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Study of Solvent Effect on Alkali catalysed Hydrolysis of Methyl nicotinate in Water-Dioxane Medium

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ABSTRACT:

At temperatures ranging from 250 to 450 degrees Celsius, the alkalicatalyzed hydrolysis of methyl nicotinate was examined in Dioxane-water combinations of varied compositions, commencing from 10% to 50% Dioxane (v/v). The rate lowers as the Dioxane content increases (aprotic solvent). The Arrhenius equation was used to calculate the isocomposition activation energy (E_c). Wynne-Jones and Eyring equations were used to compute activation enthalpy, entropy, and free energy. Researchers have discovered that the solvation mechanism can be deduced from the patterns of variation in these numbers. Additional considerations included water molecules' involvement in the transition state as well as changes in molar polarization energy.

Keywords: There is an interaction between the ion and the solvent throughout the process of dissolving the ion.

INTRODUCTION:

In this study, it was found that an increase in the composition of an aprotic constituent such as dioxane did not increase the rate of alkalicatalysed hydrolysis of methyl nicotinate in aquo-organic solvent combinations, contrary to what Parker¹ claimed. It is well known that 1, 4-dioxane is an aprotic solvent that is completely soluble in water at room temperature, making it ideal for the investigation at hand. The effect of solvents on esters' hydrolysis has been extensively studied in the literature (2-18), but the mechanism by which solvents affect the alkaline hydrolysis of esters with heterocyclic rings, which have numerous applications in biology and medicine, has received surprisingly little attention. The authors chose methyl nicotinate as an ester and 1,4-dioxane as an aprotic organic solvent because of the above considerations.

EXPERIMENTAL:

Everything that went into this experiment was CP-graded (Merck). A well-established technique was used to purify the organic solvent 1,4-dioxane. The alkaline KMnO_4 utilized in the reaction mixture was used to make the water used in the reaction mixture. The experiment's steps were laid out in detail by the author. 19 In order to calculate the rate constants, the equation was used 1

In other words, it's impossible. k t

since before adding ester, conductivity was set at 0.

The conductivity of a medium is

it's a matter of time (t),

' a ' is the molecular weight of the ester, and ' a ' is the conductivity.

concentration of alkali For alkaline hydrolysis of methyl nicotinate in dioxane-water mixtures, the specific rate constant values are provided in Table-1

Table-1

Specific rate constant (K) values for the alkaline hydrolysis of methyl nicotinate in 1,4-dioxane-water mixture.

K (lit.mol⁻¹ min⁻¹)

%	25 ⁰	30 ⁰	35 ⁰	45 ⁰
10	8.50	13.49	19.92	45.64
20	6.78	16.50	15.53	35.57
30	5.91	8.74	12.92	28.26
40	5.17	7.47	10.81	23.10
50	4.19	6.31	8.77	18.33

RESULT AND DISCUSSION:

According to Hughes and Ingold²⁰ and Amis, the specific rate constant values decrease noticeably as the amount of organic solvent increases in the reaction mixture. ²¹ Transition state concentration decreases as the dielectric constant of the medium decreases due to the addition of organic co-solvents. As a result, disintegration of the initial state is more pronounced than in the transition state, which is also supported by the decrease in activation energy

Table-2

Isocomposition Activation Energy E_a (Kcal mol⁻¹) values

%1,4-dioxane (v/v)

	10%	20%	30%	40%	50%
E_c	63.76	62.23	61.27	55.91	55.14

Wolford also determined the dielectric activation energy (ED). 22 The levels of isodielectric activation energy increased in this solvent media, according to the research. It shows that solvation effects are more important than dielectric effects in th

Table-3

Isocomposition Activation Energy (ED in Kcal mol⁻¹) values 1,4-dioxane

Dielectric constant	45	50	55	60	65	70
E_D	64.72	66.25	66.63	67.40	68.93	70.08

Table-4 Thermodynamic Activation Parameters

ΔH^* (KJ mol⁻¹), ΔS^* (JK⁻¹mol⁻¹), ΔG^* (KJmol⁻¹)

% of dioxane(v/v)	ΔH^*	25°C		30°C		35°C		45°C	
		$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*
10	61.3	21.4	67.7	21.0	67.7	21.4	67.8	20.8	67.9
20	60.7	25.3	68.2	25.2	68.3	25.4	68.5	24.9	68.6
30	57.4	37.5	68.6	37.7	68.8	37.5	68.9	38.8	69.7
40	56.7	40.9	68.9	41.3	69.2	41.3	69.4	41.1	69.8
50	49.8	65.8	69.4	65.5	69.6	65.4	69.9	64.7	70.4

It is interesting to note that the thermodynamic parameters, H^* and S^* , decrease with increasing dioxane content in the reaction media as shown in Table 4. This means that alkaline hydrolysis in water-dioxane medium is controlled by the rate of entropy decay, as shown by the equation: $G^* = H^* - T S^*$, which states that the depletion of both H^* values and the entropy of the water-dioxane medium is greater than that of the entropy of the water-dioxane medium. Dioxane's S^* and H^* do not change linearly when the molar composition of the solvent medium increases (fig. 1). A unique solvation in the medium is shown by this non-linear dependency of activation parameters on the mole percentage of

organic co-solvent. Similar variations in activation parameters have been found by Tommilla et al.²³ and Elsemongy et al.²⁴ in other aquo-organic solvent hydrolysis reactions.

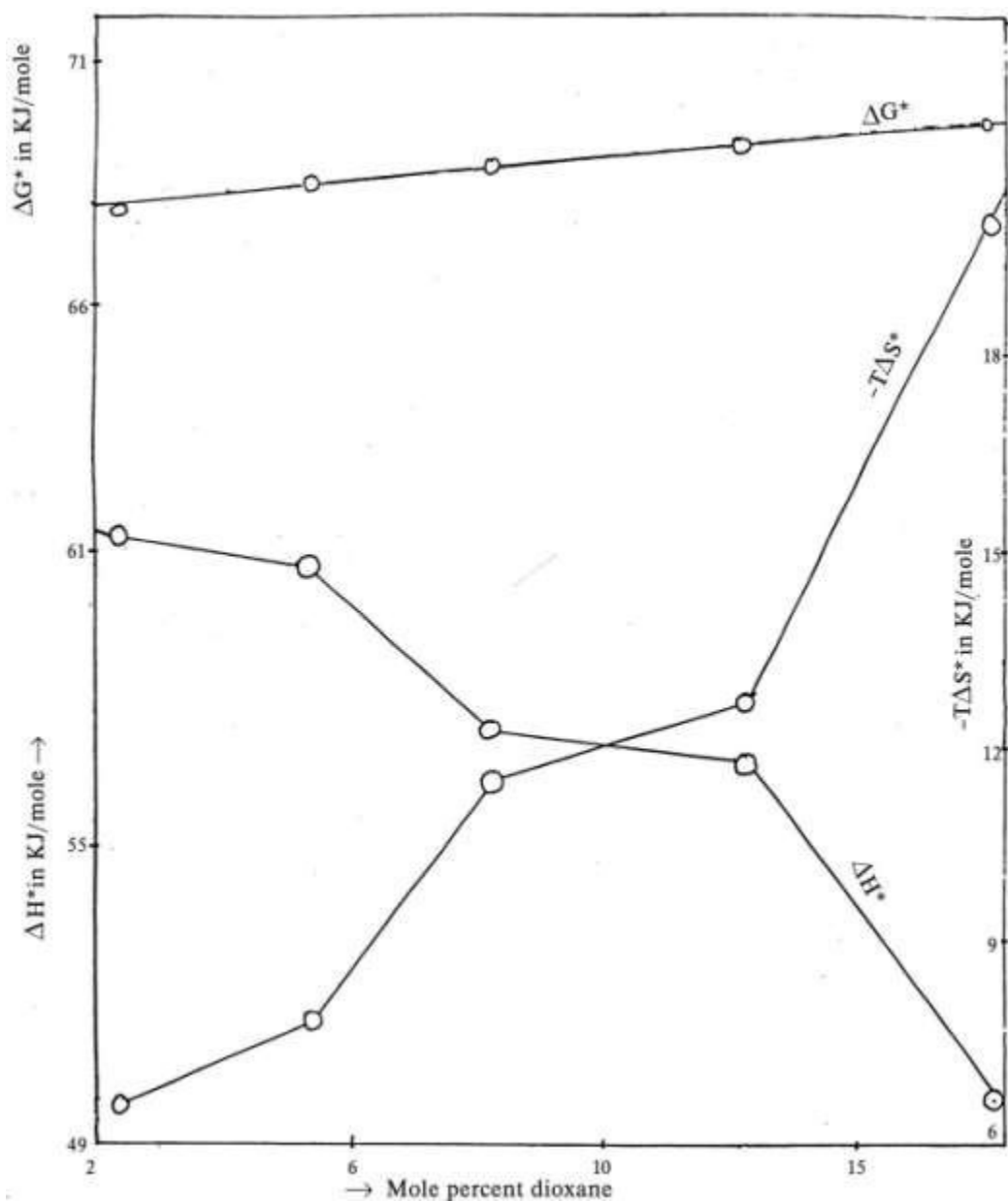


Fig. 1 : Plot of $\Delta H^\ddagger$, $-\Delta S^\ddagger$, $\Delta G^\ddagger$ Vs. Mole percent dioxane for alkaline hydrolysis of methyl nicotinate in aquo-dioxane media.

Effect of Concentration of Water on rate and mechanism of reaction:

According to Robertson, the quantity of water molecules attached to the activated complex was calculated by plotting $\log K$ against $\log H_2O$. In the equation below, $25 \log K = \log K_D n \log H_2O$

An important tool for understanding reaction mechanisms involves using the solvation number n , as seen above. The number of water molecules in the transition state should be noted.

As the temperature rises from 25°C to 45°C, it goes from 1.02 to 1.38. According to Bensen et al., for bimolecular reactions, n is below 3 and for unimolecular reactions, n is about 5. As a result, our current study is a bimolecular process.

Molar polarisation energy change:

Electronegativity variations between atoms and the composition of the solvent medium influence the distribution of electronic charge in a molecule. Because the solute molecule is transferred from one molecule to another, the polarization energy changes as a result. Singh and Jha²⁶'s modified equation was used to calculate the molar polarization energy change. Table 5 includes these data.

Table-5

Temp(°C)	E_D	Slope	(1-1/D)	$\frac{4-0.94RTA}{(1-1/D)}$	$1.8E_D$	$NZGe^2/b^3$
25	64.72	42.30	0.978	-419.62	116.49	-536.11
30	64.72	42.50	0.978	-428.67	116.49	-545.16
35	64.72	42.81	0.978	-438.93	116.49	-555.42
45	64.72	43.20	0.978	-457.31	116.49	-573.80

a starting point Molar polarisation energy change values in aquo-dioxane media were found to be negative. The researchers discovered that as the temperature rose, these levels fell. This suggests that the transition state is more polarized than previously thought.

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