

A kinetic Study of the Solvent Effect of Dipolar Aprotic Solvent Systems on the Catalysed Solvolysis of Iso-valerate Ester

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ABSTRACT

For highlighting the solvent effect of a dipolar aprotic solvent on the plastisizer and pharmaceuticals producing efficiency of the iso-valerate ester, the kinetics of alkali catalysed hydrolysis of methyl iso-valerate ester, was studied in aquo-acetone reaction media having different concentration of acetone varying from 20 to 80 % (v/v) and at different temperatures ranging from 20 to 40^o C.

The decrease and increase respectively in the values of Iso-composition and Iso-dielectric activation energies of the reaction respectively have been observed and explained on the basis of solvation and desolvation of the initial and the transition state of the reaction to different extent.

Enhancement in the values of free energy activation ΔG^ with simultaneous decrease in enhancement of activation ΔH^* and entropy of activation ΔS^* reveals that the specific solvation is taking place in the reaction media and the aprotic solvent acetone acts as a enthalpy dominating and entropy inhibiting solvent.*

Introduction:

As reported by the different researchers^{1,2} the effect of dipolar aprotic solvent like DMSO, DMF etc. have widely been studied on the alkali and acidic catalysed hydrolysis of aliphatic esters but towards the study of effect of acetone solvent having

peculiar solvating nature on the uses of a higher fatty acid ester, even a little attention has not been paid so far.

So, in order to highlight the above noted untouched research, it has been proposed to make a kinetic study of the solvent effect of acetone on the alkali catalysed hydrolysis of methyl iso-valerate.

Experimental:

Purified acetone of Merck grade and methyl Iso-valerate of USSR make were taken into use. The kinetics of alkali catalysed hydrolysis of the ester was studied as usual^{3,4} by adding 1.0 ml of ester through a syringe pipets in 100 ml of 0.01 M NaOH solution. The values of specific rate constants were evaluated by making use of second order rate equation and are tabulated in Table - I.

Results and Discussion:

From the plots of $\log k$ versus mol % acetone as shown in Fig. -1. it is obvious that with the gradual addition of the organic co-solvent (acetone) in the reaction media there is initially sharp followed by shallow depletion in the rate of reaction at all the five different temperatures.

The following two factors seem to be responsible for depletion in the rate of the reaction in solution, they are:

- (i) decreasing polarity of the medium as changing from polar water to less polar aquo-acetone medium, and
- (ii) lowering of the bulk dielectric constant values of the medium.

These interpretations have already been found in support of Hughes and Ingold⁵ and views of Laidler and Lanskoener⁶ Recently Kumar & Singh et al.⁷ and R.T. Singh⁸ have also reported similar findings and their interpretations for effect of solvent on the specific rate constants of solvolysis reaction.

Solvent effect on Iso-composition activation energy of the Reaction :

From the recorded values of variation of $\log k$ with $1/T$ as mentioned in Table - 2, their plots have been shown in Fig-2. From the slopes of the straight lines of the iso-composition activation energy (E_C) values of the reaction have been evaluated and are placed in Table - III.

From Table - III, it is clear that values of iso-composition activation energy go on decreasing sharply from 98.54 kJ/mol to 71.31 kJ/mol with gradual addition of 20 to 80% of acetone in the reaction media.

Generally, the increase in the values of iso-composition activation energy may be due to:

- (i) Simultaneous solvation of the transition state and desolvation of the initial state
- (ii) The greater solvation of the initial state than the transition state and
- (iii) The greater desolvation of transition state than the initial state.

Out of these three factors, the third one seems to be applicable in this case and it has also been supported by the decrease in the values of entropy of activation with gradual addition of the organic co-solvent in the reaction media as mentioned ahead in Table - V. Similar views has been reported earlier by Singh & Singh et al⁹. Abhay & Singh et al.¹⁰ also recent by Sushma & Singh et al.¹¹

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

From the Arrhenius plots of $\log k_D$ values against $1/T$ ($\log k_D$ values obtained from interpolation of the plots of $\log k$ values against D values), the values of iso-dielectric activation energy have been evaluated and are recorded in Table - IV. From this Table, it is inferred that E_D values go on increasing from 71.59 kJ/mol to 99.48 kJ/mol with increasing D values of the reaction media from 35 to 65. This trend of change in E_D values of the reaction media has been found in support of the earlier finding of the Welford¹². Earlier Rennu & Singh et al¹³ and recently Sinha & Singh et al¹⁴ have also reported similar

observation and inferences for effect of solvent on the E_D values of different solvolysis reactions.

Involvement of water molecules in the formation of transition state and Mechanism of the reaction:

The number of water molecules associated with the transition state has been evaluated by plotting $\log k$ values, against $\log [H_2O]$ from their values as mentioned in Table- V following the Robertson¹⁵. equation as given below:

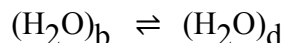
$$\log k = \log k_0 + n \log [H_2O]$$

where 'n' is the solvation number which tells about number of water molecules associated with the transition state and also hints about criterion for studying the mechanism of the reaction. On plotting $\log k$ values against $\log [H_2O]$ values as picture in Fig. - 3, two sets of intersecting straight lines both having positive slopes have been obtained. Two sets of intersecting straight lines cut each other at about 1.430 $\log [H_2O]$ value which correspond to 48.50% of water. From the values of slopes as mentioned in Table – V, it clear that when water concentration is below 48.50% in water acetone media, its values increase from 0.206 to 0.571 with increase in temperature from 20⁰ to 40⁰ C. Similarly the value of slope, when water concentration is above 48.50% in the reaction media, increases from 0.395 to 1.056 as the temperature of the reaction increases from 20⁰ to 40⁰ C.

From the above noted values of the slopes, it may be inferred that overall with rise of temperature of the reaction from 20⁰C to 40⁰C, the number of water molecules associated with the transition state vary from 0.206 to 1.056 when water concentration in the reaction increases and the concentration of organic co-solvent (acetone) decreases in the reaction media.

It may also be interpreted in reverse way that with increase in acetone content of the reaction media from 20 to 80%, the number of water molecules associated with the transition state decreases from 1.056 to 0.206 with rise in temperature of the reaction.

These observations may be attributed to the fact that equilibrium shifts from dense form of water bulky from with rise in temperature of the reaction and with addition of more acetone the reaction media.



On the guidelines proposed by Robertson et al¹⁶. it may be inferred that the mechanistic pathways followed by the alkali catalysed solvolysis of methyl iso-valerate is changed from bimolecular to unimolecular with increasing concentration of acetone in the reaction media and with increasing temperature of the reaction. These findings have also been supported earlier by Sharma & Singh et al¹⁷. Singh & Singh et al¹⁸ and recently by Sinha & Singh et.al¹⁹.

Solvent Effect on Thermodynamic Activation Parameters of the Reaction :

The famous Wynne – Jones & Eyring²⁰ equation have been applied to evaluated the three thermodynamic activation parameters namely enthalpy of activation ΔH^* , entropy of activation ΔS^* and the free energy of activation ΔG^* and their evaluated values have been recorded in Table - VI.

From the data mentioned in Table-VI, the interesting feature comes in the light is that out of all the values of three thermodynamic parameters i.e. ΔH^* , ΔS^* and ΔG^* values, the values ΔH^* and ΔS^* go on decreasing with simultaneously increasing in ΔG^* values and with increasing proportion of acetone in the reaction media. ΔG^* values go on enhancing with simultaneous depletion and ΔH^* and ΔS^* values at all the temperature of the reaction i.e. from 20° to 40°C.

From the fundamental thermodynamic equation,;

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

It may be inferred that the enhancement in the values of ΔG^* with simultaneous depletion in ΔH^* and ΔS^* values is only possible when the depletion in the values of ΔS^* is more than that found in the values of ΔH^* and from this fact, it is concluded that alkali catalysed hydrolysis of methyl iso-valerate in aquo-acetone media is enthalpy dominated and entropy controlled.

In other words, it may also be inferred that acetone by its presence in the reaction media activates the enthalpy but controls over the entropy of the reaction.

The change found in the value of the three thermodynamic activation parameters also support the fact that initial state of the reaction is desolvated and the transition state is solvated in the similar way as reported earlier by Dheeraj & Singh²¹ and recently also by Anant & Singh et al²².

Evaluation of Iso-kinetic temperature and Solvent- solute interaction in aquo-Acetone reaction media:

In the light of Barclay and Butler²³ relationship between enthalpy and entropy of activation, the value of iso-kinetic temperature of the alkali catalysed hydrolysis of methyl iso-valerate in aquo-acetone media has been evaluated from the plots of ΔH^* versus against ΔS^* value from Table VI. Which come to be $283.52 \approx 284.00$ which is less than 300.

From the value of iso-kinetic temperature which is less than 300, it is concluded that there is a considerable change in the structure of reactants or in the solvent or in both due to weak but appreciable interaction between solvent and solute present in the reaction media consisting of acetone in the similar way as reported by Leffler²⁴. similar findings and their interpretation have also been reported recently Sushma , Abhay & Singh et al²⁵ for solvent-solute interaction in the different aquo-organic solvent system.

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Table - 1

**Specific rate constant values of Alkali catalysed
hydrolysis of Methyl iso-valerate in water-Acetone media**

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

Temp in °C	% of Acetone (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20° C	86.85	80.95	77.13	73.76	70.50	66.30	61.92
25° C	169.97	154.49	142.63	132.53	123.00	112.25	100.79
30° C	329.69	293.49	265.03	238.67	213.89	188.41	163.42
35° C	599.93	534.81	468.92	410.39	355.96	304.16	256.04
40° C	1140.05	961.17	830.04	704.37	592.52	491.02	397.01

Table - 2

Variation of log k values of the reaction with $10^3/T$
in water-Acetone media.

Temp. °C	$\frac{10^3}{T}$	3 + log k values at different % Acetone (v/v)						
		20%	30%	40%	50%	60%	70%	80%
20° C	3.413	1.9388	1.9082	1.8872	1.8678	1.8482	1.8215	1.7918
25° C	3.356	2.2304	2.1889	2.1542	2.1223	2.0899	2.0502	2.0031
30° C	3.300	2.5181	2.4676	2.4233	2.3778	2.3302	2.2751	2.2133
35° C	3.247	2.7781	2.7282	2.6711	2.6132	2.5514	2.4831	2.4083
40° C	3.195	3.0569	2.9828	2.9191	2.8478	2.7727	2.6911	2.5988

Table - 3

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 value in kJ/mol	98.54	94.75	90.87	86.22	81.07	77.26	71.31

Table - 4

Evaluated values of Iso-Dielectric Activation Energy (E_D) of the reaction
at different desired 'D' values of the water-Acetone media.

D values	D = 35	D = 40	D = 45	D = 50	D = 55	D = 60	D = 65
E_D values in kJ/mol	77.59	80.76	85.04	89.65	92.85	96.50	99.46

Table - 5

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

Temperature in °C	Slope - I when log[H ₂ O] value is below 1.430	Slope - II when log[H ₂ O] value is above 1.430
20°C	0.206	0.395
25°C	0.284	0.542
30°C	0.421	0.754
35°C	0.451	0.862
40°C	0.571	1.056

Table - 6

Variation of ΔH^* , ΔG^* and ΔS^* values of the reaction with mol % of Acetone in water-Acetone media

% of Acetone (v/v)	Mol % of Acetone	ΔH^* in kJ/mol	ΔG^* in kJ/mol at 30°C	ΔS^* in J/K/mol at 30°C	$(\Delta S^* +100)$ in J/K/mol at 30°C
20%	5.79	96.39	87.37	29.77	129.77
30%	9.56	92.35	87.66	15.48	115.48
40%	14.11	88.31	87.92	1.29	101.29
50%	19.77	83.55	88.18	-15.28	84.72
60%	26.99	78.91	88.46	-31.52	68.48
70%	36.45	76.08	88.78	-41.91	58.09
80%	49.58	68.57	89.14	-67.89	32.11

