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STUDIES OF THE KINETICS OF ALKALI CATALYSED HYDROLYSIS OF BUTYL ACETATE IN AQUO-DMF REACTION MEDIA

Rashik Bihari Dubey

Assistant Professor of Chemistry, B.S. College Hatta Chenari, V.K.S. University, Ara

Abstract

The solvent effect on the rate a mechanism and the molar thermodynamics activation parameters of alkali catalysed hydrolysis of butyl acetate was studied in water-DMF media having varying concentration of DMF from 20 to 80% (v/v) at different temperatures ranging from 20 to 40°C. The rates of reaction was found to decrease with increasing proportion of the organic cosolvent in the reaction media. The number of water molecules associated with the activated complex were found increasing from 0.394 to 1.305. with increasing temperature from 20 to 40°C and from this was inferred that in water-DMF media, structure of water is being changed from its dense form tonu its bulky form. Out of the three molar thermodynanic activation parameters ΔH, ΔS* and ΔG*, ΔG* values are found to increase with simultaneous depletion in ΔH* and ΔS* values. Hence, it is concluded that in this reaction, decrease in entropy dominates over depletion in enthalpy and the reaction is entropy controlled reaction.*

Key Words:- *Catalysed, Dipolar Aprotic, Reaction media Mechanistic pathway, Solvation, Specific solvation, Initial state, Transition State, Thermodynamic Activation Parameters.*

Introduction:

Various kineticists[1-4] have reported about the solvent effect on the various types of reactions, but works on the solvent effect on the mechanism and the molar thermodynamic activation parameters of the solvolysis, particularly of esters of heavy aliphatic acids have not been reported sofar. Hence, for highlighting the above noted idea, the kinetics of alkali catalysed butyl acetate in water-DMF media having varying concentrations of DMF was studied, as it was thought important from industrial as food technological points of views.

Experimental: The kinetics of alkali catalysed hydrolysis of butyl acetate in water-DMF media was studied by keeping the concentration of alkali and ester M/10 and M/20 respectively following the method reported by Singh et al[5,6]. The specific rate constant values of the reaction were calculated using second order kinetic equation and have been tabulated in Table - I. log k and log[H_2O] values of the reaction and reaction media respectively have been recorded in Table - II and number of water molecules associated with the activated complex of the reaction have been mentioned in Table - III. Consolidated values of molar thermodynamic activation parameters have been depicted in Table - IV.

RESULTS AND DISCUSSION:

Solvent Effect on the rate of reaction:

From the Table - I, it is obvious that the rate of alkali catalysed hydrolysis of butyl acetate in water-DMF media follows decreasing trend with increasing proportion of DMF in the reaction media. Though these finding are against the view of Hughes and Ingolds[7], however, recent instances of Sinha et al.[8] and Singh et al.[9,10] are in support of our findings. the decrease in the rate is attributed jointly due to the effect of dielectric constant of the media and also due to the change in structure of water as a result of solvation change taking place in the reaction media.

Participation of Solvent (water) molecules with the activated complex and mechanism of the reaction:

Participation of water molecules of water-DMF media in the activated complex was studied for knowing the effect of change in reaction media on the rate and mechanism of the reaction. The number of water molecules associated with the activated complex were evaluated by plotting log k values against log $[H_2O]$ values, mentioned in Table - II in light of equation proposed by Robertson[11] which is as:

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

where ‘n’ is the solvation number which tells about the criterion for studying about the mechanism of the reaction. From the slopes of plots of log kagainst log$[H_2O]$ the number of water molecules associated with the activated complex were found to vary with temperature of the reaction as mentioned in Table - III.

From the values of the number of water moles associated with the activated complex which increases from 0.394 to 0.933 when log [H,O] value is below 1.45 and from 0.546 to 1.305 when log $[H_2O]$ value is above 1.45. Hence, it is inferred that with the rise of temperature, water in the water-DMF media changes its structure from dense to bulky form.

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

As the number of molecules of water associated with activated complex is enhancing with rise in temperature, hence it is inferred that in presence of DMF in the reaction media, the bimolecular of the mecanism of the reaction is changed to unimolecular in the similar way as observed by Packer and Tomilinson[12]. Such inferences are in support of the recent reports of Singh et al.[13]

Solvent Effect on the Molar Thermodynamic Activation Parameters:

The three thermodynamic activation parameters i.e. enthalpy of activation ΔH*, free energy of activation ΔG* and entropy of activation ΔS* were calculated by using Wynne-Jones and Eyring[14] equation and their consolidated values have been inserted in Table - IV.:

From the Table-IV, it is obvious that out of the three thermodynamic parameters namely ΔH*, ΔG* and ΔS*, ΔG* values are increasing with simultaneous decrease in ΔH* and AS* values with addition of DMF in the reaction media. Hence, according to one of the fundamental equations of thermodynamic for free change in cnergy, i.e.,

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

Enhancement in ΔG* values with simultaneous decrease in ΔH* and ΔS* values is only possible when extent of depletion in ΔS* value is greater than that in ΔH* value. Hence, from this observation, it is inferred that the alkali catalysed hydrolysis of butyl acetate in water-DMF media is entropy controlled.

However, non-linear variation of ΔH*, ΔG* and ΔS* values with mole % of DMF in water-DMF media are indication of specific solvation taking place in the reaction media as reported by Elsemongy et al.[15] and Singh et al.[16]. Enhancement observed in ΔG* values from 82.46 to 85.39 kJ/mole with increase in the organic cosolvent (DMF) from 20 to 80%(v/v) in the reaction media is a sign of the solvation of the reacting species as reported by Elsemongy et al.[17] and recently by Singh et al.[18]. In this case, the limit of solvation is mainy due to the non-formation of hydrogen bonding as DMF it is not very efficient and sensitive towards formation of hydrogen bond.

Moreover, further works, i.e. to test the validity of Barclay Butler rule by the reaction, to study the solvent-solute interaction in the reaction media are in progress.

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Table - I

Specific rate constant values for Alkali catalysed hydrolysis of Butyl acetate in water-DMF media

K × 10^2 in $(dm)^3$ $mole^{-1}$ min^{-1}

Temp in °C	**% of DMF (v/v)**						
	20%	**30%**	**40%**	**50%**	**60%**	**70%**	**80%**
20°C	51.93	48.10	43.15	39.71	36.86	32.73	28.04
25°C	110.08	96.85	86.68	74.30	66.07	56.22	44.34
30°C	231.18	190.99	165.12	139.35	117.63	96.45	72.11
35°C	464.09	360.91	308.18	256.63	204.27	161.47	112.25
40°C	867.16	707.62	576.77	465.69	353.92	265.03	176.93

Table - II

Variation of log k values of the reaction with log $[H_2O]$ values in water-DMF media.

% of DMF	**% of water**	**log $[H_2O]$**	**2 + log k values**				
			20°C	**25°C**	**30°C**	**35°C**	**40°C**
20%	80%	1.6478	1.7154	2.0417	2.3639	2.6666	2.9380
30%	70%	1.5898	1.6821	1.9860	2.2810	2.5680	2.8498
40%	60%	1.5229	1.6349	1.9278	2.2178	2.4888	2.7610
50%	50%	1.4437	1.5989	1.8709	2.1441	2.4093	2.6680
60%	40%	1.3468	1.5666	1.8200	2.0705	2.3102	2.5489
70%	30%	1.2218	1.5149	1.7499	1.9843	2.2080	2.4233
80%	20%	1.0458	1.4478	1.6468	1.8579	2.0501	2.2478

Table - III

Evaluated Values of number of water molecules associated with the activated complex of the reaction in water-DMF media.

Temperature in °C	Slope - I Where log[H_2O] value is below 1.45	Slope - II when log[H_2O] value is above 1.45
20°C	0.394	0.546
25°C	0.571	0.809
30°C	0.708	1.012
35°C	0.879	1.290
40°C	0.933	1.305

Table- IV

Consolidated Values of Molar Thermodynamic Activation Parameters of the reaction in water-DMF media.

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

% of DMF (v/v)	Mole% of DMF	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%	5.53	110.80	83.29	93.89	82.89	93.65	82.46	93.53	82.08	93.25	81.82	92.58
30%	9.12	103.26	83.48	67.50	83.22	67.24	82.94	67.06	82.66	66.88	82.36	66.77
40%	13.50	97.80	83.74	47.99	83.55	47.81	83.31	47.82	83.13	47.62	82.88	47.66
50%	18.96	91.50	83.95	25.76	83.87	25.60	83.74	25.61	83.59	25.68	83.45	25.71
60%	25.98	87.84	84.13	12.66	84.14	12.35	84.16	12.14	84.18	11.88	84.16	11.76
70%	35.27	79.23	84.42	-17.71	84.56	-17.88	84.66	-17.92	84.78	-18.02	84.92	-18.17
80%	48.29	72.55	84.79	-41.77	85.15	-42.28	85.39	-42.37	85.71	-42.73	85.97	-42.88