

Reaction Mechanism and Kinetic Investigation of the Substituent of 4-Amino-3-Methylphenyl Phosphate Mono-Ester via Conjugate Acid Species

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Abstract— Investigation of kinetic study of 4-amino-3-methylphenyl phosphate mono-ester has been carried out in 0.1 to 6.0 mol. dm⁻³ HCl and in buffers from 1.24 to 7.46 pH at 97 ± 0.5°C in water. The effects of temperature, solvent and substrate concentration on the rate of hydrolysis have been studied to determine the probable mechanism and reaction paths. Bond fission, molecularity and order of reaction have been supported by Arrhenius parameters, Zucker-Hammett Hypothesis, Bunnett and Bunnett-Olsen parameters. Comparative isokinetic rate data of the esters whose mechanism is known supported P-O bond fission.

Index Terms— Kinetic, 4-amino-3-methylphenyl phosphate mono-ester, conjugate acid species.

I. INTRODUCTION

Mono-ester has been found to be reactive in the form of four reactive species such as conjugate acid, neutral, mononegative and dinegative species. All the reactive species have been found to be undergo hydrolysis via P-O bond fission with bimolecular reaction path. A systematic ionic strength data shows the

presence of acid catalysis and the order of rate values correlated well with the leaving abilities of organic substituents with P-O bond fission.¹

II. EXPERIMENTAL

4-Amino-3-methylphenyl phosphate mono-ester has been prepared by the general method.² The parent compound 12.30 gms was dissolved in 200ml of dry benzene in round bottom flask and 9.0 ml of POCl₃ was added drop by drop with constant stirring to the ice cooled phenol with the help of separating funnel for about 0.5h. After the addition of POCl₃, it was refluxed for 48h on Soxhlet heater of constant temperature 85°C, in order to ensure complete reaction and distilled at reduced pressure. The first fraction of benzene and unreacted POCl₃ was removed by distillation at 40°-50°C. The second fraction was dichloride, it was dissolved in 100 ml of ice cooled water and kept at low temperature over night and extracted with solvent ether. After remaining the solvent

ether, a white colored crystalline solid was obtained, which on recrystallization with absolute ethyl alcohol gave a white crystalline solid, it was identified to be phosphate mono-ester.

III. RESULT AND DISCUSSION

The rate of hydrolysis was determined by measuring the rate of appearance of inorganic phosphate by Allen's modified Colorimetric method.³

Hydrolysis via conjugate acid species :

Pseudo first order rate coefficient have been summarized in Table-1. As seen that the rate of hydrolysis of mono-ester increases with increases in acid molarity and the rate maxima is at 4.0 mol.dm.⁻³ HCl. The initial rise in rates in the region 1.0 to 4.0 mol.dm.⁻³ HCl may be due to incursion of more reactive conjugate and species.

TABLE-1

pH-log RATE PROFILE OF MONO-4-AMINO-3-METHYLPHENYL PHOSPHATE AT 97 ± 0.5°C.

HCl (mol.dm. ⁻³)	pH	10 ⁵ .Ke (mol.dm. ⁻³ min. ⁻¹) (obsd.)	5+log Ke
6.0	-0.778	40.82	1.61
5.0	-0.669	77.14	1.89
4.0	-0.602	142.74	2.15
3.5	-0.544	130.01	2.11
3.0	-0.477	125.02	2.10
2.5	-0.397	118.46	2.07
2.0	-0.300	109.55	2.04
1.5	-0.176	92.25	1.96
1.0	0.000	85.01	1.93
0.5	0.301	66.14	1.82
0.4	0.400	63.21	1.80
0.3	0.520	60.57	1.78
0.2	0.700	69.53	1.84
0.1	1.000	82.32	1.92
Buffers :	1.24	89.32	1.95
Composition	2.20	119.46	2.08
of buffers	3.33	130.07	2.11
	4.17	133.57	2.13
	5.60	118.46	2.07
	6.43	116.02	2.06
	7.46	125.12	2.09

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IV. EFFECT OF IONIC STRENGTH

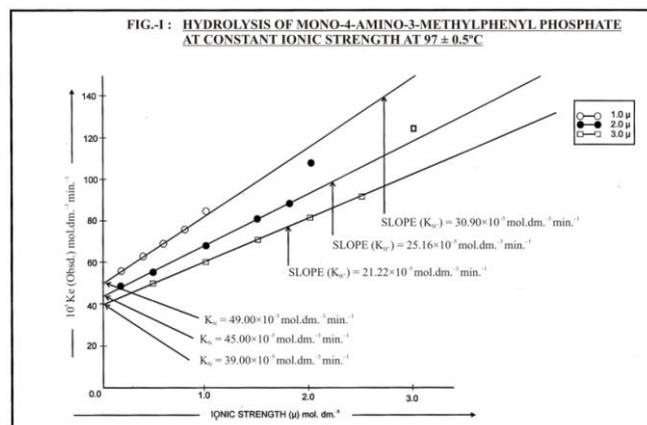
The constant ionic strength (1.0 μ , 2.0 μ and 3.0 μ) were maintained by using

the suitable mixture of KCl and HCl at 97 \pm 0.5 $^{\circ}$ C and have been summarized in Table-2 (Fig.1)

TABLE-2

HYDROLYSIS OF MONO-4-AMINO-3- METHYLPHENYL PHOSPHATE AT CONSTNAT IONIC STRENGTH AT 97 \pm 0.5 $^{\circ}$ C

Ionic Strength (μ) (mol.dm. ⁻³)	Composition		10 ⁵ K _e (mol.dm. ⁻³ min. ⁻¹) (Obsd.)
	HCl (mol.dm. ⁻³)	KCl (mol.dm. ⁻³)	
1.0	0.2	0.8	56.19
1.0	0.4	0.6	63.22
1.0	0.6	0.4	69.40
1.0	0.8	0.2	76.27
1.0	1.0	0.0	85.01
2.0	0.2	1.8	49.75
2.0	0.5	1.5	55.12
2.0	1.0	1.0	67.70
2.0	1.5	0.5	79.27
2.0	1.8	0.2	86.00
2.0	2.0	0.0	109.55
3.0	0.5	2.5	50.52
3.0	1.0	2.0	61.13
3.0	1.5	1.5	72.69
3.0	2.0	1.0	83.28
3.0	2.5	0.5	93.02
3.0	3.0	0.0	125.02



As clear from the plot (Fig.I) three linear curves were obtained on the hydrolysis of mono-ester, each curve represents the hydrolysis at different ionic strength. The kinetic law for each curve may be represented as :

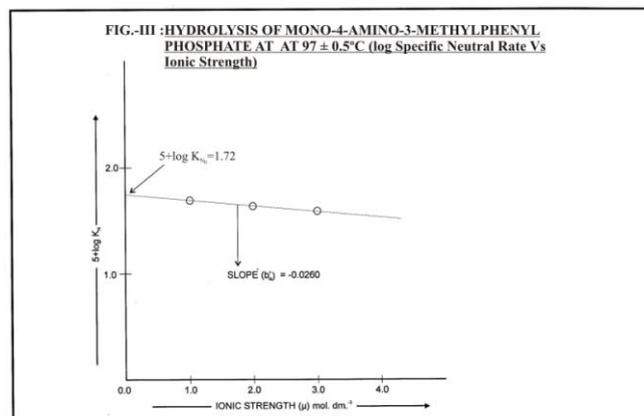
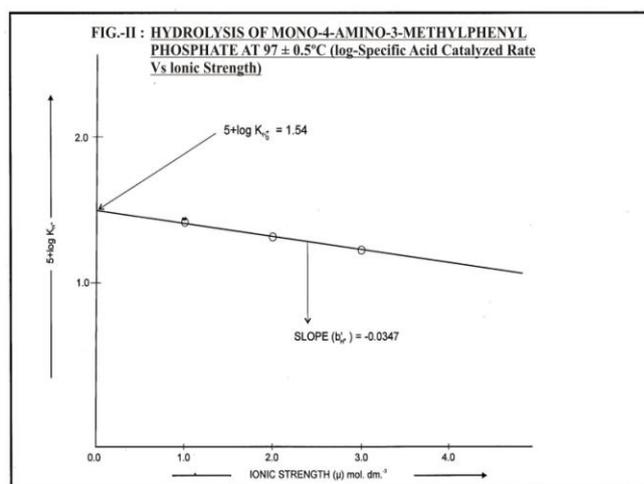
$$K_e = K_{H^+} \cdot C_{H^+} \dots(1)$$

Where,

K_e , K_{H^+} and C_{H^+} , respectively are observed rate constant, specific rate constant and acid molarities at that ionic strength, the acid catalysed rate are subjected to negative effect of ionic strength. Hence, specific and catalyzed rate (K_{H^+}) decreases with the increasing ionic strength.

One linear curve is obtained from the (Fig.2) and (Fig.3), the slopes of these curves represent the constant b'_{H^+} and b'_N

(where, $b' = \frac{b}{2.303}$), while the intercept on the rate axis represents the specific acid catalyzed rate ($\log 5 + \log K_{H^+}$) and specific neutral rate ($5 + \log K_{N_0}$) at zero ionic strength in (Fig.2) and (Fig.3) respectively.



These values can be used in the following equations to calculate the acid-catalyzed rate and neutral rate .

Acid catalysed rate :

$$5 + \log K_{H^+} \cdot C_{H^+} = 5 + \log K_{H_0^+} \cdot C_{H^+} + b'_{H^+} \cdot \mu$$

....(2)

Neutral rate:

$$5 + \log K_N = 5 + \log K_{N_0} + b'_N \cdot \mu$$

....(3)

The values obtained from these equation have been used to estimate the theoretical rate by following equation :

$$K_e = K_{H^+} \cdot C_{H^+} + K_N$$

The rates calculated by these equations are compared with the observed rates. Now there is a fairly good agreement in the entire acid region (0.1 to 6.0 mol.dm.⁻³). Thus acid hydrolysis as well as neutral hydrolysis is governed by both ionic strength and water activity.

V. MOLECULARITY :

The various correlation plot like Hammett plot⁴ (0.166), Zucker-Hammett plot⁵ (0.689), Bunnett plots⁶. ($\omega = 10.00$ and $\omega^* = 4.78$) and Bunnett Olsen plot⁷ ($\phi = 1.50$), postulates a bimolecular rate of hydrolysis, i.e. the involvement of water molecule as second reaction partner in the slow reaction step.

The Arrhenius parameter at 3.0 and 5.0 mol.dm.⁻¹ HCl, $\Delta\epsilon = 21.00$ and 21.91 K.Cal.mol.⁻¹, frequency factor $A = 5.29 \times 10^7$ and 11.31×10^7 and entropy $\Delta S^\ddagger = 25.61$ and 24.10

The above parameters at 3.0 and 5.0 mol.dm.⁻³ HCl, shows the bimolecular mode of hydrolysis with P-O bond fission¹ and by isokinetic relationship represents the conjugate acid species hydrolysis with P-O bond fission. Solvent effect and concentration effect also show the reaction to be bimolecular hydrolysis

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