

Study of Solvent Effects on Kinetics of Alkaline Hydrolysis of Methyl Nicotinate in Aquo-Propan-1-ol Medium

D.K. VERMA, PRASHANT PRIYADARSHI, PRATIBHA PRIYADARSHINI,
RAJNISH KUMAR SINGH and R.N. PANDEY^{1*}

Department of Chemistry, Patna University, Patna-800005 (INDIA)

¹P.G. Centre of Chemistry, College of Commerce (M.U.),

Patna-800020 (INDIA)

Email : rajnishkumarsingh72@gmail.com

Prashant_12289@rediffmail.com

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Abstract

The effect of mixed aqueous solvent, propan-1-ol on alkaline hydrolysis of methyl nicotinate was studied at various solvent composition at temperature ranges from 25°C to 45°C. Various thermodynamic activation parameters such as ΔG^* , ΔH^* and ΔS^* , isocomposition activation energy and the effect of dielectric constant on rate of reaction are evaluated to understand the mechanism of solvent effect on methyl nicotinate.

Key words: Methyl nicotinate, thermodynamic parameters, activation energy.

Introduction

Solvents play important role in the study of mechanism and rate of reaction and a lot of works on solvent effects has been done in recent years.¹⁻³ However a literature survey revealed that less amount of work have been done with heterocyclic acid esters.⁴⁻⁶ The present study describes a kinetic study of the effect of aqueous propan-1-ol water media on hydrolysis of methyl nicotinate.

Experimental

Methyl nicotinate and propan-1-ol of C.P. Merck grade were used and purified by known procedure. Preparation of solution and other experimental procedure are the same as reported in literature⁷⁻⁹. The conductivity bridge method is used for rate determination. In the present hydrolysis, the faster hydroxyl ions are replaced by slow nicotinate ions resulting in gradual decrease in conductance of the reaction mixture. The rate constant was

determined by suitably correlating the conductance of the reaction mixture with the concentration of the reactants. A 0.05N solution of the ester and a 0.05 N NaOH solution were used.

Results and Discussion

The rate constant values were evaluated from the equation :

$$\Lambda_t = \Lambda_\infty + \frac{1}{ak} \frac{\Lambda_0 - \Lambda_t}{t}$$

Where Λ_0 = Initial concentration of alkali before addition of ester.

Λ_t = Conductance at time t (in minute)

Λ_∞ = Conductance when ester is completely hydrolysed

a = molar concentration of the alkali
and k = specific rate constant value.

By plotting Λ_t against $\frac{\Lambda_0 - \Lambda_t}{t}$ a

straight line is obtained slope of this line is equal to $1/ak$. Since the initial concentration is known, specific rate constant k can be calculated from the relation :

$$K = \frac{1}{\text{Slope} \times a}$$

The rate constant value of alkaline hydrolysis of methyl nicotinate in aquo-propan-1-ol media at different temperatures is given in table 1.

Table 1.

% of propan-1-ol (V/V)	Temperature			
	25°C	30°C	35°C	45°C
10 %	20.92	28.92	38.85	74.32
20 %	17.01	22.47	30.15	53.82
30 %	14.21	18.28	23.90	40.86
40 %	12.10	15.60	19.92	32.43
50%	10.52	13.30	16.40	26.45

The hydrolysis of methyl nicotinate follows Bac^2 mechanism in Ingold's terminology.¹⁰ According to this theory, the rate controlling step is addition of OH^- ion to Carboxyl Carbon.¹¹ The transition state of the rate controlling step ion will not only be polar but will have two units of negative charges superimposed on it. The formation of such transition states in case of the above ester hydrolysis must be favoured by increasing dielectric constant of the medium. Therefore,

the rate should fall with increasing percentage of propan-1-ol whose dielectric constant is much smaller than water. This is on accordance with Hughes and Ingold theory.¹² In the plot of $\log k$ against mole percent of the solvent, the decrease appears to be quite gradual. The hydrolysis reaction found to obey the Arrhenius law throughout the range of temperature and composition under study. The E_c values (K cal/mole) calculated from the plot of $\log k$ Vs $1/T$ which are shown in table 2.

Table 2.
Activation energy (E_c) values

Propane -1-ol % (V/V)	10%	20%	30%	40%	50%
E_c (K cal mole ⁻¹)	12.49	11.17	10.39	9.51	9.18

The activation energy value (E_c) decreases with increasing percentage of organic co-solvent in the mixture of solvent. If the decrease is attributed to the solvation change then one of the states *i.e.* reactant or transition state is more prone to solvation than other.

Since the transition state is a large dipolar anion with negative charges on it, its solvation will increase with increasing percentage of propan-1-ol compared to the initial state.

Naturally E_c value will decrease. However it is important to note that the rate is not increasing. This may be on account of the fact that the reaction is entropy dependent.

Thermodynamic parameters :

The thermodynamic activation parameters such as ΔH^* , ΔS^* and ΔG^* were calculated using Wyne-Jones and Eyring equation.¹³ They have listed in Table 3.

Table 3.
Thermodynamic activation parameters for the alkaline hydrolysis of methyl nicotinate in aquo-propan-1-ol media at different temperatures.

% of propan-1-ol	ΔH^*	25°C		30°C		35°C		45°C	
		ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*
10 %	11.80	18.01	20.84	18.11	20.83	18.24	20.91	18.44	21.07
20%	10.82	18.13	24.53	18.25	24.52	18.39	27.82	18.65	24.62
30%	9.80	18.27	28.32	18.38	28.31	18.53	28.34	18.82	28.36
40%	9.52	18.34	29.60	18.48	29.57	18.64	29.61	18.96	29.69
50%	8.81	18.42	32.25	18.59	32.2	18.75	32.27	19.10	32.36

ΔH^* in K.Cal mole⁻¹, ΔG^* in K.Cal mole⁻¹, ΔS^* in Cal K⁻¹ mole⁻¹

From the table it is clear that ΔG^* increases very slowly as the solvent composition is increased. Thus shows that the stability of the transition state is very little affected by the addition of organic co-solvent. The graph between ΔH^* and ΔS^* is found to be a straight line which obeys according to the prediction of Barclay – Butler rule.¹⁴ The value of slope was found to be nearly 250, which clearly justifies about the weak solute – solvent interactions occurring in the reaction in this solvent system.

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

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