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Study of Variation in Activation Parameters in DMSO-H_2O Media during Alkaline Hydrolysis of Ethyl Picolinate

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Variation in activation parameters during alkaline hydrolysis of ethyl picolinate was studied in DMSO-H_2O media at different temperatures. The rate constant was found to increase with increasing percentage of DMSO indicating a somewhat less polar activated complex. Both iso-composition activation energy (E_c) and iso-dielectric activation energy (E_D) for the above mentioned hydrolysis have been found to increase with increasing composition of DMSO. The variation in other activation parameters ΔS^*, ΔH^* and ΔG^* have also been calculated and interpreted. The size of activated complex was also calculated to corroborate the above information. The polarizability of the activated complex was expressed by a new function $\Sigma NGe^2/b^3$. The stability of the activated complex was predicated by calculating the value of potential energy decrease in the activation process.

Key Words: Activation parameters, DMSO-H_2O, Hydrolysis, Ethyl picolinate.

INTRODUCTION

Several works have been reported to show that an inert solvent can influence both the rate as well as the mechanism of chemical reactions. The effect of aquo-organic solvents has been found more pronounced.

In this context a study has been made on alkaline hydrolysis of heterocyclic ester, ethyl picolinate in water-DMSO media. The results have been interpreted on the basis of a number of parameters such as dielectric constant effects, solvation effect, etc. It is believed that these effects operate simultaneously. The dominance of one effect over the other was proposed with the help of results obtained. An attempt has been made to explain it on the basis of change in polarization energy expressed by the funciton $\Sigma NGe^2/b^3$. The size of the activated complex and the potential energy decrease in the activation process was also calculated to predict the nature of the reaction intermediate.

EXPERIMENTAL

HCl, DMSO and NaOH used were of BDH, Merck/SISCO and E. Merck/BDH grade respectively. Conductivity bridge and conductivity cell used were of Elico (CM-82) mark. Purification of DMSO was carried out by the known methods.

Water used in the preparation of solutions was doubly distilled from alkaline $KMnO_4$. Standard N/5 NaOH solution was made in different solvent mixtures of DMSO varying from 10 to 40% (v/v) in water. After thermostating the solution its conductivity, Λ_0 was determined. Ester was added and change in conductivity with time, Λ_t was obtained for different compositions. The values of specific rate constant, k were found within the experimental error range (±0.05) with the values of k obtained from plot of Λ_t *vs.* $(\Lambda_0 - \Lambda_t)/t$.[1]

RESULTS AND DISCUSSION

Rate variation

Table-1 shows that the values of the specific rate constant for the alkaline hydrolysis of ethyl picolinate in DMSO-H_2O media increased gradually on increasing the percentage of DMSO at all temperatures. Similar rate enhancement has also been observed by Robert[2] in cases of alkaline hydrolysis of other simple aliphatic acid esters. The rate enhancement even by the decrease of dielectric constant of the medium in above cases have been explained by Parker[3] on the basis of special type of solvation mechanism of anions by aprotic polar solvents. However, such explanations have been criticized because many aprotic solvents including DMSO have been observed to retard the specific rate of hydrolysis in several cases. 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

k VALUES FOR THE ALKALINE HYDROLYSIS OF ETHYL PICOLINATE IN H_2O-DMSO MEDIUM

Temp. (°C)	DMSO (v/v) (%)			
	10	20	30	40
25	16.6	19.5	24.4	30.9
30	21.9	25.7	32.4	43.7
35	28.2	34.7	43.7	60.3
49	36.3	47.8	58.9	83.2

Variation of Activation Parameters

The plot of log k values against $10^3/T$ gives a straight line in each case and therefore Arrhenius equation is applicable. E_c values obtained from the slope have been shown in Table-2. The iso-dielectric activation energy, E_D values have also abeen calculated by usual procedure (Table-3). Other activation parameters such as ΔH^*, ΔS^* and ΔG^* have also been calculated and presented in Table-4. It is to be noted that both ΔH^* and ΔS^* values increase non-linearly with increasing composition of DMSO. The increase in ΔS^* values according to the views of

Hudson and Salville[4] is indicative of specific solvation phenomena. Further, the increase of specific rate even on increase in ΔS* values suggests that the hydrolysis reaction in DMSO-H_2O medium is enthalpy controlled. ΔG* values appear to decrease slightly within the experimental range of precision. The plot of ΔH* against ΔS* gives straight line and thus Barclay-Butler[5] rule is obeyed in this case. Further, the slope of the above plot is 320 and is definitely less than 400 as suggested by Leffler *et al.*[6] in case of existence of solvent-solute interaction.

TABLE-2

ISO-COMPOSITION ACTIVATION ENERGY, E_c

DMSO (vol %)	10	20	30	40
E_c (kJ mol^{-1})	40.7	46.5	48.4	51.5

TABLE-3

ISO-DIELECTRIC ACTIVATION ENERGY, E_D

Dielectric constant	70	71	72	73	74
E_D (kJ mol^{-1})	18.19	24.32	27.38	28.15	28.72

TABLE-4

ACTIVATION PARAMETERS FOR THE ALKALINE HYDROLYSIS OF ETHYL PICOLINATE IN WATER-DMSO MEDIUM

DMSO (vol. %)	ΔH* (kJ mol^{-1})	ΔS* (J mol^{-1})	Δg* (kJ mol^{-1})			
			298 K	303 K	308 K	313 K
10	37.34	131.18	76.68	77.33	78.00	78.66
20	42.70	114.44	76.67	77.24	77.81	78.38
30	44.04	111.18	77.18	77.73	78.29	78.84
40	46.68	90.31	74.50	74.95	75.40	75.85

Molar Polarization Energy Change and Size of Transition State

Jha *et al.*[7] and Singh *et al.*[8] have suggested a modified procedure to calculate the function $\Sigma NGe^2/b^3$ from the solvent effect study. The function which expresses the change in the polarization has been calculated in the case of alkaline hydrolysis of ethyl picolinate. The values are recorded in Table-5. Since the values of function are positive, the reactant molecules appear to be more polarized than the transition state in presence of DMSO. The size of the activated complex is reasonable and acceptable as it is comparable to that reported by Kumar[9] and Kumar *et al.*[10]

TABLE-5

MOLAR POLARIZATION ENERGY CHANGE, $\Sigma NGe^2/b^3$, SIZE OF THE TRANSITION STATE, b* AND POTENTIAL ENERGY DECREASE, $N\left[\frac{Z^2e^2}{b_A}-\frac{Z^2e^2}{b^*}\right]$ at D = 72

Temp. (K)	E_D (kJ mol^{-1})	$\Sigma NGe^2/b^3$ (kJ mol^{-1})	b* (A)	$N\left[\frac{Z^2e^2}{b_A}-\frac{Z^2e^2}{b^*}\right]$ (kJ)
298	27.38	41.18	4.12	39.68
303	27.38	46.05	4.10	37.83
308	27.38	51.77	4.07	35.67
313	27.38	60.02	4.03	32.54

Potential Energy Decrease

The data for the potential energy decrease (Table-5) suggest that potential energy surface at the 'col' has a definite cavity at all temperatures. It also suggests that the depth of the cavity depends upon the solvent composition as well. The occurrence of such cavity in the potential energy surface may be taken as an indication of the existence of unstable reaction intermediate. The possibility of such unstable reaction intermediate in course of ester hydrolysis in alkaline medium has also been found by other workers[11, 12].

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