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Kinetic Study of Solvent Effect on the Acid Catalyzed Solvolysis of Methanoate Ester in Water-Dioxane Media

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The solvent effect of dioxane on the acid catalyzed solvolysis of ethylmethanoate was studied by carrying out the hydrolysis of the ester in water-dioxane media of varying composition consisting of 0 to 80% dioxane (v/v) at different temperatures ranging from 20–40°C. The specific rate constant values of the reaction were found to decrease with increasing concentration of dioxane in the reaction media. It was found that up to 1.5 molecules of water are associated with the activated complex The depletion observed in the values of isocomposition activation energy of the reaction shows that the transition is solvated and the initial state is desolvated with addition of dioxane in reaction media. From enhancement and depletion found, respectively in the values of ΔG^* and in the values of both ΔH^* and ΔS^* (though up to different degrees), it is inferred that the reaction is entropy controlled and specific solvation is taking place in the water-dioxane media. From the values of isokinetic temperature, it may be concluded that water-dioxane reaction media does not check the reaction to follow Barclay-Butler rule.

Key Words: Kinetic, Solvent effect, Solvolysis, Methanoate ester.

INTRODUCTION

Studies of solvent effect of dipolar aprotic solvents such as DMSO, DMF on the alkaline hydrolysis of amides and esters have been reported by several workers[1–3]. But for acid catalyzed solvolysis reactions few efforts have been made so far. The rate of such reactions in which transition state passes through polarization should be faster in aprotic solvents than in protic solvents[4]. Roberts[5] studied the alkaline hydrolysis of a large number of esters in DMSO-H_2O mixtures and observed an enhancement in the rate by increasing the ratio of aprotic components of the binary solvent mixtures. However, this is against the quantitative prediction of Hughes and Ingold[6], as well as the theoretical prediction of Laidler and Landskroner[7]. According to them, the rate of such reactions should increase with increasing dielectric constant values of the medium. In view of this, in the present work, the kinetics and mechanism of hydrolysis of ethyl methanoate in dioxane-water system has been reported.

EXPERIMENTAL

The kinetics of the reaction was studied by adding 1 mL of the ester into 100 mL of 0.01 M HCl solution in thermostated condition at the desired temperature. The reaction was found to obey the first order kinetic equation and the evaluated values of specific rate constants have been recorded in Table-1. The values of both types of activation energies (isocomposition and isodielectric) have been mentioned in Tables 2 and 3 respectively, whereas the values of thermodynamic parameters, *i.e.*, ΔH^*, ΔG^* and ΔS^* calculated by using Wynne-Jones and Eyring[8] equation have been shown in Table-4.

RESULTS AND DISCUSSION

Table-1 shows that the rate constant values of the reaction decrease with increasing proportion of dioxane in the reaction media. On plotting log k values against mol % of dioxane, it is obvious that up to 8 mole % of dioxane in the reaction media, the rate of reaction falls rapidly but beyond 8 mol % of dioxane, the depletion in the rate follows a slow path. This decreasing trend in the values of rate constants needs to be discussed in the light of Hughes and Ingold[6] 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 construction of charges on the transition stage and causes a decrease in the rate when there is diffusion or destruction of charges in the transition stage. The values of dielectric constants of the reaction media go on decreasing with gradual addition of dioxane Here our findings are fully in accordance with the qualitative prediction of Hughes and Ingold[6]. However, our findings are also in agreement with the qualitative prediction of Laidler and Landskroener[7] who predicted that the rate of ion-dipolar reaction decreases with decrease in the dielectric constant values of the reaction media.

TABLE-1

$k \times 10^4$ min^{-1}

% of Dioxane (v/v)	Temperatures (°C)				
	20	25	30	35	40
0	22.79	30.35	46.00	63.90	91.50
10	20.07	27.90	36.23	52.90	71.50
20	18.97	25.59	34.59	45.71	61.09
30	18.40	23.99	31.62	40.36	52.60
40	17.99	22.70	29.17	36.73	46.24
50	17.18	21.38	26.49	32.36	39.63
60	16.70	19.95	23.71	28.05	33.11
70	15.85	18.24	21.23	24.21	27.67
80	15.52	17.26	19.50	22.39	23.99

TABLE-2

% of Dioxane (v/v)	0	10	20	30	40	50	60	70	80
in kJ/mol	54.28	48.75	47.84	44.82	73.35	32.68	27.67	21.71	17.96

TABLE-3

D	8	18	28	38	48	58	68
E_D in kJ/mol	42.90	52.29	64.35	84.55	95.33	104.00	114.49

TABLE-4

VALUES OF THERMODYNAMIC ACTIVATION PARAMETERS IN WATER-DIOXANE MEDIA (ΔH^* AND ΔG^* IN kJ/mol AND ΔS^* IN J/K/mol)

% of Dioxane (v/v)	Mole (%)	ΔH^* (kJ/mol)	20°C		25°C		30°C		35°C		40°C	
			ΔG^* (kJ/mol)	$-\Delta S^*$ (J/K/mol)	$-\Delta G^*$ (kJ/mol)	$-\Delta S^*$ (J/K/mol)	ΔG^* (kJ/mol)	$-\Delta S^*$ (J/K/mol)	ΔG^* (kJ/mol)	$-\Delta S^*$ (J/K/mol)	ΔG^* (kJ/mol)	$-\Delta S^*$ (J/K/mol)
0	0	46.72	96.52	169.98	97.50	170.41	98.13	169.68	98.95	169.59	99.60	168.97
10	2.28	44.42	96.83	178.89	97.71	178.83	98.73	179.26	99.43	178.62	100.23	178.31
20	4.99	39.20	96.96	197.15	97.92	197.04	98.85	196.85	99.80	196.77	100.66	196.33
30	8.27	36.10	97.04	207.98	98.08	207.98	99.07	207.82	100.13	207.86	101.05	207.48
40	12.29	32.55	97.09	220.30	98.22	220.37	99.28	220.23	100.32	220.19	101.38	219.91
50	17.37	28.72	97.21	233.76	98.37	233.72	99.52	233.73	100.69	233.68	101.78	233.43
60	23.98	24.50	97.28	248.37	98.54	248.44	99.80	248.49	101.06	248.54	102.25	248.38
70	32.91	21.44	97.40	259.26	98.76	259.46	100.08	259.52	101.44	259.72	102.72	259.66
80	45.68	15.68	97.46	278.12	98.90	279.28	101.29	279.82	101.64	279.09	103.09	279.28

Solvent effect on activation energies (Isocomposition and Isodielectric) of the reaction

From Table-2, it is obvious that E_C values go on decreasing with increasing the concentration of dioxane in reaction media. This trend is probably due to solvation charges 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 several researchers in this field[9–12]. 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 dioxane in the reaction media.

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

The transition state being a large cation (ester $+H^+$) available more for solvation by dioxane molecule than the initial stage, so the third factor seems to be operative in the present case and it also gets support when the values of entropy of activation (ΔS^*) and enthalpy of activation (ΔH^*) go on decreasing with increasing concentration of dioxane (Table-4).

Isodielectric activation energy

With a view to minimize the dielectric effect, the isodielectric activation energy was evaluated from the Arrhenius plot of log k_D values (obtained from interpolation of the plots of log k values against D values of the reaction media) against 1/T adopting the methods of Wolford[13] and Elsemongy[10] and the values thus obtained have been summarized in Table-3. From Table-3, it is found that E_D values go on increasing from 42.90–114.48 kJ/mol with increase in D values from $D = 8$ to $D = 68$. This trend of increase in E_D values is quite in agreement with changes in E_C values of reaction and also with the findings of Wolford[13].

Solvent effect on other activation parameters

The ΔH^*, ΔG^* and ΔS^* values are depicted in Table-4. The enhancement, though small increase in ΔG^* values followed by considerable larger decrease in both the ΔH^* and ΔS^* values is a sign of specific solvation of the transition state and desolvation of the initial state which is in agreement with our view. Elsemongy *et al.*[3] and Cleve[14] have also observed a similar increase in G^* values. Simultaneous increase and decrease in ΔG^* and in both of ΔH^* and ΔS^* values respectively are only possible when the extent (degree) of decrease in ΔS^* values is greater than that in ΔH^* values and from this it may be inferred that the acid catalyzed hydrolysis of ethyl methanoate is entropy controlled reaction.

Obedience of Barclay-Butler relationship

This relation is found to obey the Barclay-Butler relationship[15] as a straight line is obtained when ΔH^* values are plotted against ΔS^* and from the slope of the plot, the values of isokinetic temperature of the reaction comes to be 280.

Effect of $[H^+]$

The effect of change in hydrogen ion concentration $[H^+]$ has also been studied by keeping the ionic strength, % of dioxane and temperature of the reaction constant at $\mu = 0.9$, 60% (v/v) and 30°C respectively.

The plot of log k values against $[H^+]$ is found to have a good straight line with the value of slope equal to 1.027 which may be treated as almost equal to unity. This value of slope (equal to unity) indicates that acid catalyzed hydrolysis of ethyl methanoate in water-dioxane medium follows the pathway of A_{AC}^2 mechanism as reported by Zucker and Hammett[16].

However, further research regarding evaluation of the number of solvent molecules taking part in the formation of activated complex of the reaction is in progress.

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