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INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

SYNTHESIS & MECHANISTIC AND KINETIC INVESTIGATIONS OF MONO-2,6-DI-METHYLPHENYL PHOSPHATE IN ACID MEDIUM

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Manuscript Info

Abstract

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Manuscript History:

Received: 15 July 2015 Final Accepted: 22 August 2015 Published Online: September 2015

Key words:

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Investigations of the kinetic study of the hydrolysis of mono-2, 6-dimethylphenyl phosphate has been carried out in 0.1 to 6.0 mol.dm³.HCL and in buffers from 1.24 to 7.46 pH at 97 \pm 0.5°C in water. The monoester has been found to be hydrolyses by conjugate acid, mononegative, neutral and dinegative species. Bond fission, molecularity and order of reaction have been supported by Arrhenius parameters, Zucker Hammett hypothesis, concentration, solvent effect etc., study of the reaction and dioxane-water mixture suggested the nature of transition state in which charges are developed due to the bimolecular attack of water molecule. Comparative isokinetic rate data of similarly substituted other phosphate monoesters, whose mechanism is known, supported P-0 bond fission

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INTRODUCTION

The effect of the substituents, the hydrolysis of aryl phosphate esters - having C-O-P¹⁻⁶ linkages have been studied exhaustively by Mhala and Co workers⁵ and established that the effect of substituents of graded polarity⁷⁻⁹, not only effects of 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 (-I) and (-T) effect reduce the basicity of the ester-oxygen. Polar effects of the substituent in 2, 6-di-methyphenyl phosphate monoesater are expected to favour acid catalysis. To test the hypothesis of abnormal acid catalysis, a systematic ionic strength data shows the presence of acid catalysis and the order of rate values correlates well with the leaving abilities of the organic substituents with P-0 bond.

METHOD AND MATERIALS

2,6-di-methylphenyl phosphate monoester has been prepared by to-general methods (P.Redurt method¹⁰⁻¹¹). To 2,6-di-methylphenol (24.4 gms) dissolved in dry benzene (120 ml) and added phosphorus oxy tri-chloride (10.0 ml) 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 b_{30} , 40-45°C, unreacted benzene and POCI₃ was obtained. After this, the second fraction distilled at b_{50} , 120-140°C, was dissolved in 100 ml distilled water, extracted with ether and recrystallised by absolute alcohal, M.P 162°C (found P;15.35 required theortically P; 15.41). Finally the structure was confirmed by I.R. spectroscopy. All the chemicals used belong to B.D.H. (A.R.) and riedel quality. Hydrolysis of 2, 6-di-methyl phenyl phosphate monoester (0.0005M) was studied in distilled water and the inorganic phosphate was formed during the hydrolysis and estimated colorimetrically by Allen's modified method¹²

RESULT AND DISCUSSION (A) HYDROLYSIS VIA CONJUGATE SPECIES-



Hydrolysis of mono-2,6-di-methylphenyi phosphate has been kinetically studied in 0.1 to 6.0 mol.dnf3.HCI at 97 \pm 0.5°C. Pseudo first order rate coefficients have been summarised in tabled and (fig.-I). From the result, it may be concluded that the hydrolysis increase with increase in acid molarity.

TABLE - I
pH – log RATE PROFILE OF MONO-2, 6-DI-METHYLPHENYI,
PHOSPHATE AT 97 + 0.5 $^{\circ}$ C

HCl	рН	10 ⁵ Ke	5+log Ke				
(mol.dm ⁻³ $)$		$(mol.dm^{-3}min^{-1})$ (obsd)					
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-	1.24	98.45	1.99				
Composition of Buffers	2.20	120.84	2.11				
have been used	3.33	132.76	2.12				
	4.17	136.63	2.13				
	5.60	127.75	2.10				
	6.43	100.79	2.00				
	7.46	128.38	2.10				

The raw maxima is at 4.0 mol.dm⁻³ HCl and it gradually decreases with further increase in acid molarity. The rate maxima or bend of pH-log rate profile in acid region have also been found in some other cases. The decrease in the rates from (>4.0 mol.dm.⁻³HCl) may be due to participation of water molecule, ionic strength effect or both. The decrease in rates with increase in acidity in the region 0.1 to 0.5 mol.dm⁻³ HCL may be attributed to the decrease in concentration of more reactive mononegative species and the incursion of less reactive neutral species. The further rise in rates in the region of 0.1 to 4.0 mol. dm⁻³ HCl may be either due to incursion of conjugate acid species along with neutral species or the negative effect of ionic strength or both, whether or not the bend in the pH-log rate profile is due to ionic strength effect or water activity, could be determined by carrying out the kinetic runs at constant ionic strength. The rate coefficients have been summarised in table-2 and (fig.-II) describes a plot between rate coefficient and acid molarities.

TABLE - 2HYDROLYSIS OF MONO-2, 6-DI-METHYLPHENYL PHOSPHATEAT CONSTANT IONIC STRENGTH AT 97°C

Ionic Strength	Com	Ke x 10 ⁵	
(μ)	HCl	KCl	$(\text{mol.dm}^{-3} \text{min}^{-1})$
	mol.dm ⁻³	mol.dm ⁻³	(obsd)
1.0	0.2	0.8	42.78
1.0	0.4	0.6	48.08
1.0	0.6	0.4	58.58
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.	41.38
3.0	1.0	52.0	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

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

$$K_e = K_H^* C_H^*$$
 (1)

Where Ke, 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.

The rate of hydrolysis decreases with increase in ionic strength. The ionic strength effect is subjected to ionic retardation effect or negative salt effect. The corresponding slope values at constant ionic strength 1.0, 2.0 and 3.0μ are 30.0×10^{-5} , 26.92×10^{-5} and 25.0×10^{-5} mol dm⁻³.min⁻¹ respectively. (Fig.-III) shows specific acid catalysed rates with their logarithmic forms at the corresponding ionic strength.

A linear curve is obtained. The slope of this curve represents a constant b'_{H}^{+} , where b' = b/2.303 and intercepts on the rate axis represent the specific acid catalysed rate (log K_{H0}^{+} . Table-3 (fig.-IV) summarises the log-rate coefficients of specific neutral rates at different ionic strength with their corresponding rate constant b'_{N} .

TABLE-3SPECIFIC ACID CATLYSED [K_H⁺] AND SPECIFIC NEUTRALRATES [K_{N0}] FOR THE HYDROLYSIS OF 2,6-DI-METHYLPHENYL PHOSPHATE MONOESTER ATDIFFERENT IONIC STRENGTH AT 97°C

Ionic Strength (µ)	K _H ⁺ 10 ⁵ (mol.dm ⁻³ min ⁻¹)	K _{NO} 10 ⁵ (mol.dm ⁻³ min ⁻¹)	$5 + \log {K_H}^+$	5+log K _N	5+log K _{NO}
1.0	30.00	36.0	1.48	1.56	
2.0	26.92	33.0	1.43	1.52	1.728
3.0	25.00	28.0	1.40	1.44	

The linearity of the curves of (fig.-III and IV) shows the following relation of rate constant with ionic strength. This is an empirical form of Debye-Hucket equation^{5,13-14}

$$K = K_0 \cdot exp. b. \mu$$

The specific acid catalysed rate may be shown as:

1000

$$K_{\rm H}^{+} = K_{\rm Ho}^{+} \exp (b_{\rm H}^{+}, \mu)$$
 (3)

And acid rates are as:

$$K_{\rm H}^{+}, C_{\rm H}^{+} = K_{\rm Ho}^{+}, C_{\rm H}^{-}, \exp, b_{\rm H}^{+}, \mu$$

or its logarithmic form can be shown as:

 $5 + \log K_{\rm H}^{+}$, $C_{\rm H}^{+} = 5 + \log K_{\rm Ho}^{+} + \log C_{\rm H}^{+} + b_{\rm H}^{+}$, μ (5)

where K_{H}^{+} , K_{Ho}^{+} , b'_{H}^{+} and μ are specific acid catalysed rate at that ionic strength, at zero ionic strength and a constant respectively. Similarly the specific neutral rates may be represented as follows;

$$K_N = K_{No} \exp[b_N], \mu$$
(6)

And its logarithmic form may be shown as:

$$5 + \log K_N = 5 + \log K_{No} + b'_N, \mu$$
 (7)

Where K_{No} , b'_N and μ are the specific neutral rate, a constant and the ionic strength respectively, where b'N = b/2.303

The equations (5) and (7) may be used to computed the acid catalysed and the neutral rates at each experimental rates.

Therefore, the total hydrolysis of 2,6-di-methylphenyl phosphate monoester can be represented by:

$$K_e = Acid rates + Neutral rates or$$

$$K_e = K_H^* \cdot C_H^* + K_N$$
 (8)

In the above expression the terms K_{H}^{+} , K_{N} are the specific rates at that ionic strength, while K_{Ho}^{+} ; and K_{No} are the specific acid catalysed rate and specific neutral rates at zero ionic strength respectively. With the help 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 a remarkable similarities between them upto 4.0 mol.dm⁻³.HCL.

The values of specific acid catalysed rates, $(5 + \log K_{Ho}^+ = 1.52)$ and specific neutral rates $(5 + \log K_{No} = 1.70)$ can be obtained from the intercept on the rate axis, while $b_{H}^+ = (-0.0189)$ and $b'_N = (-0.0394)$ can be obtained from the slope of the (Fig.-III & IV). Equations (5), (7) and (8) have been used to calculate the theoretical rates. Table-4 summarised both the observed and calculated rates of hydrolysis for the acid region from 1.0 to 6.0 mol. din⁻³, HCl.

TABLE - 4 CALCULATED AND OBSERVED RATES FOR THE HYDROLYSIS OF MONO-2, 6- DI-METHYLPHENYL PHOSPHATE AT 97°C

HCl (mol.dm ⁻³)	K _N 10 ⁵ (mol.dm ³ min ⁻¹)	5+log K _N	K _H ⁺ C _H ⁺ 10 ⁵ (mol.dm ⁻³ min ⁻¹)	K _H ⁺ C _H ⁺ 10 ⁵ (mol.dm ⁻³ min ⁻¹)	K _N 10 ⁵ (mol.dm ⁻³ min ⁻¹)	K _E 10 ⁵ (mol.dm ⁻³ min ⁻¹)	K _E 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	93.53
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

It is clear from the result, there is fairly good agreement between the calculated and experimentally observed rate upto 4.0 mol. dm^{-3} HCl, but beyond 4.0 mol. dm^{-3} . HCl, there is a steep fall in the rates which has been presumed due to participation of water molecule as the 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 parameter. In this way both acid catalysed and neutral rates have been calculated by the modified form of equation (4) and (6) suggested by Bronsted and Bjerrum¹⁵

Table-5 summarize the comparative isokentic rate data of other similarly substituted anyl phenol phosphate monoester.

TABLE-8
COMPARATIVE KINETIC RATE DATA FOR THE HYDROLYSIS OF SOME PHOSPHATE
MONOESTERS VIA THEIR CONJUGATE ACID SPECIES

S.No	Phosphate mono	Temp ⁰ C	E.K	$-\Delta S^+$	Fission	Ref.
	ester	_	(cals./mol)			
1.	Naphthyl	100	30.48	-1.79	P-O	11
2.	p-chlorophenyl	80	28.46	5.57	P-O	11
3.	2,3-dimethoxyphenyl	80	22.50	20.88	P-O	16
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	5
6.	2,4-dichlorophenyl	98	16.90	31.30	P-O	17
7.	p-bromophenyl	-	18.38	34.83	P-O	18
8.	α – naphthyl	80	15.10	41.00	P-O	19
9.	1- nitro 2- naphthyl	98	10.49	49.76	P-O	6
10	2,6-dimethylphenyl	97	19.67	29.17	P-O*	This
		97	19.22	31.29	P-O*	work

MACHANISM OF CONJUGATE ACID SPECIES





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