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Hydrolysis of Mono 2,5-Diethoxy Aniline Phosphate in Buffer Medium: A Kinetic Study

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The kinetics of the hydrolysis of mono 2,5-diethoxy aniline phosphate was studied in acidic and buffer media. Hydrolysis was carried out in buffer media of pH ranging from 1.24-7.46. In both acidic and buffer media, hydrolysis was carried out at three different temperatures keeping other parameters unchanged. The values of Arhenius parameters, energy of activation and change of entropy reflects the bimolecular nature of hydrolysis.

Key Words: Kinetic, Mono 2,5-diethoxy aniline phosphate, Hydrolysis.

INTRODUCTION

Organo phosphate esters[1-4] known for their biochemical significance were the molecules of interest in 19th century. The biochemical reactions related to the carbohydrate and nucleoprotein metabolism involve the formation and cleavage of phosphate bonds. The process in turn provide necessary energy for many biochemical changes.

Organo phosphate esters are the derivatives of organo phosphoric acid and infinite raminifications are possible by making changes in substituent groups attached to phosphorus atom through specific linkages such as C-N-P[5-8] C-O-P[9-14] and C-S-P[15]. Hence, they constitute a large family, which display a great role in biological, industrial, agricultural medicinal and academic field. In present studies, the kinetics of the hydrolysis of mono 2,5-diethoxy aniline phosphate in different buffer medium has been reported.

EXPERIMENTAL

Phosphate esters, on hydrolysis, produce inorganic phosphates and its quantitative estimation was made possible by Allen's modified method[16]. The inorganic phosphates react with ammonium molybdate and forms a complex which is reduced to molybdate blue by addition of bisulphite solutions. The blue colour took 10 min to reach its maximum intensity. The intensity of blue colour is directly proportional to the amount of free phosphoric acid. The optical density of the colour produced was measured by single cell type Systronix photoelectric colorimeter.

Solutions required: Ammonium molybdate, hydrochloric acid, amidol, potassium dihydrogen phosphate for calibration of colorimeter, buffer solutions used-suggested by Stene[17].

Buffer solutions used: The buffer solutions were used to maintain different pH values. Stene[17] determined the pH values of buffer solutions at 20 and 150 °C (Table-1). The interpolated values of these buffer solutions mentioned at 100 °C have been correspondingly used at 98-100 °C.

TABLE-1
COMPOSITION AND pH VALUES OF DIFFERENT BUFFER

Buffer composition	pH measured		Calculated
	20 ºC	150 ºC	100 ºC
0.05 M KCl + 0.0645 M HCl	1.20	1.26	1.24
0.05 M KCl + 0.0263 M HCl	1.60	1.62	1.61
0.05 M KCl + 0.0067 M HCl	2.20	2.20	2.20
0.05 M-P + 0.0147 M HCl	3.20	3.41	3.33
0.05 M-P + 0.00261 M NaOH	3.97	4.26	4.17
0.05 M-P + 0.0075 M NaOH	4.40	5.11	4.10
0.05 M-P + 0.0300 M NaOH	5.20	5.88	5.60
0.05 M-P + 0.0455 M NaOH	6.00	6.70	6.43
0.05 M-P + 0.05 M KCl	7.80	7.26	7.46

Hydrolysis of monoester in buffer medium:

Concentration of mono -2.5 Diethoxy aniline	
Phosphate	0.0005 M
Medium	2.2 pH
Temperature	90 ± 05 °C M
Solvent	Water
Infinite reading	0.42

TABLE-2
BUFFER HYDROLYSIS (pH 2.20) OF THE MONOESTER

Time (min)	Optical density (x)	(a-x)	log K_c	10^3 K_c (min^{-1})
43	0.05	0.37	3.5345	3.43
49	0.10	0.32	3.5370	3.44
98	0.14	0.28	3.5528	3.57
200	0.20	0.22	3.5098	3.23
280	0.26	0.16	3.5374	3.45
400	0.32	0.10	3.5548	3.59

Average value of $K_c = 3.45 \times 10^{-3}$ min^{-1}

RESULTS AND DISCUSSION

Hydrolysis of the monoester at 98 °C in buffers pH 1.24-6.43 has been shown by the log rate-pH profile (Fig. 1). In the region of pH 1.24-4.17 all the monoesters get dissolved and there is an equilibrum between neutral, mononegative species and a proton.

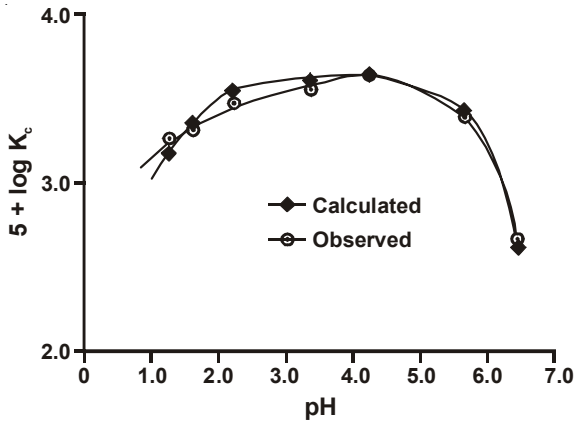

Fig. 1. log rate-pH profile for the hydrolysis of mono-2,5-diethoxyaniline phosphate at 98 ºC

The corresponding rate data for the buffer range is accumulated in Table-3. The rate rises with rise in pH due to the incursion of more reactive mononegative species of monoester upto pH 4.17. The maximum is considered to be arising as due to the sole governing mononegative species.

TABLE-3
CALCULATED FRACTIONS AND RATES (min^{-1}) OF NEUTRAL AND MONONEGATIVE SPECIES FOR THE HYDROLYSIS OF MONO 2,5-DIETHOXY ANILINE PHOSPHATE AT DIFFERENT pH VALUES AT 98 °C

pH	$\frac{M}{M+N}$	$\frac{N}{M+N}$	$10^3 K_M$	$10^3 K_N$	$10^3 K_c$ calc.	$10^3 K_c$ expt	5 + log K_c calc.	5 + log K_c expt.
1.24	0.540	0.460	1.95	1.21	3.16	3.24	2.4997	2.5105
1.61	0.733	0.267	2.65	0.70	3.35	3.30	2.5250	2.5185
2.20	0.914	0.086	3.31	0.22	3.53	3.45	2.5478	2.5378
3.33	0.933	0.007	3.59	0.01	3.60	3.52	2.5563	2.5465
4.17	0.999	0.001	3.62	0.00	3.62	3.62	2.5587	2.5587
	$\frac{D}{M+D}$							
5.60	0.944	0.056	3.42	-	3.42	3.36	2.5340	2.5263
6.43	0.712	0.288	2.58	-	2.58	2.46	2.4116	2.3909

At minimum pH (pH-1.24) only neutral species is present and concentration of mononegative one is much less Fig. 1. Contribution of neutral species continues in the pH region upto pH 4.17 but its contribution decreases rapidly after pH 3.33 while that of mono-negative species increase till it attains the maximum value at pH 4.17 The rise in rates in pH 1.24 to 4.17 may be accounted for as due to hydrolysis *via* both neutral and mononegative species.

The result proves the validity of the presumption that their exists an equilibrium between neutral and mononegative species in pH range 1.24-4.17 and that the dissociation is over at pH 4.17.

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