A Kinetic Studies of Alkaline Hydrolysis of Ethyl Nicotinate

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Abstract

The rate of alkaline hydrolysis of ethyl nicotinate was measured over the temperature range of 20^oC to $40\ ^oC$ in water-ethanol mixture at different composition 30 to 70% (v/v). The influence of solvent variation on reaction rate was examined in term of changes in the Activation parameter .increase of $\Box\ H^{\ast}$ and $\Box\ S^{\ast}$ values with simultaneous increase in $\Box\ G^{\ast}$ of the reaction in media, reveals that the reaction is Enthalpy controlled and

Entropy domination.

The Values of Iso-kinetic which is equal to 360, clearly indicates that there is appreciable interaction between solvent and solute present in the reaction media, i.e. reaction is ion-dipole.

Key word: Activation Parameter, solvent-solute interaction, Iso-kinetic temperature, specific solvation.

Ethyl nicotinate.

Introduction

Though the solvent effect on the rate and mechanism of the various type of reaction has been reported[1,2,3], but very little attention has been paid towards the study of the solvent effect on the thermodynamic activation parameter and solvent- solute interaction, particularly solvolysis of Ethyl nicotinate which is important for medicinal use. It has been proposed to make a kinetic study of the solvent effect on the base catalyzed hydrolysis Ethyl nicotinate in water-ethanol media of various compositions.

Experimental

The kinetics of base catalyzed hydrolysis of ethyl nicotinate has been carried out in water-ethanol having different concentration of solvent (Ethanol) varying from 30 to 70% (v/v) at five different temperatures ranging from 20^oC to $40\ ^o\ C$ at regular interval of $5^o\ C$. The specific rate constant calculated using second order reaction was found decrease with increase of ethanol content, tabulated in Table-1. The evaluated thermodynamic activation parameter has been tabulated in Table-2.

Result and Discussion

1. Solvent Effect on Thermodynamic Activation Parameters on the Reaction:

The thermodynamics Activation parameter such as Enthalpy of Activation ($\square H^*$), Entropy of Activation ($\square S^*$) and free energy of Activation ($\square G^*$), are better indicator of the solvent effect exerted by the solvent on the solvolysis reaction. These thermodynamics Activation parameter has been calculated with help of Wayne-Jones Eyring[4] equation and absolute rate theory.[5]

On careful observation of the data Tabulated in table 2. water-Ethanol media, the interesting feature come in light is that out of the values of all the three thermodynamic activation parameters namely free energy of activation ($\square G^*$) enthalpy of activation ($\square H^*$), and entropy of activation ($\square S^*$) increases with increasing mole% of ethanol content.

For highlighting the solvent effect on these activation parameters i.e. ($\square G^*$) ($\square H^*$) ($\square S^*$), all these parameters are plotted against mole% of ethanol as shown in Fig-1,2 and fig-3 respectively. The non linear variation of in ($\square H^*$) and ($\square S^*$) fig-1 and fig-3, give information of the fact that specific solvation take place in water-ethanol media as reported by Savilla et al.[6]. From the fundamental thermodynamic equation.

$$\square G^* = \square H^* - T\square S^*$$

It may be inferred that the enhancement in the value of $\square G^*$ with simultaneous increase in $\square H^*$ and $\square S^*$ value is only possible when the quantitative increase in the value of $\square H^*$ is greater than $\square S^*$ and from this fact, it is concluded that base catalyzed hydrolysis of Ethyl Nicotinate in water-ethanol media is Enthalpy dominating and Entropy controlled. The enhancement found in the values of enthalpy of activation (ΔH*) and entropy of activation ΔS*) also supported the fact that transition state of reaction is more solvated than initial state as similar was as recently reported by Singh R T et al.[7]

2. Evaluation of Iso-kinetic Temperature and Solvent- Solute Interaction:

In the light of Barclay[8] and Butler relationship between Enthalpy and Entropy of Activation, which is as follows

$$\delta m\ (\square H^*) = \beta\delta m(\square S^*)$$

It is straight line equation representing the relationship between Enthalpy and Entropy of Activation. β is the Iso-kinetic temperature.

From the data available in the table-2, the plot of $\square H^*$ and $\square S^*$ in the solvent system in Fig. 4 and from the slope of straight line, the value of Iso-kinetic temperature was calculated to be 360 (water-ethanol)) which is equal to 360.

From the value of Iso-kinetic temperature which is equal to 360, it is concluded that there is more change in the structure of the reactant or in the solvent or in both due to strong interaction between solvent and solute present in the reaction media in similar way as reported by Leffler[9] Our this conclusion has been recently supported by[10] singh R.T. et al.

Conclusion

In this research work the results indicate that the rate of hydrolysis of Ethyl Nicotinate is enthalpy dominating.

It may be inferred that the simultaneous increase in the value of, $\Box H^*$ and $\Box S$ with enhancement of $\Box G^*$ value is only possible when the quantitative increase in the value of $\Box H^*$ is greater than that found in the values of $\Box S^*$ and from this fact ,it is concluded that acid hydrolysis of ethyl Nicotinate in water ethanol media is enthalpy dominating. The Values of Iso-kinetic which is equal to 360, clearly indicates that there is appreciable interaction between solvent and solute present in the reaction media, *i.e.* reaction is ion-dipole.

Table 1. Specific rate constant [k x10^3(dm)^3/mole/mint]values of alkali catalyzed Hydrolysis of Ethyl-Nicotinate in water-ethanol media.

Temp in ^{o}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. Thermodynamics Activation Parameters of the Reaction in Water- ethanol Media

($\Box H^*$ and $\Box G^*$ in KJ/Mole, $\Box S^*$ in J/K/Mole)

| % OF EtOH (V/V)	Mole %	☐ H* in k j /mole	20 ^{0}C		25 ^{0}C		30 ^{0} C		35 ^{0} C		40 ^{0}C	
			☐ G*	-☐ S*	☐ G*	-☐ S*	☐ G*	- ☐ S*	☐ G*	- ☐ S*	☐ G*	- ☐ S*
30 %	11.69	35.36	89.98	186.41	90.91	186.40	91.92	186.66	92.81	186.52	93.77	186.61
40 %	17.04	39.66	90.60	173.85	91.51	173.99	92.52	174.45	93.35	174.31	94.32	174.63
50 %	23.59	40.89	91.11	171.39	92.03	171.61	93.05	172.14	93.82	171.85	94.68	171.85
60 %	31.96	43.92	91.73	163.17	92.72	163.75	93.69	164.25	94.59	164.51	95.52	164.85
70 %	46.87	47.97	92.38	151.57	93.29	152.08	94.15	152.40	95.23	153.44	96.19	154.05
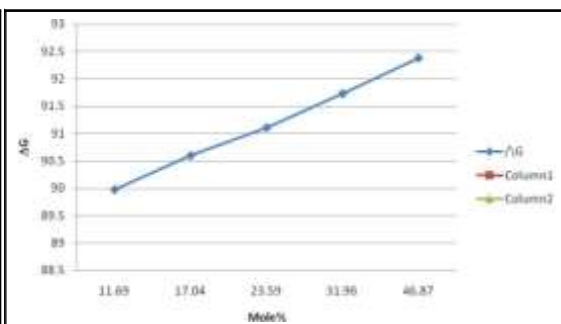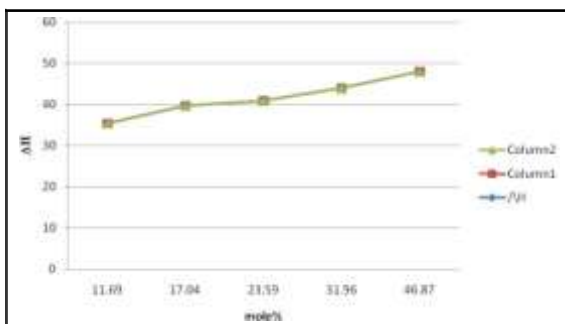
Figure 1 Variation of ΔH value with mole% at 20^{0} C   Figure 2. Variation of mole% with ΔG* at 20^{0}C in   water-ethanol media.
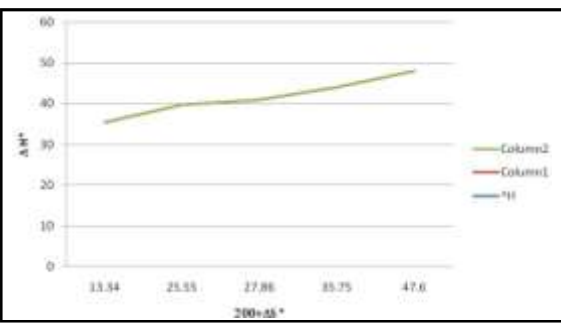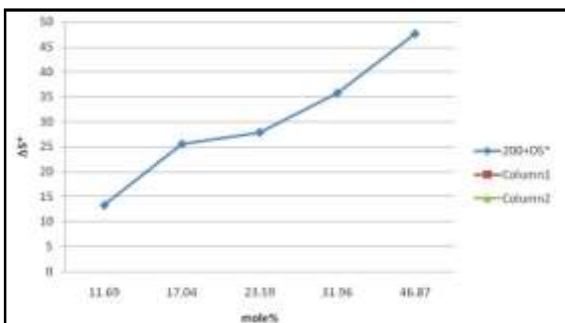

Figure 3 Variation of ☐ S* +200 with mole % at 200C   Figure 4 Variation of verses200+ΔS*

at 20^{0}C

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