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Study the effect of temperature and substarate concentration on the rate of hydrolysis of 2 ethyl-6-methyl anline phosphate monoester

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***Abstract*-** The kinetic study, cover all the important aspects of chemical reaction including mechanism. The outcome of investigations indirectly explain the path of certain complex biochemical processes. The role of the organic phosphate ester in chemistry and particularly in biochemistry were recognized quite early because of common C—N—P linkages present in nucleotides. With this view, investigations of the kinetic study of the hydrolysis of 2-ethyl, 6-methylaniline phosphate ester has been made in a wide range of various experimental conditions at pH 1.24. The rate of coefficents of temperature effect have been determined. The reactive species has been found to undergo hydrolysis with common P—N bond fission, with bimolecular reaction path, since the entropy of a activation energy falls in the range.

I. INTRODUCTION

Organic phosphate ester play an important role in various branches of chemistry, recent biochemical researches on nucleotides have added to the organic compounds of phosphate esters[1,2] are very important due to their wide range of applications in various branches of chemistry. They are essential constituent of protoplasm and play an significant role in the maintenance of life. They are artificially synthesised for their practical use as lubricants,[3] oil additives,[4] plasticizers[5] and pesticides[6]. Thus, organophosphate esters have significant chemical, physical and biological properties. Phosphate ester transformation being metabolic process appreciated biochemists as well as physico-organic chemists, to study the complexity and variety of mechanistic aspects of the ester reaction. Recent bio-chemcial researches on nucleotides[7], which possess ester linkages, have proved the significance of chemistry of phosphate esters. There is a growing interest of investigators in the mechanism of biochemical processes, in which individual phosphate ester play important roles. Much work has been done on phosphate esters of C—O—p[8,9] linkage and some of their paths have been understood, but the kinetic study of phosphates having C—N—p[10] linkages have received comparitively less attention, even though, their significance as industrially important compounds has been recognized.

II. MATERIAL AND METHODS

PREPARATION OF MONO-2-ETHYL, 6-METHYL-ANILINE PHOSPHATE:

13.5 ml. of 2-ethyl, 6-methylaniline was dissolved in 200 ml. of dry benzene in a round bottom flask, 10.0 ml. of phosphorus oxy-trichloride ($POCl_3$) was added drop by drop with constant stirring to the ice-cooled amine with the help of separating funnel for about half an hour. After the addition of $POCl_3$, it was refluxed for about 50 hours on the soxhlet heater at constant temperature 45°C in order to ensure complete reaction and then distilled at reduced pressure. The first fraction of benzene and unreacted $POCl_3$ was removed by distillation at b_{66}, 50-55°C. The second fraction was dichloridate. It was dissolved in 100 ml. of ice cooled water and kept at low temperature overnight. The 2-ethyl, 6-methylaniline phosphorodichloridate converted into 2-ethyl, 6-methylaniline dihydrogen phosphate, which was extracted with solvent ether. After removing the solvent ether a light brown coloured crystalline solid was obtained, which on recrystallisation with absolute ethyl alcohol gave a white crystalline solid and it was identified to be 2-ethyl, 6-methylaniline phosphate mono-ester with the following physical characteristics:

Table 1 Analysis of elements

Complex	% C	% H	% O	% P	M. pt.	Yield %
2E6MAPME	50.23 (50.20)	6.51 (6.48)	22.32 (22.38)	14.88 (14.92)	226°C	15.02 (14.62)

Table 2 The infrared spectrum of mono-ester

Complex	N-H stretching	C—H stretching	Aromatic ester	—C = C—	—P=0	—P—OH	Substit. A. ring
2E6MAPME	3450 cm^{-1}	2960 cm^{-1}	1718 cm^{-1}	1560 cm^{-1}	1280 cm^{-1}	1170cm^{-1}	770 cm^{-1}

III. RESULTS & DISCUSSION

Contribution of the hydrolysis via neutral species of 2-ethyl, 6-methylaniline phosphate mono-ester has been found in acid and alkaline medium. The hydrolysis of neutral species has been found to associated with conjugate acid species as well as mononegative species in alkaline media respectively. Therefore, the hydrolysis of neutral species in acid region from 1.0 to 6.0 mol. $dm.^{-3}$ HCl. The overall rate of hydrolysis in alkaline region can be estimated at different hydrogen ion concentration, Almost all the phosphate mono-ester have been found to dissociate almost completely at about pH 4.17. The maxima at pH 4.17, where the hydrolysis of mono-ester may be presumed to occur by exclusively it's mononegative species. Consequently, the fractions of mononegative species at this pH value may be taken to almost unity (0.999).

IV. EFFECT OF TEMPERATURE

Kinetic study of the hydrolysis of 2-ethyl, 6-methylaniline phosphate mono-ester has been made at 97°, 90°, 85° and 80°C at pH 1.24, where major contribution to the overall hydrolysis is made by neutral species. A series of systematic kinetic runs were performed to ascertain the molecularity of the reaction or bond fission. The rate coefficients of temperature effect have been determined and summarised in Table-3.

Linearity of the plot shows the uniformity of the reaction in the temperature ranges used. The plot of (Fig. I) gave a negative slope, the values of which have been used to determine Arrhenius parameters by the equation Table-4 summarises the Arrhenius parameters for the neutral species. The reaction via neutral species have been found to hydrolyse bimolecularly, since, the entropy of activation (S*=30.74 e.u.) fall in the range of bimolecular hydrolysis, because the value of entropy is found to be highly negative, the value of frequency factor ($A=4.01x10^6$ sec^{-1}) is not greater than 10^{12} and energy of activation (AE= 19.22 $KcaLmol^{-1}$) is less than 25 $K.Cal.mol^{-1}$. Hence, the reaction proceeds via neutral species, shows bimolecular nature of hydrolysis. Fission of the P—N bond in the hydrolysis of neutral species may be difficult without the help of water because even conjugate acid species have been found to hydrolyse bimolecularly. Therefore, the probability of bimolecular hydrolysis via neutral species is more expected with the above range of the Arrhenius parameters.

V. EFFECT OF SUBSTRATE CONCENTRATION

Determination of kinetic order has been done by carrying out kinetic runs at 1.24 pH using different substrate concentration. The rate coefficients have been summarised in Table-5, which have decreased the value of rate constant. The results show that the rate constants have been found to be independent of the initial concentration of mono-2-ethyl, 6-methylaniline phosphate, which is apparent from the table. Consequently the solvatic reaction proceeds via. Pseudo first order reaction.

TABLE-3 ARRHENIUS PLOT DATA FOR THE RATE OF HYDROLYSIS OF MONO-2-ETHYL. 6-METHYLANILINE PHOSPHATE AT DIFFERENT TEMPERATURES VIA NEUTRAL SPECIES.

pH	t°C	T.K (abs.)	$10^5 X \frac{1}{T}$	$10^5.K_e$ (mol.$dm.^{-3}$ min^{-1}) (Obsd.)	$5+\log K_e$
1.24	97	370	270.3	107.03	2.03
1.24	90	363	275.5	33.65	1.53
1.24	85	358	279.3	13.50	1.13
1.24	80	353	283.3	5.72	0.76

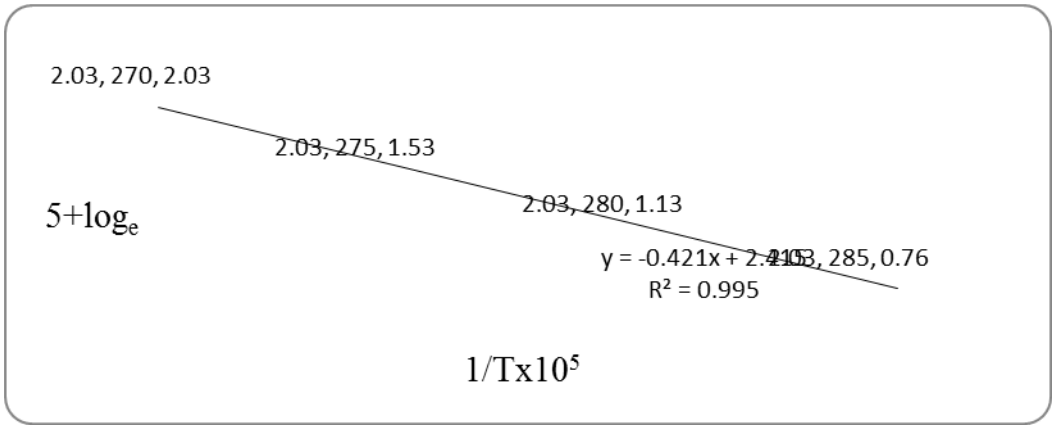
TABLE-4 Arrehenius parameters fot the rate of hydrolysis of mono-2ethyl 6 methyl phosphate via neutral species

HC1 (mol.$dm.^3$)	PARAMETERS		Entropy - S (e.u.)
	Energy of activation (E) (K.cal. $mol.^{-1}$)	Frequency factor (A) (Sec^{-1})	
1.24	19.22	$10.39 x10^6$	30.74

TABLE – 5 Effect of substarte concentration on the rate of hydrolysis of of mono-2ethyl 6 methyl phosphate via neutral species at 97 + 0.5ºC.

pH	Mono-ester Concentration (mol.dm.-3)	$10^5.K_e$ (mol.dm.$^{-3}$ min.$^{-1}$) (Obsd.)
1.24	0.00025	109.00
1.24	0.00050	107.03
1.24	0.00075	106.17

FIG. I Effect of temperature on the rate of hydrolysis of of mono-2ethyl 6 methyl phosphate via neutral species at 97 + 0.5ºC.



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