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Kinetic study of hydrolysis of 2,6-di-propylaniline phosphate esters catalysed by hydrochloric acid

[1] BK Tiwari, [2] Siyaram, *[3] RB Singh

[1, 2] Department of Chemistry, Agra College, Agra, Uttar Pradesh, India
[3] Department of Zoology, School of Life Sciences, Dr. B. R. Ambedkar University, Khandari Campus, Agra, Uttar Pradesh, India

Abstract

The kinetic study of acid catalyzed hydrolysis of 2,6-di-propylaniline phosphate was studied in the acid region from 0.1 to 6.0 mol.dm^{-3} hydrochloric acid at 97±0.5^{0}C in 20% dioxane-water mixture. The rate of reaction increases with increase in HCl acid molarity upto 4.0 mol.dm^{-3} HCl which was largely contributed by the conjugate acid species. Rate data at constant ionic strength was used to identify the reactive species and to determine the theoretical rates. Hydrolysis of di-ester via conjugate acid species was assigned the biomolecular behaviour of the reaction on the basis of Arrhenius parameters. Solvent effect on hydrolytic reaction was found to indicate the formation of a transition state in which charge dispersion occurs. The first order rate coefficient have been calculated by using integrated form of corresponding rate equation.

Keywords: kinetic study of hydrolysis of di phosphate ester

1. Introduction

Phosphate ester are play an important role in the physiology of cells as a structural and functional part of DNA, RNA and its monomeric building blocks. The occurrence as a post-translational signal in proteins and as a head group in phospholipids [1]. Phosphate is an indispensable nutrient that is usually taken up by plant cells and stored interacellularly [2] which helps in photosynthesis, energy transformation and activity of some hormone in both plants and animals [3]. These esters are artificially synthesized for their practical uses as lubricants [4], presence of oxygen [5], fertilizers [6] and smoke generation [7]. They are also used in human medicines by professional operations and general public [8]. Other significant applications are as environmentally degradable pesticides due to their toxicity to a wide range of insects in the environment [9]. They are found throughout the environment and in close contact with humans. The facile hydrolysis of these esters is found everywhere on account of their great values in various chemical and biochemical reactions [10]. Kinetics of the reaction of simple organic phosphates provides an insight into more complicated reactions during their metabolism. Determination of mechanism of hydrolysis of organic phosphate is expected to reveal possible correlation between the reaction path of chemical and enzymatic hydrolysis of biologically important phosphate esters [11]. Kinetic study deals all the important aspects of chemical reaction including mechanism. Various reviews regarding the kinetics and mechanisms of hydrolysis of phosphate esters in neutral alkaline and acidic media have been reported time to time [12-13]. In present investigation mainly deals with the kinetic study of acid catalyzed of 2, 6-di-propylaniline phosphate ester in acid medium.

2. Experimental

The preparation of 2, 6-di-propylaniline phosphate was prepared [14] in our Chemical Research Laboratory, Agra College, Agra, U.P. (INDIA) which involves the reaction of 2,6-propylaniline with phosphorylating agent phosphorous oxychloride in 2:1 molar ratio in benzene solvent. All solutions were prepared in triple distilled water and chemicals used were of AR grade.

Hydrolytic reactions of 2, 6-di-propylaniline phosphate were performed at 97±0.5^{0}C by employing 5.6×10^{-4} mol. dm^{-4} solution in 20/70 (v/v) dioxane-water medium. The progress of kinetics of hydrolytic reaction was studies spectrophotometrically of Allens modified method [15] at 735nm. The method involves the measurement of inorganic phosphate formed from the ester, during the course of its hydrolysis.

3. Results and Discussion

Hydrolysis of 2, 6-di-propylanilene phosphate was carried out in acid region from 0.1 to 6.0 mol. dm^{-3} hydrochloric acid at 97±0.5^{0}C. Pseudo first order rate constants were obtained at different acid molarities are summarized and results are shown in Table-1.

Table 1: Specific acid catalysed rates for the hydrolysis of 2, 6-di-propylaniline phosphate via conjugate acid and neutral species.

S. No.	Ionic Strength (μ)	$K_{H^+} \times 10^5$ (mol. dm^{-3} & min^{-1})	5 ±log K_{H^+}	$K_{N^+} \times 10^5$ (mol. dm^{-3} & min^{-1})	5 + log K_{N^+}
1.	1.0	22.00	1.34	25.00	1.40
2.	2.0	17.86	1.25	22.00	1.34
3.	3.0	13.64	1.13	19.00	1.28

It is clear from the results that the rate of reaction increases with increase in acid molarity upto 5.0 mol dm^{-3} hydrochloric acid. Further rise in acid molarity decreases the rate of reaction. The maximum rate at 5.0 mol dm^{-3} HCl was attributed to complete conversion of substrate into its conjugate acid species. The decrease in rate after 5.0 mol dm^{-3} HCl was attributed to lowering in concentration of attacking nucleophile (water) taking part in the reaction.

In order to determine whether or not there is effect of ionic strength or acid catalysis, kinetic runs were made at six different ionic strength from 0.5 to 3.0μ using an appropriate mixture of sodium chloride and hydrochloric acid. The accelerating ionic effect indicates that 2, 6-di-propylaniline phosphate undergoes hydrolysis with positive effect of ionic strength. The specific acid catalyzed rate and neutral rate at constant ionic strength are shown in Table-2.

Table 2: Calculated and observed rates for the acid catalyzed hydrolysis of 2, 6-di-propylaniline phosphate.

HCl (mol. dm^{-3})	**$10^5 K_N$ (mol. dm^{-3} min^{-1})**	**5 + log K_N**	**$10^5 K_N C_N^+$ (mol. dm^{-3} min^{-1})**	**$10^5 K_N$ (mol. dm^{-3} min^{-1})**	**$10^5 K_N$ (mol. dm^{-3} min^{-1})**	**10^5 Ke mol. dm^{-3} min^{-1}**	**5 +log K^e (Cal cld.)**	**10^5 Ke (mol. dm^{-3} min^{-1}) (obsd.)**
0.1	29.32	1.47	2.73	-	-	32.05	1.51	26.52
0.2	29.13	1.46	5.38	-	-	29.13	1.46	28.13
0.5	28.58	1.45	13.08	-	-	41.66	1.62	36.63
1.0	27.64	1.44	24.83	-	-	52.56	1.72	49.18
1.5	26.79	1.43	35.36	-	-	62.15	1.79	56.41
2.0	25.94	1.41	44.67	-	-	70.61	1.85	64.92
2.5	25.12	1.40	53.03	-	-	78.15	1.89	73.26
3.0	24.32	1.39	60.53	-	-	84.85	1.93	86.00
3.5	23.56	1.37	67.07	-	-	90.63	1.96	93.37
4.0	22.80	1.36	72.78	-	-	95.58	1.98	105.03
5.0	21.38	1.33	82.04	40.18*	10.47*	50.65	1.70	55.09
6.0	20.04	1.30	88.72	20.68*	6.67*	25.32	1.40	28.40

Neutral rate (Kn_o), buffer solution equal to 31.00 × 10^{-5} mol. dm^{-3} min^{-1}
Where, solution with Kn_o = 31.62 × 10^{-5} mol. dm^{-3} min^{-1} value
Determine by ionic strength effect
4.0 mol. dm^{-3} HCl
Kinetic rate low for hydrolysis neutral species

$$K_N = Kn_o \frac{N}{N+M}$$

Kinetic rate low for the hydrolysis via mononegative species

$$K_M = K_{Mo} \frac{M}{M+N}$$

The order of hydrolytic reaction has been found to be Pseudo first order.

3.1 Effect of temperature

In order to determine Arrhenius Parameters [16] for acid catalysed hydrolysis for 2, 6-di-propylaniline phosphate ester. A series of kinetic runs were made at 4 different temp. (95^0, 90^0, 85^0 and 80^0C). The effect has been made examined at 3 and 5 mol. dm^{-3} hydrochloric acid. Arrhenius parameters determine in Table-3 can be calculated the falls in the range of biomolecular reaction.

Table 3: Arrhenius parameters for acid hydrolysis of 2, 6-di-propylaniline phosphate.

S. No.	**HCl mol. dm^{-3}**	**Parameters**		**Entropy -ΔS^{-1} (e.u.)**
		Energy of activation (E) (K. Cal. Mol.$^{-1}$)	**Frequency Factor (A) (Sec^{-1})**	
1.	3.0	18.99	2.36 × 10^6	31.80
2.	5.0	19.68	3.84 × 10^6	30.83

It may be concluded from the result that the magnitude of Arrhenius parameters fall in the range of biomolecular reactions and bend in pH –log rate profile is not due to maximum protonation of di-esters.

4. Conclusion

The 2, 6-di-propylaniline phosphate ester in 0.1-6.0 mol. dm^{-3} hydrochloric acid was found to hydrolyze via neutral and conjugate acid species. The acid catalysed hydrolysis is subjected to positive effect of ionic strength. Biomolecular nature of hydrolysis was supported by Arrhenius parameters. Biomolecular hydrolysis with P-N bond fission of phosphate ester was proposed in di-esters.

5. References

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