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Study of the Solvent Effect on Acid Catalysed Hydrolysis of Ethyl Formate in Water—DMF Medium

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Acid catalysed hydrolysis of ethyl formate was studied in DMF—water mixtures of varying compositions, starting from 0 to 60% of DMF (v/v) at different temperatures ranging from 20° to 40°. The rate decreases with increasing percentage of DMF. The isocomposition activation energy, E_{exp}, was evaluated using Arrhenius equation. Enthalpy of activation ΔH^*. free energy of activation ΔG^* and entropy of activation ΔS^*, were calculated using Wynne-Jones and Eyring equation. The trends of variation of these values have been found to reveal the solvation mechanisms by the medium. The variation in rates and activation parameters of the reaction in the medium have been compared with that of water-DMSO medium. The effects of variation of hydrogen ion and back-ground electrolyte were also studied.

THIS work is in continuation of our previous paper[1] on solvent effects in which it was observed that the view of Parker[2] was not wholly true and that the rates of acid catalysed hydrolysis of ethyl formate in aquo-organic solvent mixtures were not enhanced with an increase in the composition of aprotic constituent such as DMSO throughout the whole range. The rate, no doubt, enhanced in the lower concentration region of DMSO but it started decreasing steadily beyond 8 mole percent of the above organic cosolvent.

The exigency of further work in this line was felt on account of this irregular change of specific rate in case of acid catalysed hydrolysis[1] of ethyl formate in water-DMSO mixture. It was thought essential to study the effect of some other aprotic solvent constituent, in place of DMSO, on the acid catalysed hydrolysis of ethyl formate in binary solvent system. It is well established that DMF is an aprotic solvent like DMSO, miscible with water in all proportions at ordinary temperature, forming a homogeneous system and therefore very suitable for the above mentioned study. For this reason the authors have selected the aqueous-DMF solvent mixture to study the same solvolysis reaction in order to explore the pronounced specific effect of the solvent mixture on the reaction.

Experimental

Ethyl formate and DMF were of BDH and E.Merck L. R. grade. These were adequately purified before use. Preparation of solution and other experimental procedure were the same as published earlier[1]. The specific rate constants were determined in different solvent mixtures containing 0 to 60% DMF (v/v) at temperatures ranging from 20° to 40°. Table 1 shows the data for the specific rate constants in above conditions.

The precision in the value of k was determined by repeating an experiment five times at the different temperatures and solvent compositions. The standard deviation σ was found to be not more than 0.05×10^4 min^{-1} in any case. Therefore the reliability of k values is taken to be $\pm 0.05 \times 10^4$ min^{-1} in each case.

Reliabilities in E_{exp} and E_D values (Table 2 and 3) have been calculated with the help of Vector formula[3] using the values of k and T and considering their reliabilities equal to $\pm 0.05 \times 10^4$ min^{-1} and $\pm 0.05°$ respectively. E_{exp} and E_D values were found to be reliable within the limits of ± 0.1 K.cal in all the solvent compositions.

TABLE 1

SPECIFIC RATE CONSTANT, k VALUES FOR HYDROLYSIS OF ETHYL FORMATE IN WATER—DMF MEDIA

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

Temp. (°C)	% of DMF (v/v)								
	0	5	10	15	20	30	40	50	60
20	10.55	9.99	9.56	9.02	8.72	7.92	7.33	6.87	6.19
25	16.17	15.23	14.55	13.40	12.66	11.28	10.47	9.66	8.61
30	24.55	22.96	21.88	19.72	18.30	16.11	14.79	13.41	11.75
35	36.32	34.32	32.58	28.87	26.60	22.65	20.65	18.41	15.85
40	54.17	50.88	48.26	41.71	37.32	31.53	28.51	25.12	21.38

TABLE 2

ISOCOMPOSITION ENERGY OF ACTIVATION (E_{exp})

% of DMF (v/v)	0	5	10	15	20	30	40	50	60
K. cal/ mole	14.93	14.84	14.77	14.00	13 33	12.64	12.40	11.88	11.29

TABLE 3

ISODIELECTRIC ENERGY OF ACTIVATION (E_D)

Dielectric Constant Values	70	68	66	64	62	60
E_D Values in K. cal/ mole	14.27	13.71	13.51	13.22	12.84	12.74

Reliabilities in ΔG^* and ΔS^* values (Table 4) were calculated using the various values of k in a particular condition of temperature and solvent composition.

TABLE 4 — ACTIVATION PARAMETERS FOR ETHYL FORMATE IN DIFFERENT WATER—DMF MIXTURES

ΔH^* in K.cal/mole, ΔG^* in K.cal/mole and $-\Delta S^*$ in cal/mole/degree

% of DMF (v/v)	ΔH^*	20°		25°		30°		35°		40°	
		ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$
0	14 35	23.52	31.30	23.68	31.31	23.83	31.30	24.00	31.33	24.15	31.31
5	14 29	23.55	31.59	23.71	31.61	23.83	31 62	24.03	31.62	24.19	31.61
10	14.12	23.58	32.29	23.74	32.30	23.89	32.27	24.06	32.30	24.22	32.28
15	13.39	23.61	32.88	23.79	34.89	23.96	34.89	24.14	34.89	24.31	34.89
20	12.68	23.63	37.39	23 82	37.40	24.01	37.41	24.19	37.38	24.38	37.39
30	12.03	23.69	39.77	23.89	39.79	24.09	39.78	24.29	39.78	24.48	39.78
40	11.76	23.73	40.87	23.93	40.87	24.14	40.86	24.34	40.86	24.55	40.86
50	11.22	23.77	42.82	23.98	42.82	24.20	42 82	24.41	42.82	24.63	42.82
60	10.70	23.83	44.80	24.05	44.80	24.28	44.80	24.50	44.82	24.73	44.81

They were found to be ±0.05 K.cal and ±0.02 cal/deg/mole respectively.

Results and Discussion

It is evident from Table 1 that the rate constant values decrease at all the temperatures with increasing proportion of DMF in the mixture. The graphical representation of the variations of rate constant (log k) with mole percent of DMF in the mixture have been shown in Fig. 1. The log k values are found to decrease almost uniformly with increasing mole percent of DMF in the mixture.
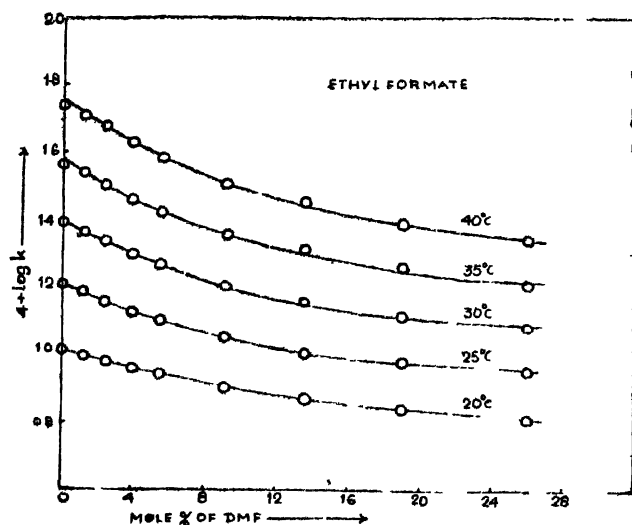

Fig. 1. Variation of log k with mole percent of DMF in the mixture.

Thus the acid catalysed hydrolysis of ethyl formate in water-DMSO as well as in water-DMF shows clearly that the rate constants may or may not be enhanced by increasing the mole percent of the aprotic constituent. Most probably the organic cosolvent exerts two types of opposite effects on the rate. The first type of effects enhancing the rate, are the greater solvation of the transition state and the increase of freewater molecules from water clusters, while the other type of effects responsible for depressing the rate constant are (i) decrease in the bulk dielectric constant of the medium, (ii) decrease of the polarity of the solvent and (iii)

depletion of H_3O^+ due to the formation of DMFH⁺-like species by the reaction given below :

$$H_3O^+ + DMF \rightleftharpoons H_2O + DMFH^+$$

Now the rate constant variation can be explained on the basis of the above effects. Initially, the reacting molecules including the hydrogen ion and the transition state are all solvated by water molecules alone, in water enriched regions, and the change in solvation due to the organic co-solvent is small. The possibility of generation of free water molecules from clusters by DMF is expected only after a critical amount of it has been added into water. Therefore, both the rate enhancing factors are either negligible or very small in the range of solvent mixtures studied. Among the rate decreasing factors the first two are quite in operation from the very beginning. The third factor is bound to decrease the rate as the H_3O^+ concentration is decreased. Thus the rate decreasing factors are more prominent throughout the region of the mixture studied and this explains the decrease of rate constant in general with increasing mole percent of DMF. However, the slow decrease in the rate constant beyond 8 mole percent of DMF in the medium might be due to greater extent of solvation changes in the transition state compared to the initial state. The effect though small at the beginning, becomes appreciable after the above amount of DMF is added.

Arrhenius activation energy (E_{exp}) : Arrhenius activation energy (E_{exp}) also called isocomposition activation energy, E_c, was calculated from the slope of the straight line obtained by plotting log k against $\frac{1}{T}$. The values are tabulated in Table 2.

From the table it appears that E_{exp} values decrease with increasing percent of DMF in the solvent mixture. However, the plot of E_{exp} against mole percentage of DMF (fig. not shown), reveals that the decrease in E_{exp} values is inconsistent upto 10 mole percent of DMF and only after that particular molar composition the decrease seems to be uniform. If one attributes this activation energy decrease only to solvation changes, it has to be concluded that one of the states (either reactant or activated complex) changes its solvation more rapidly than the other. However, the process of solvation changes is quite slow in the mixture upto 8 mole percent of DMF. Since the activated complex is a large cation, it is more vulnerable to be solvated com-

pared to the reactants by aprotic solvents. This view regarding greater solvation of transition state by increasing percent of DMF gets support from entropy of activation change. It is noticed that entropy of activation decreases with increasing DMF which is in conformity with the above view.

Iso-dielectric activation energy (E_D) : In order to annul the effect of dielectric variation on activation energy the iso-dielectric activation energy was calculated from the data as described by Wolford[4]. The variation of E_D values with composition is tabulated in Table 3. The trend in decrease in the E_D values for acid catalysed hydrolysis of ethyl formate in water-DMF medium are in agreement with that observed by Wolford[4] in water-acetone system.

Thermodynamic activation parameters : The thermodynamic activation parameters $\triangle H^*$, $\triangle S^*$ and $\triangle G^*$ were calculated by usual methods[5] and have been mentioned in Table 4. Although the effect of variation of solvent composition on $\triangle G^*$ is negligible, the effect on $\triangle S^*$ and $\triangle H^*$ can not be ignored. The variation of $\triangle S^*$ and $\triangle H^*$ with increasing molar composition of DMF in solvent medium (Fig. 2) is not linear. This non-linear dependence of the activation parameters on the mole percentage of the organic co-solvent is indicative of specific solvation[6] taking place in the medium. Tommila[7], Hyne *et al*[8] and Elsemongy *et al*[9] have also reported similar variation in activation parameters in different hydrolysis reaction in various aquo-organic solvents.
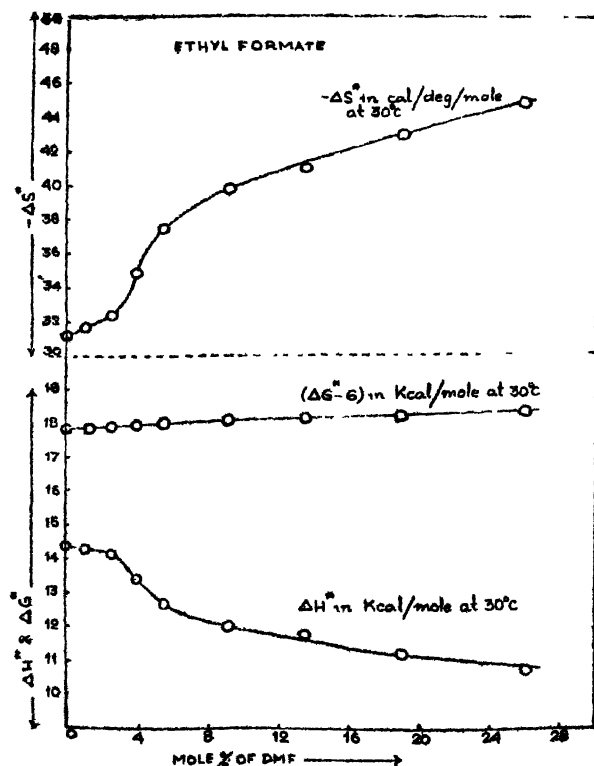
The trend of variation of the activation parameters in the solvent mixtures are quite interesting. In aqueous DMSO medium obvious maxima in rate and minima in the activation parameters are observed[1] with increasing mole percent of organic component while no such maxima or minima are observed in water-DMF system. On the other hand the k values and activation parameters go on decreasing with increasing mole percent of DMF. It, thus, appears that the solvation change is a greater influencing factor on rate changes in case of water-DMSO and the dielectric constant variation plays a secondary role. However, the situation is reversed in case of water-DMF system where the dielectric decrease influences the rate more than the solvation changes and consequently the observed rate show a decrease with increasing mole percent of DMF.

Effect of $[H^+]$ *on specific rate constant* : The effect of $[H^+]$ on the acid catalysed hydrolysis of ethyl formate was studied using HCl solution of different concentrations varying from $0.005N$ to $0.05N$ at a fixed ionic strength $(\mu=0.1)$ and solvent composition (10% DMF v/v) of the medium at 30°. The k values are shown in Table 5. On plotting log k against log $[H^+]$, a straight line having a positive slope equal to 1.004 has resulted. This value of the slope almost equal to unity is indicative of $A_{Ac}2$ mechanism of hydrolysis according to the hypothesis of Zucker and Hammett[10].

TABLE 5—DEPENDENCE OF RATE CONSTANT ON [HCl] AT CONSTANT $\mu(0.1)$ IN 10% DMF (v/v) AT 30°

[HCl]	$k \times 10^4$ in min^{-1}
0.005	12.44
0.01	22.80
0.02	45.77
0.025	55.38
0.03	67.88
0.04	90.12
0.05	113.17

Effect of added salt : The effect of back ground electrolyte with varying concentrations of potassium chloride ranging from $0.05M$ to $0.5M$ was also studied in 10% DMF-water (v/v) medium at a fixed $[H^+]=0.01N$. The results are tabulated in Table 6.

TABLE 6—EFFECT OF ADDED SALT ON RATE CONSTANT IN 10% DMF (v/v) AT 30°. [HCl] = 0.01N

[KCl]	$k \times 10^4$ in min^{-1}
0	21.88
0.05	22.38
0.10	23.00
0.20	23.30
0.30	24.07
0.40	24.30
0.50	25.37

Fig. 2. Variation of activation parameters with mole percent of DMF in the mixture.

Neither the graphical representation of log k versus $\mu^{\frac{1}{2}}$ nor that of log k vs μ gave straight line relationship.

On the other hand the data obey the equation :

$$k = k_0^\beta(1 + b \ \mu)$$

giving straight line having a slope equal to 7.31.

Further studies are in progress to apply the results of this investigation in testing the various equations suggested[10-13] from time to time for evaluating the size of Laidler-Landskroener equation[14].

Acknowledgement

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