A Kinetic Study of the Biochemical Efficiencies of the Solvolysis Products of the Iso-Amyl Formate in Aquo-Glycerol Reaction Media

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ABSTRACT

The biochemical efficiencies of iso-Amyl formate is due to formation of formic acid as its solvolysis product. It is best highlighted by studying the kinetics of acid catalysed solvolysis of iso-amyl formate in aquo-Glycerol reaction media having different concentration of Glycerol (trihydric alcohol) from 20 to 80% (v/v) and at different temperatures ranging from 20 to 40°C.

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 addition of Glycerol 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 283.0, it may be concluded that in water-Glycerol reaction media, the reaction follows Barclay-Butler rule and there is weak but acceptable interaction between solvent and solute.*

KEYWORDS: Protic Solvent, Substituted Formate, Iso-dielectric, Iso-kinetic, specific solvation, Leffler's rule, Desolvation, Solvent-solute interaction, Mechanistic pathways.

INTRODUCTION

The kineticists[1-2] have reported in their works on the solvent effect of dipolar aprotic solvents like DMSO, DMF, Dioxan on the acid catalysed hydrolysis of aliphatic formate, but the studies on the solvent effect of the polyhydric alcohol on the biochemical potential of iso-Amyl formate have not been communicated yet.

Hence it is thought essential to study the solvent effect of a polyhydric alcohol Glycerol (trihydric alcohol) on the acid catalysed hydrolysis of Iso-Amyl formate, as its biochemical use as flavouring agent seems to be very useful in the food technology and also in manufacturing of soft drinks.

EXPERIMENTAL & CALCULATION

Export quality of Iso-Amyl formate Fluka grade packed in Switzerland and Merk grade of high purity were used. The kinetics of reaction was studied by adding 0.70 ml of ester 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 bvalues of specific rate constants have been recorded in Table – I. The variation of log k values with mol% of Glycerol 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 by using Wynne-Jones & Eyring equation[3] 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:

Table – I shows that the rate constant values of the reaction decrease with increasing proportion of Glycerol in the reaction media. On plotting log k values against mole% of Glycerol (from recorded values in Table – II), it is obvious that up to 17.80 mol% of Glycerol in the reaction media, the rate of reaction falls rapidly but beyond (above) 17.80mol% of Glycerol, the depletion in the rate follows slow path. From Table – I, 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 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 Glycerol. So the findings are fully in accordance with the qualitative prediction of Hughes and Ingold[4]. However, these findings are in agreement with the qualitative prediction of Laidler and Landskroener[5] and also with the earlier views of Singh and Sweety *et al.*[6], Kumari and Singh et. al.[7], and Akanksha & Singh et. al.[8] and also with the recently reported findings of Priyanka & Singh *et. al.*[9], who predicted that the rate of ion-dipolar reaction decreases with the decrease in the dielectric constant values of the reaction media.

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

Robertson[10] has derived 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.*[11] 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 Table – IV, it is clear that at each temperature two intersecting straight lines are obtained at $\log[H_2O]$ value 1.475 which corresponds to 53.70% of water concentration (v/v) in aquo-Glycerol 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 1.475, which corresponds to 53.70% of water in the reaction media, the number of water molecules associated with the activated complex increases from 0.290 to 0.842 with increase in temperature of the reaction from 20 to 40^0C. Similarly, for above 53.70% water concentration in the reaction media, the number of water molecules involved in the formation of the activated complex increases from 0.450 to 1.565 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 0.290 to 1.565 with rise in temperature from 20°C to 40°C and from this trend, in the light of the guidelines of Robertson *et al.*[11], 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 Glycerol content of the reaction media and also with increase in the temperature of the reaction.

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

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

Similar observations and inferences and have been earlier reported by Priyanka & Singh *et al.*[12] and Pathak & Singh et. al.[13] and also recently by Kumari Sushma[14].

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 101.43 to 62.85 kJ/mol with increasing the concentration of Glycerol 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.*[15] 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 Glycerol in the reaction media:

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

The transition state being large cation (ester $+H^+$) is available more for solvation by Glycerol 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 interpretations for depletion in E_C value have also been reported earlier by Singh & Hafizee *et al.*[16] and recently by Laxmi & Singh *et al.*[17].

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

With a view 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 the Table – VI, it is found that E_D values go on increasing from 75.03 to 122.51 kJ/mol with increase in D values from D = 50 to D = 75. 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[18] and with the earlier findings of Monalisa & Singh *et al.*[19]. However, recently Laxmi & Singh[18] and Sinha &

Singh et. al.[20] 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^*), entropy of activation (ΔS^*) and the free energy of activation (ΔG^*) of the reaction were evaluated using Wynne-Jones and Eyring equation[3] 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, these were plotted against mol% of Glycerol which have been found to vary non-linearly to the considerable extent with the increasing concentration (mol%) of Glycerol and this is the indication of specific solvation taking place in the reaction media according to Saville and Hudson[21].

The evaluated ΔH^* and ΔS^* values 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 82.73 to 85.10 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 $\Delta H^*$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-Amyl formate in aquo-Glycerol media is entropy controlled and enthalpy dominating reaction.

Similar findings and inferences have also been reported earlier by Kumar & Singh *et al.*[22] and in recent years by Sabita & Singh[23].

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

For highlighting solvent-solute interaction for a solvolysis reaction, Barclay and Butler[24] 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 30^0C). The plot consists of a straight line whose slope values has been evaluated to be $282.59 \approx 283.0$ which is less than 300. On the guidelines of Leffler[25], it is concluded that there is weak but considerable solvent-solute interaction for acid catalysed hydrolysis of Iso-Amyl formate in aquo-Glycerol reaction media.

Similar interpretations for solvent-solute interaction have also been reported earlier by Singh & Kumari *et al.*[26] and recently also by Rakesh & Singh et. al.[27].

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

In order to investigate the effect of change in acid concentration of the reaction media (H^+ in concentration) on

the acid catalysed hydrolysis of Iso-Amyl formate in aquo-Glycerol 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 $25^{o}C$ in the reaction media having 20% (v/v) concentration of Glycerol 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 it 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 0.998 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[28] that acid catalysed hydrolysis of Iso-Amyl formate in aquo-Glycerol media follows $A_{AC}2$ mechanism.

Similar conclusions have also been reported earlier by Singh & Navendu *et al.*[29] and in recent years by Azad & Singh et. al.[30].

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Table - I

Specific Rate Constants Values of Acid Catalysed Hydrolysis of Isi-Amyl Formate in Water-Glycerol Media

$k \times 10^3$ in $(dm)^3\ mol^{-1}\ min^{-1}$

Temp in ^oC	% of Glycerol (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20^0C	53.55	50.65	48.36	45.43	41.68	38.89	34.59
25^0C	106.56	96.23	87.82	79.41	70.50	62.16	52.80
30^0C	207.87	183.32	159.44	138.74	118.20	100.72	81.21
35^0C	390.03	331.28	276.44	231.05	191.69	158.03	120.98
40^0C	737.73	602.28	478.85	386.99	311.03	242.94	179.80

Table II

Variation of log k values of the reaction at different temperature with mol% of Iso-Amyl Formate in Water-Glycerol Media

% of t-Glycerol (v/v)	Mol% of t-Glycerol	3 + log k values				
		20^0C	25^0C	30^0C	35^0C	40^0C
20%	5.81	1.7288	2.0276	2.3178	2.5911	2.8679
30%	9.56	1.7046	1.9833	2.2632	2.5202	2.7798
40%	14.12	1.6845	1.9436	2.2026	2.4416	2.6802
50%	19.79	1.6573	1.8999	2.1422	2.3637	2.5877
60%	27.01	1.6199	1.8482	2.0726	2.2826	2.4928
70%	36.54	1.5898	1.7935	2.0031	2.1987	2.3855
80%	49.67	1.5390	1.7226	1.9096	2.0827	2.2548

Table III

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

% of Glycerol	% of H_2O	log [H_2O]	3+ log k values				
			20^{0}C	25^{0}C	30^{0}C	35^{0}C	40^{0}C
20%	80%	1.6478	1.7288	2.0276	2.3178	2.5911	2.8679
30%	70%	1.5898	1.7046	1.9833	2.2632	2.5202	2.7798
40%	60%	1.5229	1.6845	1.9436	2.2026	2.4416	2.6802
50%	50%	1.4437	1.6573	1.8999	2.1422	2.3637	2.5877
60%	40%	1.3468	1.6199	1.8482	2.0726	2.2826	2.4928
70%	30%	1.2218	1.5898	1.7935	2.0031	2.1987	2.3855
80%	20%	1.0458	1.5390	1.7226	1.9096	2.0827	2.2548

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 1.475	Slope – II when log [H_2O] value is above 1.475
20^{0}C	0.290	0.450
25^{0}C	0.437	0.778
30^{0}C	0.595	0.996
35^{0}C	0.730	1.251
40^{0}C	0.842	1.565

Table - V

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

% of Glycerol (v/v)	20%	30%	40%	50%	60%	70%	80%
E_C values in kJ/Mol	101.43	95.59	89.08	82.84	76.90	71.04	62.85

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

D value	D=50	D=55	D=60	D=65	D=70	D=75
E_D values in kJ/Mol	75.03	84.52	90.71	101.48	112.52	122.51

Table VIII
Effect of [H⁺] on the Specific Rate Constant Values of Acid Catalysed Hydrolysis of Iso-Amyl Formate in Water-Glycerol Media at Constant Ionic Strength (μ=0.9)

Concentration of Glycerol=20% (v/v) **Temp 25°C**

[H⁺]	[KCl]	μ	k×10³ 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	21.24	1.0000	1.3271	
0.15	0.75	0.90	31.64	1.1761	1.5003	
0.20	0.70	0.90	42.38	1.3010	1.6272	
0.25	0.65	0.90	53.47	1.3979	1.7281	
0.30	0.60	0.90	63.43	1.4771	1.8023	0.998
0.40	0.50	0.90	84.10	1.6021	1.9248	
0.50	0.40	0.90	106.56	1.6990	2.0276	
0.60	0.30	0.90	128.03	1.7782	2.1073	
0.70	0.20	0.90	148.46	1.8451	2.1716	
0.80	0.10	0.90	171.83	1.9030	2.2351	

Table VII

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

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

% of Glycerol	Mol% of Glycerol	△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%	5.81	97.42	83.22	48.44	82.98	48.45	82.73	48.47	82.53	48.34	82.25	48.46
30%	9.56	92.46	83.36	31.08	83.23	30.98	83.05	31.08	82.94	31.91	82.78	30.95
40%	14.12	86.12	83.47	9.06	3.46	8.94	83.39	9.01	83.41	8.82	83.37	8.91
50%	19.79	80.07	83.62	-12.12	83.71	-12.20	83.75	-12.14	83.87	-12.33	83.93	-12.39
60%	27.01	74.73	83.83	-31.06	84.00	-31.11	84.15	-31.09	84.35	-31.22	84.50	-31.34
70%	36.54	68.22	84.00	-53.87	84.31	-54.01	84.56	-53.92	84.84	-53.96	85.14	-54.06
80%	49.67	61.27	84.29	-78.56	84.72	-78.70	85.10	-78.65	84.52	-78.76	85.92	-78.77