



Kinetic hydrolysis of mono-2,4,5-tri-methyl phenyl phosphate ester in Buffer medium

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Abstract: Kinetic study of the hydrolysis of mono-2,4,5-tri-methyl phenyl phosphate ester has been investigated in pH 0.00 to 7.46 at $97 \pm 0.5^\circ\text{C}$ in dioxane-water medium 40% (v/v). The pH log rate profile has maximum at pH 4.17. Hydrolysis of mono-ester carried out in buffer solution shows that the neutral and mono negative species are reactive in the range of pH 0.00 to 2.20 and only mono negative species in the range of pH 2.20 to 7.46. The theoretical rate determined from specific rates and fractions of the neutral and mono negative species agree closely with the experimental rates. Biomolecular nature of hydrolytic reaction has been supported on the basis of temperature and solvent effect study. The mono-2,4,5-tri-methyl phenyl phosphate ester involves P-O bond fission, which is strengthened by isokinetic relationship. Probable reaction mechanism has been proposed for the hydrolysis of mono-2,4,5-tri-methyl phenyl phosphate ester with neutral and mono negative species.

Keywords: Hydrolysis, mono-2,4,5-tri-methyl phenyl phosphate, bond fission, neutral and mono negative species.

I. Introduction

Phosphorous is one of the most abundant elements on the earth. Phosphorus has a broad role in living system and the reaction of phosphate esters in solution and in enzyme are of the great importance^[1]. Most of the phosphorus in living system exists in the form of phosphate. It is a part of many essential biological components such as lipids, bones, genetic materials, energy rich molecules (ATP) and signaling molecules (GTP)^[2]. Phosphate esters are very essential in life processes^[3] in living organism for growth, development and maintenance of plants and animals. Phosphate esters have wide range of application in industrial, agricultural and medicinal chemistry owing to their biological and physical properties as well as their utility as synthetic intermediates^[4]. These esters are important surfactants, which are widely used in many fields such as chemical fibers, chemical products, plastic and paper-making^[5]. These are also used in textile and clothing dyeing industry. Extreme toxicity, broad spectrum activity and low cost of organophosphorus compounds have made them as insecticides, pesticides, bactericides and antibiotics^[6]. The mechanisms of hydrolysis of phosphate diesters are of great interest because phosphate diester linkage is highly stable towards solvolytic cleavage and is widely utilized throughout the nature^[7-8]. Hydrolysis of phosphate ester in biology, being involved in protein synthesis, energy transduction and replication of genetic material^[9].

II. Experimental

The mono-2,4,5-tri-methyl phenyl phosphate ester was synthesized by the Rudert method^[10] in Chemical Research Laboratory, Agra College, Agra which involves the reaction of mono-2,4,5-tri-methyl phenyl phosphate with phosphorylating agent phosphorus oxychloride in 2:1 molar ratio in benzene solvent medium. All reactions were carried out at $97 \pm 0.5^\circ\text{C}$ employing 2.0×10.0^{-4} mol. dm^{-3} concentration of the mono-2,4,5-tri-methyl phenyl phosphate ester in 40% (v/v) dioxane-water medium. Buffer solution were proposed using appropriate mixture of KCl, COOH C_6H_4 , COOK, NaOH and H_3BO_3 ^[11]. The progress of the hydrolysis of mono-2,4,5-tri-methyl phenyl phosphate was followed by the estimation of inorganic phosphate spectrophotometrically^[12].

III. Results and Discussion

A. Hydrolysis of neutral and mono negative species

Kinetics of the hydrolysis of mono-2,4,5-tri-methyl phenyl phosphate ester was studied in the range of pH 0.00 to 7.46 in 40% (v/v) dioxane-water medium at 100°C . The pH range of hydrolysis of mono-2,4,5-tri-methyl phenyl

phosphate ester has been found to be governed by two reactive species neutral and mono negative. Both species are participating in hydrolysis but the reactive nature of neutral species decreases due to its conversion into mono negative species. The appearance of mono negative species starts at pH 0.00 and attains maximum value at pH 7.46 as shown in Table-1.

Table-1: Measurement of pH values.

S. No.	Buffer Composition	Measured pH at		Calculated pH at 100°C
		20°C	150°C	
1.	0.05 KCl +0.0645 HCl	1.20	1.26	1.24
2.	0.05 KCl +0.0263 HCl	1.60	1.62	1.62
3.	0.05 KCl +0.0067 HCl	2.20	2.20	2.20
4.	0.05 P ¹ +0.1147 HCl	3.20	3.41	3.33
5.	0.05 P ¹	3.97	4.28	4.17
6.	0.5 P ¹ + 0.03 NaOH	5.20	5.88	5.60
7.	0.5 P ¹ +0.0455 NaOH	6.00	6.70	6.43
8.	0.05 H ₃ PO ₃ +0.05 HCl + 0.1 NaOH	7.80	7.26	7.46

B. Solvent effect

The effect of solvent on the rate of hydrolysis of mono-2,4,5-tri-methyl phenyl phosphate ester has been studied in aqueous dioxane mixture. Pseudo first order rate coefficients have been summarized in Table-2.

Table-2: Effect of solvent on the rate of hydrolysis of mono-2,4,5-tri-methyl phenyl phosphate at 97±0.5°C.

S.No.	HCl (mol.dm ⁻³)	H ₂ O percentage (v/v)	Dioxane (v/v) percentage	10 ⁵ K _c (mol. dm. ⁻³ min. ⁻¹)
1.	3.0	100.00	00.00	126.81
2.	3.0	60.00	40.00	81.18
3.	3.0	50.00	50.00	51.34
4.	5.0	100.00	00.00	81.13
5.	5.0	60.00	40.00	59.88
6.	5.0	50.00	50.00	42.78

The changes in rate with the change in solvent of a reaction have been used to determine the nature of transition state^[13]. The observed significant rise on rates of hydrolysis may be attributed to better proton donating property of dioxane media.

C. Bond Fission

From Arrhenius parameters it is clear that the present mono-2,4,5-tri-methyl phenyl phosphate ester may undergo hydrolysis via P-O or C-N bond fission. The probability of P-O bond fission is also supported by comparative isokinetic rate data of other similarity substituted aryl amino phosphate tri-ester involving P-O bond fission as shown in Table-3.

Table-3: Comparative isokinetic rate data for hydrolysis of mono-2,4,5-tri-methyl phenyl phosphate tri ester via conjugate acid species.

S. No.	Phosphate tri-ester	Medium	Tem. °C	E K.Cal/m	-Δ S ⁻¹ (e.u.)	Bond Fission
1.	p-Chloro-m-methyl phenyl amine	4.0	80	27.46	4.20	P-O
2.	p-chloro phenyl amine	3.0	80	27.465	4.7s1	P-O
3.	5-chloro-2-methylaniline	3.0	80	21.50	21.22	P-O
4.	4-chloro-3-nitroaniline	3.0	97	19.67	29.87	P-O
5.	m-toluidine	4.0	80	14.62	32.94	P-O
6.	m-nitroaniline	3.5	98	16.83	34.57	P-O
7.	Cylohexylamine	2.0	50	15.69	37.47	P-O
8.	p-nitroaniline	2.0	98	15.25	42.71	P-O
9.	p-chloroaniline	4.0	90	11.44	47.68	P-O
10.	p-phenatidine	3.0	98	7.59	52.20	P-O
11.	α-naphthylamine	3.0	98	8.89	55.43	P-O
12.	2,4,5-tri-methyl aniline	3.0	97	18.99	31.80	P-O

*Bond fission assumed

D. Temperature effect

The effect of temperature gives valuable information about the energy requirements of reaction. In order to determine the Arrhenius parameters^[14], kinetic runs were carried out at different temperature in pH 1.24 and pH 4.17. Prediction of the molecularity of the reaction may be made by determining. Arrhenius parameters for hydrolysis via neutral and mono negative species summarized in Table-4 are in the favour of a biomolecular reaction^[15].

Table-4: Arrhenius parameters for the hydrolysis of mono 2,4,5-tri methyl phosphate via neutral and mono negative species.

S. No.	pH	Parameters		
		E (Kcal. mol ⁻¹)	A (Sec ⁻¹)	-Δ S ⁺ (e. u)
1.	4.17	15.26	10.56×10 ⁴	34.56
2.	4.17	16.47	12.20×10 ⁴	36.78

IV. Conclusion

The mono-2,4,5-tri-methyl phenyl phosphate ester in the range of pH 0.00 to 7.46 was found to hydrolysis via neutral and mono negative species. The maximum value at pH 4.17 is due to the hydrolysis via mono negative and neutral species. The pH log rate profile shows that the estimated rates closely agreed well with those experimental rates-Biomolecular nature of the hydrolytic reactions has been supported by Arrhenius parameters. The mono-2,4,5-tri-methyl phenyl phosphate esters involves P-O bond fission, which is strengthened by comparative kinetic rate data.

V. References

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