



A KINETIC STUDY OF THE SOLVENT EFFECT OF AQUO-ETHANOL SOLVENT SYSTEMS ON THE MECHANISM AND THERMODYNAMIC FUNCTIONS OF CATALYSED SOLVOLYSIS OF HIGHER BUTANOATE

Rashik Bihari Dubey

Assistant Professor of Chemistry, B.S. College Hatta Chenari, V.K.S. University, Ara

Abstract

The values of Iso-composition activation energy of the reaction were found to decrease with increasing proportion of EtOH in the reaction media. The plausible explanation for such depletion is due to solvation and desolvation of transition and initial states of the reaction respectively.

From increase observed in ΔG^* values with simultaneous decrease in the values of ΔH^* and ΔS^* of the reaction, it is inferred that the organic cosolvent EtOH acts as entropy controller solvent.

From the evaluated values of water molecules associated with the activated complex of the reaction, it is concluded that bimolecular mechanistic path is changed to unimolecular in presence of the organic components of the reaction media.

The numerical value of iso-kinetic temperature of the reaction, which comes to be 286.31 indicates that there is weak but considerable solvent-solute interaction in the reaction media.

Key Words:- Aquo-Ethanol, Mechanism, Catalysed, Thermodynamic functions, Solvation number, Iso-kinetic Temperature, Barclay-Butler Rule uni and Bimolecular, solvent-solute Interaction.



Scholarly Research Journal's is licensed Based on a work at www.srjis.com

Introduction: Though a large number of works on the solvent effect on the rates and thermodynamic properties have been reported by various workers¹⁻⁴, but a little attention has been paid towards the studies of solvent effect on the thermodynamic functions, mechanism of the reaction and solvent-solute interaction for alkali catalysed solvolysis of esters having high number of carbon atoms.

In order to highlight the above noted facts, it has been proposed to study the kinetics of alkali catalysed hydrolysis of propyl butanoate in water EtOH media. The kinetic of alkali catalysed hydrolysis of propyl butanoate was carried out separately in the different aquo-organic co-solvent media (water-EtOH) prepared by adding different volumes of organic co-solvent (20 to 80% v/v). The strength of the solution was kept 0.1 M with respect of NaOH and 0.05 M with respect to the ester. The reaction was found to follow the second order kinetic equation and the evaluated values of specific rate constants have been recorded in Table - I.

The iso-composition activation energy values of the reaction, have been mentioned in Table - II. For studying the mechanism of the reaction, the number of water molecules associated with the transition state of the reaction in reaction media at different temperatures have been evaluated by the use of Robertson⁵ equation and are depicted in Table - III. The thermodynamic activation parameters such as ΔH^* , ΔG^* and ΔS^* have been evaluated using Wynne-Jones and Eyring equation⁶ and their consolidated values have been shown in Table - IV.

RESULTS AND DISCUSSION:

Effect of Solvent on the Specific Rate Constant:

In order to elaborate the effect of the solvent on the specific rate constant values of the reaction, the log k values were plotted against the mole % of the organic co-solvent (EtOH).

From the plots it is found that variation of k values (log k values) follows decreasing trends.. However, the depletion found in the rate with increasing mole of the organic co-solvent at all the temperatures follows smooth path following two intersecting straight lines having different numerical values of the slope (of similar nature) before and after the point of intersection at about 18 mole % of EtOH in the reaction media. It is also clear from the plot that with increasing the temperature of the reaction, the rate of depletion in the rate becomes deeper or sharper. After all, in the views of Elsemongy⁷ and Singh et al.⁸ the depletion in the specific rate constant values with different values of slopes may be attributed partly due to the dielectric effect of the media and partly due to solvation changes taking place in the reaction media.

Effect of Solvent on the Iso-composition Activation Energy:

By using the method of Arrhenius plots, the values of the iso-composition activation energies of the reaction have been evaluated and are recorded in Table - II.

On perusal of the data mentioned in Table - II, we observe that the value of iso-composition activation energy of the reaction go on decreasing from 123.06 kJ/mole to 75.05 kJ/mole with increasing concentration of EtOH from 20 to 80%(v/v), in the reaction media.

The depleting trend in E_C values of the reaction in water-EtOH media may be due to either of the following three causes:

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

(iii) The transition state is more solvated than the initial state.

Among these three factors, the third factor seems to be operative in this case as from the values of thermodynamic activation parameters of the reaction in Table - IV, both ΔH^* and ΔS^* values of the reaction are found to decrease with increasing proportion of EtOH in the reaction media (ΔH^* values decreases from 120.55 kJ/mole to 72.01 kJ/mole and ΔS^* values deplete from 125.68 J/K/mole to -43.69 J/K/mole at 30°C). Our such findings are in accordance with the recent reports of Singh et al.⁹

Participation of water molecules in the transition state and mechanism of the reaction:

The number of water molecules associated with the formation of transition state has been evaluated by plotting log k values of the reaction against log [H₂O] values in the light of relation proposed by Robertson⁵.

$$\log k = \log k_0 + n \log [\text{H}_2\text{O}]$$

Slopes of the plots the evaluated values of number of water molecules associated with the transition state are noted in Table - III. From Table - III, it is clear that before log[H₂O] value 1.475 which corresponds to about 53.70% water in water-EtOH reaction media, the number of water molecules associated with the transition state increases from 0.264 to 1.075 with increase in temperature from 20 to 40°C while in case of water concentration above 53.70% in the reaction media, the number of water molecules associated with the transition state increases from 0.547 to 1.768 with rise in temperature.

From the above noted values of the number of water molecules, it may be inferred that overall, the number of water molecules associated with the transition state increases from 0.264 to 1.768 with increase in temperature from 20 to 40°C of the reaction

According to observation and findings of Robertson et al.¹⁰ it has been suggested that number of water molecules associated with the transition state is fairly high for unimolecular reaction while that for bimolecular reaction will be very low.

Hence in the light of findings of Robertson et al.¹⁰, it may be inferred that with rise in temperature of the reaction, the mechanistic path of the reaction changes from bimolecular to unimolecular in water-EtOH media. Such findings are also in support of the recent report of Dubey and Singh.¹¹

Solvent Effect on Thermodynamic Activation Parameters:

From Table IV, on operusal of the values of thermodynamic activation parameters, namely ΔG^* , ΔH^* and ΔS^* , it is found that ΔG^* values (free energy of activation) of the

reaction increases with simultaneous decrease in its ΔH^* and ΔS^* values. At 30°C, ΔG^* values have been observed increasing from 82.47 k cal/mole to 85.25 k cal/mole with increasing concentration of ethyl alcohol (EtOH) from 20 to 80%(v/v) in the reaction media. Though this enhancement is not very large, however, it must be taken into consideration.

From the plots of ΔG^* values against mole % of EtOH, it is found that ΔG^* values go on increasing simultaneously but non-linearly with gradual addition of EtOH in the reaction media. This finding is indicative of desolvation of reactants as explained by Elsemony et al.¹²

So far as the variations in ΔH^* and ΔS^* are concerned, on observing their values from Table - IV, it is interestingly found that both of them decrease with gradual addition of EtOH in the reaction media.

From the thermodynamic relation:

$$\Delta G^* = \Delta H^* - T\Delta S^*,$$

it can be easily concluded that simultaneous increase in ΔG^* values, with decrease in both of ΔH^* and ΔS^* is only possible when ΔS^* values deplete more than ΔH^* values. From such findings, it is inferred that in presence of ethyl alcohol, the alkali catalysed hydrolysis of propyl butanoate becomes entropy controlled reaction.

Moreover, non-linear variation in ΔH^* and ΔS^* values with increasing mole % of EtOH in the reaction media, gives information of the fact that the specific solvation is taking place in water-EtOH systems similar to that as reported by Saville et al.¹³ and recent report of Singh et al.¹⁴

Solvent Effect on Iso-kinetic Temperature and Solvent-Solute Interaction in the Reaction Media:

The value of the iso-kinetic temperature of the reaction was evaluated by using BarcleyButler relationships¹⁵ which is expressed as

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

It is a straight line equation representing the relationship between enthalpy and entropy of activation values of the reaction. ' β ' is known as iso-kinetic temperature. From the values of ΔH^* and ΔS^* values available in Table - IV, the plots of ΔH^* versus ΔS^* at 30°C were made. From the slope of the straight line of the plots, the value of the kinetic temperature was evaluated to be 286.31. Thus, in the light of Lefler's¹⁶ guidelines, from the values of the isokinetic temperature (which is lower than 300), it can safely be concluded that there is no

large but considerable change in the structure of the reactant or in the solvent or in both the reactant and solvent due to weak interaction between solvent and solute present in the reaction media (water - EtOH) in the similar way as reported recently by Singh et al.^{17,18}

Table - I

Alkali catalysed hydrolysis of Propyl-butanoate in water-EtOH media.

$K \times 10^2$ in $(\text{dm})^3 \text{mole}^{-1} \text{min}^{-1}$

Temp in °C	% of propanol (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20°C	43.8	40.47	38.12	35.50	33.20	31.05	27.87
25°C	100.02	88.37	79.47	70.83	63.08	56.13	45.94
30°C	230.14	192.35	166.34	141.32	122.10	97.75	76.40
35°C	500.96	399.94	330.29	270.52	218.83	167.92	124.70
40°C	1019.19	837.14	657.96	516.77	398.42	288.40	197.24

Table II

Values of Iso-composition Activation Energy of the reaction at different concentrations of EtOH in water-EtOH media.

% of EtOH	20%	30%	40%	50%	60%	70%	80%
E_c value in kJ/mole	123.03	115.93	120.07	102.49	95.94	86.33	75.05

Table - III

Evaluated Values of number of water molecules associated with the activated complex of the reaction in water-EtOH media.

Temperature in °C	Slope - I	Slope - II
	Below $\log[\text{H}_2\text{O}] = 1.475$	Above $\log[\text{H}_2\text{O}] = 1.475$
20°C	0.264	0.547
25°C	0.451	0.873
30°C	0.657	1.139
35°C	0.765	1.438
40°C	1.075	1.768

Table- IV
Consolidated Values of Enthalpy of activation (ΔH^*), Free energy of activation (ΔG^*) and Entropy of activation(ΔS^*) of the reaction at different mole % of EtOH in water-EtOH media.

ΔH^* and ΔG^* in kJ/mol, ΔS^* in J/K/mole

% of EtOH (v/v)	Mole% of EtOH	ΔH^*	20°C		25°C		30°C		35°C		40°C	
			ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*
20%	07.17	120.55	83.71	125.75	83.14	125.56	82.47	125.68	81.89	125.55	81.23	125.63
30%	11.69	113.29	83.91	100.30	83.44	100.16	82.93	100.22	82.46	100.10	81.92	100.23
40%	17.07	106.83	84.05	77.74	83.70	77.62	83.29	77.68	82.95	77.52	82.55	77.58
50%	23.59	100.43	84.22	55.30	83.99	55.16	83.70	55.20	83.46	55.08	83.17	55.12
60%	31.65	95.75	84.39	38.79	84.28	38.51	84.07	38.56	84.01	38.14	83.85	38.02
70%	41.89	82.03	84.55	-8.60	84.57	-8.52	84.63	-8.59	84.68	-8.62	84.69	-8.51
80%	55.35	72.01	84.81	-43.68	85.06	-43.79	85.25	-43.69	85.33	-43.25	85.68	-43.66

References

1. Singh, Lallan, Singh, R. T. Singh, R.K. and Jha, R. C.: *J. Indian Chem. Soc.*, **55**, 372, 1978 2.
Singh, P., Mishra, S. K., Sinha, D. K., Prasad, D. and Singh, R. T.: *ARJ Phys. Sci.*, **7**, 87
89, 2004
3. Kiranmayee and Singh, R. T.: *Asian Journal of Chemistry*, **18**, No. **2**, 1050-1054, 2006 .
4. Tabassum, N., Upadhyay, M. K., Singh, A. K. and Singh, R. T.: *NIRJ Sci.*, **1**, No.(1), 115118, 2008
5. Robertson, R. E., : *Prog. Phy. Org. Chem.* **4**, 213, 1967
6. Wynne-Jones, W.F. K. and Eyring, H.: *J. Chem. Phys.* **3**, 492, 1935
7. Elsemongy, M. M.: *Z. Physik. Chem. (Neue Folge)* **84**, 295, 1973
8. Singh, Lallan, Singh, R. T. and Jha, R.C. : *J. Indian Chem. Soc.* **58**, 966-969, 1981
9. Kumar, K., Pandey, S., Singh, A. and Singh, R. T.: *NIRJ Sci.*, **4**, 87-94, 2010
10. Robertson, R. E. and Scott. J. M. W. : *Canad. J. Chem. Soc.*, **55**, 372, 1978
11. Dubey, R.B, Singh, A. K., Singh, P. K. and Singh, R. T. : *NIRJ Sci.*, **4**, 133-139, 2010
12. Elsemongy, M. M., Elamayam, M. S. and Moussa, M.N.H.: *Z. Physik. Chem. (New Folge)* **84**, 295, 1973
13. Saville, B. J. and Hudson, R. F. : *J. Chem. Soc.*, 4114, 1955
14. Kumari, K., Upadhyay, M. K., Kumar, A. and Singh, R. T.: *NIRJ Sci.*, **4**, 65-72, 2010
15. Barclay, I. A. and Butler, J. A. V. : *Trans, Faraday Soc.*, **34**, 1445, 1938
16. J. E. Leffler : *J. Org. Chem.*, **20**, 1201, 1955
17. Singh, A. K., Rai, C. L., Singh, Y. P. and Singh, R. T. : *ARJ Phys. Sci.*, **11**, No. (1-2), 167
170, 2008
18. Kumari, V., Kumari, S., Kumari, K. and Singh, R. T. : *NIRJ Sci.*, **3**, 87-91, 2009