

Solvent Effect on Solvolysis Rate in Water-Methanol and Water-Ethanol Mixed Solvent System

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Abstract

Different solvents can affect the equilibrium constant of a reaction by differential stabilization of the reactant or product. The equilibrium is shifted in the direction of the substance that is preferentially stabilized. Stabilization of the reactant or product can occur through any of the different non-covalent interactions with the solvent such as H-bonding, dipole-dipole interactions, van derwaals interactions etc. Although the Solvent Effect on the Rate and Mechanism of the various type of reaction has been reported but very little attention has paid towards the study of the Solvent Effect on the Thermodynamic Activation Parameter and the solvent-solute interaction, particularly for an ion-dipolar reaction. In order to highlight the above noted idea, it has been proposed to make the kinetic study of the solvent effect on the alkali catalysed hydrolysis of Ethyl Acetate has not been paid even a little attention so far.

Keywords:Equilibrium Constant;Little Attention;Preferentially Stabilized

Introduction

Though the solvent effect on the rate and mechanism of the various type of reaction has been reported, 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 acetate 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 acetate in water-ethanol media of various compositions. The effect of solvent on the rate and mechanism of alkali catalyzed hydrolysis of ester have received continued attention, but the explanation put forward is not satisfactory. So, in order to explore the above idea, it was thought essential and useful to investigate about the fact that how ethyl cinnamate is useful as flavor and fragrance agent in cigarettes and cut tobacco. This compound is also used as food additive for human beings.

Experimental

The base catalyzed hydrolysis of ethyl benzoate was estimated volumetrically in water-methanol solvent system at different degree of composition from 30 to 70% (v/v), ranging from 20°C to 40°C at regular interval of 5°C. Pure ethyl benzoate (Merck) was used for kinetics. Distilled water is used throughout and the experiment is carried out by keeping strength of solution 0.1M with respect to NaOH and 0.05M with respect to ester. The detail of procedure was mentioned in my previous communication. Using second order kinetics, specific rate constant was calculated and inserted in Table-1.

Enthalpy of Activation, Entropy of Activation and Free energy Activation is calculated with Wynne-Jones and Eyring equation and tabulated in Table-2

Result and Discussion

(A) Effect of solvent composition on rate:

The kinetic result of hydrolysis of ethyl benzoate in water-methanol solvent system follows second order kinetic and calculated values are inserted in Table-1. The specific rate constant values decrease with increasing temperature may be attributed partly due to dielectric effect of reaction media and partly due to solvation taking place in media which is in good agreement with Hughes and Ingold.

Table – I Rate constant as function of solvent medium composition

Temp in °C	% of Methanol				
	30%	40%	50%	60%	70%
20°C	37.15	30.54	25.70	21.87	18.62
25°C	74.13	57.54	48.97	41.68	35.48
30°C	147.91	112.20	88.10	74.13	64.56
35°C	278.61	211.34	165.95	136.45	112.20
40°C	543.25	316.22	301.99	245.47	199.52

$k \times 10^2$ (dm³/mole/min)] values of hydrolysis of Ethyl benzoate in water-methanol media

(B) Observed values of Iso-composition Activation Energy (E_c) of the reaction in water-methanol media. The iso composition activation energy is calculated with Arrhenius plot which decreases with increasing solvent composition, inferred solvation in transition state and desolvation in initial.

(C) Calculated values of Iso- Dielectric Activation Energy. The value of Iso-dielectric Activation energy (E_D) is calculated by plotting Arrhenius plot of $\log k_D$ values against $1/T$. Iso-dielectric

Activation energy (E_D) values goes on increasing from 109.95 to 120.12 kJ/mole with increasing dielectric value in reaction media. This is also supported by past view of Wolford recently supported by Singh R T. et al.

(D) Rate and thermodynamic activation Parameters of reaction:

The thermodynamic activation parameter plays an important role in determining properties of activated complex and solvating power of medium. The activation parameter (ΔG^*), ΔH^* and ΔS^* is calculated with help of Wynne-jones and Eyring equation and inserted in Table-2. The nonlinear increase in (ΔG^*) and decrease in (ΔH^*) and (ΔS^*) with mole % fig-1,2 and 3 represent the specific solvation taking place in process of solvation already proposed by Saville and Hudson [15]. The nonlinearity in (ΔG^*) with mole % curve in water-methanol media also indicate that random distribution of component is not acceptable. The noted data in Table-2 it is observed that Free energy of activation (ΔG^*) increases with simultaneous decrease in enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) with mole%.

According to thermodynamic relation of free energy and entropy $\Delta G^* = \Delta H^* - \Delta S^*$

On the basis of above thermodynamic relation it is clear that increase in ΔG with simultaneous decrease in ΔH and ΔS possible only when extent of depletion in ΔS is greater than ΔH . The regular decrease in these activation parameter that is entropy of activation and enthalpy of activation also indicate that the reaction is enthalpy dominating and entropy control.

Table-II Activation Parameters as a function of composition for reaction in Water- Methanol Media ΔH^* and ΔG^* in KJ/Mole, ΔS^* in J/K/Mole.

% of MEOH	Mole %	ΔH^* in KJ/Mole	20 ⁰ C		25 ⁰ C		30 ⁰ C		35 ⁰ C		40 ⁰ C	
			ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*
30%	16.03	90.68	84.42	21.36	84.15	21.91	83.85	22.54	83.58	23.05	82.04	23.36
40%	22.90	89.65	84.83	16.45	84.76	16.48	84.55	16.83	84.32	17.30	84.55	17.57
50%	30.82	89.64	85.25	14.98	85.16	15.03	85.08	14.78	84.94	15.25	84.27	17.15
60%	40.06	89.06	85.65	11.63	85.56	11.74	85.60	11.41	85.44	11.75	84.82	13.54
70%	50.97	88.47	86.04	8.2	85.96	8.45	85.95	8.31	85.95	8.18	85.36	9.90

Fig (1)- Variation of ΔH^* with mole % at 25⁰c (water-methanol)

Fig (2)- Variation of ΔG^* with mole % at 25⁰c (water-methanol)

Fig (3)- The enhancement in the value of and ΔG^* with Variation of ΔS with mole % at 25⁰c (water-methanol)

Fig. 4: Variation of ΔH^* with ΔS^* at 25⁰C (water-methanol) system

Evaluation of Iso-Kinetic Temperature and Solvent-Solute Interaction

In the light of Barclay and Butler relationship between Enthalpy and Entropy of Activation, this is as follows:

$$\delta_m(\Delta H^*) = \beta \delta_m(\Delta S^*)$$

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 4 the plot of ΔH^* and ΔS^* in the solvent system in Figure 5 and from the slope of straight line, the value of Iso-kinetic temperature was calculated to be 244 (water-acetone) and which is less than 300. From the value of Iso-kinetic temperature which is much less than 300, it is concluded that there is slow change in the structure of the reactant or in the solvent or in due to weak interaction between solvent and solute present in the reaction media in similar way as reported by Lefler. Our this conclusion has been recently supported.

Conclusion

This method can be used to produce FA from γ -oryzanol in soapstock from rice bran oil processing at a low temperature and in a short time using low-frequency and high-power irradiation. In hydrolysis of ethyl benzoate, the decrease in rate constant with mole percentage of co solvent either decreases in bulk dielectric constant value or it decreases in polarity of reaction media by the addition of less polar methanol to it. Decreasing trend of activation energy (E_c) with increase cosolvent inferred the salvation in transition state and desolvation in initial state. The increasing number of water molecule associated with activated complex with increasing temperature shows that the mechanism of reaction media changes from bio molecular to unimolecular with addition of the solvent (methanol).

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