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Kinetic study of acid hydrolysis of Di-4-chloro, 3-methyl phenyl phosphate esters catalysed by hydrochloric acid

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Abstract

Kinetic study of acid catalyzed hydrolysis of di-4-chloro, 3-methyl phenyl phosphate was studied in the acid region from 0.1 to 6.0 mol.dm^{-3} hydrochloric acid at 97 ± 0.5^0C in 20% dioxane- water mixture. The rate of reaction increase with increase in hydrochloric 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 as to determine the theoretical rates. Hydrolysis of di-ester via conjugate acid species was assigned the biomolecular behavior 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 acid hydrolysis of di-phosphate ester

Introduction

Phosphate ester are play an important role in the physiology of cells is the participation of phosphate esters 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 which helps in photosynthesis, energy transformation and activity of some hormone in both plant and animals [2]. These esters are artificially synthesized for there practical uses as lubricants [3], presence of oxygen [4], fertilizers [5], fire retardants [6] and smoke generation [7]. They are also used in human medicines in various public hygienic product for use by professional operators and general public. Other significant applications are as environmentally degradable pesticides due to their toxicity to a wide range of insects in the environment [8]. 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 [9, 10]. Phosphoryl and thiophosphoryl transfer reactions are of prime importance for transfer of a phosphoryl group between ATP and ADP is the fundamental mechanism for energy transfer that allows the processes of synthsis and nurve function in biological system [11]. 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 [12]. Kinetic study are mainly deals all the important aspects of chemical reaction including hydrolysis of 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 by various workers [13, 14, 15, 16]. In present investigation was mainly deals with the kinetic study of acid catalyzed of di-4-chloro, 3-methyl phenyl phosphate ester in acid medium. (HCl).

Materials and Methods

The preparations of di-4-chloro, 3-methyl phenyl phosphate was prepared [7] in our Chemical Research Laboratory, Department of Chemistry, Agra College, Agra U.P. (INDIA) which involves the reaction of di-4-chloro, 3-methyl phenyl with phosphorylating agent phosphorous oxychloride in 2:1 molar ratio in benzene solvent. All solutions were prepared in triple distilled water and all chemicals used were of AR grade.

Hydrolytic reactions of di-2-chloro, 3-methyl phenyl phosphate were performed at 97±0.5^0C by employing 5.6x10^{-4} mol. dm^{-4} solution in 20/70 (v/v) dioxane-water medium and pH 1.24 to 7.46. The progress of kinetics of hydrolytic reaction was studies spectrophotometrically of Allens modified method [18] at 735nm. The method involves the measurement of inorganic phosphate formed from thester, during the course of its hydrolysis.

Results and Discussion

Acid hydrolysis of di-2-chloro, 3-methyl phenyl phosphate was carried out in acid region from 0.1 to 6.0 mol. dm^{-3} hydrochloric acid at97±0.5^0C and pH 1.24 to 7.46. Pseudo first order rate constants were obtained at different acid molarities ard summarized and results are given in Table-1.

Table 1: Specific acid catalysed rates for the acid hydrolysis of di-2-chloro, 3-methyl phenyl 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.	0.5	19.00	1.36	20.00	1.50
2.	1.0	15.86	1.28	18.00	1.48
3.	1.5	12.64	1.16	16.00	1.26
4.	2.0	10.26	1.12	13.00	1.18
5.	2.5	08.12	0.86	11.00	1.12

It is clear from the above results that the rate of reaction increases with increases 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} hydrochloric acid was attributed to complete conversion of substance into its conjugate acid species. The decrease in rate after 5.0 mol dm^{-3} hydrochloric acid was attribute to lowering in concentration of attacking nucleophile part in the reaction due to the variation in water activity.

In order to determine whether or not there is effect of ionic strength or acid catalysis,a series of kinetic runs were made at six different ionic strength from 0.5 to 3.0 μ using an appropriate mixture of sodium chloride and hydrochloric acid. The accelerating ionic effect indicated that di-2-chloro, 3-methyl phenyl phosphate undergoes hydrolysis with positive effect of ionic strength. The specific acid catalyzed rate and neutral rate at constant ionic streagth are shown in Table-2.

Table 2: Calculated and observed rates for the acid catalyzed acid hydrolysis of di-2-chloro, 3-methyl phenyl phosphate.

HCI (mol.dm^{-3})	10^5K_N (mol. dm^{-3} & min^{-1})	5+log K_N	$10^5K_N C_N^+$ (mol. dm^{-3} min^{-1})	10^5K_N (mol. dm^{-3} min^{-1})	10^5K_N (mol. dm^{-3} min^{-1})	10^5Ke (mol. dm^{-3} min^{-1})	5+log K^e (Cal cld.)	10^5Ke (mol. dm^{-3} min^{-1}) (obsd.)
0.1	28.32	1.47	2.73	-	-	32.05	1.51	25.52
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	98.03
5.0	21.38	1.33	82.04	38.18	9.48	50.65	1.70	54.09
6.0	20.04	1.30	88.72	19.62	6.52	25.32	1.40	26.40

Neutral rate (Kn_0), Buffer solution equal to 31.00 x 10^{-5} mol. dm^{-3} min^{-1} value Where, solution with Kn_0= 31.00 x 10^{-5} mol. dm^{-3} min^{-1} value Determine by ionic strength effect are as follow:

4.0 mol. dm^{-3} HCI Kinetic rate low for hydrolysis neutral species given in equation (1)

$$K_N = Kn_0 \frac{N}{N+M} \qquad (1)$$

Kinetic rate low for the hydrolysis via mononegative species shown in equation. (2)

$$K_M = K_{M0} \frac{M}{M+N} \qquad (2)$$

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

Effect of temperature

In order to determine Arrhenius Parameters [19] for acid catalysed hydrolysis of di-2-chloro, 3-methyl phenyl 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 di-2-chloro, 3-methyl phenyl phosphate.

S. No.	HCI mol. dm^{-3}	Parameters		Entropy - ΔS^{-1} (e.u.)
		Energy of activation (E) (K. Cal. $Mol.^{-1}$)	Frequency Factor (A) (Sec^{-1})	
1.	0.29	12.82	2.36×10^6	30.80
2.	0.86	10.24	3.84×10^6	29.83

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

Conclusion

The di-2-chloro, 3-methyl phenyl phosphate ester in 0.1-0.6 mol. dm^{-3} hydrochloric acid was found to hydrolyzed 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-O bond fission of di-2-chloro, 3-methyl phenyl phosphate ester was proposed in di-esters.

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