

The Kinetic Study of the Solvent Effect of Hydrogen Bonding of Aquo-protic Solvent Systems on the Acid Catalysed Hydrolysis of Secondary Aliphatic Methanoate

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ABSTRACT

The effect of hydrogen bonding existing in the reaction media has been highlighted by studying the acid catalysed solvolysis of iso-propyl methanoate in aquo-ethanol solvent systems.

The depletion and enhancement observed respectively in iso-composition and iso-dielectric activation energies reveal that the transition state is solvated and initial state is desolvated with gradual addition of Methanoate in reaction media.

Almost unity value of the 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, which comes to be 284.17, it may be inferred that in aquo-EtOH reaction media, the reaction follows Barclay-Butler rule and there is weak but considerable interaction between solvent and solute in aquo-EtOH (aquo-ethanol) reaction media.

KEYWORDS: Protic Solvent, Secondary aliphatic methanoate, Iso-dielectric, Iso-kinetic, specific solvation, Barclay-Butler rule, Desolvation, Solvent-solute interaction, Mechanistic pathways.

INTRODUCTION

In order to explore the effect of hydrogen bonding present in aquo-dipolar-protic solvent systems on the biochemical use as a flavouring agent of higher substituted methanoate, it has been proposed in the best interest of mankind and society to study the kinetics of $[H^+]$ ion catalysed solvolysis of iso-propyl methanoate in aquo-EtOH

reaction media.

EXPERIMENTAL & CALCULATION

Export quality of Iso-Pentyl methanoate made in U. S. S. R. and Merk grade of ethyl alcohol of high purity (absolute alcohol) were used. The kinetics of reaction was studied by adding 0.60 ml of ester Iso-propyl methanoate through a German make graduated syringe pipette into 50ml of 0.5 M solution of HCl. 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 variation of $\log k$ values with mol% of EtOH have been tabulated in Table – II and variation of $\log k$ with $\log [H_2O]$ of the reaction media are recorded in Table – III. From the slopes of the plots of $\log k$ versus $\log [H_2O]$, the number of water molecules associated with the transition state of the reaction have been evaluated and are placed in Table – IV.

The values of both the iso-composition and iso-dielectric activation energies have been enlisted in Table – V and Table – VI respectively. The numerical values of thermodynamic activation parameters were calculated using Absolute Rate Theory¹ and Wynne-Jones & Eyring equation² and are synchronised in Table – VII. Effect of change in $[H^+]$ ion concentration of the reaction media on the specific rate constants of the reaction has been shown in Table – VIII.

RESULTS AND DISCUSSION:

From Table – I it is obvious that the specific rate constants of the

reaction decrease with increasing proportion of EtOH in the reaction media. On plotting $\log k$ values against mol% of EtOH (from recorded values in Table – II), it has been found that up to approx 30.0 mol% of EtOH in the reaction media, the rate of reaction falls rapidly but beyond (above) 30.0mol% of EtOH, the depletion in the rate follows slow path. From the plots, it is also apparent that with increase in temperature of the reaction, the rate of reaction decreases more sharply. The decreasing trend in the values of the specific rate constants needs to be discussed in the light of the theory of Hughes and Ingold³, 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 EtOH. So the findings are fully in accordance with the qualitative prediction of Hughes and Ingold³. However, these findings and their interpretations have been found fully in agreement with the qualitative prediction of Laidler and Landskroener⁴ and also with the earlier reported findings R. T. Singh⁵. In recent years Sinha⁶ and Namrata & Singh⁷ have also communicated similar findings and inferences for depletion observed in the rate of different catalysed solvolysis reactions.

Evaluation of number of water molecules involved in the formation of activated complex of the reaction and Establishment of the mechanisms of the reaction:

Robertson⁸ has formulated an equation, which is as:

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

where 'n' is the salvation number, i.e., the number of water molecules associated with the transition state of the reaction and is evaluated from the slopes of the plots of $\log k$ versus $\log[H_2O]$.

Robertson *et al.*⁹ have suggested that value of 'n' for unimolecular reactions is fairly high while that of bimolecular reactions, it will be low.

From the recorded values of $\log k$ and $\log[H_2O]$ in Table – III, the $\log k$ values were plotted against $\log[H_2O]$ and the evaluated values of the slopes of the straight lines have been enlisted in Table – IV.

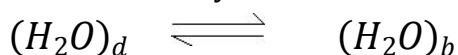
From the plots, it is clear that at each temperature two intersecting straight lines are obtained at $\log[H_2O]$ value -1.433 which corresponds to 49.00% of water concentration (v/v) in aquo-ethanol reaction media.

From the recorded values of the slopes of the plots of $\log k$ versus $\log[H_2O]$ in Table – IV, it is clear that below or before $\log[H_2O]$ value 1.433, which corresponds to 49.00% of water in the reaction media, the number of water molecules associated with the activated complex increases from 0.262 to 0.592 with increase in temperature of the reaction from 20 to 40°C. Similarly, for above 49.00% water concentration in the reaction media, the number of water molecules involved in the formation of the activated complex increases from 0.416 to 1.018 with rise in temperature from 20 to 40°C.

Overall, it is concluded that number of water molecules associated with the activated complex increases from 0.262 to 1.018 with rise in temperature from 20°C to 40°C and from this trend, in the light of the guidelines of Robertson *et al.*⁹, it is inferred that the mechanistic pathway of the reaction is changed from bimolecular to unimolecular with increase in water concentration or with

decrease in ethanol content of the reaction media and also with increase in the temperature of the reaction.

From the enhancing trend of number of water molecules involved in the formation of the activated complex, it is also inferred that on addition of EtOH in the reaction media, the equilibrium of water is shifted from its dense form to bulky form.



Such observations and inferences and their interpretations have been earlier reported by Singh & Singh *et al.*¹⁰ and also recently by Sushma & Singh *et al.*¹¹ and Ojha & Singh *et al.*¹².

Solvent Effect on Iso-composition Activation energy (E_c) of the Reaction:

From the slopes of Arrhenius plots of $\log k$ versus $10^3/T$, the values of iso-composition activation energy (E_c) of the reaction have been evaluated and are tabulated in Table – V. From Table – V, it is obvious that E_c values go on decreasing from 95.09 to 70.09 kJ/mol with increasing the concentration of EtOH from 20 to 80% (v/v) 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 Elsemongy *et al.*¹³ 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 EtOH in the reaction media:

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

The transition state being large cation (ester +H⁺) is available more for solvation by ethanol molecule than the initial state, so the first factor seems to be operative in this case and it is also supported by the decrease in entropy of activation (ΔS^*) of the reaction as shown in Table – VII. So situation first is more plausible explanation for decrease in E_c values of the reaction as recorded in Table – V.

It is, therefore, inferred that E_c values of the reaction go on decreasing due to solvation of the transition state and desolvation of initial state. Similar findings and interpretations have also been reported earlier by Dubey & Singh *et al.*¹⁴ and recently by Laxmi & Singh *et al.*¹⁵.

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

In order to minimise the dielectric effect, the iso-dielectric activation energy was evaluated from the slopes of the Arrhenius plots of $\log k_D$ values (obtained from interpolation of plots of $\log k$ values against D values of the reaction media) against $1/T$. The values thus obtained have been tabulated in Table – VI. From this table, it is observed that E_D values go on increasing from 77.58 to 100.23 kJ/mol with increase in D values from $D = 35$ to $D = 65$. This trend of increase in E_D values is quite in agreement with changes (decrease) in E_c values of this reaction and also with the findings of Welford¹⁶ and earlier Singh & Perween *et al.*¹⁷ as well as recently Laxmi & Singh *et al.*¹⁸ have also reported similar interpretations for the effect of reaction media on the Iso-dielectric Activation energy (E_D) of the solvolysis reactions.

Solvent Effect on Thermodynamic Activation Parameters of the Reaction:

The three thermodynamic activation parameters namely enthalpy

of activation (ΔH^*), the free energy of activation (ΔG^*) and entropy of activation (ΔS^*) of the reaction were evaluated using Wynne-Jones and Eyring equation² and have been mentioned in Table – VII. From the values enlisted in Table – VII, it is clear that ΔG^* values of the reaction go on increasing with simultaneous decrease in both the ΔH^* and ΔS^* values of the reaction.

In order to study the variations in these thermodynamic parameters more clearly, they were plotted against mol% of EtOH. From the plots, it is clear that all of them vary non-linearly to the considerable extent with the increasing concentration (mol%) of EtOH and this is the indication of specific solvation taking place in the reaction media according to Saville and Hudson¹⁹.

The ΔH^* and ΔS^* are complimentary to each other as the resulting net property of ΔG^* in Table – VII is a well behaved function. From the values of ΔG^* in Table – VII, it is clear that ΔG^* is being little affected by the solvent composition (mol%). However there is considerable enhancement (from 82.20 to 84.04 kJ/mol at 30°C) in ΔG^* values.

From Table – VII, it is also clear that ΔG^* values are found to increase simultaneously with depletion in both the ΔH^* and ΔS^* values.

From the thermodynamic relation:

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

it is apparent that enhancement in ΔG^* values with simultaneous decrease in both of ΔH^* and ΔS^* values of the reaction is only possible when the extent of depletion in ΔS^* values is greater than in ΔH^* values. From these findings, it is concluded that the acid catalysed hydrolysis of Iso-propyl methanoate in aquo-ethanol media is entropy controlled and enthalpy dominated reaction.

Similar findings and inferences have also been reported earlier by Prashansa & Singh *et al.*²⁰.

Solvent Effect on Solvent-Solute Interaction in the Aquo-Methanoate Reaction media:

For evaluating the solvent-solute interaction for a solvolysis reaction, Barclay and Butler²¹ have correlated the enthalpy of activation (ΔH^*) and the entropy of activation (ΔS^*) by means of the relationship:

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

where, β is a constant called iso-kinetic temperature and it is evaluated from the slope of plots of ΔH^* values against ΔS^* value.

From the recorded values of ΔH^* and ΔS^* in Table – VII, ΔH^* values were plotted against ΔS^* (at 30°C). The plot consists of a straight line whose slope value has been evaluated to be $280.17 \approx 280.0$ which is less than 300. Following the guidelines of Leffler²², it is concluded that there is weak but considerable solvent-solute interaction for acid catalysed hydrolysis of Iso-propyl methanoate in aquo-ethanol reaction media.

Similar interpretations for weak solvent-solute interaction have also been reported earlier by Singh & Singh *et al.*²⁴, Kumar & Sharma *et al.*²⁵ and recently by Sabita & Singh²⁵.

Effect of Change of [H⁺] in concentration of the Reaction Media on the Mechanism of the Reaction:

In order to investigate the effect of change in acid concentration of the reaction media (H^+ in concentration) on the specific rate constant of the acid catalysed hydrolysis of Iso-propyl methanoate in aquo-ethanol media, experiments were performed to study the kinetics at various concentration of HCl (from 0.1M to 0.8M), keeping the temperature, solvent composition and ionic strength of the reaction media constant. The reactions were carried out

at 25° C in the reaction media having 20% (v/v) concentration of ethanol and the evaluated values of specific rate constants have been tabulated in Table – VIII. From the tabulated values of log k and log [H⁺] in Table – VIII, log k values were plotted against log [H⁺] and from the plot it is clear that the plot is an excellent straight line showing linear dependence of rate of reaction on [H⁺] ion concentration. The slope of the log k versus log [H⁺] plot is evaluated to be 1.004 which is almost equal to unity.

From this value of slope (unity), it may be inferred on the basis of the hypothesis of Zucker and Hammett²⁶ that acid catalysed hydrolysis of Iso-propyl methanoate in aquo-ethanol media follows A_{AC^2} mechanism.

Similar observations, inferences and their interpretations have also been reported in recent years by Ashutosh & Singh²⁸.

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Table - I
Specific Rate Constants Values of Acid Catalysed Hydrolysis of Iso-Propyl Methanoate in Water-EtOH Media
 $k \times 10^3$ in min^{-1}

Temp in °C	% of EtOH (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20°C	71.46	67.00	63.58	59.50	55.31	52.07	48.00
25°C	134.83	124.97	115.40	105.83	95.26	86.78	77.30
30°C	256.68	230.89	208.40	185.69	163.49	143.45	123.40
35°C	467.52	411.91	387.44	314.27	271.08	230.78	191.12
40°C	855.85	734.85	631.10	534.69	447.20	369.91	296.07

Table II
Variation of log k values of the reaction at different temperature with mol% of Iso-Propyl Methanoate in Water-EtOH Media

% of EtOH	Mol% of EtOH	3 + log k values				
		20°C	25°C	30°C	35°C	40°C
20%	7.17	1.8541	2.1298	2.4094	2.6698	2.9324
30%	11.69	1.8261	2.1037	2.3634	2.6148	2.8662
40%	17.07	1.8033	2.0622	2.3189	2.5882	2.8000
50%	23.59	1.7752	2.0246	2.2688	2.4973	2.7281
60%	31.06	1.7428	1.9789	2.2135	2.4331	2.6505
70%	41.87	1.7166	1.9384	2.1567	2.3632	2.5681
80%	55.85	1.6812	1.8882	2.0913	2.2813	2.4714

Table III

Variation of log k values of the reaction with log [H₂O] values of Water-EtOH system (media) at different temperatures

% of EtOH	% of H ₂ O	log [H ₂ O]	3+ log k values				
			20°C	25°C	30°C	35°C	40°C
20%	80%	1.6478	1.8541	2.1298	2.4094	2.6698	2.9324
30%	70%	1.5898	1.8261	2.1037	2.3634	2.6148	2.8662
40%	60%	1.5229	1.8033	2.0622	2.3189	2.5882	2.8000
50%	50%	1.4437	1.7752	2.0246	2.2688	2.4973	2.7281
60%	40%	1.3468	1.7428	1.9789	2.2135	2.4331	2.6505
70%	30%	1.2218	1.7166	1.9384	2.1567	2.3632	2.5681
80%	20%	1.0458	1.6812	1.8882	2.0913	2.2813	2.4714

Table - IV

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

Temp. in °C	Slope - I when log [H ₂ O] value is below 1.433	Slope - II when log [H ₂ O] value is above 1.433
20°C	0.262	0.416
25°C	0.305	0.647
30°C	0.459	0.766
35°C	0.506	0.894
40°C	0.592	1.018

Table - V

Evaluated Values of Iso-Composition Activation Energy (E_c or E_{exp}) of the reaction in Water-EtOH Media

% of EtOH (v/v)	20%	30%	40%	50%	60%	70%	80%
E _c values in kJ/Mol	95.09	92.64	88.59	84.67	80.57	75.67	70.09

Table - VI
Evaluated Values of Iso-Dielectric Activation Energy (E_D) of the reaction at different Desired 'D' Values of the Water-EtOH Media

D value	D=35	D=40	D=45	D=50	D=55	D=60	D=65
E_D values in kJ/Mol	77.58	81.75	85.26	89.21	94.15	96.44	100.23

Table VIII
Effect of $[H^+]$ on the Specific Rate Constant Values of Acid Catalysed Hydrolysis of Iso-Propyl Methanoate in Water-EtOH Media at Constant Ionic Strength ($\mu=0.9$)

Concentration of EtOH=20% (v/v)

Temp 25°C

$[H^+]$	$[KCl]$	μ	$k \times 10^3$ in min^{-1}	$2 + \log[H^+]$	$3 + \log k$	Value of the Slope of the Plots of $\log k$ versus $\log [H^+]$
0.10	0.80	0.90	26.98	1.0000	1.4311	
0.15	0.75	0.90	40.44	1.1761	1.6068	
0.20	0.70	0.90	53.69	1.3010	1.7299	
0.25	0.65	0.90	67.58	1.3979	1.8298	
0.30	0.60	0.90	80.32	1.4771	1.9048	1.004
0.40	0.50	0.90	107.45	1.6021	2.0312	
0.50	0.40	0.90	134.83	1.6990	2.1298	
0.60	0.30	0.90	162.63	1.7782	2.2112	
0.70	0.20	0.90	190.46	1.8451	2.2798	
0.80	0.10	0.90	217.67	1.9030	2.3378	

Table VII

Consolidated Values of Activation Parameters (ΔH^* , ΔG^* , ΔS^*) of the reaction in Water-EtOH System at different temperatures

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

% of EtOH	Mol% of EtOH	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%	7.17	93.38	82.52	37.07	82.40	36.86	82.20	39.90	82.06	36.74	81.86	36.80
30%	11.69	89.46	82.68	23.15	82.55	23.20	82.47	23.08	82.39	22.96	82.26	23.00
40%	17.07	85.69	82.80	9.83	82.78	9.74	82.72	9.77	82.54	10.20	82.66	9.68
50%	23.59	81.71	82.96	-4.27	83.00	-4.32	83.02	-4.31	83.08	-4.45	83.09	-4.40
60%	31.06	78.64	83.14	-15.37	83.26	-15.50	83.34	-15.49	83.46	-15.64	83.55	-15.69
70%	41.87	73.79	83.29	-32.43	83.49	-32.55	83.67	-32.59	83.87	-32.73	84.05	-32.77
80%	55.85	67.83	83.49	-53.45	83.78	-53.51	84.04	-53.52	84.35	-53.65	84.63	-53.66