A KINETIC STUDY OF THE SOLVENT EFFECT OF AQUO-TERTIARY ALCOHOL MEDIA ON THE SOLVOLYSIS OF AN ISO-BUTYRATE ESTER

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Abstract

Solvent effect of a tertiary alcohol on the kinetics of alkali catalysed solvolysis of mehyl iso-butyrate (substituted ester) was studied in water-t-butanol media of varying composition ranging from 20 to 80% of t-butanol in the reaction media at different temperatures varying from 20 to 40°C. The rate of the reaction was found to decrease with increasing proportion of the t-butanol al all the temperatures. It was observed that the values of activation energy (Iso-composition) go on increasing with gradual addition of the organic co-solvent. For variation in rate and activation energy of the reaction, it inferred that effect of change in dielectric constant values and selective solvation of reactants are responsible for depletion in rate while solvation and desolvation of the initial and the transition states respectively are the causes for enhancement in the values of iso-composition activation energy of the reaction.

From the decreasing number of water molecules from 1.678 to 0.355 involved information of the transition state with increaing temperature of the reaction, it is inferred that t-butanol changes its mechanistic path from unimolecular to bimolecular.

Key Words:- *Solvolysis, Substituted ester, uni and bimolecular Mechanism, Specific solvation, Iso-composition, Iso-dielectric, Iso-kinetic.*

INTRODUCTION:

Various researchers[1-4] have reported about the solvent effect on the solvolysis of simple esters but the study of the effect of solvent on the solvolysis of ester of subsitituted acid has not been paid adequate attention so far. It seems essential to study the solvent effect on the alkaline solvolysis of the methyl iso-butyrate (substituted ester) ester as it is fruitful from food technological as well as medicinal points of views. Hence, in order to highlight the above noted untouched work, it was thought useful and necessary to study the solvent effect on the alkaline solvolysis methyl isobutyrate in water-t-butanol media.

Experimental:

The kinetics of alkail catalysed solvolysis of methyl isobutyrate was studied in water-t-butanol media having varying composition of the reactant media, separately prepared by adding 20 to 80% oft-butanol in it. The reaction mixture was prepared such that its strength in terms of ester as well as alkali were kept 0.05 M and 0.1 M respectively. The temperatures of the reaction were varied from 20 to 40°C. The reaction was found to follow the second order kinetic equation and the evaluated values of specific rate constants are recorded in Table - I. The evaluated values of iso-composition activation energy have been mentioned in Table-II.

From the slopes of the plots of log k values versus $\log[H_2O]$ values, the evaluated values of no. of water molecules associated with the activated complex have been inserted in Table - III. The consolidated values of the thermodynamic activation parameters have been tabulated in Table -IV.

Results and Discussion:

Effect of Solvent on the Specific Rate Constants of the Reaction:

From Table - I, it is clear that specific rate constant values of the reaction go on decreasing with increasing t-butanol content of the reaction media. From the plots of log k with mole % of organic co-solvent it is observed that the plot follows a sharp decreasing trend upto 17.5 mole % of t-butanol at all temperatures. After 17.5 mole %, which corresponds to 52.80% (v/v) of t-butanol in the reaction media, the depletion in the rate becomes slow at all the temperatures. The trend of variation in the values of specific rate constant may be discussed in light of the Hughes and Ingold[5] theory. According to the theory, increase in dielectric constant values of the reaction media results in increase in the rate when there is concentration of charges on the transition state and causes a decrease in the rate when there is diffusion or destruction of charges on the transition state.

It is true fact that there is decrease in the dielectric constant values of the aquo-t-butanol mixtures with the gradual addition of organic co-solvent. In the alkali catalysed hydrolysis of methyl iso-butyrate, due to participation of OH⁻ ion (Negative ion) the negative charge is dispersed on the larger area of the transition state, so in water-t-butanol mixtures the rate of the reaction should decrease with increase in the dielectric constant of the media according to the Hughes and Ingold theory. But, in our case, the specific rate constant values were found obeying decreasing trend with decrease in the dielectric constant values of the

medium or with the addition of organic co-solvent (t-butanol) in the reaction mixture. Thus our inferences are against the Hughes and Ingold theory.

For retardation in the rate of reaction in water-t-butanol systems, the following factors seem to have been responsible:

(i) lowering of the bulk di-electric constant of the medium after adding more and more t-butanol to it,

(ii) decreasing the polarity of the medium as changing from polar water to less polar water-t-butanol medium.

Both of the above noted factors are found to be responsible for depletion in the rate throughout the region of the water-t-butanol media in which the kinetics of the reaction were studied.

However, recently many instances have been reported[6-8] in which the rate decreases in the similar way as observed in this case.

Effect of Solvent on Iso-composition Activation Energy (E_C or E_{exp}):

After making observation of the values of E_{exp} in Table - II, it is clear that there is enhancement in the E_{exp} values with increase in the concentration of t-butanol in the reaction media. The E_{exp} values increases from 49.57 kJ/mole to 72.73 kJ/mole. It has been established that changes in the values of activation energy are obviously noticeable only when the solvation changes take place either in the initial state level or at the transition state level or at both the

Table – I Specific rate Constant values of Alkali catalysed hydrolysis of Methyl isobutyratein water-t butanol media.

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

Temp in °C	% of t-butanol (v/v)						
	20%	**30%**	**40%**	**50%**	**60%**	**70%**	**80%**
20°C	72.19	57.82	45.40	32.96	25.64	19.11	12.60
25°C	137.44	121.65	95.04	72.96	59.99	47.11	33.36
30°C	280.09	229.72	198.20	161.85	139.03	115.37	87.74
35°C	501.42	438.63	394.91	342.85	304.93	267.30	216.87
40°C	909.91	824.14	785.42	720.94	671.74	609.82	534.69

Table – II Values of Iso-composition Activation Energy (E_C) of the reaction in Water-t-butanol media.

% of t-butanol (v/v)	20%	30%	40%	50%	60%	70%	80%
E_{exp} values in k/J/mol	49.57	50.81	54.48	59.49	62.76	67.33	72.73

Table – III The Values of the slopes of the plots of log k versus log [H_2O] in water-t-butanol reaction media.

Temperature in °C	Slope - I Where log[H_2O] is below 1.43	Slope - II when log[H_2O] is above 1.43
20°C	1.011	1.678
25°C	0.884	1.429
30°C	0.671	1.001
35°C	0.534	0.732
40°C	0.355	0.427

levels. The increase in the activation energy of the reaction with decrease in the specific rate constant values may seems to be quite natural. The following three possibilities may be held responsible for enhancement in the values of E_{exp}:

      (i)   The initial state is solvated and the transition state is desolvated.

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

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

           Out of these three factors, the first seems to be applicable in our case as this factor is supported by the increase in the values of entropies of activation as depicted ahead in

Table - IV. This conclusion has also been supported by recent works of Kumari & Singh et al[9]. and Kumar & Singh et al[10].

EFFECT OF CONCENTRATION OF WATER [H_2O] ON THE RATE AND MECHANISM:

The effect of water concentration [H_2O], of the water-t-butanol mixture, on the rate and mechanism of alkali catalysed hydrolysis of methyl isobutyrate has been studied. For this, the number of water molecules associated with the activated complex was determined by plotting log k against log [H_2O] according to the relation proposed by Robertson[11],

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

Here 'n' is the solvation number which tells about the criterion for studying about the mechanism of the reaction.

The values of slopes of the plots of log k versus log [H_2O] at all the temperatures are noted in Table - III

From the noted values of the slopes in Table - III, it may be inferred that with rise in temperatures, the values of slopes go on decreasing from 1.011 to 0.355 when log [H_2O] value is below 1.43 which corresponds to 48.80% of water in water-t-butanol media. Similarly, above log [H_2O] value 1.43, the number of water molecules associated with the activated complex decreases from 1.678 to 0.427 with rise in temperature of the reaction. Overall, it may be inferred that number of water molecules involved with the transition state decreases from 1.678 to 0.355 with rise in the temperature of the reaction from 20 to 40°C.

These observation may be attributed to the fact that the equilibrium of the reaction shifts from bulky form of water to its dense form with the rise of temperature.

$$(H_2O)_b \ \rightleftharpoons \ (H_2O)_d$$
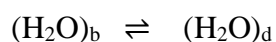
Finally, it is inferred that with rise of temperature the number of water molecules associated with the activated complex decreases as the proportion of organic co-solvent increases in the water-t-butanol mixture and it explains that when t-butanol is added to water butanol media the mechanistic path of the reaction is changed from unimolecular to bimolecular in the similar way as observed by packer and Tomilinson[12] and recently by Sinha & Singh.[13]

SOLVENT EFFECT ON THE THERMODYNAMIC ACITVATION PARAMETERS:

The thermodynamic activation parameters such as enthalpy of activation ΔH^*, entropy of activation ΔS^* and free energy of activation ΔG^* are supposed to be better indicators of the solvent effects displayed by the solvent on the solvolysis reactions. These thermodynamic activation parameters have been evaluated with the help of Wynne Jones and Eyring[14] equation.

The values of all these three thermodynamic parameters i.e. ΔH, ΔS^* and ΔG^* at different mole % of the organic component of the reaction media have been synchronized in Table - IV. The variation in ΔH, ΔG^* and ΔS^* with mole % of the organic component of the water-t-butanol mixtures may be seen with their plots against mole % of t-butanol in the reaction media. On careful observation of the data, it is found that ΔG^* value increases from 81.98 kJ/mole to 84.96 kJ/mole with change of proportion of t-butanol from 20 to 80%(v/v) at 30°C. Though the enhancement is not very large, however it cannot be ignored but must be taken into consideration.

A similar variation in ΔG^* values with increasing mole %of organic Co-solvent has also been reported recently by Tabassum & Singh[15]. This gradual non-linear increase in

Table- IV Consolidated Values of Thermodynamic Activation Parameters of the reaction 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	93.61	82.49	37.93	82.35	37.78	81.98	38.38	81.88	38.7	81.70	38.04
30%	7.51	97.63	83.03	49.79	82.65	58.25	82.44	50.13	82.22	58.00	81.96	50.05
40%	11.21	106.59	83.62	79.39	83.26	77.08	82.81	78.50	82.51	78.19	82.09	78.30
50%	15.93	115.32	84.40	105.52	83.92	103.75	83.36	105.48	82.86	105.44	82.31	105.47
60%	22.13	122.87	85.02	129.19	84.40	127.03	83.34	129.14	83.16	128.95	82.49	129.01
70%	30.66	130.08	85.73	151.36	85.00	148.82	83.92	151.38	83.49	151.26	82.47	151.24
80%	43.11	140.46	86.75	183.31	85.86	183.22	84.96	183.34	84.03	183.21	83.09	183.29

ΔG* values with increase in mole % of the organic component in the reaction media is indicative of solvation or desolvation of reactants as explained by Absolute Reaction Rate Theory[16].

So far as the variation in ΔH* and ΔS* are concerned, it is clear from Table - IV that both of them increase with increasing mole % of t-butanol in the reaction media. However, on perusal of the Table -IV, it is interestingly observed that out of all the three thermodynamic parameters of the reaction namely ΔG*, ΔH* and ΔS*, all of them are found to be enhanced simultaneously with increase in mole % of t-butanol of the reaction media.

According to the relation,

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

it can be easily concluded that increase in ΔG* values with simultaneous enhancement in ΔH* and ΔS* values is only possible when the extent of enhancement in ΔH* values is greater than : that of ΔS*. The regular enhancement to the greater extent in ΔH* values in comparison to the AS* values clearly indicates that the alkali catalysed hydrolysis of methyl iso-butyrate in water-t-butanol media is entropy controlled. Moreover non linearity in ΔH* and ΔS* curves give information of the fact that specific solvation is taking place in water-t-butanol systems as reported by Saville et al.[17] and it also indicates that the random distributions of the components are not acceptable. The similar non linear variations in ΔH* and ΔS* values with increasing mole % of the organic component in the reaction media have also been reported by Tommila et al.[18] and recently by Upadhyay & Singh.[19]

Solvent Effect and Iso-Kinetic Relationship

Barclay and Butler[20] have developed iso-kinetic relationship between enthalpy of activation AH* and entropy of activation ΔS* as follows:

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

where 'β' is a constant called iso-kinetic temperature. Leffler[21] has pointed out that plot of ΔH* against ΔS* results in a straight line and the slope of the line gives the value of iso-kinetic temperature. He pointed out that in many solvolysis reactions, the values of slope of plots of ΔH* versus ΔS* come in between 300 and 400 and this foretells about the considerably strong interaction between solvent and solute of the reaction mixture.

In the present study also, plots of ΔH* versus ΔS* has been found to be linear which is conformity with Barclay-Butler relationship. The numerical value of the slope of the straight line is found to be 324.0. Thus, in light of Leffler's guidelines, from the value of the slope, it can easily be concluded that there is appreciable change in the structure of the reactant or in the solvent or in both the reactant and the solvent due to strong interaction

between solvent and solute present in the reaction mixture (water-t-butanol media) in the similar way as reported by Leffler[21]. The structural changes with increasing proportion of the t-butanol in water-t-butanol solvent system are responsible for the decrease in the specific rate constant values. However, similar conclusion has also been reported earlier by Singh et al[22]. and recently by RT. Singh [23].

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