

Studies on the Solvent Effect of Aquo-DMSO Reaction Media on the Catalysed Solvolysis of Ethyl Iso-Valerate Ester

Ashutosh Abhay¹, and R. T. Singh²

1. Assistant Professor of Chemistry, Shri Shankar College, Sasaram

2. Professor & Formerly HOD Chemistry and the Dean of the Faculty of Science,
V. K. S. University, Ara

ABSTRACT

The kinetics of the alkali catalysed hydrolysis of Ethyl Iso-valerate (Aliphatic iso- valerate) were studied in aquo-aprotic solvent systems (aquo-DMSO) and the specific rate constants of the reaction were found decreasing with increasing concentration of the organic content (DMSO) of the media. It is inferred that dielectric effect and the solvation changes are the causes of depletion in the rate of the reaction.

The Iso-composition activation energy (E_C) and the Iso-dielectric activation energy (E_D) of the reaction were found to increase and decrease respectively and from this, it is inferred that the transition state of the reaction is desolvated and its initial state is solvated.

From the depletion observed in the solvation number of the water content of the aquo-DMSO solvent systems with increase in the temperature of the reaction, it is inferred that unimolecular mechanistic path of the reaction is changed to bimolecular mechanistic path. Increase observed in free energy of activation with simultaneous increase in the values of both the ΔH^* and ΔS^* , it is inferred that in the presence of DMSO with reaction media, the reaction becomes enthalpy dominating and entropy controlled.

From the evaluated values of iso-kinetic temperature of the reaction which comes to be 330.0, it is concluded the Barclay-Butler rule is obeyed by the reaction and there is strong solvent-solute interaction in presence of DMSO in the reaction media

KEYWORDS: Iso-valerate ester, Dipolar aprotic solvent, Iso – kinetic temperature, Iso-composition and Iso-dielectric activation energy, Transition state, Entropy controlled, Enthalpy dominating, Solvent-Solute Interaction.

INTRODUCTION

The kinetics of alkali catalysed hydrolysis of Ethyl Iso-valerate in aquo-DMSO media has been planned to be carried out, as this reaction is very useful from commercial as well as from the hygienic points of views and also because it has not been paid adequate attention by the researchers so far.

The alkali catalysed solvolysis of the said ester was studied in aquo-DMSO media having varying concentration of DMSO from 20-80%(v/v) at five different temperatures, i.e., 20,25,30,35 and 40°C.

Experimental

Export quality Ethyl iso-valerate ester packed in Switzerland and SISCO grade of DMSO were taken in use. The kinetics of alkali catalysed hydrolysis of Ethyl Iso-valerate were studied using earlier reported process^{1,2} keeping the strength of alkali and esters as 0.1 M and 0.05 M respectively. The concentration of the organic solvent DMSO was varied from 20 to 80% (v/v) and hydrolysis was carried out at five different temperatures at 20,25,30,35 and 40°C. The reaction was found to follow second order kinetic equation and the evaluated values of the specific rate constants were enlisted in Table-I. The evaluated values of iso-composition activation energy (E_C) and iso-dielectric activation energy (E_D) have

been recorded respectively in Table -II and III. From the slopes of the plots of $\log k$ values versus $\log [H_2O]$ (values as recorded in Table-IV), The evaluated values of number of water molecules associated with the activated complex of the reaction have been tabulated in Table-V. The three thermodynamic activation parameters namely ΔH^* , ΔG^* and ΔS^* were calculated by applying Wynne-Jones and Eyring equation³ and their values are synchronised in Table -VI.

Results and Discussion:

Solvent Effect on the Rate of Reaction:

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 mol % of DMSO, it is found that rates of reaction go on depletion with gradual addition of DMSO in the reaction media. The depletion in the rate follows smooth depleting path. From the plots of $\log k$ versus mol% of DMSO in the reaction media, two intersecting straight lines having different values of slopes are obtained. The decrease in the rate with increasing mol % of DMSO at all the five temperatures are found to follow deep depletion path up to 19.50 mol% of the DMSO in the reaction media and after its 19.50 mol % in the reaction media, the rate of depletion becomes slow. IT is clear that sharpness in the depletion of the rate becomes slow with increase in temperature of the reaction. This decreasing trend in the values of the rate constants needs to be discussed in the light of Hughes and Ingold⁴ predictions and the theory of Laidler and Landskroener⁵. The values of dielectric constant 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 Ingold⁴.

However, our findings are in agreement with the qualitative prediction and views of Singh & Jha et al.^{6,7} and also with the recent reports of Narendra & Singh et al.⁸ and Rakesh & Singh et al.⁹, who predicted that the rate of ion dipolar reaction decreases partly with decrease in the dielectric constant values of the reaction media and partly due to the solvation changes taking place in the reaction media.

Solvent effect on the Iso-composition Activation Energy (E_C) of the reaction:

The values of iso-composition activation energy (E_C) of the reaction were evaluated from the slopes of Arrhenius plots of $\log k$ values of the reaction against $10^3/T$ and have been tabulated in Table-II.

From Table-II, it is obvious that E_C values go on increasing from 97.01 kJ/mol to 134.16 kJ/mol with increase in concentration of DMSO from 20 to 80% (v/v) in reaction media. This change 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 states as reported earlier by Elsemongy¹⁰ in this field. Considering the extent of solvation to be a dominant factor, The following three factors seem to be responsible for increase in E_C values with gradual addition of DMSO in the reaction media:-

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

The transition state being large anion (ester +OH) not available more for solvation by DMSO molecule than the initial state, so the first factor seems to be operative in this case and it also gets support when the values of entropy of activation (ΔS^*) and enthalpy of

activation (ΔH^*) go on increasing with concentration of DMSO as shown in Table-VI. Such observations and inferences have been reported earlier by Chandra & Singh et al.¹¹ and Singh & Priyanka et al.¹² and also in recent years by Singh & Singh et al.¹³ and Prashansa & Singh et al.¹⁴.

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

On perusal of the data of Table-III, it is found that iso-dielectric energy (E_D) values of the reaction are decreasing from 149.70 kJ/mol to 118.09 kJ/mol with increase in dielectric constant values of the reaction media from $D = 60$ to $D = 75$ respectively. Since D values of the aquo-DMSO reaction media go on decreasing with gradual addition of DMSO to it, hence it may also be concluded that like E_C values, E_D values are also increasing with decrease in D Values of the reaction media or with adding more and more DMSO to it. Thus it also may be inferred that E_C and E_D values of the solvolysis reactions are complimentary to each other.

Such findings and their interpretations have been found in support of the past views of Elsemongy et al.¹⁵, Wolford¹⁶ and the recent reports in support of Singh & Singh et al.¹³, Prashansa & Singh¹⁴ and Abha & Singh et al.¹⁷.

Effect of Solvent on the Solvation number and on the Mechanistic pathways of the reaction:

The solvation number i.e. the number of water molecules involved in the formation of the activated complex of the reaction were evaluated from the slopes of the plots of $\log k$ values of the reaction against $\log[H_2O]$ values of the reaction media. By using Robertson¹⁸ equation which is –

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

where 'n' is the solvation number.

The $\log k$ and $\log [H_2O]$ are enlisted in Table-IV and the numerical values of the slopes of the plots have been enlisted in Table-V.

Robertson et al.¹⁹ have established that the numerical value of solvation number 'n' i.e. the number of water molecules associated with the activated complex in its formation are fairly high for reaction following unimolecular mechanistic pathway and are low for reaction following bimolecular mechanistic pathway.

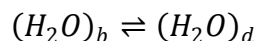
From the values recorded in Table-V, it is clear that at all the temperatures of the reaction, the plots of $\log k$ versus $\log[H_2O]$, there are two straight lines having different slopes which meet at $\log [H_2O]$ value 1.480 which corresponds to 54.40% of water in aquo-DMSO media.

From the evaluated values of slopes as recorded in Table -V, it is clear that before $\log [H_2O]$ value 1.480 which corresponds to 54.40% of water concentration in the reaction media, their values are decreasing from 0.888 to 0.342 with rise in temperature of the reaction from 20 to 40°C. Similarly, after $\log [H_2O]$ values 1.480 i.e. above 54.40% of water in the reaction media, the numerical values of the slopes i.e. the number of water molecules associated with the activated complex in its formation decrease from 1.792 to 0.606 with increase in temperature from 20 to 40°C.

Overall, it may be concluded that number of water molecules associated with the activated complex of the reaction in the formation decrease from 1.792 to 0.342.

Thus, on the guidelines of Robertson et al.¹⁹, it may be inferred that with rise in temperature of the reaction, the mechanistic pathways of the reaction is changed from unimolecular to bimolecular in presence of DMSO in the reaction media.

About the change in the structure of water in presence of DMSO and with rise in temperature of the reaction, water components of the reaction media changes its structure from its bulky form to dense form at equilibrium.



Such observations and inferences have earlier been reported by Singh & Mishra et al.²⁰ and recently by Laxmi & Singh et al.²¹ and Raghaw & Singh et al.²².

Effect of Aquo-DMSO solvent system on the Thermodynamic Parameters of the Reaction:

The three thermodynamic activation parameters namely ΔH^* , ΔG^* and ΔS^* of the alkali catalysed hydrolysis of Ethyl Iso-valerate were evaluated using Wynne-Jones and Eyring equation³ and their values have been synchronised in Table-VI.

From Table -VI, it is clear that out of the three thermodynamic activation parameters ΔH^* , ΔG^* and ΔS^* , all of them are found increasing with increasing mol % of DMSO in the reaction media.

For better understanding of the effect of solvent DMSO on these three thermodynamic activation parameters, their values were plotted against mol % of the solvent DMSO shows the variation in ΔH^* , ΔG^* and ΔS^* respectively with mol % of DMSO in the reaction media.

The reasonable and considerable increase in ΔG^* values (from 81.81 to 84.24 kJ/mol at 30°C) as found in Table -VI and non-linear variation in ΔH^* , ΔG^* and ΔS^* with mol% of DMSO are indication of specific solvation taking place in the process of activation as reported by Saville and Hudson²³, Tommila et al.²⁴ and Hyne et al.²⁵. Enhancement observed in both the ΔH^* and ΔS^* also justifies that transition state of the reaction is desolvated and the initial state of the reaction is solvated. Simultaneous increase in ΔG^* values with

increase in ΔH^* and ΔS^* values is only possible when the extent (degree) of enhancement in ΔH^* values is more than that of ΔS^* values and from this, it may be inferred that alkali catalysed hydrolysis of Ethyl Iso-valerate is entropy suppressing or controlled and enthalpy dominating reaction. Such findings and interpretations have earlier been reported by Singh & Kumari et al.²⁶, Singh & Bano et al.²⁷ and Monalisa & Singh et al.²⁸ and recently Verma²⁹ and Hafizee & Singh³⁰ have also reported similar observations and inferences.

Solvent effect of Aquo-DMSO solvent media on Iso-kinetic Temperature and Solvent-Solute Interaction:

This reaction is found to obey Barclay and Butler³¹ rule and straight line is obtained when ΔH^* values of the reaction is plotted against ΔS^* and from their values tabulated in Table-VI.

The Barclay and Butler equation is

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

It is a relation between enthalpy (ΔH^*) and entropy (ΔS^*) of activation values of the reaction and ' β ' is called iso-kinetic temperature of the relation which is also called Leffer-Grunwald solvent stabilizer operator³². From the values of slope of the plot, the values of Iso-kinetic temperature was evaluated which came to be $330.02 \approx 330.0$.

In the light of Leffler's³³ guidelines, from the values of iso-kinetic temperature which is greater than 300, it is inferred that there is a considerable change in the structure of the reactant or in the solvent or in both the reactant and the solvent due to appreciably strong interaction between the solvent and the solute present in the reaction media. The structural changes with increasing proportion of DMSO in aquo-DMSO reaction media are responsible for the depletion observed in the values of the specific rate constant of the reaction.

Earlier Singh & Singh et al.³⁴, Singh & Kumari et al.³⁵, Singh & Navendu et al.³⁶ and Singh & Wats et al.³⁷ and in recent years Ojha & Singh et al.³⁸ and Sabita & Singh et al.³⁹ have also reported similar conclusions about the solvent-solute interaction in the reaction media.

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Table – I

Specific rate constant values of Alkali catalysed hydrolysis of Ethyl Iso-valerate in water-DMSO media
 $k \times 10^3 \text{ in (dm)}^3 \text{ mole}^{-1} \text{ min}^{-1}$

Temp in °C	% of DMSO (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20°C	88.11	69.74	53.41	42.48	33.58	26.84	18.96
25°C	169.79	137.15	111.25	91.96	75.25	61.12	46.51
30°C	323.67	272.14	231.79	197.83	168.81	143.02	114.18
35°C	602.28	523.48	450.56	407.47	360.25	316.15	262.30
40°C	1105.10	999.54	914.32	834.07	766.13	687.23	613.06

Table - II

Evaluated values of Iso-composition Activation Energy (E_C or E_{exp}) of the reaction in water-DMSO media.

% of DMSO	20%	30%	40%	50%	60%	70%	80%
E_C values in kJ/mol	97.01	102.97	109.17	113.96	119.34	125.28	134.16

Table - III

Evaluated Values of Iso-Dielectric Activation Energy (E_D) of the reaction at Different-Desired 'D' values of water-DMSO media.

D values	D= 60	D = 62.5	D = 65	D =67.5	D = 70	D = 72.5	D = 75
E_D values in kJ/mol	149.70	139.84	136.45	129.61	126.27	122.09	118.09

Table – IV

Variation of log k values of the reaction with log[H₂O] values of water-DMSO media at different temperatures.

% of DMSO (v/v)	% of H₂O	log[H₂O]	3+ log k values				
			20°C	25°C	30°C	35°C	40°C
20%	80%	1.6478	1.9450	2.2299	2.5101	2.7798	3.0434
30%	70%	1.5898	1.8435	2.1372	2.4348	2.7189	2.9998
40%	60%	1.5229	1.7276	2.0463	2.3651	2.6614	2.9611
50%	50%	1.4437	1.6282	1.9636	2.2963	2.6101	2.9212
60%	40%	1.3468	1.5861	1.8765	2.2274	2.5560	2.8843
70%	30%	1.2218	1.4288	1.7862	2.1554	2.4999	2.8371
80%	20%	1.0458	1.2778	1.6675	2.0576	2.4188	2.7875

Table - V

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

Temperature in °C	Slope - I Where log [H₂O] value is below 1.480	Slope – II where log [H₂O] value is above 1.480
20°C	0.888	1.792
25°C	0.730	1.487
30°C	0.590	1.181
35°C	0.495	1.027
40°C	0.342	0.606

Table- VI
Consolidated Values of Thermodynamic Activation Parameters (ΔH^* , ΔG^* and ΔS^*) of the reaction in water-DMSO solvent system at different temperatures.
 ΔH^* and ΔG^* in kJ/mol, ΔS^* in J/K/mol

% of DMSO (v/v)	Mol% 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	95.25	88.01	45.20	81.83	45.06	81.81	45.02	81.41	44.94	81.20	44.91
30%	9.77	99.55	85.58	57.84	82.35	57.62	82.05	57.68	81.77	57.65	81.46	57.73
40%	14.40	104.94	83.23	74.09	82.87	74.04	82.46	74.20	82.11	74.11	81.73	74.15
50%	20.17	112.31	87.79	97.33	83.34	97.21	82.85	97.23	82.41	97.08	81.93	97.06
60%	27.49	117.05	84.36	111.56	83.84	111.42	83.25	111.54	82.73	111.42	82.15	111.49
70%	37.09	122.71	84.91	129.02	84.36	128.70	83.67	128.83	83.06	128.72	82.43	128.68
80%	50.27	131.12	86.02	154.10	85.03	154.83	84.24	154.88	83.54	154.64	82.73	154.76