935)
5. N. Goldenberg and E.S. Amis Physik. Chem. 31, 145 (1962)
6. L.P. Hammett J. Am. Chem. Soc. 59, 96 (1937)
7. N. Bjerrum Physik. Chem. 102, 169 (1922)
8. J.B. Hyne, J.Am. chem. Soc. 82, 5129(1960)
9. J. G. Kirkwood J. Chem. Phys. Soc. 75,5735 (1953)
10. N. Bjerrum, Physik. Chem. 108, 82 (1924)
11. L.R.Fedor and T. B. Bruice, J.Am. chem. Soc. 89,4138(1965)

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