

Study of Solvent Effect on Kinetics of Alkaline Hydrolysis of Ethylpicolinate in Water-Acetone Medium

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ABSTRACT: An attempt has been made to study the kinetics of alkaline hydrolysis of ethylpicolinate in water-acetone medium evaluating rate constant of varying composition (10% to 50% acetone (v/v)) at temperature range 25°C to 45°C. The rates were found to decrease with increasing percentage of acetone at all the temperatures. The isocomposition activation energy and thermodynamic activation parameters were evaluated to explain solvation. The reaction is basically entropy controlled.

Keyword:- Ethylpicolinate, Acetone, Thermodynamic activation parameters, solvent stabilisation operator.

authors^{1,5,7,8}. In the present study, we have attempted to see the effect of aprotic solvent mixture (water-acetone) on alkaline hydrolysis of ester (ethylpicolinate) which has immense medicinal importance. When the mineral is a picolinate, minerals uptake by tissues is far greater. It is demonstrated that a commonly used pancreatic extract contains a substantial concentration of picolinic acid. Higher concentration of picolinic acid in human milk results in the formation of picolinic acid-zinc complexes which are more easily absorbed. Due to aforesaid medicinal importance, we have selected ethylpicolinate as ester.

I. INTRODUCTION

A number of papers¹⁻¹⁹ have been published regarding solvent effect on hydrolysis of ester in binary solvent mixtures. Some of them²⁻³ have supported the views of Parker⁴ which states about the rate enhancement by aprotic solvent constituent of binary solvent system. However, decrease in the hydrolysis rate by several aprotic solvents has also been noticed by several

II. MATERIAL AND METHODS

Ethylpicolinate and acetone of B.D.H. and E. Merck L.R. Grade were used and purified by known procedures. The experimental procedure is the same as previous communication.⁹ The specific rate constants were determined in different solvent mixtures containing 10 to 50% acetone (v/v) at temperature range from 25°C to 45°C. The reliability of k values were found to be $\pm 0.1 \times 10^{-2}$.

TABLE -1: SPECIFIC RATE CONSTANTS (K) IN WATER-ACETONE MEDIA
K(Lmol⁻¹ min⁻¹)

Temp. (°C)	Acetone/. (v/v)				
	10	20	30	40	50
25	17.8	13.2	11.2	10.0	8.5
30	25.1	18.6	15.9	13.5	11.2
35	35.5	25.7	21.4	18.2	15.1
45	70.8	50.1	39.8	33.1	26.3

III. RESULTS AND DISCUSSION

The hydrolysis of ethylpicolinate follows BAC² mechanism. According to this mechanism, the rate determining step is addition of OH⁻ ion to carbonyl carbon. The formation of transition state is Polar in such case. However dielectric constant of the medium is decreasing with increasing percentage of acetone. According to the first clause of Ingold theory¹⁰, rate should fall. This is in

conformity with the experimental observation. Such decrease in rate has been observed by Anantkishnan et.al.¹¹. They have stated that in a medium of dielectric constant higher than 10, solvent-solute interaction is more influencing than dielectric constant-so, it is concluded that decrease in rate in water-acetone medium is the combined effect of decrease in dielectric constant as well as solute-solvent interaction.

Activation Energy

The activation energy value decreases with increasing Percentage of acetone.

TABLE-2 : ACTIVATION ENERGY (E_c) VALUES

Acetone% (v/v)	10	20	30	40	50
E _c (kJ mol ⁻¹)	58.0	55.5	52.1	49.6	45.8

Here, the transition state formed is a large dipolar anion with two units of negative charge on it, its solvation will increase as compared to the initial state with increasing percentage of acetone. Hence, E_c values will certainly decrease. But it is important to note that rate of reaction is not increasing. This may be on account of the fact that the reaction is entropy controlled.

THERMODYNAMIC PARAMETERS

The thermodynamic activation parameters ΔH^{*}, ΔS^{*} and ΔG^{*} Calculated by usual procedures have been given in table-3

From the table, it is obvious that ΔG^{*} increases very slowly with the increase in the proportion of acetone in solvent medium. This indicates that stability of transition state is little affected by the addition of organic Cosolvent. The variation of ΔH^{*} with ΔS^{*} gives straight line plot which follows Barclary-Butler rule¹². The slope of this straight line called solvent stabilization operator comes to be 255. This suggests that only little solute-solvent interaction is taking place.

TABLE – 3 : Thermodynamic Activation parameters in Water-Acetone Medium ΔH^{*}, ΔG^{*}, in kJ mol⁻¹, ΔS^{*} in J mol⁻¹ k⁻¹

Acetone% (v/v)	25°C			30°C		35°C		45°C	
	ΔH [*]	ΔG [*]	ΔS [*]	ΔG [*]	ΔS [*]	ΔG [*]	ΔS [*]	ΔG [*]	ΔS [*]
10	56.5	76.0	65.7	76.5	65.9	76.9	66.1	77.7	66.5
20	53.7	76.8	77.6	77.2	77.6	77.8	77.9	78.6	78.2
30	49.3	77.2	93.7	77.6	93.1	78.1	93.7	79.2	93.9
40	48.2	77.5	98.30	78.0	98.5	78.6	98.6	79.7	98.2
50	44.7	77.9	111.4	78.7	112.5	79.2	111.7	80.3	112.1

Effect of Ionic Strength

The small effect of ionic strength suggests that the reaction is not of ion-ion type but ion-molecule type.

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