Solvent Effect Alkali *Catalysed* Hydrolysis of Ethyl picolinate in Aquo-Acetone Medium

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ABASTRACT: *Interpreting solvent effect on the alkali catalysed reaction is still an intriguing problem. As a part of a broad programme, the alkali catalysed hydrolysis of ethylpicolinate has been investigated conductometrically in acetone (10 to 50% v/v) at different temperatures (298 to 318 K). Several interesting observations of solvent effect have been observed. Acetones have a rate decreasing effect. The results are discussed in terms of the solvent structure, thermodynamic properties of binary aqueous mixtures and dielectric behaviour of the medium. The activation parameters ΔH*, ΔS* and ΔG* have been calculated and discussed in terms of salvation effect. The value of molar polarization energy change and size of the transition state indicates relative polarity and salvation of initial state as compared to the transition state.*

I. INTRODUCTION

Solvent effects on ion-dipole type of reaction have been reported earlier. But a clear understanding about the microscopic changes taking place during activation process has not been interpreted satisfactorily. Solvent effect on alkali catalysed hydrolysis of ethyl picolinate using a variety of co-organic solvents had been studied under different conditions in our laboratory. It gave interesting results; due to the dielectric constant effect, salvation effect etc. in each case of study. Now we propose to study the solvent effect on alkali catalysed hydrolysis of ethyl picolinate in aquo-acetone medium.

II. EXPERIMENTAL

The alkali hydrolysis of ethyl picolinate was followed by conductometric method. In aquo-acetone system the study was made up to 50% (v/v) of organice co-solvent.

The specific rate constant was calculated by deriving the equations relating specific rate constant with conductance for a second order reaction. The activation parameters were calculated by usual method. The values of b* and $N\Sigma Ge^2/b^3$ were obtained by using simple modified methods of Singh et.al.

III. RESULTS AND DISCUSSION

Variation of Rate constant

The specific rate constant have been found to decrease with increasing percentage of acetone in reaction media (table-1) in accordance with the qualitative prediction of many worker. In ion – dipole type of reactions, the transition state is supposed to be highly polar. The formation of transition state is inhibited on decreasing the polarity of the medium. As the proportion of acetone is progressively increased the dielectric constant of the medium decreases and consequently the rate decreases. Therefore, the initial state is expected to be less desovated than the transition state. A simultaneous operation of both dielectric constant effect and solvation change effect proposed in some recent publications appears to be more reasonable in the present case.

Table-1

Specific Rate Constant, k for Alkaline Hydrolysis of Ethyl picolinate in Aquo-cetone Medium.

Temp. (K)	% of Acetone (v/v)				
	10	20	30	40	50
298	22.4	21.0	19.4	18.2	17.1
303	24.8	23.1	21.0	19.3	18.2
308	27.2	25.4	22.9	20.7	19.2
313	30.2	27.5	24.4	22.4	20.6
318	32.3	29.9	26.1	24.4	21.7

Effect of Water Concentration on the Rate of reaction

The effect of $[H_2O]$ on specific rate in aquo-acetone medium was studied by poltting log k vs log (H_2O). The variation was found to be a straight line with a slope value less than 2. Confirming that reaction going on is of bimolecular in nature.

Variation of Activation Parameters

The alkaline hydrolysis of ethyl picolinate was found to obey the Arrhenius law in acetone – water mixture and the values of activation energy for each composition were calculated. On increasing the percentage of organic co-solvent the value of E_c decreases.

The large change in E_c values indicates strong solute – solvent interactions. The decreases in activation energy due to the effect of concentration of water molecules suggest progressive desolvation of the transition state with the increase of organic co-solvent of the reaction mixture. This fact has been also supported by the decrease in ΔS^* values.

ΔS^* and Δh^* appear to be will defined parameters as are expected to compensate each other, so that to keep ΔG^* almost constant. The non-linearity of ΔS^* and ΔH^* values are indicative of specific salvation taking place with change of composition as well as change ΔS^* dielectric constant of the media.

Table-II

Activation Parameters for the Alkaline Hydrolysis of Ethyl Picolinate in Water-Acetone Medium

Acetone (vol.%)	E_c (kJmol^{-1})	ΔH^* (kJmol^{-1})	ΔS^* (kJmol^{-1})	ΔG^* (kJmol^{-1})				
				298K	303K	308K	313K	318K
10	15.51	11.68	-213.93	75.43	76.50	77.57	78.64	79.71
20	14.55	11.11	-216.40	75.60	76.68	77.76	78.84	79.93
30	12.26	9.38	-222.88	75.80	76.91	78.03	79.14	80.26
40	11.68	7.28	-230.58	75.99	77.15	78.30	79.45	80.50
50	9.96	6.32	-234.11	76.08	77.36	78.43	79.60	80.77

ΔH^* values were plotted against ΔS^* with view to study the iso-kinetic relationship. The plot is linear one as expected and obeys Barclays-Butler Rule. The slope comes about 302 which suggest weak interactions taking place between solvent – solute as well as solvent – solvent molecules.

The iso-dielectric activation energy, E_D, was obtained by plotting log k_D against 1/T. table –III shows that the E_D values increase with increasing dielectric constant. On perusal of E_D values at different dielectric constant it is evident that the effect of salvation appears to be quite considerable as change in E_D value is very large.

Table- III

Iso-dielectric Activation Energy, ED

Dielectric Constant	50	55	60	65	70	75
ED(in kJ/mole)	18.96	18.19	17.04	15.89	14.36	13.79

Molar Polarisation Energy Change and Size of Transition State

The molar Polarization energy change was found to be positive confirming the earlier conclusion of more polar initial state. The decreasing trend of the value (table-IV) with increasing temperature suggests greater desolvation of initial state.

Table-IV

Molar Polarisation Energy Change, Size of the Transition state and Potential Energy

Decrease (at D= 60)

Temp. (K)	$N\Sigma\ Ge^2/b^3$(kJmol^{-1})	$N[Z^2e^2/bA - Z^2e^2/b*]$ (in kJ)	b* (in A)
298	285.33	-73.65	2.11
303	258.78	-63.60	2.50
308	254.38	-61.93	2.53
313	204.11	-42.90	2.91
318	153.85	-23.87	3.17

The decrease in potential energy values suggests that in a bimolecular reaction as OH- ion approaches the ester molecule the symmetry of both the units are distorted which is even more pronounced at higher temperatures. It also suggested that potential energy surface at the 'col' has a definite cavity. The existence of such cavity at the potential energy surface may be considered as an indication of formation of unstable reaction intermediate.

The size of the transition state is reasonable and acceptable.

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