

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

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**Abstract**— The solvent effect of aquo-dipolar protic solvent system was highlighted by studying the kinetics of base catalyzed solvolysis of ethyl cinnamate in water-methanol media of various compositions having 20 to 70% (v/v) of ethanol at different five temp ranging from 20 to 40°C. Fast decrease of specific rate constant with gradual addition of organic co solvent in the reaction media and also with increasing temperature of the reaction has been explained in light of solvation in initial and transition state to different extent. The change in Iso-composition Activation energy ( $E_C$ ) and Iso-dielectric Activation energy ( $E_D$ ) also explained the solvation and desolvation of initial and transition states to different extent. The decrease in number of water molecule (1.59 to 1.42) associated with the activated complex is found to be decrease in water-MEOH system and this tells about the fact that in presence of MEOH the mechanistic path of reaction is change from bio-molecular to uni-molecular. Increase in numerical value of free energy of activation ( $\Delta G^*$ ) simultaneous decrease in entropy of activation ( $\Delta S^*$ ) and enthalpy of activation ( $\Delta H^*$ ), of reaction media reveals that ethanol acts as entropy inhibitor and Enthalpy stimulator.

**Keywords** - Solvent effect, ethyl cinnamate, Hydrolysis water-methanol mixture. Specific rate constant, Iso-composition and Iso-dielectric Activation energy, Activated complex.

## I. 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.

## II. EXPERIMENTAL

Kinetic of alkali catalyzed solvolysis of ethyl cinnamate was studied by adding different concentrations of the protic organic co solvent (methanol) from 30 to 70% (v/v) in reaction media at five different temperature i. e. 20°, 25°, 30°, 35° & 40° 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-I. Variation of specific rate constant with different mole% and different temperature are inserted in Table-2.

The value of slopes of Arrhenius plot of  $\log k$  versus  $1/T$  (Table-3) (Iso-composition activation energy ( $E_C$ ) and plots of  $\log k$  versus  $D$  (Iso-dielectric activation energy) were evaluated and inserted in Table-4&5 respectively. From the plots of  $\log k$  versus  $\log [H_2O]$  Table-6, the value of slopes were evaluated and tabulated in Table-7. Thermodynamic Activation Parameter were also calculated and inserted in Table-8

## III. RESULT AND DISCUSSION

### 3.1 Solvent Effect on Specific Rate

In order to highlight the effect of the solvent on specific rate constant values (Tab-I) of the reaction, the  $\log k$  values were plotted against the mole% of organic co-solvent (their values from Table-2 as shown in fig-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 Elsemomy [5], and recently by Singh A K [6].

TABLE I. SPECIFIC RATE CONSTANT K X103(DM)3/MOLE/MINT] VALUES OF ALKALI CATALYZED HYDROLYSIS OF ETHYL-CINAMATE IN WATER-METHANOL

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	13.96	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 II. VARIATION OF 3 + LOGK VALUE AGAINST MOLE %, (WATER-METHANOL) SYSTEM

Temp in °C	Mole%	3 + Logk				
		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

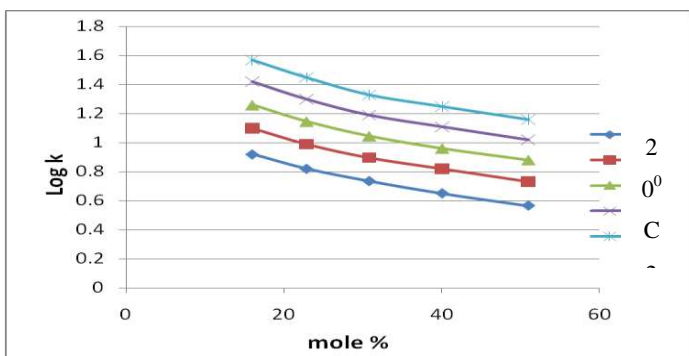


Figure 1. Variation of 3+Log k with mole% (water-methanol system)

### 3.2 Solvent effect on Iso-composition Activation Energy of the reaction

From Tab- 4, (Fig-2) it is found that the values of Iso-composition Activation Energy goes on increasing [52.16 to 57.37kj/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 desolvated.

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

TABLE III. 3 + LOGK VALUE AGAINST  $10^3/T$ , WATER-METHANOL SYSTEM

Temp in °C	$10^3/T$	3 + Logk				
		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

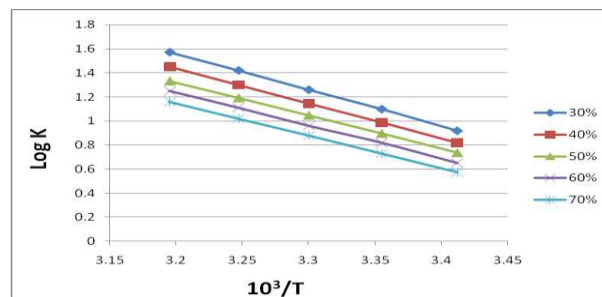


Figure 2. Variation of 3+Logk against  $10^3/T$  (Water-methanol) system

TABLE IV. VALUES OF ISO-COMPOSITION ACTIVATION ENERGY (WATER-MEOH MEDIA)

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

### 3.3 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 Tab-5. From the table-5 and Fig-3, 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) (Tab-5) with gradual addition of more solvent in reaction media. This interpretation was supported by past view of Wolford [8] recently supported by Singh R. T. et al.[9]

TABLE V. VALUES OF ISO-DIELECTRIC ACTIVATION ENERGY (WATER-METHANOL)

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

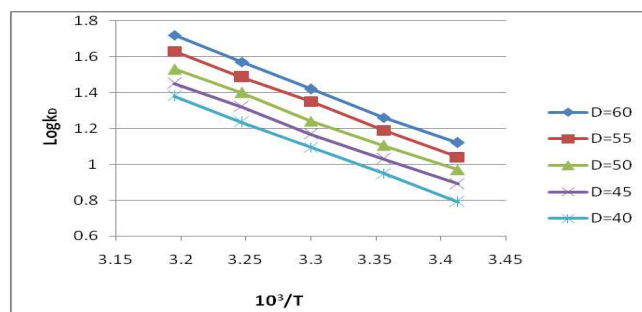


Figure 3. Variation of 3+Logko against  $10^3/T$  (Water-methanol) system

3.4. EFFECT OF CONCENTRATION OF WATER MOLECULES [H<sub>2</sub>O], ASSOCIATED WITH THE ACTIVATED COMPLEX ON MECHANISTIC PATH OF THE REACTION

The effect of water concentration [H<sub>2</sub>O] of the water-ethanol mixture, on rate and mechanism of alkali catalysed hydrolysis of ethyl cinnamate has been studied. For this, the number of water molecule associated with activated complex was determined by plotting Log k against Log[H<sub>2</sub>O], 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<sup>0</sup>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.



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 A K [12]

TABLE VI. VARIATION OF 3+ LOG K WITH LOG [H<sub>2</sub>O] (WATER – METHANOL) AT DIFFERENT TEMPERATURE

% of Acet one	% of H <sub>2</sub> O	Log [H <sub>2</sub> O]	3 + Log k				
			20 <sup>0</sup> C	25 <sup>0</sup> c	30 <sup>0</sup> c	35 <sup>0</sup> c	40 <sup>0</sup> 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

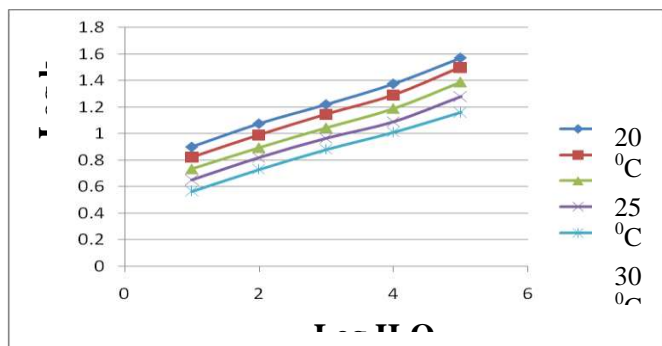


Figure 4. Variation of 3+Logk against 10<sup>3</sup>/T (Water-methanol) system

TABLE VII. CALCULATED VALUES OF SLOPES (PLOT OF LOG K VERSES LOG [H<sub>2</sub>O] ) OF WATER-METHANOL MEDIA

Temp <sup>0</sup> C	20 <sup>0</sup> c	25 <sup>0</sup> c	30 <sup>0</sup> c	35 <sup>0</sup> c	40 <sup>0</sup> c
Slope	2.08	2.16	2.21	2.29	2.56

TABLE VIII. CONSOLIDATED VALUES OF THERMODYNAMICS ACTIVATION PARAMETERS(ΔH\* AND ΔG\* IN KJ/MOLE, ΔS\* IN J/K/MOLE) OF THE REACTION IN WATER- METHANOL MEDIA

% of MEOH	Mole %	ΔH* in KJ/Mole	20 <sup>0</sup> C		25 <sup>0</sup> C		30 <sup>0</sup> C		35 <sup>0</sup> C		40 <sup>0</sup> C	
			ΔG*	-ΔS*	ΔG*	-ΔS*	ΔG*	-ΔS*	ΔG*	-ΔS*	ΔG*	-ΔS*
30%	16.03	53.31	93.64	13.76	94.27	13.74	94.98	13.75	95.60	13.73	96.31	13.73
40%	22.90	52.95	94.20	14.07	94.91	14.84	95.65	14.08	96.31	14.07	97.03	14.08
50%	30.82	52.87	94.68	14.26	95.44	14.03	96.23	14.31	96.96	14.31	97.75	14.33
60%	40.06	51.28	95.16	14.97	95.88	14.72	96.72	14.99	97.43	14.98	98.23	15.00
70%	50.97	50.51	95.64	15.40	96.39	15.14	97.19	15.40	97.96	15.25	98.77	15.41

IV. 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 57.37kj/mole] with increasing concentration of MEOH from 30% to 70%(v/v) in reaction media indicate Transition state is solvated and initial state desolvated. Increase in the value of and ΔG\* with simultaneous increase in ΔH\* & ΔS\* for the hydrolysis ethyl cinanimite 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 biomolecular to unimolecular due to increase in number of water molecule associated with activated complex (2.08to 2.56).

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