Effect of Aquo-DMSO Solvent Systems on the Activation Energies, Thermodynamic Activation Parameters and the Mechanistic Pathways of Catalysed Solvolysis of Propyl Formate

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ABSTRACT

With a view to study the solvent effect on activation energies, mechanistic pathways and Thermodynamic Activation Parameters of the solvolysis of formates, the solvent effect of DMSO on the acid catalysed solvolysis of propyl fromate was studied by carrying out the hydrolysis of the ester in water-DMSO media of varying compositions consisting of 20 to 80% (v/v) of DMSO at different temperatures ranging from 20 to 40°C.

The specific rate constant values of the reaction were found to decrease with increasing concentration of DMSO in the reaction media. It was found that from 0.267 to 1.642 molecules of water are associated with the activated complex and from this, it is concluded that in the presence of DMSO in the reaction media, the mechanistic pathways if the reaction is changed from bimolecular to unimolecular. The depletion observed in the values of the reaction shows that the transition state is solvated and initial state is desolvated with addition of DMSO in reaction media. The unity value of slope of the plots of log k *values against log* $[H^+]$ *values shows that the reaction follows* $A_{AC}2$ *mechanism. From the values of iso-kinetic temperature, i.e. 290, it may be concluded that in water-DMSO reaction media, there is weak but considerable solvent-solute interaction.*

KEYWORDS: Iso-kinetic temperature, Activated complex, Solvation, Desolvation, Structure Breaker, Activation Energies, Enhancement, Depletion, Ionic Strength

INTRODUCTION

In our previous reported works[1,2], effect of dipolar aprotic solvents like DMSO and DMF on the acid catalysed solvolysis of lighter methanoate has been studied but on heavier, aliphatic formate, very few reports are available up till now.

Hence it is thought essential to study the effect of a dipolar aprotic solvent, DMSO on the acid catalysed hydrolysis of propyl formate, as its use as flavouring agent and as a food additive is expected to be discussed in detail for food industry.

EXPERIMENTAL

Export quality of propyl formate, made in USSR and SISCO grade and a Bayer German product of DMSO high purity were used. The kinetics of the reaction was studied by adding 0.5 ml of ester into 50 ml of 0.5M solution of HCl in thermostated condition at desired temperature. The reaction was found to obey the first order kinetic equation and the evaluated values of specific rate constants have been recorded in Table – I. The values of both iso-composition and iso-dielectric activation energies have been mentioned in Table – II Table – III respectively.

The evaluated values of the water molecules associated with the transition state of the reaction at different temperatures have been tabulated in Table-IV. The consolidated values of thermodynamic activation parameters of ΔG*, ΔH* and ΔS* were evaluated using Wynne-Jones and Eyring[3] equation and are enlisted in Table –V.

Results and Discussion:

Table – I shows that the constant values of the reaction decreases with increasing proportion of DMSO in the reaction media. On plotting log k values against mol% of DMSO, it is obvious that up to 15 mol% of the DMSO in the reaction media, the rate of the reaction falls rapidly but beyond 15mol% of DMSO, the depletion in the rate follows slow path.

From the plot, it is apparent that on gradual addition of DMSO in the reaction media at lower temperature, the depletion in the rate of reaction is low but it becomes sharper with increase in temperature of the reaction.

The decreasing trend in the values of the rate constants needs to be discussed in the light of Hughes and Ingold[4] predictions according to which an increase in the dielectric constant values of the reaction media causes an increase in the rate when there is concentration or constructions 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. The values of dielectric constants of the reaction media go on decreasing with gradual addition of DMSO, so our findings are fully in accordance with the qualitative prediction of Hughes and Ingold. However, our findings are also in agreement with the qualitative prediction of Laidler and Landskroener[5] and also with the earlier report of Kiranmayee[6] and Kumar & Singh *et al.*[7] who predicted that the rate of ion dipolar reaction decreases with decrease in the dielectric constant values of the reaction media. However, it is concluded that in this case, both the dielectric effect and solvation effect (solvation of the transition state) are responsible for slow and sharp depletion in the reaction rate. In recent years Lal & Singh *et al.*[8] have also reported similar findings and their interpretations for solvent effect on the solvolysis of different esters.

Solvent effect on activation energies (Iso-composition and iso-dielectric) of the reaction:

From Table – II, it is obvious that E_C values go on decreasing with increasing the concentration of DMSO in reaction media. This trend 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 initial and transition states as reported earlier by several researchers[9,10] in this field. Considering the extent of solvation to be a dominant factor, the following three factors seem to be responsible for decrease in E_C values with gradual addition of DMSO in the reaction media:

(i) The transition state is desolvated less than the initial state,
(ii) The transition state is solvated more than the initial state, and
(iii) The transition state is solvated and the initial state is desolvated

The transition state being large cation (ester $+H^+$) is available more for solvation by DMSO molecule than the initial state, so the third factor seems to be operative in this case and it is also supported by the recent reports of Ojha & Singh *et al.*[11].

Iso-dielectric Activation Energy:

With a view to minimise the dielectric effect, the iso-dielectric activation energy was evaluated from Arrhenius plots of log k_D values (obtained from interpolation of plots of log k values against D values of the reaction media) against 1/T adopting the methods of Wolford[12] and Elsemongy *et al.*[13] and the values thus obtained have been tabulated in Table – III. From the table, it is found that E_D values go on increasing from 63.15 to 107.32 kJ/mol with increase in D values from D = 64 to D = 74 respectively. This trend of increase in E_D values is quite in agreement with changes in E_C values of this reaction and also with the findings of Wolford[12] and the recent reports of Raj Laxmi & Singh *et al.*[18].

Effect of Solvent on the Mechanism of the Reaction:

For establishing the mechanistic pathways of the reaction, Robertson[14] gave an idea of solvation number 'n' which is the number or the number of water molecules involved in the formation of the activated complex and for its evaluation he proposed the equation:

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

Robertson et al[15] have established the principle that the values of solvation number (n) for the reaction following unimolecular mechanistic pathway is fairly high but for the reaction following bimolecular path, it will be low.

The number of water molecules 'n' involved in the formation of the activated complex of the reaction were determined by plotting log k values against log $[H_2O]$ value for alkali catalysed hydrolysis of methyl nicotinate in aquo-ethanol media. The value of log k and log $[H_2O]$ have been tabulated in Table – V. The numerical values of the slopes of plots have been recorded in Table - VI.

From the plot, it is clear that at each temperature of the reaction, the plots of log k versus log $[H_2O]$, two intersecting straight lines having, different values of slopes are obtained at log $[H_2O]$ value at about 1.475 which corresponds to 53.70% of water in aquo-ethanol media.

From the values recorded in Table - VI, it is clear that below log $[H_2O]$ value 1.475, which corresponds to 53.70% of water in the reaction media, the number of water molecules associated with the activated complex decreases from 0.930 to 0.329 with rise in temperature of the reaction from 20 to 40°C. Similarly, in case of above, 53.70% of water concentration in the reaction media, the values of slopes decreases from 1.341 to 0.329 with increase in temperature from 20 to 40°C of the reaction. Overall, it may be inferred that number of water molecules associated with the activated complex in its formation decreases from 1.341 to 0.329.

In the light of guidelines of Robertson *et al.*[15] from the decreasing number of water molecules from 1.341 to 0.329 involved in the formation of the activated complex, it may be inferred that the mechanistic pathway followed by the reaction is changed from unimolecular to bimolecular in presence of ethanol in the reaction media and with increase in temperature of the reaction from 20 to 40°C.

Regarding the changes in the structure of water, it is obvious that in presence of ethanol and with rise in temperature, water components of the reaction media, changes its structure from bulky to dense form.

$$(H_2O)_b \; ; \; (H_2O)_d$$

Such findings and inferences have also been reported earlier by Singh and

Wats *et al.*[16] and recently by Prashansa & Singh *et al.*[17].

Solvent effect on Thermodynamic Activation Parameters of the Reaction:

The solvation number, i.e., the number of water molecules associated with the activated complex evaluated from the slopes of the plots of log k versus log [H_2O] have been mentioned in Table – IV.

From the plot and Table – IV, it is apparent that before and after log [H_2O] value approx. 1.5 which corresponds to 56.90% of water in the reaction media, the values of the slopes of the two intersecting straight lines are different.

Before log [H_2O] value 1.5 which corresponds to approx. 56.90% of water in the reaction media, the values of the solvation number (n), i.e., the number of water molecules associated with the Transition state (activated complex of the reaction increases from 0.267 to 1.006, whereas after log [H_2O] value 1.5, the values of n increases from 0.490 to 1.642 with increase in temperature of the reaction from 20 to 40^OC.

Thus, the guidelines of Robertson et. al.[15] which suggests that the value of 'n' for unimolecular reaction is fairly high while that for bimolecular reaction it will be low, it is inferred that the mechanistic pathways of the acid catalysed hydrolysis of propyl formate is changed from bimolecular to unimolecular in presence of DMSO in the reaction media and also with increasing temperature of the reaction from 20 to 40^OC.

It is also inferred that on gradual addition of DMSO in the reaction media at equilibrium, the dense form of water is changed to its bulky form.

$$(H_2O)_d \rightleftharpoons (H_2O)_b$$

Our such interpretations and inferences have also recently been supported by Sabita & Singh *et al.*[16].

Effect of change of DMSO concentration on the Thermodynamic Activation Parameters of the Reaction:

The evaluated values of three thermodynamic activation parameters, i.e., ΔH*, ΔG* and ΔS* are depicted in Table-V. From their values in Table -V, it is evident that enhancement observed in ΔG* values is followed by simultaneous depletion in both the values of ΔH* and ΔS*. The variations observed in ΔH*, ΔG* and ΔS* with mol % of DMSO in the water-DMSO media have been plotted. The non-linear variation of the plots is sign of specific solvation and desolvation of transition and initial state respectively as reported earlier by Saville and Hudson[17], Tommila *et al.*[18] and Hyne *et al.*[19].

Simultaneous increase in $\Delta G*$ values followed by decrease in ΔH^* and ΔS^* is only possible when the degree of depletion in ΔS* values is greater than that observed in ΔH* values. From this, it may be inferred that the acid catalysed hydrolysis of propyl formate in presence of DMSO in reaction media is enthalpy stimulator and entropy deactivator. These findings are found in support of the recent findings of Sinha & Singh[20].

Effect of [H^+]:

The effect of change in hydrogen ion concentration [H+] has also been studied by keeping the ionic strength, % of DMSO and temperature of the reaction constant at μ=0, 30% DMSO (v/v) and 30^OC respectively. The evaluated k values at different [H^+] ion strength in the reaction have been mentioned in Table – VI.

The plot of log k values against log [H^+] are found to have a good straight line with the value of slope equal to 1.018 which may be treated as almost equal to unity. This value of slope (equal to unity) indicates that acid catalysed hydrolysis of propyl formate in water DMSO media follows the pathway of $A_{AC}2$ mechanism as reported by Zucker and Hammett[21].

Similar conclusions have also been reported by Raghaw & Singh et. al.[22].

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Table – I

Specific rate constant values of Acid catalysed hydrolysisof Propyl Formate in water-DMSO media [HCl]=0.5M

$k \times 10^4$ min^{-1}

Temp in °C	% of DMSO(v/v)						
	20%	30%	40%	50%	60%	70%	80%
20°C	52.60	49.22	46.78	44.47	41.99	38.73	35.05
25°C	104.28	93.35	83.75	78.58	68.56	59.90	51.05
30°C	206.16	178.24	153.85	133.69	113.01	92.92	74.13
35°C	386.46	328.10	270.46	220.80	180.03	140.31	115.08
40°C	738.07	594.29	468.81	369.83	285.89	209.41	151.39

Table - II

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 kJ/mol	100.53	95.23	89.27	81.80	73.87	64.48	57.94

Table - III

Values of Iso-Dielectric Activation Energy (E_D) of the reactionat desired 'D' values of water-DMSO media

D values	**D= 64**	**D = 66**	**D = 68**	**D =70**	**D = 72**	**D = 74**
E_D values in kJ/mol	63.15	72.08	83.22	89.63	102.11	107.32

Table - IV

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

Temperature in °C	Slope - I Where log [H_2O] value is below 1.5	Slope – II where log [H_2O] value isabove 1.5
20°C	0.267	0.490
25°C	0.430	0.819
30°C	0.665	0.966
35°C	0.724	1.340
40°C	1.006	1.642

Table – VI

Effect of [H^+] on the Specific rate constant values of Acid Catalysed Hydrolysis of Propyl Formate in water-DMSO media at constant ionic strength ($\mu = 0.9$) DMSO=20% (v/v)

Concentration of Glycerol=20% (v/v)

Temp 25°C

[H^+]	[KCl]	μ	$k \times 10^4$ in min^{-1}	2+log[H^+]	4 + log k	Value of the Slope of the Plots of log k versus log [H+]
0.10	0.80	0.90	40.00	1.0000	1.6021	
0.15	0.75	0.90	60.10	1.1761	1.7789	
0.20	0.70	0.90	80.87	1.3010	1.9078	
0.25	0.65	0.90	101.88	1.3979	2.0081	1.018
0.30	0.60	0.90	122.46	1.4771	2.0880	
0.40	0.50	0.90	163.68	1.6021	2.2140	
0.50	0.40	0.90	201.16	1.6990	2.3142	
0.60	0.30	0.90	250.09	1.7782	2.3981	
0.70	0.20	0.90	291.41	1.8451	2.4646	
0.80	0.10	0.90	331.97	1.9030	2.5211	

Table- V

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)	Mol%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	98.82	94.46	14.89	94.11	15.80	94.11	15.80	94.01	15.62	93.90	15.72
30%	9.77	93.03	94.62	-5.42	94.38	-4.54	94.38	-4.47	94.43	-4.52	94.46	-4.57
40%	14.40	85.78	94.74	-30.75	94.65	-30.43	94.76	-29.77	93.92	-29.82	95.08	-29.84
50%	20.17	78.07	94.87	-57.34	94.88	-56.40	95.11	-56.24	95.44	-56.41	95.69	-56.31
60%	27.49	70.46	95.01	-83.79	95.15	-82.85	95.57	-82.75	95.96	-82.80	96.36	-82.76
70%	37.09	62.16	95.02	-112.79	95.48	-111.83	96.02	-111.77	96.60	-111.82	97.17	-111.86
80%	50.27	52.30	95.39	-147.06	95.88	-146.22	96.59	-146.16	97.10	-145.46	98.01	-146.03