Studies on the Kinetics of [H⁺] ion Catalysed Solvolysis of Higher Formate in Aquo-Aprotic Solvent Reaction Media

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ABSTRACT

The solvent effect of a dipolar aprotic solvent has been highlighted by studying the kinetics of acid catalysed solvolysis of iso-pentyl formate in aquo-acetone 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 acetone 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 286.93, it is be inferred that in aquo-acetone reaction media, the reaction follows Barclay-Butler rule and there is weak but acceptable interaction between solvent and solute in aquo-acetone reaction media.

KEYWORDS: Solvolysis, Dipolar aprotic, Solvent, Solvation and Desolvation, Iso-kinetic temperature, Flavouring agent, Weak interaction, Catalysed solvolysis.

INTRODUCTION

In order to explore the effect of dipolar aprotic solvent on the biochemical use as a flavouring agent of higher substituted formate, it has been proposed in the best interest of mankind and the society to study the kinetics of [H⁺] ion catalysed solvolysis of iso-pentyl formate in aquo-acetone reaction media.

EXPERIMENTAL & CALCULATION

Export quality of Iso-Pentyl formate made in U. S. S. R. and Merk grade of acetone of high purity were used. The kinetics of reaction was studied by adding 0.70 ml of ester Iso-pentyl formate 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 acetone 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 slope 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 Wynne-Jones & Eyring equation[1] 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 acetone in the reaction media. On plotting log k values against mol% of acetone (from recorded values

in Table – II), it has been found that up to 22.50 mol% of acetone in the reaction media, the rate of reaction falls rapidly but beyond (above) 22.50 mol% of acetone, 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 Ingold[2], 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 acetone. So the findings are fully in accordance with the qualitative prediction of Hughes and Ingold[2]. However, these findings and their interpretations have been found fully in agreement with the qualitative prediction of Laidler and Landskroener[3] and also with the earlier reported findings Raghaw & Singh et. al.[4], Singh & Perween et. al.[6], Abhay & Singh et. al.[6] and R. T. Singh[7]. In recent years Renu & Singh et. al.[8] 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:

Robertson[9] 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 values recorded in Table - IV, it is clear that at each temperature two intersecting straight lines are obtained at $\log[H_2O]$ value -1.470 which corresponds to 53.10% of water concentration (v/v) in water-acetone reaction media.

From the recorded values of the slopes of the plots of log k versus $\log[H_2O]$ in Table – III, it is clear that below or before $\log[H_2O]$ value 1.470, which corresponds to 53.10% of water in the reaction media, the number of water molecules associated with the activated complex increases from 0.258 to 0.592 with increase in temperature of the reaction from 20 to 40^0C. Similarly, for above 53.10% water concentration in the reaction media, the number of water molecules involved in the formation of the activated complex increases from 0.569 to 1.136 with rise in temperature from 20 to 40^0C.

Overall, it is concluded that number of water molecules associated with the activated complex increases from 0.258 to 1.136 with rise in temperature from 20°C to 40°C and from this trend, in the light of the guidelines of Robertson *et al.*[10], 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 acetone 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 acetone in the reaction media, the equilibrium of water is shifted from its dense form to bulky form.

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

Such observations and inferences and their interpretations have been earlier reported by Kumar & Singh *et al.*[11], Singh & Singh et. al.[12] and also recently by Laxmi & Singh *et al.*[13].

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 109.55 to 67.97 kJ/mol with increasing the concentration of acetone 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.*[14] 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 Acetone in the reaction media:

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

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

(iii) The transition state is desolvated less than the initial state

The transition state being large cation (ester $+H^+$) is available more for solvation by acetone 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.*[15], Singh & Singh et. al.[16], Achari & Singh[17] and also recently by Prashansa & Singh *et al.*[18].

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 79.23 to 105.34 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 Wolford[19] and with the earlier reports of Singh & Singh *et al.*[20] and Singh & Pathak et. al.[21], Singh & Hafizee[22] and recently Sinha & Singh[23] have also reported similar interpretations for the changes in 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 equation[1] 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 acetone. From the plots, it is clear that $\Delta H^*, \Delta G^*$ and ΔS^* vary non-linearly to the considerable extent with the increasing concentration (mol%) of acetone and this is the indication of specific solvation taking place in the reaction media according to Saville and Hudson[24].

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 98.94 to 100.92 kJ/mol at $30^0 C$) 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-pentyl formate in aquo-acetone media is entropy controlled and enthalpy dominated reaction.

Such observations, inferences and interpretations have also been reported earlier by Choubey & Singh *et al.*[25], Sharma & Singh et. al.[26] and recently by Rakesh & Singh et. al.[27].

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

With a view to highlight the solvent-solute interaction for a solvolysis reaction, Barclay and Butler[28] 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^oC). The plot consists of a straight line whose slope value has been evaluated to be $286.93 \approx 287.0$ which is less than 300. Following the guidelines of Leffler[29], it is concluded that there is weak but considerable solvent-solute interaction for acid catalysed hydrolysis of Iso-pentyl formate in aquo-acetone reaction media.

Such interpretations for weak solvent-solute interaction have also been reported earlier by Priyanka & Singh *et al.*[30], Sharma & Singh *et al.*[31] and recently by Manju & Singh et. al.[33].

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

For investigating 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-pentyl formate in aquo-acetone 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 $30^{o}C$ in the reaction media having 20% (v/v) concentration of acetone 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^+]. From the plots 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 0.984 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 Hammett[34] that acid catalysed hydrolysis of Iso-pentyl formate in aquo-acetone media follows A_{AC^2} mechanism.

Similar observations, inferences and their interpretations have also been reported earlier by Singh & Singh et. al.[35], Navendu & Singh et. al.[36], Singh & Parween et. al.[37] and in the recent years by Kishor & Singh[38] and Azad & Singh et. al.[39].

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Table - I

Specific Rate Constants Values of Acid Catalysed Hydrolysis of Iso-Pentyl Formate in Water-Acetone Media

$k \times 10^3$ in min^{-1}

Temp in ^oC	% of Acetone (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20^0C	87.12	81.04	75.58	71.67	68.49	62.92	56.82
25^0C	165.88	150.18	137.47	125.95	113.37	104.14	90.95
30^0C	316.15	282.68	249.80	223.92	195.57	169.20	
35^0C	575.17	509.45	439.95	383.52	319.60	267.18	
40^0C	1049.98	916.64	771.08	649.08	521.19	424.42	

Table II

Variation of log k values of the reaction at different temperature with mol% of Acetone in Water-Acetone Media

% of Acetone	Mol% of Acetone	3 + log k values				
		20^0C	25^0C	30^0C	35^0C	40^0C
20%	5.79	1.9401	2.2198	2.4999	2.7598	3.0212
30%	9.56	1.9087	2.1766	2.4513	2.7071	2.9622
40%	14.11	1.8784	2.1382	2.3976	2.6434	2.8871
50%	19.77	1.8553	2.1001	2.3501	2.5838	2.8123
60%	26.99	1.8356	2.0545	2.2913	2.5046	2.7170
70%	36.45	1.7988	2.0176	2.2284	2.4268	2.6278
80%	49.58	1.7545	1.9587	2.1588	2.3467	2.5336

Table III

Variation of log k values of the reaction with log [H_2O] values of Water-Acetone system (media) at different temperatures

% of Acetone	% of H_2O	log [H_2O]	3+ log k values				
			20^0C	25^0C	30^0C	35^0C	40^0C
20%	80%	1.6478	1.9401	2.2198	2.4999	2.7598	3.0212
30%	70%	1.5898	1.9087	2.1766	2.4513	2.7071	2.9622
40%	60%	1.5229	1.8784	2.1382	2.3976	2.6434	2.8871
50%	50%	1.4437	1.8553	2.1001	2.3501	2.5838	2.8123
60%	40%	1.3468	1.8356	2.0545	2.2913	2.5046	2.7170
70%	30%	1.2218	1.7988	2.0176	2.2284	2.4268	2.6278
80%	20%	1.0458	1.7545	1.9587	2.1588	2.3467	2.5336

Table – IV

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

Temp. in ^{0}C	Slope – I when log [H_2O] value is below 1.470	Slope – II when log [H_2O] value is above 1.470
20^0C	0.258	0.569
25^0C	0.404	0.666
30^0C	0.512	0.810
35^0C	0.550	1.037
40^0C	0.663	1.136

Table - V

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

% of Acetone (v/v)	20%	30%	40%	50%	60%	70%	80%
E_C values in kJ/Mol	109.55	93.88	88.42	84.42	79.00	74.68	67.97

Table - VI

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

D value	D=35	D=40	D=45	D=50	D=55	D=60	D=65
E_D values in kJ/Mol	79.23	82.32	88.03	94.26	97.21	101.17	105.34

Table VII

Consolidated Values of Activation Parameters (△H*, △G*, △S*) of the reaction in Water-Acetone System at different temperatures

△H*, △G* in kJ/Mol and △S* in J/K/ Mol

% of Acetone	Mol% of Acetone	△H* in kJ/Mol	20°C		25°C		30°C		35°C		40°C	
			△G*	△S*	△G*	△S*	△G*	△S*	△G*	△S*	△G*	△S*
20%	5.79	93.49	98.73	-17.88	98.86	-18.02	98.94	-17.99	99.08	-18.15	99.16	-18.12
30%	9.56	91.07	98.91	-26.76	99.12	-27.01	99.22	-26.90	99.39	-27.01	99.52	-27.00
40%	14.11	86.82	99.08	-41.84	99.33	-41.98	99.53	-41.95	99.77	-42.05	99.97	-42.01
50%	19.77	82.54	99.21	-56.89	99.55	-57.08	99.81	-57.00	100.12	-57.08	100.42	-57.12
60%	26.99	72.24	99.32	-92.42	99.81	-92.52	100.15	-92.11	100.59	-92.05	100.99	-91.85
70%	36.45	69.64	99.53	-102.01	100.02	-102.55	100.51	-101.88	101.05	-101.98	101.52	-101.85
80%	49.58	65.67	99.77	-116.38	100.35	-116.38	100.92	-116.33	101.52	-116.40	102.09	-116.36