



Synthesis, Mechanistic Interpretation and Kinetic Study of 2,6 Di-methylphenyl Phosphate Monoester in Acid Medium

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ABSTRACT

Extensive kinetic study has been carried out on the hydrolysis of mono-2,6-dimethylphenyl phosphate ester in acid 0.1 to 6.0 mol. dm⁻³.HCl and buffers from 1.24 to 7.46 pH at 97± 0.5°C in water. Systematic ionic data proves the presence of acid catalyzed hydrolysis. The monoester has been found to be hydrolysis by conjugate acid, mono-negative, neutral and di-negative species. The inorganic phosphate obtained in overall hydrolysis has been estimated by Allen's modified method. Study of the reaction and dioxane- water mixture suggested the nature of transition state in which charges are developed due to bimolecular attack of water molecule. Comparative isokinetic rate data of similarly substituted other phosphate monoesters, whose mechanism is known, supported P-O bond fission.

Key words: Mechanistic Interpretation, Kinetic study, Acid medium.

INTRODUCTION

The effect of the substituents, the hydrolysis of aryl phosphate esters having C-O-P¹⁻⁷ linkages have been studied exhaustively by Mhala and Co-workers^{1,8-9} and established that the effect of substituents of graded polarity¹⁰⁻¹¹, not only effects the reaction rates but also alter the course of the reaction paths. The substituents having positive inductive effect (+I) and tautomeric effect (+T) increase the electron density at the oxygen of the ester linkage. Consequently conjugate acid species is readily formed which enhances the reaction rate. On the other hand substituents having negative inductive effect (-I) and tautomeric effect (-T) reduce the basicity of the ester-oxygen. Polar effects of the

substituents in 2,6-dimethyl phenyl phosphate monoester are expected to favour acid catalysis.

MATERIAL AND METHODS

2,6-dimethylphenyl phosphate monoester has been prepared by general methods (P. Redurt Method¹²⁻¹³). 2,6-dimethyl phenol (24.4 gms) dissolved in dry benzene (120ml) and added POCl₃ (10ml) drop by drop slowly. During 15 minutes with constant stirring, the reaction mixture was refluxed and distilled at reduced pressure. The first fraction distilled at b₃₀, 40-45°C, unreacted benzene and POCl₃ was obtained. After this, the second fraction distilled at b₅₀, 120-140°C, was dissolved in 100ml distilled water, extracted with ether and

recrystallised by absolute alcohol, M.P 162°C (found P:15.35 required theoretically P: 15.41) finally the structure was confirmed by I.R.Spectroscopy. Hydrolysis of 2,6-dimethylphenyl phosphate monoester (0.0005 M) was studied in distilled water and inorganic phosphate was formed during the hydrolysis and estimated colorimetrically by Allen's modified method¹⁴.

RESULTS AND DISCUSSION

Hydrolysis via conjugate acid species

Hydrolysis of mono-2,6-dimethylphenyl phosphate has been kinetically studied in 0.1 to 6.0 mol. dm⁻³. HCl at 97± 0.5°C. Table 1 and (Fig 1) summarises the pseudo first order rate coefficient of the hydrolysis of monoester.

Results shows that the rate increases with

the increases in acid concentration upto 4.0 mol.dm.⁻³HCl,further rise in acidity brings about lowering in rates. The rate maxima or bend of pH-log rate profile in due to ionic strength effect could be determined by carrying out kinetic runs at constant ionic strength. The cause of bend may not be the maximum protonation as ester as a class, which are very feebly basic substances. Bend may also be caused due to water activity effect or ionic effect or due to both.

Plot of log rate constant Vs. acid molarity (Fig 2) and Table-2 gives a linear curves indicating the presence of acid catalysis. Different intercepts on the rate axis are the neutral rate at corresponding ionic strength. Variation of the neutral rates with the ionic strength is governed by the following rate expression.

Table 1: pH- log rate profile of mono-2,6-dimethylphenyl phosphate at 97±0.5°C

HCl(mol.dm ⁻³)	pH	10 ⁵ .Ke(mol.dm ⁻³ .min ⁻¹) (obsd)	5+logKe
6.0	-0.778	43.06	1.63
5.0	-0.699	81.13	1.90
4.0	-0.602	146.68	2.16
3.5	-0.544	135.58	2.13
3.0	-0.477	126.81	2.10
2.5	-0.397	118.99	2.07
2.0	-0.300	107.73	2.03
1.5	-0.176	93.59	1.97
1.0	-0.000	80.26	1.90
0.5	0.301	60.20	1.77
0.4	0.400	58.49	1.76
0.3	0.520	53.93	1.73
0.2	0.700	74.65	1.87
0.1	1.000	88.79	1.94
Buffers-Composition of Buffers have been used	1.24	98.45	1.99
	2.20	128.84	2.11
	3.33	132.76	2.12
	4.17	136.63	2.12
	5.60	127.75	2.10
	6.43	100.79	2.00
	7.46	128.38	2.10

Linear curves represents the reaction at the specific ionic strength by the following rate equation:

$$K_e = K_H^+ \cdot C_H^+ \quad \dots(1)$$

Where K_e , K_H^+ and C_H^+ are the observed rate coefficient and specific acid catalysed rate at that ionic strength and concentration of hydrogen ion respectively.

$$K_H^+ = K_{H_0}^+ \exp.b_{H^+} \cdot \mu \quad \dots(2)$$

$$\text{Or, } K_H^+ \cdot C_H^+ = K_{H_0}^+ \cdot C_H^+ \cdot \exp.b_{H^+} \cdot \mu \quad \dots(3)$$

or

$$5 + \log K_H^+ \cdot C_H^+ = 5 + \log K_{H_0}^+ + \log C_H^+ + b_{H^+}' \cdot \mu \quad \dots(4)$$

Where K_H^+ , $K_{H_0}^+$, b_{H^+}' and μ are specific acid catalysed rate at that ionic strength, at zero ionic strength and a constant respectively.

$$K_N = K_{N_0} \exp.b_{N^+} \cdot \mu \quad \dots(5)$$

or

$$5 + \log K_N = 5 + \log K_{N_0} + b_{N^+}' \cdot \mu \quad \dots(6)$$

Where K_N , K_{N_0} , b_{N^+}' and μ are specific neutral rate at that ionic strength, at zero ionic strength, a constant and ionic strength respectively where b_{H^+}' and $b_{N^+}' = b/2.303$.

The equation(4) and (6) may be used to compute the acid catalysed and neutral rates at each experimental molarity. Thus both acid catalysed and neutral rates may be represented as-

$$K_e = K_{H^+} \cdot C_{H^+} + K_N \quad \dots(7)$$

The specific acid catalysed and specific neutral rates for the hydrolysis of monoester have been summarized in Table-3

With the helps of above equations, theoretical rates can be calculated which then be compared with the experimental rates of mono-2,6-dimethylphenyl phosphate and there is remarkable similarities between them upto 4.0 mol.dm⁻³ HCl. The values of acid catalysed rate ($5 + \log K_{H_0}^+ = 1.52$)

Table 2: hydrolysis of mono-2,6 dimethylphenyl phosphate at constant ionic strength at 97°C

Ionic Strength μ	Composition		$K_e \times 10^5$ (mol. dm ⁻³ min ⁻¹)
	HCl mol.dm ⁻³	KCl mol.dm ⁻³	
1.0	0.2	0.8	42.78
1.0	0.4	0.6	48.08
1.0	0.6	0.4	55.58
1.0	0.8	0.2	60.26
1.0	1.0	0.0	78.53
2.0	0.2	1.8	41.87
2.0	0.5	1.5	48.29
2.0	1.0	1.0	60.41
2.0	1.5	0.5	73.43
2.0	1.8	0.2	76.86
2.0	2.0	0.0	107.73
3.0	0.5	2.5	41.38
3.0	1.0	2.0	52.58
3.0	1.5	1.5	62.77
3.0	2.0	1.0	80.65
3.0	2.5	0.5	91.54
3.0	3.0	0.0	126.81

Table 3: Specific acid catalysed(KH+) and specific neutral rates(k_{n0}) for the hydrolysis of 2,6-dimethylphenyl phosphate monoester at different ionic strength at 97°C

Ionic strength μ	105.K _{H⁺} mol. dm ⁻³ min ⁻¹	105.K _{N₀} mol dm ⁻³ min ⁻¹	5+log K _{H⁺}	5+logK _N	5+logK _{N₀}
1.0	30.00	36.0	1.48	1.56	
2.0	26.92	33.0	1.43	1.52	1.72
3.0	25.00	28.0	1.40	1.44	

and specific neutral rates ($5+\log K_{N_0}=1.70$) can be obtained from the intercept on rate axis, while $b'_{H^+} = -0.0189$ and $b'_N = -0.0394$ can be obtained from the slope (fig-III&IV) respectively

Table-4 summarises both the observed and calculated rates of hydrolysis in the acid region from 1.0 to 6.0 mol.dm⁻³HCl. It is clear from the results that there is a fairly good agreement between calculated and experimentally observed rates upto 4.0 mol.dm⁻³HCl. There is a steep fall in the rates, which has been presumed due to participation of

water molecule as a second reaction partner in the nucleophilic substitution reaction. Moreover, the rates are also retarded due to negative ionic strength effect. Therefore, the agreement between the theoretical and experimental rates have been sought by introducing water activity parameters. In this way both acid catalysed and neutral rates have been calculated by the modified form suggested by Bronsted-Bjerrum¹⁵⁻¹⁶.

Table 5 Summarizes the comparative isokinetic rate data of other similarly substituted aryl

Table 4: Calculated and observed rates for the hydrolysis of mono-2,6-dimethylphenylphosphate at 97°C

HCl mol. dm ⁻³	10 ⁵ .K _N mol.dm ⁻³ min ⁻¹	5+log K _N	10 ⁵ .K _{H⁺} .C _{H⁺} mol.dm ⁻³ min ⁻¹	10 ⁵ .K _{H⁺} .C _{H⁺} mol.dm ⁻³ min ⁻¹	10 ⁵ .K _N mol.dm ⁻³ min ⁻¹	Ke.10 ⁵ mol.dm ⁻³ min ⁻¹	Ke.10 ⁵ mol.dm ⁻³ min ⁻¹
1.0	47.92	1.68	31.70	-	-	79.62	80.26
1.5	45.80	1.66	46.52	-	-	92.32	93.59
2.0	43.77	1.64	60.56	-	-	104.33	107.73
2.5	41.83	1.62	74.08	-	-	115.91	118.99
3.0	39.97	1.60	87.15	-	-	127.12	126.81
3.5	38.20	1.58	99.50	-	-	137.70	135.58
4.0	36.50	1.56	111.27	-	-	147.77	146.68
5.0	33.34	1.52	133.19	65.22*	16.33*	81.56	81.13
6.0	30.45	1.48	152.96	35.61*	7.08*	42.69	43.06

Where n* = 2 and n*=3 for 5.0 and 6.0 mol.dm⁻³.HCl

Table 5: Comparative kinetic rate data for the hydrolysis of some phosphate monoesters via their conjugate acid species

S No.	Phosphate monoester	Temp °C	E.K (Cals/mol.)	-ΔS*	Fission	Ref
1	Naphthyl	100	30.48	-1.79	P-O	12
2	p-chlorophenyl	80	28.46	5.57	P-O	12
3	2,3-dimethoxyphenyl	80	22.50	20.88	P-O	17
4	Pentabromophenyl	97	22.42	21.56	P-O	4
		97	21.50	24.99	P-O	4
5	p-nitrophenyl	80	18.70	24.00	P-O	2
6	2,4-dichlorophenyl	98	16.90	31.30	P-O	18
7	p-bromophenyl	-	18.38	34.83	P-O	19
8	á-naphthyl	80	15.10	41.00	P-O	20
9	1-nitro2-naphthyl	98	10.49	49.76	P-O	3
10	2,6-dimethylphenyl	97	19.67	29.17	P-O*	This work
		97	19.22	31.29	P-O*	

*Bond fission assumed

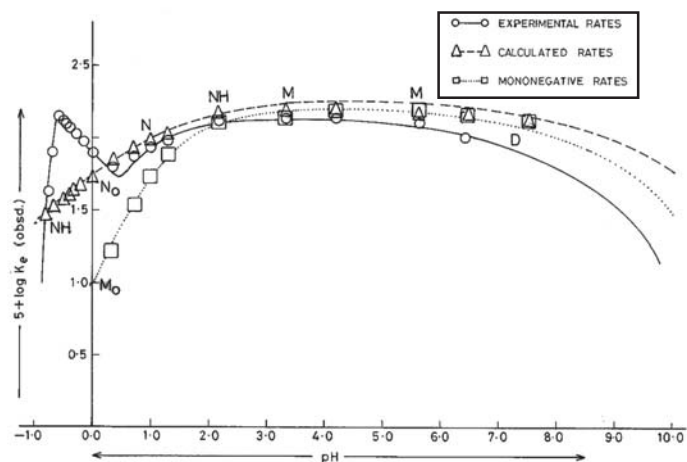
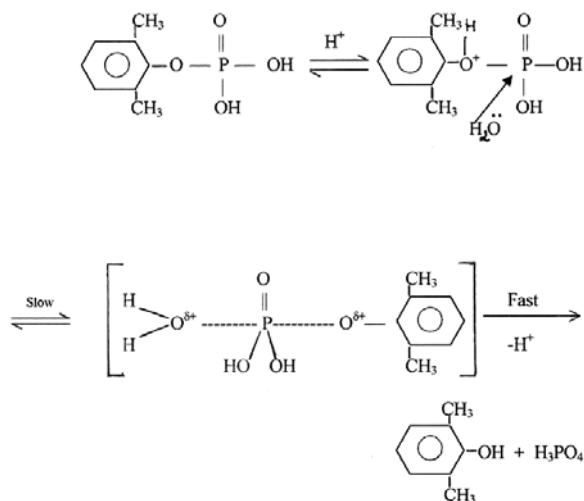


Fig. 1: pH-log rate profile of mono-2,6-di-methylphenyl phosphate at 97°C

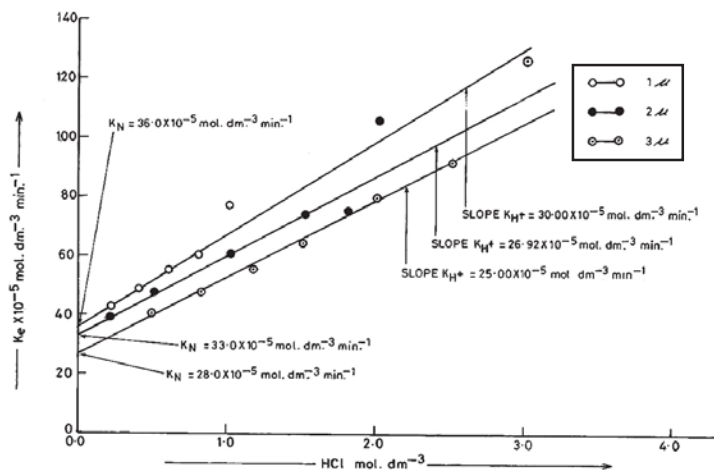


Fig. 2: Hydrolysis of mono mono-2,6-di-methylphenyl phosphate at constant ionic strength (μ) at 97°C

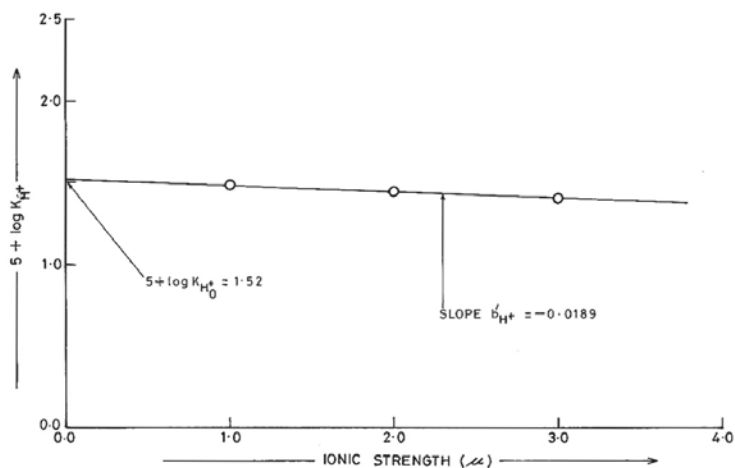


Fig. 3: Hydrolysis of mono-2,6-di-methylphenyl phosphate (Plot between log acid catalysed rate) vs ionic strength at 97°C

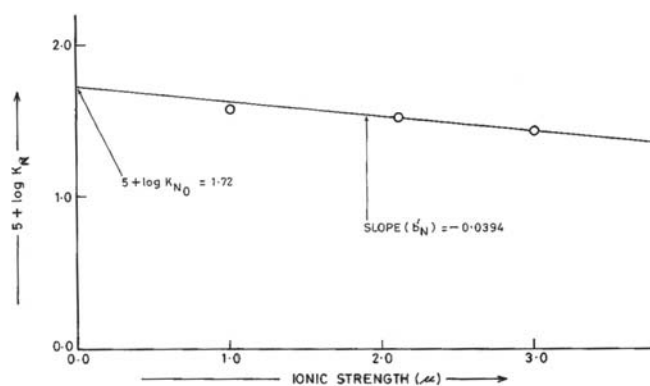


Fig. 4: Hydrolysis of mono-2,6-di-methylphenyl phosphate (Plot between log natural rate) vs ionic strength at 97°C

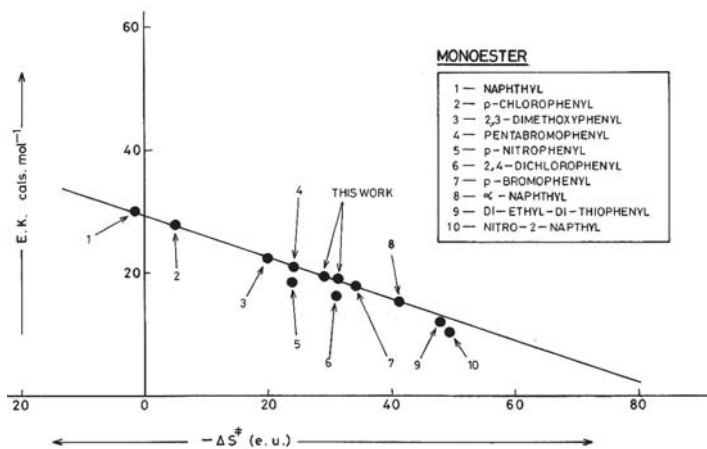


Fig. 5: Comparative kinetic rate data for the hydrolysis of some monoester via their conjugate acid species

phenol phosphate monoester, the bond fission and molecularity of which is known. (Fig V) describes a relationship and linearity of the curve shows similarity of mechanism. The point of mono-2,6-

domethylphenylphosphate lies on the same line on which other phosphate monester that is of known mechanism to undergo bimolecular hydrolysis with P-O bond fission for the acid catalyzed hydrolysis.

REFERENCES

- Mhala, M.M. Patwardhan, M.D. and Kasturi (Mrs), G., *India J.Chem.*, 7: 149 (1969).
- Barnard, P.W.C. Bunton,C.A., Killerman,D., Mhala,M.M, Silver, B., Vernon,C.A. and Welch,V.A., *J. Chem. Soc. Sec-B*, 227-235 (1966)
- Pandey, P.N., Ph.D. Thesis, Jiwaji Univ., Gwalior (1972) .
- Tyagi, K; Ph.D Thesis, Dr B.R. Ambedkar Univ; Agra (1999).
- Humphry, T.M; Forconi Marcello ; William Nicholos, Hengge, H.Alvan, C; *Journal of American Chemical Society*, **124**(50):14860-15861 (2002)
- Kadam, R; Dixit, V.K; Agrawal, Anupam ; Parihar, P.S; *Asian Journal of Chemistry*, 3758 Vol. (XVI) (2004) .
- Tiwari,B.K; Singh, Ruchi; Chem Abst. National Seminar on Polymer Science and Technology Vision and Scenario, 3rd Dec 2008 .
- Mhala .M.M ; Holla, C.P; Kasturi.G; and Gupta, K. ' Hydrolysis of Organic Phosphate' Part III, *Indian J Chem*; **6**: 332-336 (1970) .
- Mhala. M.M, Prabha (Miss) S, *Indian J. Chem* **10**: 1073-1076 (1972).
- Jachak, C.K; Ph.D Thesis, Jiwaji Univ. ; Gwalior (1972).
- Ingold, C.K; ' Structure and Mechanism in Organic Chemistry' Bell and Sons, London, p.346 (1953).
- Patwardhan,M.D; ' Hydrolysis of Organic Phosphate' Ph.D Thesis Jiwaji Univ. Gwalior (1967).
- Rudert, P; *J.Chem. Soc .a.1*: 323-324 (1893).
- Allen ,R.J.L; Bio-Chem, *J.Am. Chem. Soc*; **79**: 2365 (1957).
- Bronsted, J.N; *Z. Physik. Chem*; **102**: 169 (1922), **115**: 237 (1925).
- Bjerrum, N; *Z. Physik. Chem*; **108**: 82 (1924), 118,251 (1925).
- Prabha (Miss) S Ph.D Thesis, Jiwaji Univ. ; Gwalior (1971).
- Batwadhekar,S.S; Ph.D Thesis, Jiwaji Univ. ; Gwalior (1972).
- Kasturi (Miss) G Ph.D Thesis, Jiwaji Univ. ; Gwalior (1971).
- Cooper, K.A; Dhav, M.L; Huges, E.D; Ingold, C.K Machutty,B.J and Woolf,L.I; *J.Chem Soc* 2043 (1948).