EFFECT OF SOLVENT DMSO ON THE MECHANISM AND ACTIVATION ENERGIES OF THE CATALYSED SOLVOLYSIS OF SUBSTITUTED VALERATES

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ABSTRACT

The kinetics of the alkali catalysed hydrolysis of Ethyl Iso-valerate (Aliphatic iso-valerater) was studied in aquo-aprotic solvent systems(aquo- DMSO) and the specific rate constants of the reaction were found decreasing with increasing concentration of the organic content (DMSO) of the media. It is inferred that dielectic effect and the solvation changes are the causes of depletion in the rate of the reaction.

The Iso-composition activation energy (E_C) and the Iso-dielectric activation energy(E_D) of the reaction were found to increase and decrease respectively and from this, it is inferred that the transitionn state of the reaction is desolvated and its initial state is solvated. From the evaluated values of iso-kinetic temerature of the reaction which comes to be 330.0, it is concluded the Barclay-Butler rule is obeyed by the reaction and there is strong solvent-solute interaction in presence of DMSO in the reaction media

Key Words :- *Mechanism Specific rate constants, Activation Energies, Iso-composition, Iso dielectric Extensive Properties Enthalpy Dominating, Entropy controlled, specific Soclvation, Substituted valerates*

INTRODUCTION:

The kinetics of alkali catalysed hydrolysis of Ethyl Iso-valerate in aquo-DMSO media has been planned to be carried out, as this reaction is very useful from commercial as well as from the hygenic points of views and also because it has not been paid adequate attention by the researchers so far.The solvolysis of the said ester was studied in

aquo-DMSO media having varying concentration of DMSO from 20-80%(v/v) at five different temperatures i.e. 20,25,30,35 and 40°C.

Experimental :

Export quality of Ethyl Iso-valerate ester of USSR make and SISCO grade of DMSO were taken in use. The kinetics of alkali catalysed hydrolysis of Ethyl Iso-valerate were studied using reported process[1,2] keeping the strength of alkali and esters as 0.1 M and 0.05 M respectively. The concentration of the organic solvent DMSO was varied from 20 to 80% (v/v) and hydrolysis was carried out at five different temperatures at 20,25,30,35 and 40°C. The reaction was found to folloow second order kinetic equation and the evaluated values of the specific rate constants were enlisted in Table-I. The evaluated values of iso-composition activation energy (E_C) and iso-dielectric activation energy (E_D) have

Table – I

Specific rate constant values of Alkali catalysed hydrolysis

of Ethyl Iso-valerate in water-DMSO media

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

Temp in °C	% of DMSO (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20°C	88.11	69.74	53.41	42.48	33.58	26.84	18.96
25°C	169.79	137.15	111.25	91.96	75.25	61.12	46.51
30°C	323.67	272.14	231.79	197.83	168.81	143.02	114.18
35°C	602.28	523.48	450.56	407.47	360.25	316.15	262.30
40°C	1105.10	999.54	914.32	834.07	766.13	687.23	613.06

Table - II

Evaluated values of Iso-composition Activation Energy (E_C or E_{exp}) of the reaction in water-DMSO media.

% of DMSO	20%	30%	40%	50%	60%	70%	80%
E_C values in K/J/mol	97.01	102.97	109.17	113.96	119.34	125.28	134.16

Table - III

Evaluated Values of Iso-Dielectric Activation Energy (E_D) of the reaction at Different- Desired 'D' values of water-DMSO media.

D values	D= 60	D = 62.5	D = 65	D =67.5	D = 70	D = 72.5	D = 75
E_D values in kJ/mole	149.70	139.84	136.45	129.61	126.27	122.09	118.09

been recorded respectively in Table -II and III. From the slopes of the plots of log k values versus log[H_2O] (valuus as recorded in Table-IV), The evaluated values of number of water molecules associated with the activated complex of the reaction have been tabulated in Table -V. The three thermodynamic activation parameters namely ΔH*, ΔG* and ΔS* were calculated by applying Wynne-Jones and Eyring equation[3] and their values are synchronised in Table -VI.

RESULTS and Discussion:

Solvent Effect on the Rate to Reaction:

Table-I shows that the specific rate constant values of the reaction decrease with increasing proportion of DMSO in the reaction media. On plotting log k values against mol % of DMSO. it is obvious that rates of reaction go on depletion with gradual addition of DMSO in the reaction media. The depletion in the rate follows smooth deplecing path. From the plots of log k versus mol% of DMSO in the reaction media, two intersection gstraight lines having different values of slopes are obtained. The decrease in the rate with increasing mol % of DMSO at all the five temperatures are found to follow deep depletion path up to 19.50 mol% of the DMSO in the reaction meedia and after its 19.50 mol % in the reaction media, the rate of depletion becomes slow. IT is clear that sharpness in the depletion of the rate becomes slow with increase in temperature of the raction. This decrasing trend in the values of the rate constants needs to be discussed in the light of Hughes and Ingold[4] predictions and the theory of Laidler and Landskroener[5]. The values of dielectric constant of the reaction media go on decreasing with gradual addition of DMSO. So these findings are fully in accordance with the qualitative prediction of Hughes and Ingold.

However, these findings are also in agreement with the qualitative prediction and views of Singh & Jha et al.[6,7] and reacent reports of Singh & singh et al.[8] and Singh & Rashmi et al.[9], who predicted that the rate of ion dipolar reaction decreases partly with decrease in the dielectric constant values of the reaction media and partly due to the solvation changes taking place in the reaction media.

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

The values of iso-composition activation energy (E_C) of the reaction were evaluated from the slopes of Arrhenius plots of log k values of the reaction against $10^3/T$ and have been tabulated in Table-II. The plots of log k versus $10^3/T$ from Table-II, it is obvious that E_C values go on increasing from 97.01 kJ/mol to 134.16 kJ/mol with increase in concentration of DMSO from 20 to 80% (v/v) in reaction media. This change is probably due to solvation changes taking place either at initial state level or at the transition state level or

at the level of both the states as reported earlier by several reserchers[10,11] in this field. Considering the extent of solvation to be a dominant factor, The following three factors seem to be responsible for increase in E_C values with gradual addition of DMSO in the reaction media:-

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

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

(ii)   The transition state is desolvated more than initial state.

The transition state being large anion (ester +OH) not available more for solvation by DMSO molecule than the initial state, so the first factor seems to be operative in this case and it also gets support when the values of entropy of activation (ΔS^*) and enthalpy of activation (ΔH^*) go on increasing with concentration of DMSO as shown in Table-VI. Such observations and inferences have been supported earlier by Chandra & Singh et al.[12] and also recently by Singh & Priyanka et al.[13].

Solvent Effect on the Iso-dielectric Activation Energy (E_D) of the Reaction:

On perusal of the data of Table-III, it is found that iso-dielectric energy(E_D) values of the reaction are decreasing from 149.70 kJ/mol to 118.09 kJ/mol with increase in dielectric constant values of the reaction media from D = 60 to D = 75 respectively. Since D values of the aquo-DMSO reaction media go on decreasing with gradual addition of DMSO to it, hence it may also be concluded that like E_C values, E_D values are also increasing with decrease in D Values of the reaction media or with adding more and more DMSO to it. Thus it also may be inferred that E_C and E_D values of the solvolysis reactions are comlimentary to each other.Such findings and their interpretations are in support of the past views of Elsemongy et al.[14], Wolford[15] and are also supported by the recent reports of Kumari & Singh et al.[16] and Singh & Wats et al.[17].

Effect of Solvent on the Solvation number and on the Mechanistic pathways of the reaction:

The solvation number i.e. the number of twater molecules involved in the formation of the activated complex of the reaction were evaluated from the slopes of the plots of log k values of the reaction against log[H_2O] values of the reaction media. By using Robertson[18] equation which is –

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

where 'n' is the solvation number.

The log k and log [H_2O] are enlisted in Table-IV and the numerical values of the slopes of the plots have been enlisted in Table-V. Robertson et al.[19] have established that the numerical value of solvation number 'n' i.e. the number of water molecules associated with the activated complex in its formation are fairly high for reaction following unimolecular mechanistic pathway and are low for reaction following bimolecular mechanistic pathway. from the values recorded in Table-V, it is clear that at all the temperatures of the reaction, the plots of log k versus log[H_2O], there are two straight lines having different slopes which meet at log [H_2O] value 1.480 which corresponds to 54.40% of water in aquo-DMSO media.

Table – IV

Variationof log k values of the reaction with log[H_2O] values of water-DMSO media at different temperatures.

| % of DMSO (v/v)	% of H_2O	log[H_2O]	3+ log k values				
			20°C	25°C	30°C	35°C	40°C
20%	80%	1.6478	1.9450	2.2299	2.5101	2.7798	3.0434
30%	70%	1.5898	1.8435	2.1372	2.4348	2.7189	2.9998
40%	60%	1.5229	1.7276	2.0463	2.3651	2.6614	2.9611
50%	50%	1.4437	1.6282	1.9636	2.2963	2.6101	2.9212
60%	40%	1.3468	1.5861	1.8765	2.2274	2.5560	2.8843
70%	30%	1.2218	1.4288	1.7862	2.1554	2.4999	2.8371
80%	20%	1.0458	1.2778	1.6675	2.0576	2.4188	2.7875

Table - VI

Values of the slopes of the plots of log k versus log [H₂O] values at different temperatures

Temperature in °C	Slope - I Where log [H_2O] value is below 1.480	Slope – II when value log[H_2O] is above 1.480
20°C	0.888	1.792
25°C	0.730	1.487
30°C	0.590	1.181
35°C	0.495	1.027
40°C	0.342	0.606

From the evaluated values of slopes as recorded in Table -V, it is clear that before log[H_2O] value 1.480 which corresponds to 54.40% of water concentration in the reaction media.their values are decreasing from 0.888 to 0.342 with rise in temmerature of the reaction from 20 to 40°C . Similarly, after log[H_2O] values 1.480 i.e. above 54.40% of water in the reaction media, the numerical values of the slopes i.e. the number of water molecules associated with the activated complex in its formcation decrease from 1.792 to 0.606 with increase in temperature from 20 to 40°C.

Overall, it may be concluded that number of water molecules associated with the activated complex of the reaction in the formation decrease from 1.792 to 0.342. Thus, on the guidelines of Robertson et al.[19], it may be inferred that with rise in temperature of the reaction, the mechanistic pathways of the reaction is changed from unimolecular to bimolecular in presence of DMSO in the reaction media.

About the change in the structure of water in presence of DMSO and with rise in temperature of the reaction, water components of the reaction media changes its structure from its bulky form to dense form at equilibrium.

$$(H_2O)_b \rightleftharpoons (H_2O)_b$$
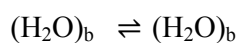
Such observations and inferences have been supported earlier by Singh & Mishra et al.[20] and recently by Singh & Singh et al.[21].

Effect of Solvent on the Thermodynamic Activation Parameters of the Reaction:

The three thermodynamic activation parameters namely ΔH^*, ΔG^* and ΔS^* of the alkali catalysed hydrolysis of Ethyl Iso-valerate were evaluated using Wynne-Jones and Eyring equation[3] and their values have been synchronised in Table-VI.

Table- VI

Consolidated Values of Thermodynamic Activation Parameters (ΔH^*, ΔG^* and ΔH^*) of the reaction in water-DMSO solvent system at different temperatures.

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

% of DMSO (v/v)	Mole% of DMSO	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%	5.94	95.25	882.01	45.20	81.83	45.06	81.81	45.02	81.41	44.94	81.20	44.91
30%	9.77	99.55	85.58	57.84	82.35	57.62	82.05	57.68	81.77	57.65	81.46	57.73
40%	14.40	104.94	83.23	74.09	82.87	74.04	82.46	74.20	82.11	74.11	81.73	74.15
50%	20.17	112.31	87.79	97.33	83.34	97.21	82.85	97.23	82.41	97.08	81.93	97.06
60%	27.49	117.05	84.36	111.56	83.84	111.42	83.25	111.54	82.73	111.42	82.15	111.49
70%	37.09	122.71	84.91	129.02	84.36	128.70	83.67	128.83	83.06	128.72	82.43	128.68
80%	50.27	131.12	86.02	154.10	85.03	154.83	84.24	154.88	83.54	154.64	82.73	154.76

From Table -VI,. it is clear that out of the three thermodynamic activation parameters ΔH^*, ΔG^* and ΔS^*, all of them are found increasing with increasing mol % of DMSO in the reaction media. For better understanding of the effect of solvent DMSO on these three thermodynamic activation parameters, their values were plotted against mol % . The variation in ΔH^*, ΔG^* and ΔS^* respectively with mol % of DMSO in the reaction media. The reasonable and considerable increase in ΔG^* values (from 81.81 to 84.24 kJ/mol at 30°C) as

found in Table -VI and non-linear variation in ΔH^*, ΔG^* and ΔS^* with mol% of DMSO. The

are indication of specific solvation taking place in the process of activation as reported by Saville and Hudson[22], Tommila et al.[23] and Hyne et al.[24]. Enhancement observenin both the ΔH^* and ΔS^* values is only possioble when the extent (degree) of enhancement in ΔH^* values is more than that of ΔS^* values and from this, it may be inferred that alkali catalysed hydrolysis of Ethyl Iso-valerate is entroy suppressing or controlled and enthalpy dominatin reaction. Such findings and interpretaions have earlier been reported by Singh & Kumari et al[25]. Recently Singh & Bano et al.[26] and Monalisa & Singh et al.[27] have also reported similar observations and inferences

Solvent effect on Iso-kinetic Temperature and Solvent-Solute Interactio:

This reaction is found to obey Barclay and Butler[28] rule and straight line is obtained when ΔH^* values of the reaction is plotted against ΔS^* and from their values tabulated in Table-VI.

The Barcaly and Butler equation is -

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

It is a relation between enthalpy (ΔH^*) and entropy (ΔS^*) of activation values of the reaction and 'β' is called iso-kinetic temperature of the relation which is also called Leffer-Grunwald solvent stabilizer operator[29]. From the values of slope of the plot, the values of Iso-kinetic temperature was evaluated which came to be $330.02 \approx 330.0$. In the light of Leffler's[30] guidelines, from the values of iso-kinetic temperature which is greater than 300, it is inferred that there is a considerable change in the structure of the reactant or in the solvent or in both the reactant and the solvent due to appreciably strong interaction between the solvent and the solute preasent in the reaction media. The structureal chages with increasing proportion of DMSO in aquo-DMSO reaction media are responsible for the depletion observed in the values of the specific rate constant of the reaction. Earlier Singh & Singh et al.[31] and in recent years Haider & Singh et al[32] have also reported similar conclusions about the solvent-solute interaction in the reaction media.

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