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Effect of water-tertiary alcohol solvent system on The molar thermodynamic properties of solvolysis of caprate Ester

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Key Words:- *Tertiary alcohol, molar, Solvolysis, caprate. Ester, Iso-kinetic temperature Transition state, Enthalpy stimulator, Entropy controlled.*

ABSTRACT

The kinetic study of solvent effect of tertiary butanol war carried out on the Themodynamic Activation parameters, Activation energy and Iso-kinetic temperatures of the alkali catalysed hydrolysis of Ethyl caprate in water-t-butanol media of varying composition ranging from 20% to 80% (t-butanol) and at five different temperatures ranging from 20 to 40°C. The number of water molecules associated with the activated complex of the reaction were found to increase from 0.471 to 1.508 and from this, it is inferred that t-butanol acts as structure breaker of water converting its(water) dense form into bulky form and it changes the mechanistic path way of the reaction from bimolecular to unimolecular, With gradual addition of t-butanol to the reaction media, enthalpy of activation(ΔH^*) and entropy of activation (ΔS^*) were found decreasing with simultaneous increase in free energy of activation (ΔG^*). On the basis of this observation, it has been inferred that the entropy of activation depletes to greater extent than enthalpy of activation and initial state of the reaction is desolvated more than the transition state.

The Iso-composition activation energy values of the reaction were found to be depleted from 108.05 kJ/mole to 70.26 kJ/mole with increasing concentration of t-butanol in the reactin media. From this depletion, it has been inferrea that the initial state of the reaction is desolveted and its transition state is solvated.

Introduction

In the kinetic field, the fact which is widely accepted is that the rate as well as mechanism of the solvolysis reaction have thermodynamically been affected by the presence of organic co-solvent in aquo-organic co-solvent media.

Though various researchers[1-5] have reported on the solvent effect on various types of reaction but the study of solvent effect on the mechanism, thermodynamic activation parameters,activation energy and iso-kinetic temperature of alkali catalysed hydrolysis of an ester having longer carbon chain has not been paid wide attention so far.

So, in order to highlight the above noted idea, it was thought essential to investigate about the fact that how the mechanism, thermodynamic activation parameters including activation energies (Iso-composition and Iso-dielectric) and iso-kinetic temperature of alkali catalysed hydrolysis of ethyl caprate (having longer carbon chain) have been affected in water-t-butanol reaction media having varying concentrations of t-butanol. It was thought essential also because the study of such reaction seems very important and much useful from the medicinal as well as biological points of views.

Experimental:

The kinetics of alkali catalysed solvolysis of ethyl caprate was studied by adding different concentration of the organic co-solvent (t-butanol) from 20 to 80%(v/v) in the reaction media at five different temperatures i.e. 20, 25, 30, 35 and 40°C as usual methods.[6-7] The specific rate constants were evaluated using second order kinetic equation and have been mentioned in Table - I. From the plots of log k values versus log [H,O] values as mentioned in Table - II, their slopes value were evaluated and have been inserted in Table - III. From the values of the specific rate constant values, thermodynamic activation parameters namely free energy of activation (ΔG^*), enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) of the reaction were determined by using Wynne-Jones and Eyring equation[8] and are synchronised in Table - IV. From the slopes of the Arrhenius plots of log k versus 1/T, its Iso-composition activation energies for different composition of water-t-butanol reaction media were evaluated and have been inserted in Table - V.

RESULTS AND DISCUSSION:

Effect of Solvent on the Mechanism of the reaction:

The mechanism of the reaction was decided by evaluating the number of water molecules involved in the formation of activated complex. It was done by plotting logk against log[H_2O] by using the relation proposed by Robertson[9], which is as:

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

where 'n' is the solvent number (number of water molecules associated with the activated complex) which is evaluated from the slopes of the plots of log k versus log [H_2O] and tells about the criterian for studying about the mechanism of the reaction. From the values mentioned in Table - II, the plots of log k versus log [H_2O] were found having two intersecting straight lines having different values of positive slopes at each temperature are mentioned in Table - III.

From Table - III, it is clear that below log [H_2O] value 1.45 which corresponds to 45.20% of water in water-t-butanol media, the number of water molecules associated with the activated complex increases from 0.421 to 0.970. Similarly, above log [H_2O] value 1.45 i.e. above 42.20%, concentration of water in the reaction media, the number of water molecules involved in the formation of the activated complex increases from 0.657 to 1.508. From the increasing number of water molecules involved in the formation of the activated complex, it is inferred that tertiary butanol in the reaction media acts as structure breaker and it shifts the equilibrium of water from its dense form to its bulky form and in the light of guidelines of Robertson et al.[10], it is concluded that the mechanistic pathways of the reaction in presence of t-butanol is changed from bimolecular to unimolecular. Singh et al.[11-12] have also reported similar findings and inferences:

Table - I

Alkali catalysed hydrolysis of Ethyl caprate in water-t-butanol media

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

Temp in °C	% of t-butanol (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20°C	98.92	93.82	85.43	75.61	65.81	57.57	48.32
25°C	172.27	148.32	137.44	120.20	98.90	82.93	69.68
30°C	303.25	257.10	219.84	177.91	146.59	125.34	92.94
35°C	485.40	380.01	328.32	275.55	221.92	162.22	123.17
40°C	843.33	645.95	533.46	415.05	316.08	239.66	169.97

Table - II

Variation of log k values with log[H_2O] values in water-t-butanol reaction media at different temperatures

% of t-butanol(v/v)	% of water	log[H_2O]	Temp. °C				
			20°C	25°C	30°C	35°C	40°C
20%	80%	1.6478	1.9953	2.2362	2.4818	2.6861	2.9260
25%	70%	1.5898	1.9723	2.1712	2.4101	2.5798	2.8102
30%	60%	1.5229	1.9316	2.1381	2.3421	2.5163	2.7271
40%	50%	1.4437	1.8786	2.0799	2.2502	2.4402	2.6181
50%	40%	1.3468	1.8183	1.9952	2.1661	2.3462	2.4998
60%	30%	1.2218	1.7602	1.9187	2.0981	2.2101	2.3796
70%	20%	1.0458	1.6841	1.8431	1.9682	2.0905	2.2121

Table - III

Values of the slopes of the plots of log k values against log [H_2O] values at different temperatures

Temperature in °C	Slope - I Where log[H_2O] value is below 1.45	Slope - II when log[H_2O] value is above 1.45
20°C	0.471	0.657
25°C	0.542	0.865
30°C	0.640	1.111
35°C	0.886	1.188
40°C	0.978	1.508

Solvent effect on the Thermodynamic Activation Parameters:

On perusal of the data mentioned in Table - II, it is found that the values of free energy of activation (ΔG^*) increases with increasing t-butanol content of the reaction at all the temperature at which the reaction was studied. At 30°C, values of ΔG^* were reported to increase from 87.58 kJ/mole to 90.56 kJ/mole with increasing proportion of t-butanol from 20 to 80% (v/v). Though the enhancement in ΔG^* values is not very high, however, it is up to mark for taking into consideration.

A similar variations in ΔG^* values with increasing mole% of organic solvent has also been reported by Singh et al.[13] From the plot of ΔG^* against mole % of organic co-solvent, it is found that ΔG^* values increases smoothly and non-linearly with gradual addition of t-butanol in the reaction media. This finding is indicative of desolvation of reactants as explained and also supported by Elsemongy et al.[14] So far as the variation in ΔH^* and ΔS^* values are concerned, on going through Table -IV, it is interestingly observed that both of them decrease with gradual increase in the concentration of t-butanol in the reaction media at all the temperatures.

On ne basis of the relation:

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

it can be concluded that simultaneous enhancement in ΔG^* values with depletion in the values of both ΔH^* and ΔS^* values is only possible when the extent of depletion in ΔS^* is more than that of ΔH^*. The regular depletion to the greater extent in ΔS^* values in comparison to that of ΔH^* values clearly indicates that the alkali catalysed hydrolysis of ethyl caprate in water-t-butanol media is entropy controlled. Moreover, non-linear variation in ΔS^* and ΔH^* values with increasing mole% of t-butanol in the reaction media, gives information of the fact that the specific solvation is taking place in water-t-butanol systems, similar to that as reported by Saville et al.[15] and it also indicates that the random distribution of the components are not permissible. The similar non-linear variations in ΔS^* and ΔH^* values with increasing mole % of the organic component in the reaction media have also been reported by Kumar & Singh et al[16.] The depletion in both ΔH^* and ΔS^* values justifies that transition state is less desolvated in comparison to initial state in water-t-butanol media.

Solvent Effect and evaluation of Iso-composition Activation Energy:

From Table - V, it is obvious that iso-composition activation energy values of the reaction go on decreasing from 81.39 kJ/mole to 46.57 kJ/mole with increasing concentration of t-butanol in the reaction media.

The decreasing trend in the E_{exp} value may be due to either of the following three causes:

(i) The initial state is less solvated than the transition state,

(ii) The initial state is desolvated more than the transition state, and

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

Out of these three causes, the third factor seems to be operative in this case as both ΔH^* and ΔS^* values of the reaction as mentioned in Table - IV, are found to decrease. Similar findings have also been reported recently by Singh et al,[17-18].

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Table - IV

Values of Iso-composition Activation Energy of the reaction in water-t-butanol media.

% of t-butanol(v/v)	20%	30%	40%	50%	60%	70%	80%
E_C or E_{exp} values in K/J/mol	81.39	72.45	69.63	65.29	61.21	55.31	46.51

Table- V

Consolidated Values of Thermodynamic Activation Parameters (,ΔG*,ΔH* and ΔS*) on the reaction at different mole % of t-butanol in water-t-butanol media

ΔH* and ΔG* in kJ/mol, ΔS* in J/K/mol

% of t-butanol	Mole% of -t butanol	ΔH* in kJ/mol	20°C		25°C		30°C		35°C		40°C	
			ΔG*	ΔS*	ΔG*	ΔS*	ΔG*	ΔS*	ΔG*	ΔS*	ΔG*	ΔS*
20%	4.52	79.65	87.34	26.24	87.49	26.33	87.58	26.18	87.86	26.67	87.89	92.58
30%	7.51	71.02	87.47	56.12	87.86	56.52	87.99	56.01	88.49	56.70	88.59	66.77
40%	11.21	66.60	87.69	72.01	88.05	72.01	88.39	71.93	88.86	72.30	89.08	47.66
50%	15.93	62.52	87.99	86.94	88.38	86.71	88.92	87.15	89.31	86.99	89.74	25.71
60%	22.13	58.15	88.33	102.99	88.87	103.08	89.41	103.16	89.87	102.96	90.45	11.76
70%	30.66	51.64	88.65	126.33	89.31	126.39	89.80	125.96	90.67	126.71	91.17	-18.17
80%	43.11	46.66	89.08	144.79	89.74	144.56	90.56	144.89	91.37	145.18	92.17	-42.88

Solvent effect on Iso-kinetic Temperature:

The values of the Iso-kinetic temperature of the reaction was evaluated by using Barclay and Butler[19] relationship which is as follows:

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

It is a straight line equation presenting the relationship between enthalpy and entropy of activation. 'β' is iso-kinetic temperature. From the data available in Table - IV, the plots of ΔH* versus ΔS* at 30°C were made and from the slope of the obtained straight line, the value of iso-kinetic temperature was found to be 271.20 which is apparently less than 300. In the light of Leffler's[20] guidelines, from the value of iso-kinetic temperature which is less than 300, it is concluded that in water-t-butanol media, there is appreciable but weak solvent-solute interaction for alkali catalysed solvolysis of ethyl caprate. Similar findings have also recently been reported by Pandey & Singh[21].

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