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A kinetics study of dipolar protic solvent in alkaline hydrolysis of ethyl Nicotinate in water-ethanol media- A Solvent effect

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Abstract

A kinetic study of dipolar protic solvent on ethyl nicotinate was highlighted by carrying out the varying composition from 30% to 70% (v/v) at five different temperature ranging from 20°C to 40°C. The specific rate constant values of the reaction found to decrease with gradual addition of ethyl alcohol in water- ethanol media. The value of iso composition activation energy (E_c) and iso-dielectric energy (E_p) values of the reaction were found increase with increase proportion of ethyl alcohol in water- ethanol media. The number of water molecule associated with the activated complex is found to be decrease (1.230 to 1.178) in water -ethanol media. The thermodynamic activation parameter such as ΔH^* , ΔS^* , and ΔG^* values of the reaction have been calculated.

Key word : Solvent effect, protic and a-protic solvent, ethyl nicotinate , water-ethanol media, Activation Parameter, solvent-solute interaction, , Solvation number.

2. Introduction

In study of our earlier reported work (1), (2) & (3) the effect of dipolar a -protic solvent like dioxan, Acetone, DMSO, DMF, etc have widely used on the alkali and acidic catalysed hydrolysis of aliphatic ester but towards the study of effect of dipolar protic solvents like [methanol ethanol etc] having special nature on the aromatic ester even a little attention has not been drawn yet. Kinetic study on the solvent effect of dipolar protic solvent were also thought useful in order to highlight , dipolar protic solvent effect of ethyl

alcohol on Nicotinate in water-ethanol media. Cigarette smoking produces inflammatory response on skin by irritants and rube facients. But there is thousand of component of cigarette smoke that may pharmacologically important. Nicotinate play an important role in the observed effect on inflammatory process. Thermodynamic Activation parameter and solvent- solute interaction has been noticed.

3. Experimental

The entire chemical was used either of BDH or Merck grade. The water used doubled distilled. The

kinetic of alkali catalysed hydrolysis of Ethyl Nicotinate was carried out volumetric in the water- ethanol media, prepared by adding different volumes of organic co-solvent ethanol from 30-70% (v/v) temperature. ranging from 20 to 40°C. The specific rate constant value was calculated was found decreased with increasing of organic co-solvent. The calculated value of specific rate constants have been recorded in table 1. The variation of $\log k$ against mole% of ethanol in reaction media are inserted in Table-2. The evaluated values of iso-composition and iso-dielectric activation energies (E_C and E_D) of the reaction in water-ethanol media have been reported in table -4&,7 respectively. To study the mechanism of the reaction, the number of water molecules associated with the transition state of the reaction in the reaction media at different temperature have been evaluated in by using Robertsen equation and slopes of $\log[H_2O]$ verses $\log k$ is tabulated table-6. The thermodynamic activation parameter such as ΔH , enthalpy ΔS Entropy and free energy of activation ΔG . These parameter have been calculated with the help of wynne jones Eyring equation (4)

4. Result and Discussion:

A. Solvent Effect on Specific Rate:

From observation of table-1, the specific rate constant value of reaction show decreasing trend with gradual addition organic solvent-ethanol in reaction mixture. From the plot of $\log k$ with mole% (Table-2) of organic co-solvent, it was observed that plots follows decreasing trend at all temperature in linear ways (fig-1), indicate that with increase of temperature the reaction become slower. However, the rate depleting factor are either due to decrease in bulk dielectric constant value of medium or decreasing in polarity of reaction media on adding less polar ethanol to it which is in light of Laidler and Landskroener⁵ finding and recently by Singh A K⁶

B. Effect of solvent on iso-composition activation energy E_C or E_{exp} :

Using Arrhenius equation, the (E_C) for alkaline hydrolysis of Ethyl Nicotinate in (water-ethanol) media was evaluated from the values of the

slopes of the linear plot of $\log K$ against $1/T$ and are enlisted in (Table-4). From the value of slopes of the straight line, the iso- composition activation energy E_{exp} was calculated.

After making observation of the values of E_{exp} , Table-4 & fig-2, it is clear that there is enhancement in the E_{exp} values with increase in the concentration of the organic co-solvent in the reaction media. The E_{exp} values increase from 36.41 kJ/mole to 43.93 kJ/mole with increase in the concentration of EtOH in the reaction media. It has been established that changes in the values of activation energy are obviously noticeable only when the solvation changes take place either at the initial state level or at the transition state level or at both the levels. The increase in the activation energy of the reaction with decrease in the specific rate constant values seems to be quite natural. The following three possibilities may be held responsible for increase in the values of E_{exp} .

- (i) the initial state is more solvated than the transition state,
- (ii) the transition state is more desolvated than the initial state,
- (iii) the transition state is desolvated and the initial state is solvated.

Out of these three factors, the third one seems to be applicable in our case as these factors is supported by the increase in the values of entropies of activation. This conclusion has also been supported by Singh *et al.*⁷

B. Effect of concentration of Water [H_2O] on the rate and mechanism:

The mechanistic pathways of reaction was determined by evaluating the solvation number (n) of water molecules involved in formation of activated complex. It was done by plotting $\log [H_2O]$ by using the relation proposed by Robertson⁸ which is as follows:

$$\log K = \log k_o + n \log [H_2O]$$

Where 'n' is the solvent number (number of water molecule associated with activated complex) which is evaluated from the slopes of $\log k$ verses $\log [H_2O]$

Table-6, tells about the criteria for studying about the mechanism of reaction and is tabulated in Table-6 and their plots in Fig.-3. From the Table-6 it is clear that the number of water molecule involved in the formation of activated complex decreases from 1.230 to 1.178 as the temperature rises from 20°C to 40°C. The decreasing number of water molecules involved in the formation of activated complex, it is inferred that ethanol in the reaction media acts as structure reformer and in so, it shift the equilibrium of water from bulky form to its dense form and in light of Robertson⁹. So it is concluded that mechanistic pathway of reaction in presence of ethanol is change from unimolecular to bimolecular. Our such finding is recently supported by Singh AK¹⁰.

C. Effect of Solvent on Iso-dielectric Activation energy (E_D):

From the slope of Arrhenius plot of $\log k_D$ values against $1/T$, the value of iso-dielectric activation energy have evaluated and recorded in Tab- 7. From this, it is inferred that E_D value goes on increasing from 46.12 to 49.97 KJ/mole with increasing D. This trend of variation is similar as E_c values (Tab-4) with gradual addition of more solvent in reaction media. This interpretation was not supported by past view of Wolford (11) but recently supported by Singh AK.

Table- 1. Specific rate constant value of alkali catalysed hydrolysis of ethyl nicotinate in water- ethanol media ($k \times 10^3 \text{ (dm)}^3 \text{ mole}^{-1} \text{ min}^{-1}$)

Temp in °C	% of Et-OH (v/v)				
	30%	40%	50%	60%	70%
20°C	37.23	28.906	23.44	18.19	13.96
25°C	48.19	38.106	30.974	23.49	18.62
30°C	60.81	47.97	38.90	30.19	23.49
35°C	77.80	63.09	52.48	38.90	30.26
40°C	97.94	79.43	69.18	50.23	38.90

Table - 2. Variation of $\log k$ values with mole % of water-ethanol media at different temperature

% of EtOH (v/v)	Mole % of EtOH	3 + $\log k$ value				
		2°C	25°C	30°C	35°C	40°C
30%	11.69	1.571	1.683	1.784	1.891	1.991
40%	17.04	1.461	1.581	1.681	1.800	1.900
50%	23.59	1.370	1.491	1.590	1.720	1.800
60%	31.96	1.260	1.371	1.480	1.590	1.701
70%	46.87	1.145	1.270	1.371	1.481	1.590

Table : 3 variation of $\log k$ verses $10^3/T$ in (water -ethanol) media

Temp in °C	$10^3/T$	3+LogK				
		30%	40%	50%	60%	70%
20 °C	3.413	1.571	1.461	1.370	1.260	1.145
25 °C	3.356	1.683	1.581	1.491	1.371	1.270
30 °C	3.300	1.784	1.681	1.590	1.480	1.371
35 °C	3.247	1.891	1.800	1.720	1.590	1.481
40 °C	3.195	1.991	1.900	1.840	1.701	1.590

Table 4: Values of Iso-composition activation Energy of Alkaline Hydrolysis of ethyl Nicotinate in water-ethanol media

% of ethyl Alcohol (v/v)	30%	40%	50%	60%	70%
E_{exp} in kj/mole	36.41	37.39	38.43	39.53	43.93

Table- 5: Variation of 3+ Log k with log [H₂O] (water -ethanol) at different temperature

% of EtOH	%o of H ₂ O	log [H ₂ O]	3+ log k value				
			2°C	25°C	30°C	35°C	40°C
30%	70%	1.5690	1.571	1.683	1.784	1.891	1.991
40%	60%	1.5229	1.461	1.581	1.681	1.800	1.900
50%	50%	1.4437	1.370	1.491	1.590	1.720	1.840
60%	40%	1.3468	1.260	1.371	1.480	1.590	1.701
70%	30%	1.2218	1.145	1.270	1.371	1.481	1.590

Table : 6 The value of slope of plot of log k versus log[H₂O] of reaction in water-ethanol media.

Temp. In C	Value of slopes
20°C	1.230
25°C	1.215
30°C	1.197
35 °C	1.187
40 °C	1.178

Table 7: Values of Iso-dielectric Activation Energy at different Dielectric Constants (D) Values in water- ethanol media

Dielectric	D=40	D=45	D=50	D=55	D=60
E_D in kj/mole	46.12	48.16	48.55	49.59	49.97

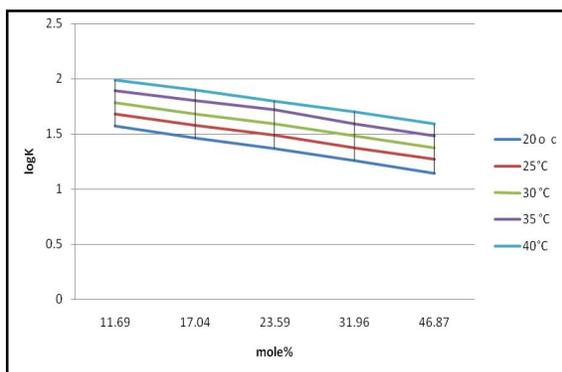


Figure :-1 variation of 3+logk with mole %

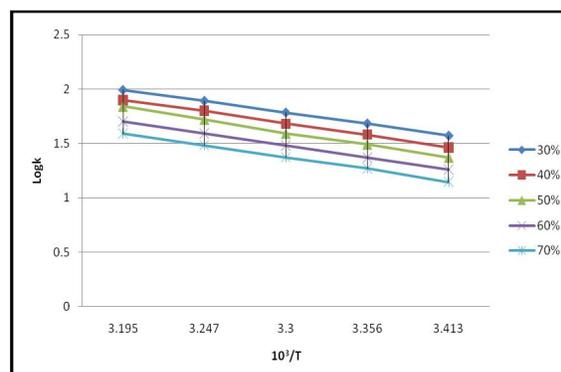


Fig.2: Variation of 3 + logk value with $10^3/T$ water-ethanol media.

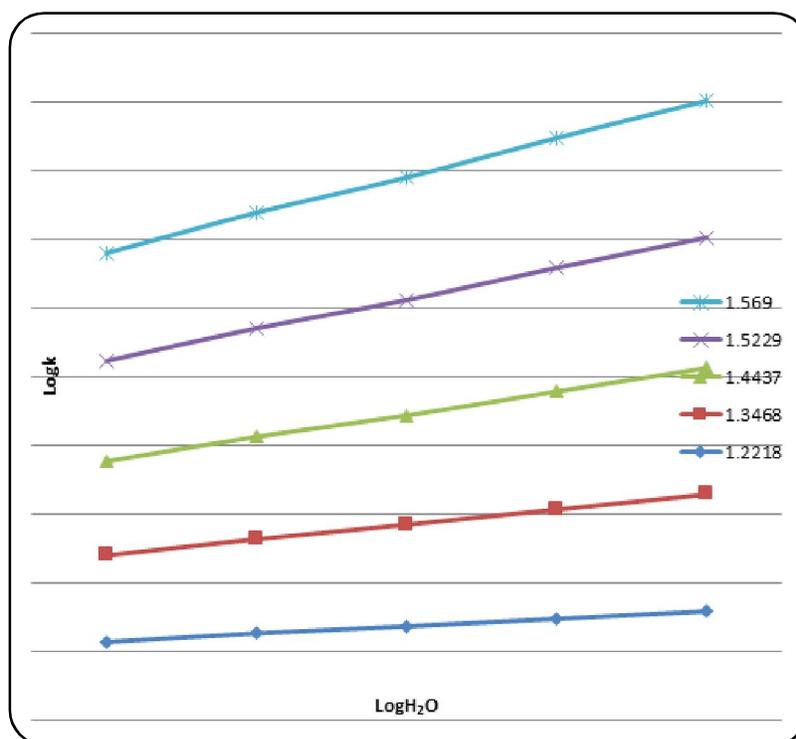


Fig. 3 Variation of $3 + \log k$ values with $\text{Log} [\text{H}_2\text{O}]$ (water-ethanol) media

5. Conclusion

In this research work the results indicate that the rate of hydrolysis of Ethyl nicotinate, decreasing trend at all temp with increasing mole% of co-solvent which appear that transition state is more desolvated than initial state. The enhancement in the values of Iso composition activation energy ($E_{\text{exp.}}$) indicate that initial state is solvated and the transition state is desolvated. The decreasing trend of number of water molecule with increase of temperature is indication that EtOH change the mechanism of the reaction from uni molecular to bimolecular. Increasing trend of E_D values with increase of D is against the view of Wolford R K. J. Phys. Chem., 1964, 68.

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