

A Kinetic Study of the Solvent Effect of Aquo-propan-1-ol Systems on the Catalysed Solvolysis of Caproate Ester

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ABSTRACT

In the present study, on the solvolysis of Propyl caproate in water propan-1-ol media, it reveals that the gradual addition of the organic component (propan-1-ol), produces depletion in the rate as well as in the activation energy of the reaction. There is depletion also in the values of ΔH^* and ΔS^* with simultaneous enhancement in ΔG^* values of the reaction, and from this, it may be inferred that reaction is entropy controlled but enthalpy dominating. The values of Iso-kinetic temperature of the reaction has been evaluated to be 280.1 which indicates that there is weak but considerable interaction between solvent and solute in the aquo-propan-1-ol solvent systems.

KEYWORDS: Better indicators, Entropy controlled, Enthalpy dominating, Enhancement Depletion, Interaction, Iso-kinetic, Desolvation, Solvation, Barclay-Butler Equation.

INTRODUCTION

Though a good number of workers have reported¹⁻² about the solvent effect on simpler ester, acid chlorides and amides, but a little attention has been found to be paid towards the kinetic study of solvent

effect on the esters of fatty acids having longer carbon chain.

In order to highlight this fact, the alkali catalysed hydrolysis of Propyl caproate was carried out in aquo-propan-1-ol solvent systems of different composition varying from 30 to 80% (v/v) of the organic co-solvent (propan-1-ol) at five different temperatures ranging from 20⁰C to 40⁰C.

The depletion in the values of specific rate constants with decrease in the activation energy (Iso-composition) of the reaction has been explained in the light of solvation and desolvation of initial and transition states Iso-kinetic temperature of the reaction has been evaluated quantitatively by using Barclay-Butler³ formula.

EXPERIMENTAL

The kinetics of alkali catalysed hydrolysis of Propyl caproate was studied as usual⁴⁻⁵. The reaction was found to follow the path of second order reaction and the evaluated specific rate constant values have been tabulated in Table – I. From Arrhenius plots of log k values against 1/T values, the values of Iso-composition activation energy were determined which are recorded in Table – II. The thermodynamic activation

parameters of the reaction have been evaluated using Wynne-Jones and Eyring.⁶ equation and are depicted in Table – III.:

Discussion over the Results:

Effect of Solvent on the Activation Energy (Iso-composition) of the reaction:

From the Table-II, it is found that the values of Iso-composition activation energy go on depleting from 114.96 kJ/mole to 77.74 kJ/mole with gradual addition of the organic content (propan-1-ol) of the reaction media. The decrease in the values of iso-composition activation energy may be attributed in the following factors.

- (1) The initial state is desolvated and the transition state is solvated,
- (2) The initial state is more desolvated than the transition state, and
- (3) The initial state is less solvated than the transition state.

Out of these three possibilities, the first factor is expected to be operative in this case which gets support from the fact that the values of entropy of activation go on depleting with increasing the concentration of n-propan-1-ol in the reaction media as recorded in Table – III. This gives information of the fact that disorderness in the reaction media decreases. This conclusion has also been found in support of the findings of Rai and Singh⁷ *et al.* in case of alkaline hydrolysis of the dimethyl phthalate in water-EG media and also in support of the earlier findings of Singh & Singh⁸ in case of

alkali catalysed solvolysis of ethyl caprate in water-t-butanol solvent system.

Effect of Solvent on Thermodynamic Activation Parameters:

From Table – III, which includes the values of the three thermodynamic activation parameters i.e. ΔH^* , ΔS^* and ΔG^* , it is obvious that values of free energy of activation ΔG^* enhance from 86.07 kJ/mole to 88.79 kJ/mole with gradual addition of propan-1-ol from 30 to 80% (v/v) in the reaction media at 30°C. Though the enhancement in ΔG^* values is not very high, but, it is very much liable to be taken into consideration. Similar variations in ΔG^* values have also earlier been reported by Tommila⁹ and by Dubey and Singh¹⁰. From the plots of ΔG^* values with mole% of propan-1-ol, a smooth curve is obtained which is indicative of solvation or desolvation of reactants as explained by Elsemongy et al¹¹.

While variation in ΔH^* and ΔS^* are concerned, it is clear from Table – III, that both of them decrease with increasing mole% of propan-1-ol in the reaction media. However, from Table – III, it is interesting to observe that out of all the three thermodynamic activation parameters of the reaction, namely ΔG^* , ΔH^* and ΔS^* , there is depletion in both the ΔH^* and ΔS^* values with simultaneous increase in ΔG^* with gradual addition of propan-1-ol in the reaction media.

According to relation

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

it can easily be concluded that the simultaneous enhancement in ΔG^*

values with decrease in ΔH^* and ΔS^* values is only possible when the extent of depletion in ΔS^* values is greater than that of ΔH^* . The regular depletion to the greater extent in ΔS^* values in comparison to the ΔH^* values clearly indicates that the alkali catalysed solvolysis of Propyl caproate in water-propan-1-ol media is enthalpy dominating and the organic co-solvent propan-1-ol plays the role of entropy controlling solvent.

Moreover, the non-linear variation (depletion) in ΔH^* and ΔS^* values with gradual addition of propan-1-ol in the reaction media gives information of the fact that the specific solvation is taking place in water-n-propanol solvent systems which is in accordance with the observation of Tommila et al.⁹, Singh and Jha¹², and also with the recent reports of Laxmi & Singh et al.¹³

Solvent effect and evaluation of Iso-kinetic temperature:

With the help of iso-kinetic relationship developed by Barclay and Butler³, the value of the iso-kinetic temperature was evaluated.

The Barclay and Butler equation is:

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

It is a relationship between enthalpy and entropy of activation and ' β ' is called Iso-kinetic temperature which is also called Leffler-Grunwald¹⁴ solvent stabilizer operator.

In the light of the above mentioned relationship, the value of Iso-kinetic temperature of the reaction was

evaluated from the slope of the plots of ΔH^* against ΔS^* from their values as recorded in Table – IV and comes to 280.10. In the light of Leffler's¹⁵ guidelines, it is concluded from the numerical value of the slope that there is considerable change in the structure of the reactant or in the solvent or in both the reactant and the solvent due to weak but appreciable interaction between solvent and solute present in the reaction mixture (water-n-propan-1-ol media).

The interference has also been supported earlier by Dubey and Singh¹⁰ and recently by Kumar & Singh et al.¹⁶

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Table - I

The Specific rate constant values of Alkali Catalysed Hydrolysis of Propyl Caproate in Water-n-propan-1-ol media

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

Temp in °C	% of propan-1-ol (v/v)					
	30%	40%	50%	60%	70%	80%
20°C	111.92	100.95	95.26	89.15	81.66	66.04
25°C	240.21	204.17	190.64	166.65	144.51	111.46
30°C	551.32	459.30	347.54	314.49	285.34	187.15
35°C	1118.41	885.32	677.64	564.94	442.59	306.41
40°C	2318.46	1750.25	1271.11	1017.42	757.01	498.65

Table - II

Values of Iso-composition Activation Energy (E_c) in water-propan-1-ol media.

% of propan-1- ol (v/v)	30%	40%	50%	60%	70%	80%
E_c value of kJ/mol	114.96	109.72	100.90	93.15	85.17	77.74

Table - III

Consolidated Values of Enthalpy of activation (ΔH^*), Free energy of activation (ΔG^*) and Entropy of activation (ΔS^*) at different temperatures in water-propan-1-ol media.

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

% of propan-1-ol (v/v)	Mole% of propan-1-ol	ΔH^* in kJ/mol	20°C		25°C		30°C		35°C		40°C	
			ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*
30%	9.36	113.85	87.04	91.5	86.67	91.20	86.07	91.70	85.73	91.30	85.25	91.30
40%	13.85	106.85	87.29	66.7	87.07	66.40	86.53	67.10	86.33	66.60	85.99	66.60
50%	19.43	96.77	87.43	31.9	87.24	32.00	87.23	31.50	87.01	31.70	86.83	31.70
60%	26.56	90.66	87.59	10.5	87.58	10.30	87.49	10.50	87.48	10.30	87.41	10.40
70%	36.01	82.86	87.89	-16.9	87.93	-17.00	87.98	-16.90	88.10	-17.00	88.18	-17.00
80%	49.01	76.39	88.32	-40.7	88.57	-40.90	88.79	-40.90	89.04	-41.10	89.26	-41.10

Table - IV

Variation of ΔH^* , ΔG^* and ΔS^* values of the reaction with mole% of propan-1-ol in water-propan-1-ol media

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

% of propan-1-ol (v/v)	Mole% of propan-1-ol	ΔH^* in kJ/mol	30°C		
			ΔG^* in kJ/mole	ΔS^* in J/K/mole	(ΔS^*+50) in J/K/mole
30%	9.36	113.85	86.07	91.70	141.70
40%	13.85	106.85	86.53	67.10	117.10
50%	19.43	96.77	87.23	31.50	81.50
60%	26.56	90.66	87.49	10.50	60.50
70%	36.01	82.86	87.98	-16.90	33.10
80%	49.01	76.39	88.79	-40.90	9.10