Kinetics and Solvent Effect in Hydrolysis of Ethyl Cinnamate in Water-Methanol Mixture

Singh AK*

Department of Chemistry, Teerthanker Mahaveer University, Moradabad, Uttar Pradesh, India

Abstract

The solvent effect of ethanol on the alkali catalyzed solvolysis reaction was studied by carring out of the hydrolysis of ester namely ethyl cinnamate in water-methanol media of varying composition consisting of 30 to 70% of methanol (v/v) at different Temperature ranging from 20°C to 70°C. The Specific rate constant values of the reaction were found to depleted with increasing concentration of methanol in reaction media. Enhancement in ΔG^* with simultaneous depletion in ΔH^* and ΔS^* of the reaction, it has been concluded that reaction is enthalpy stimulating and entropy inhibiting and specific salvation take place in water-methanol media. From the evaluated value of Iso kinetic temperature, which is less than 300 indicates that this reaction in water-methanol media obey Barclay-Butler rule and there is weak but considerable solvent –solute interaction taking place in reaction media.

Keywords: Solvent effect; Ethyl cinnamate; Hydrolysis water-methanol mixture; Specific rate constant; Iso-composition; Iso-dielectric activation energy; Activated complex

Introduction

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 [1-3]. 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

Kinetic of alkali catalyzed solvolysis of ethyl cinnamate was studied by adding different concentrations of the protic organic co solvent(Ethanol) from 30 to 70% (v/v) in reaction media at five different temperature i.e., 20°C, 25°C, 30°C, 35°C and 40°C using volumetric method. All chemicals used were either of BDH or Merck grades. The strength of the solution was kept 0.1M with respect to NaOH and 0.05 M with respect to ester. The reaction rates were determined by titrating the sample at different time interval using phenolphthalein indicator. The specific rate constant value was calculated using second order reaction and tabulated in Table 1. Variation of specific rate constant with different mole% and different temperature are inserted in Table 2. The value of slopes of Arrhenius plot of logk verses 1/T (Table 3) (Iso-composition activation energy (E_c) and plots of logk verse D(Iso-dielectric activation energy) were evaluated and inserted in Tables 4 and 5 respectively. From the plots of Logk verses Log [H_2O] Table 6, the value of slopes were evaluated and tabulated in Table 7. Thermodynamic Activation Parameter were also calculated and inserted in Table 8.

Results and Discussion

Solvent effect on specific rate

In order to highlight the effect of the solvent on specific rate constant values (Table 1) of the reaction, the logk values were plotted against the mole% of organic co-solvent (their values from Table 2 as shown in Figure 1) and were found to show decreasing trend. The plots show, that with increase in the temperature of the reaction, the degree of depletion in the rate constant of the reaction becomes slower.

However, the possible rate depleting factors in the rate can be enlisted as follows:

1. Decrease in bulk dielectric constant value of medium,

2. Decrease in the polarity of the reaction media by adding less polar methanol to it.

The above noted two depleting factors are quite in operation and are with good agreement with theory of Hughes and Ingold [4] that rate ought to decrease with decreasing dielectric constant of the reaction media. Such decrease in rate constant with increasing proportion of organic co-solvent like methanol have also reported by Elsemongy [5], and recently by Singh [6].

Solvent effect on iso-composition activation energy of the reaction

From Table 4, (Figure 2) it is found that the values of Iso-composition Activation Energy goes on increasing [52.16 to 57.37 kj/mole] with increasing concentration of MEOH from 30% to 70% (v/v) in reaction media. The increasing trend in the E_{exp} values can be explained by any of the following three situations.

1. Transition state is desolvated less than Initial state

2. Transition state is solvated more than the initial state

3. Transition state is solvated and initial state desolveted.

The transition state being large cat ion (ester+H⁺) is available more for solvation by ethanol molecule than the initial state, so third factor seem to operative in my case and is also supported by decrease in entropy of activation (ΔS^*). This conclusion is also supported recently by Singh et al. [7].

*Corresponding author: Singh AK, Department of Chemistry, Teerthanker Mahaveer University, Moradabad, Uttar Pradesh, India, Tel: 07351318000; E-mail: anilkumar2_singh@yahoo.com

Solvent effect and iso- dielectric activation energy

From the slope of Arrhenius plot of $\log k_D$ values against $1/T$, the value of iso-dielectric activation energy has been evaluated and recorded in Table 5. From the Table 5 (Figures 3 and 4), it is inferred that E_D value goes on increasing from 55.45 to 65.09 kj/mole with increasing D values. This trend of variation is similar as E_c values (62.31 to 64.88 KJ/mole) (Table 5) with gradual addition of more solvent in reaction media. This interpretation was supported by past view of Wolford [8] recently supported by Singh et al. [9].

Effect of concentration of water molecules [H_2O], associated with the activated complex on mechanistic path of the reaction

The effect of water concentration [H_2O] of the water-ethanol mixture, on rate and mechanism of alkali catalysed hydrolysis of ethyl cinnamate has been studies. For this, the number of water molecule associated with activated complex was determined by plotting Log k against Log[H_2O], According to Robertson [10] relation

$\log k = \log k_0 + n \log[H_2O]$

Here n is the solvation number and decide the criteria about the mechanism of reaction.

From noted value of slope mention in Table 7, it may be seen that with rise of temperature from 20 to 70°C, the value of slope (number of water molecule associated with activated complex) goes on increasing from (2.08 to 2.56). This observation may be attributed to the fact that with addition of ETOH in reaction media, the equilibrium of water component reaction media shifted from its dense form to its bulky form with rise of temperature.

Temp in °C	% of Methanol				
	30%	40%	50%	60%	70%
20°C	8.31	6.60	5.43	4.46	3.75
25°C	2.56	9.74	7.85	6.59	5.37
30°C	18.15	3.96	11.09	9.12	7.58
35°C	26.24	19.90	15.48	12.88	10.47
40°C	27.15	28.18	21.57	17.78	14.45

Table 1: Specific rate constant $k \times 10^3$ (dm)^3/mole/mint values of alkali catalyzed hydrolysis of Ethyl-Cinamate in water-Methanol.

Temp in °C		3+Logk				
	Mole%	20°C	25°C	30°C	35°C	40°C
30%	16.03	0.920	1.099	1.259	1.419	1.570
40%	22.90	0.820	0.989	1.145	1.299	1.450
50%	30.82	0.735	0.895	1.045	1.190	1.330
60%	40.06	0.650	0.819	0.960	1.110	1.250
70%	50.97	0.565	0.730	0.880	1.020	1.160

Table 2: Variation of 3+Logk Value against mole %, (Water-methanol) System.

Temp in °C		3+Logk				
	10^3/T	30%	40%	50%	60%	70%
20°C	3.412	0.920	0.820	0.735	0.650	0.575
25°C	3.355	1.099	0.989	0.895	0.819	0.730
30°C	3.300	1.259	1.145	1.045	0.960	0.880
35°C	3.247	1.419	1.299	1.190	1.110	1.020
40°C	3.195	1.570	1.450	1.330	1.250	1.160

Table 3: 3+Logk Value against 10^3/T, Water- methanol System.

% of MEOH	30%	40%	50%	60%	70%
E_{exp} in KJ/mole	52.16	52.74	54.30	54.30	57.37

Table 4: Values of Iso-composition Activation Energy (water-MEOH media).
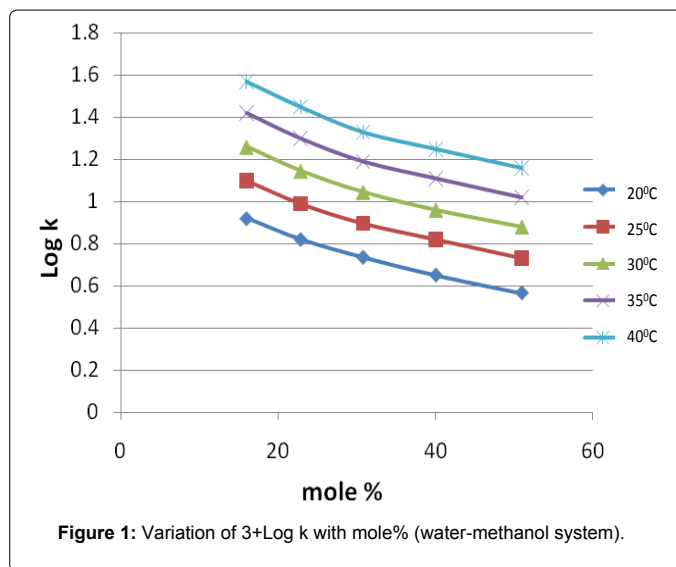

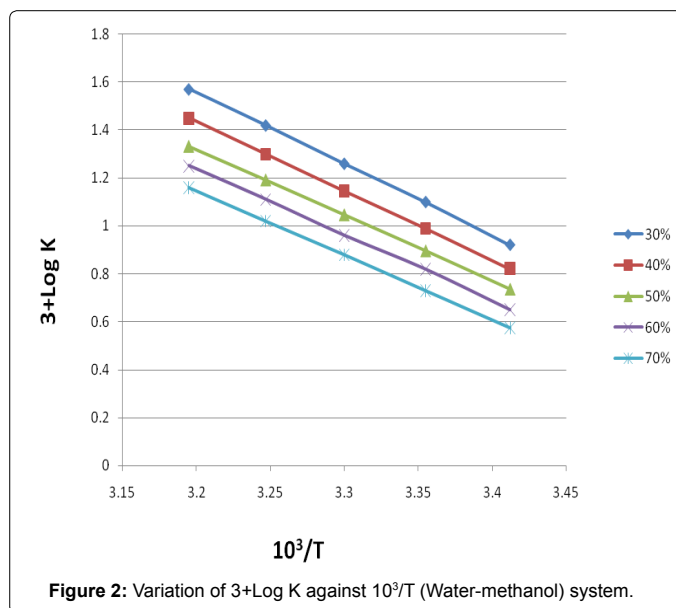**Figure 1:** Variation of 3+Log k with mole% (water-methanol system).

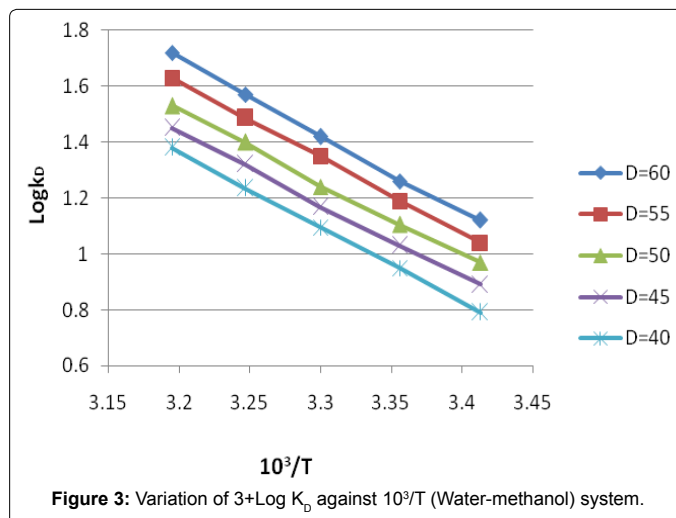**Figure 2:** Variation of 3+Log K against 10^3/T (Water-methanol) system.

Figure 3: Variation of 3+Log K_D against 10^3/T (Water-methanol) system.
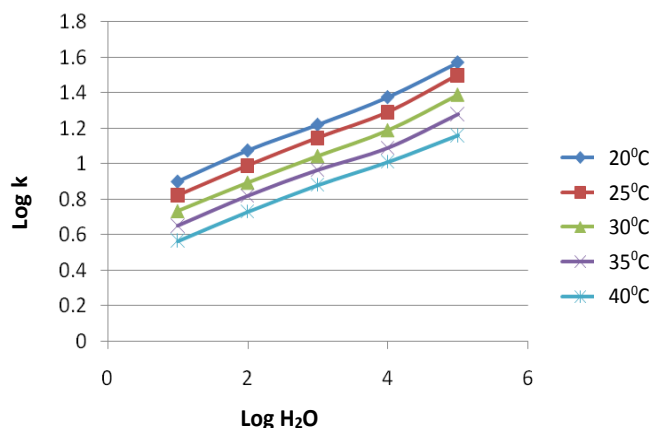
Figure 4: Variation of 3+logk against log[H_2O] water-methanol system.

Dielectric constant(D)	D=45	D=50	D=55	D=60	D=65
E_{exp} in KJ/mole	55.45	57.95	62.19	62.76	65.09

Table 5: Values of Iso-Dielectric Activation Energy (water-methanol).

% of Acetone	% of H_2O	Log [H_2O]	3+Log k				
			20°C	25°C	30°C	35°C	40°C
30%	70%	1.5690	0.890	1.075	1.210	1.70	1.570
40%	60%	1.5229	0.820	0.989	1.145	1.290	1.500
50%	50%	1.4437	0.735	0.895	1.045	1.190	1.390
60%	40%	1.3468	0.650	0.819	0.965	1.090	1.280
70%	30%	1.2218	0.565	0.730	0.880	0. 980	1.160

Table 6: Variation of 3+Log k with log [H_2O] (water – methanol) at different temperature.

Temp. °C	20°C	25°C	30°C	35°C	40°C
Slope	2.08	2.16	2.21	2.29	2.56

Table 7: Calculated values of slopes (Plot of log k verses log[H_2O]) of water-methanol media.

% of MEOH	Mole %	ΔH^* in Kj/Mole	20°C		25°C		30°C		35°C		40°C	
			ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$
30%	16.03	53.31	93.64	137.64	94.27	137.44	94.98	137.52	95.60	137.30	96.31	137.38
40%	22.90	52.95	94.20	140.78	94.91	138.42	95.65	140.89	96.31	140.77	97.03	140.83
50%	30.82	52.87	94.68	142.6	95.44	140.30	96.23	143.10	96.96	143.14	97.75	143.38
60%	40.06	51.28	95.16	149.76	95.88	147.24	96.72	149.96	97.43	149.83	98.23	150.00
70%	50.97	50.51	95.64	154.02	96.39	151.44	97.19	154.05	97.96	152.56	98.77	154.18

Table 8: Consolidated values of Thermodynamics Activation Parameters (ΔH^* and ΔG^* in KJ/Mole, ΔS^* in J/K/Mole) of the reaction in Water- methanol Media.

$$[H_2O]_d \, \Delta[H_2O]_b$$

Finally, it is inferred that with rise of temperature, the number of water molecule associated with activated complex increases as the proportion of bulky form of water molecule increase with increase in MEOH content in the water-ethanol mixture and it explain that when MEOH is added to water, the mechanistic path of reaction is changed from biomolecular to unimolecular in similar way as observed by parker and Tomilinson [11] and recently by Singh [12].

Conclusion

In hydrolysis of Ethyl cinnamate, the decreasing trend of specific rate constant at all temp with increasing mole % of co-solvent which show that the decrease is either due to bulk dielectric constant value of medium or decrease in the polarity of the reaction media by adding less polar methanol to it. The values of Iso-composition Activation Energy goes on increasing [52.16 to 57.37 kj/mole] with increasing concentration of MEOH from 30% to 70%(v/v) in reaction media indicate Transition state is solvated and initial state desolveted. Increase in the value of and ΔG^* with simultaneous increase in ΔH^* and ΔS^* for the hydrolysis ethyl cinanimate in water- Methanol is enthalpy dominating and Enthalpy control. The linear plots obtained by plotting logk as function of D represent the different electrostatic interaction for the ion-dipole as well as dipole - dipole reaction. Solvating power of MEOH change the mechanism of the reaction from bio-molecular to unimolecular due to increase in number of water molecule associated with activated complex (2.08 to 2.56).

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