Int. J. Chem. Sci. : 2 (1), 2004, 52–56

A KINETIC STUDY OF THE EFFECT OF AQUO–ETHANE–1, 2–DIOL ON ALKALINE HYDROLYSIS OF ETHYL PYRIDINE–2–CARBOXYLATE.

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ABSTRACT

Alkaline hydrolysis of several esters has been studied in aquo–organic solvent systems. In the present work, ethyl pyridine –2– carboxylate was hydrolysed utilizing S_N2 mechanism in water–ethane–1,2–diol binaries at different temperatures. The experimental findings were in good agreement with the theoretical predictions. The rate of reaction was determined at different temperatures and solvent compositions alongwith the corresponding dielectric values. The various kinetic parameters were calculated and suitable explanations have been given. The size of the transition state as well as potential energy decrease were calculated on the basic of recently developed equation.

Key word : Kinetics, Alucline hydrolysis, Ethyl pyridine-2-carboxylate.

INTRODUCTION

The work is an extension of our study on alkaline hydrolysis of ethyl pyridine–2–carboxylate in DMSO–water media. Ethane–1,2–diol is miscible with water in all proportions. Since the dielectric constant of ethane–1,2–diol is less than that of water (82), hence, the dielectric constant values at varying compositions of water solvent mixtures will be different[1] and lower than water. The effect of aquo–organic solvent on the kinetic behaviour of heterocyclic ester hydrolysis has not been studied thoroughly and explanations put forward from time to time for the effect is far from satisfactory. Since the ester hydrolysis is ion–dipole type of reaction and assuming the predominance of electrostatic effect, a fall in the rate with decreasing dielectric constant of the medium is predicted. However, little attention has been given by workers in elucidating the effect of aquo–ethane–1,2–diol on the rate as well as the various activation parameters in alkaline hydrolysis of ethyl pyridine–2–carboxylate at different temperatures. As such, attention is being paid to study the effect of solvent on reaction kinetics and also to evaluate size of the transition state. The potential energy decrease in the activation process was also calculated to predict the nature of the reaction intermediate.

EXPERIMENTAL

The reaction was followed by the conductometic method[2,3]. The composition of ethane–1, 2–diol–water system in the study ranges from 10 to 40% (v/v).

The specific rate constant was calculated using equation for a second order reaction. The activation parameters were calculated by usual method.

RESULTS AND DISCUSSION

The specific rate constant values appreciably decrease with the increasing proportion of ethane–1,2–diol in the reaction mixture (Table 1) in accordance with the view of many workers[4–7]. The decrease in rate constant is sharp up to 50% (v/v) and beyond this, it is slow down up to 90% (v/v).

Table 1. Specific rate constant, k (lit.mol^{-1}. min^{-1}) and dielectric constant, D values for alkaline hydrolysis of ethyl pyridine–2–carboxylate in ethane–1,2–diol–water medium.

Temp. (°C)	Specification	% of Ethane–1, 2–diol (v/v)			
		10	20	30	40
25	D	75.3	72.2	69.1	65.8
30	k	26.3	19.5	15.8	13.2
	D	73.5	70.4	67.2	64.0
35	k	38.0	27.5	21.9	18.2
	D	71.8	68.7	65.5	62.3
40	k	52.5	36.3	29.5	24.0
	D	70.1	67.1	63.9	60.7
	k	72.4	47.9	38.9	30.9

With the increase in the proportion of ethane–1, 2–diol in the medium, the dielectric constant values decrease, which has more pronounced effect than the solvation factor. Thus there is greater desolvation of the inital state than the transition state, which is also supported by the fall in the activation energy (Table 3).

Table 2. Iso–composition activation energy, E_C

% of Ethane–1, 2– diol (v/v)	10	20	30	40
E_c in kJ. Mol^{-1}	52.8	47.7	46.5	44.9

Effect of temperature: The specific rate constant values were found to increase with increasing temperature (Table 1) which is in accordance with the Arrhenius Law, showing a straight line plot for log k against $10^3/T$ in ethane–1, 2–diol–water medium.

Effect of water concentration: The effect of $[H_2O]$ on specific rate in ethane–1, 2–diol–water medium was studied by plotting log k vs log $[H_2O]$. The plot was found to be a straight line with a slope close to 1.5, which is indicative of the fact that the reaction going on is bimolecular[8].

The iso–composition activation, E_c values (Table 2) decrease appreciably in ethane–1, 2–diol. Sinha[9] has also reported similar decrease in the case of alkaline hydrolysis of methyl nicotinate in ethane ethane–1, 2–diol–water media.

The iso–dielectric activation energy, E_D are also calculated by usual method (Table 3) and it was found to increase with increasing dielectric constant. It indicates that here solvation effects play more dominant role than dielectric effect.

Table 3. Iso–dielectric activation energy, E_D

Dielectric Constant	64	65	66	67	68	69	70
E_D in kJ. Mol^{-1}	61.27	61.86	61.90	63.76	63.95	67.40	71.80

Thermodynamic activation parameters

The entropy of activation, ΔS^* and enthalpy of activation, ΔH^* has been reported in Table 4 for the hydrolysis of ethyl pyridine–2–carboxylate in ethane–1, 2–diol system.

The entropy and enthalpy change values show considerable variations. The plot of ΔH^* against ΔS^* in aquo–organic media is straight line, which is in accordance with Barclay –Butler rule[9]. The decrease in ΔS^* values suggests the formation of non–mobile transition state indicating the solvation of transition state or desolvation of initial state. The free energy change, ΔG^* values have also been determined (Table 4) and found almost constant. This is in agreement with our view that with the gradual addition of the solvents, transition state gets more solvated than initial state. Cleve[11] observed a similar trend in free energy change values.

Table 4. Values of ΔH^*, ΔS^* and ΔG^*

% of Ethane –1, 2–diol (v/v)	10	20	30	40
ΔH^* (k.J. mol^{-1})	49.40	43.75	42.89	40.78
$-\Delta S^*$ (J. mol^{-1})	91.84	112.14	113.10	115.59
ΔG^* (kJ. mol^{-1})	77.22	77.69	77.13	75.93

Size of transition state, b* and molar polarization energy change $N\Sigma Ge^2/b^3$

A modified equation of Jha *et al.*[12] was used to calculate b* and $N\Sigma Ge^2/b^3$, which accounted for the dielectric constant value near the solute molecules. The corresponding values are given in Table 5. The b* value compared well with that Singh and Kumar.[13] and Kumar *et al.*[14]. The negative value, $N\Sigma Ge^2/b^3$ indicate that transition state is more polarized than initial state in aquo–ethane–1,2–diol.

Potential energy decrease: Since the size of the transition state is larger than the initial state, the potential energy in an ion–dipolar molecule reaction is expected to decrease. The quantitative value of this decrease was calculated using the equation Jha *et al.*[12]

The data (Table 5) suggest that potential energy surface at the "col" has a definite cavity at all temperatures. It also suggests that the depth of the cavity depends upon the solvent composition as well. The occurrence of such activity in potential energy surface may be taken as an indication of the existence of unstable reaction intermediate. The possibility of such unstable reaction intermediate in course of ester hydrolysis in alkaline medium has been found by other workers too[15,16]

Table 5. Molar polarization energy change, size of the transition state and potential energy decrease (at D = 67).

Temp. (K)	E_D (kJ.mol^{-1})	$N\Sigma Ge^2/b^3$ (kJ. mol^{-1})	b* (Å)	$N\left[\frac{Z^2e^2}{b_A} - \frac{Z^2e^2}{b^*}\right]$ (kJ)
293	63.76	–128.16	6.96	177.23
303	63.76	–127.98	6.95	177.16
308	63.76	–126.86	6.94	176.73
313	63.76	–126.11	6.93	176.45

Salt effects: The influence of the charged species derived from the salts on the rate of the reaction has very small effect. This indicates that the reaction is ion–molecule or molecule–molecule type and not ion–ion type.

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Accepted : 4.8.2003