

KINETIC STUDIES OF THE SOLVENT EFFECT OF AQUO-DMSO SOLVENT SYSTEMS ON THE EXTENSIVE THERMODYNAMIC PROPERTIES OF ACID CATALYSED SOLVOLYSIS OF HIGHER METHANOATES

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Abstract

With a view to study the solvent effect on the extensive thermodynamic properties of Acid catalysed solvolysis of higher methanoate, the kinetics of the reaction was studied in water-DMSO media of varying composition 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 of the reaction is changed from bimolecular to unimolecular. The depletion observed in the values of iso-composition activation energy of the reaction shows that the transition state is solvated and initial stage 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: - Extensive, solvolysis, Mechanism, Iso-composition, and iso-dielectric, solvated, Desolvated, Weak Interaction.



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INTRODUCTION: In the previously reported works¹⁻⁴, effect of dipolar aprotic solvents like DMSO and DMF on the acid catalysed solvolysis of lighter methanoate have been studied but on heavier and aromatic methanoate, 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 methanoate, as its use as flavouring agent and as a food additive is expected to be discussed in detail for food industry.

Experimental & Calculation: Export quality of propyl methanoate, made in USSR and SISCO grade and a Bayer German product of DMSO were used. The kinetics of the reaction was studied by adding 0.5 ml of the ester into 50 ml of 0.5 M HCl solution 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 and 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 Δ^* , ΔH^* and ΔS^* were evaluated using Wynne-Jones and Eyring⁵ equation and are enlisted in Table - V.

Results and Discussion :

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 mole % of

Table – I Specific rate constant values of Acid catalysed hydrolysis of Propyl methanoate in water-DMSO media [HCl] = 0.5M
K × 10⁴ in 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 (v/v)	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 reaction at Desired D values of water-DMSO media.

Dielectric constant values	D= 64	D = 66	D = 68	D =70	D = 72	D = 74
E_D values in kJ/mole	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 [H₂O] in water-DMSO media at different temperatures

Temperature in °C	Slope - I Where log[H ₂ O] is below 1.5	Slope - II when log[H ₂ O] is above 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

DMSO it is obvious that up to 15 mole % of the DMSO in the reaction media, the rate of the reaction falls rapidly but beyond 15 mole % of DMSO, the depletion in the rate follows slow path.

From the plots 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 Ingold⁶ 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 stage and causes a decrease in the rate when there is diffusion or destruction of charges on the transition stage. The values of

dielectric constants 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 of Laidler and Landskroener⁷ and also with the recent report of Kiranmasyee⁸ and Kumar and Singh⁹ 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

Table- V Consolidated Values of Enthalpy of activation (ΔH^*), Free energy of activation (ΔG^*) and Entropy of activation (ΔS^*) of the reaction at different mole % of DMSO in water-DMSO media.

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	98.82	94.46	14.89	94.11	15.80	93.98	15.98	94.01	15.62	93.60	15.72
30%	9.77	93.03	94.62	-5.42	94.38	-4.54	94.39	-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	94.92	-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	95.20	-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

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 charges 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 researchers^{10,11} 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 desolated 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 desolated.

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 report of Kumar and Singh⁹.

Iso-dielectric Activation Energy:

With a view to minimise the dielectric effect, the iso-dielectric activation energy was evaluated from the Arrhenius plot of $\log k_D$ values (Obtained from interpolation of the plots of $\log k$ values against D values of the reaction media) against $1/T$ adopting the methods of Wolford¹² and Elsemongy et.al.¹³ and the value 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 Wolford¹² and the report of Kumar and Singh⁹.

Effect of Solvent on the Mechanism 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.

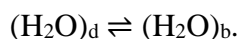
From Table - IV it is apparant that before and after $\log [H_2O]$ value approx. 1.5 which corresponds to 56.90% of water in the reaction media, the values of the slopes of the two intersecting straight lines are different.

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 [H₂O] 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°C.

Thus, the guidelines of Robertson et al.,¹⁴ 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 methanoate is changes from bimolecular to unimolecular in presence of DMSO in the reaction media and also with increasing temperature of the reaction from 20 to 40°C.

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.



our such interpretations and inferences have also recently been supported by Singh & Bala et al¹⁵ and Kumar & Singh et al¹⁶.

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

The evaluated values of three thermodynamic activation parameters i.e. ΔG^* , ΔH^* 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 non linear variations observed in ΔH^* , ΔG^* and ΔS^* were observed with mole % of DMSO in water-DMSO. The non-linear variation is sign of specific solvation and desolvation of transition and initial state respectively as reported earlier by Tommila et al.¹⁷, Saville et al.¹⁸ and Hyne et al.¹⁹.

Simultaneous increase in ΔG^* values followed by decrease in ΔH^* and ΔS^* is only possible when the degree of depletion in ΔS^* value is greater than that observed in ΔH^* values. From this, it may be inferred that the acid catalysed hydrolysis of propyl methanoate in presence of DMSO in reaction media is enthalpy stimulator and entropy deactivator. These findings are supported recently by Kumar and Singh⁹ and Singh et al.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 u=0.90, 30% DMSO(v/v) and 30°C 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 methanoate in water DMSO media follows the pathway of A_{AC}² mechanism as reported by Zucker and Hammett²¹.

Similar conclusions have also been reported earlier by Pandey and Singh et al.²². and recently by Abhay & Singh et al²².

Table – VI Effect of (H⁺) on the specific rate constant values of Acid catalysed hydrolysis of Propyl methanoate in water-DMSO media at constant ionic strength (μ = 0.9)

DMSO - 20% (v/v)

Temp. 30°C

[H ⁺]	[KCl]	μ	k × 10 ⁴ in min ⁻¹	2 + log[H ⁺]	4 + log k	Value of the slope of the plot 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	25211	

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