

# Synthesis, Reaction Mechanism and Kinetic Study of the Reaction of Hydrolysis of Mono-P-Propoxy Aniline Phosphate

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**Abstract** - Kinetic measurements of the hydrolysis of mono-p propoxy aniline phosphate has been carried out both in acid as well as in the buffer medium at  $97 \pm 0.5^\circ\text{C}$ . The rate of hydrolysis was measured by determining the rate of appearance of inorganic phosphate by Allen's modified calorimetric method [1]. The concentration of monoester in all the kinetics runs was  $(5.0 \times 10^{-4}) \text{ mol dm}^{-3}$ .

Throughout the process of hydrolysis pseudo first order rate coefficients were observed. Factors such as hydrogen ion concentration, solvent, ionic-strength, temperature, substrate concentration etc. on the rate of hydrolysis have been studied in detail. Presumption of  $pK$  values and ionic strength data were used to estimate theoretical rates of the reactive species in various zones of pH log rate profile. These rates are found in the close agreement with the observed rates. Molecularity of the reaction has been discussed by employing recent concepts such as Hammett acidity function [2, 3], Zucker hammett Hypothesis [4] and bunnett parameters [5] etc. Probable mechanism of the hydrolysis of mono-p-propoxy aniline phosphate via different reactive species has been suggested on the basis of kinetic rate data and isokinetic relationship [6, 7]. It has been observed that the hydrolysis of mono-ester takes place through its conjugate acid, neutral, mononegative species in different ranges of acid and buffer medium.

## I. INTRODUCTION

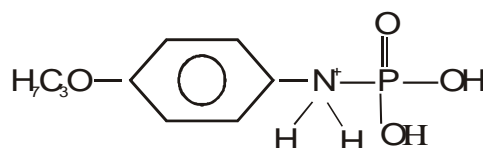
The effect of substituent on the hydrolysis of aryl phosphate ester having C-N-P linkages [8-21] have been studied exhaustively by Mhala and co-workers [22] and established that the effect of substituents of graded polarity [23-27] not only effect the reaction rates but also alter the course of the reaction path. The rate of hydrolysis of relevant phosphate esters p-chloro aniline phosphate ester [10], mono 3, 4-di chloroaniline phosphate ester [28], 5 chloro-2-methyl aniline phosphate ester [29] was shown to be the least in the series of the others esters studied.

## II. METHODS AND MATERIALS

Monoester of p-propoxy aniline phosphate has been prepared by general methods [30-31]. 15.1 of pure p-propoxy aniline was dissolved in 100 ml of dry benzene in a round bottom flask .90 ml of phosphorus oxy-trichloride ( $\text{POCl}_3$ ) was added dropwise with constant stirring to the ice-cooled amine in about half an hour with the help of separating funnel. After the addition of  $\text{POCl}_3$ , mixture was refluxed for about 25 hours in order to ensure complete reaction and then distilled at reduced pressure. The first fraction of benzene and unreacted  $\text{POCl}_3$  was removed by distillation at  $160^\circ\text{C}$ . The second fraction of pungent smelling liquid was distilled at  $160-180^\circ$ . It was dissolved in 100 ml ice cooled distilled water extracted with solvent ether After removing the solvent ether a crystalline solid obtained which on recrystallisation with absolute ethyl alcohol gave a white crystalline solid and it was identified to be mono-p-propoxy aniline phosphate with following physical properties. Melting point (observed)  $238^\circ\text{C}$ , Theoretical percentage of 'p' 13.42 and observed percentage of 'p' 13.33 Finally the structure of the monoester was confirmed by IR spectrum. Hydrolysis of p-Propoxy aniline phosphate monoester ( $0.0005 \text{M mol dm}^{-3}$ ) was studied in distilled water and the inorganic phosphate are formed during the hydrolysis was estimated by Allens colorimetric method [1].

## III. RESULT AND DISCUSSION

Hydrolysis of p-propoxy aniline phosphate mono-ester has been studied kinetically in  $0.1$  to  $6.0 \text{ mol dm}^{-3}$  HCl at  $97 \pm 0.5^\circ\text{C}$ . Pseudo first order rate coefficients of the hydrolysis are summarised in Table I and fig. 1.

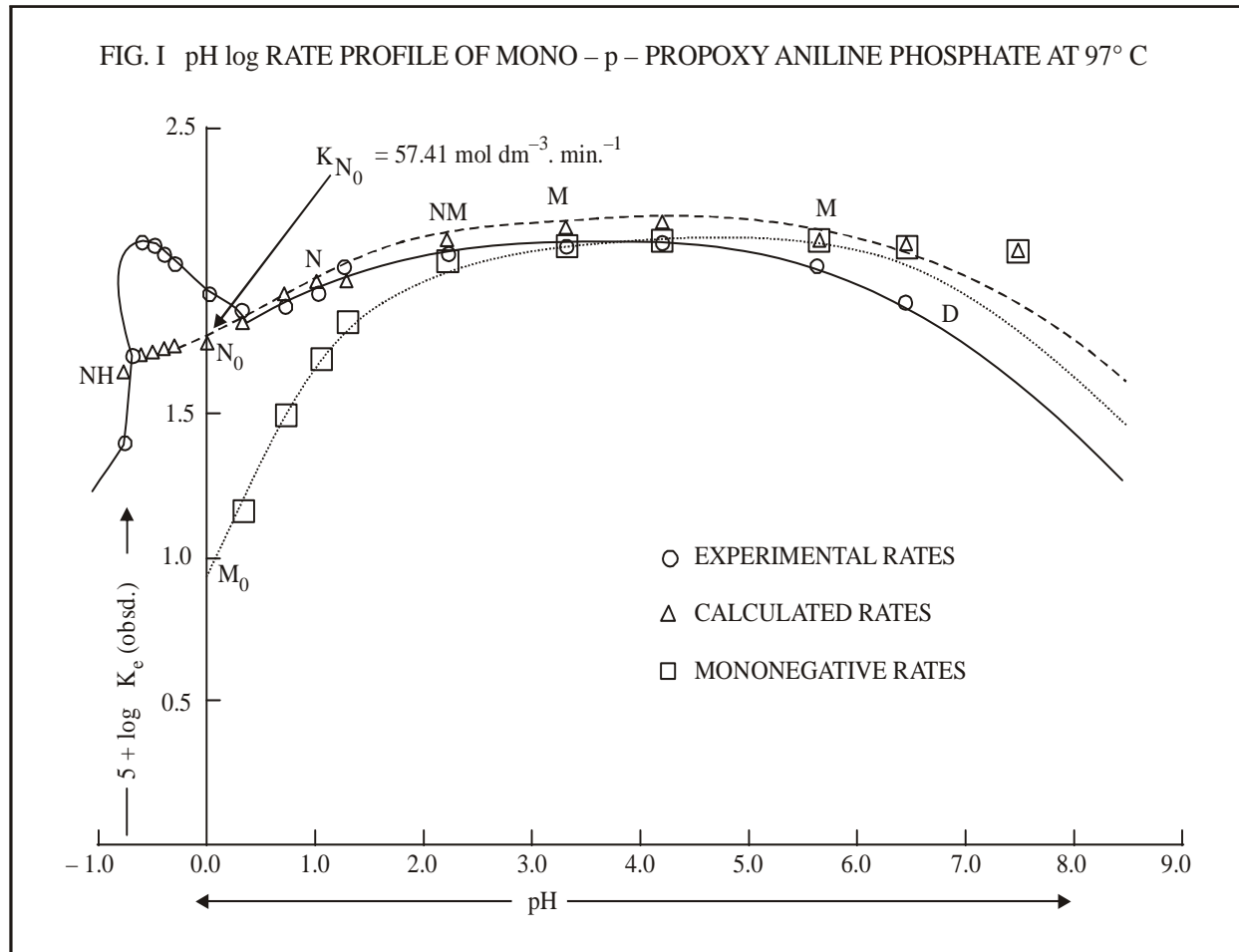


(Conjugate Acid Species)

describes the acid and pH log rate profile. Results show that the rate of hydrolysis decreases with the increase in acidity for 0.1 to 0.5 mol dm<sup>-3</sup> HCl. Further increase in acid molarity brings about rise in the rate of reaction upto 4.0 mol dm<sup>-3</sup> HCl and further increase in acid molarity brings down the rates passing through a maxima. The decrease in the rates from (> 4.0 mol dm<sup>-3</sup> HCl) may be due to the participation of water molecule, ionic strength effect or both.

TABLE 1. pH log RATE PROFILE OF MONO-p-PROPOXY ANILINE PHOSPHATE AT 97°C

HCl (mol dm <sup>-3</sup> )	pH	10 <sup>5</sup> Ke (mol dm <sup>-3</sup> min <sup>-1</sup> )	5 + log ke
6.0	-0.778	24.92	1.40
5.0	-0.699	50.23	1.70
4.0	-0.602	129.22	2.11
3.0	-0.477	120.31	2.08
2.5	-0.400	112.30	2.05
2.0	-0.300	103.21	2.01
1.0	-0.000	83.42	1.92
0.5	0.301	69.86	1.84
0.2	0.700	76.78	1.88
0.1	1.000	82.26	1.92
Buffers :	1.24	102.24	2.00
	2.20	116.54	2.06
	3.30	120.04	2.08
	4.17	121.63	2.09
	5.60	104.24	2.02
	6.43	78.50	1.89
	7.46	112.72	2.05



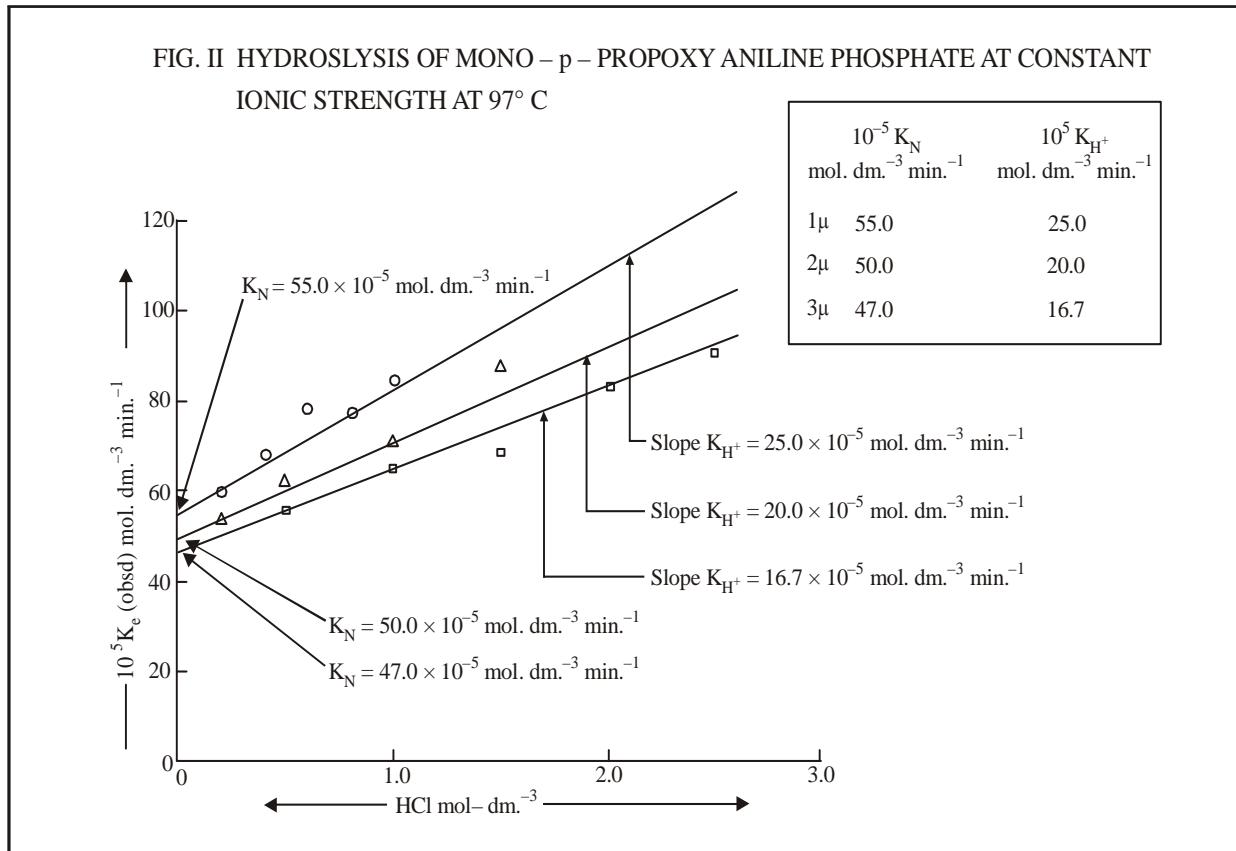
In the organic amide system [32-34] similar rate maxima were observed which were supposed due to full conversion into their conjugate acid species. After complete conversion into protonate species the rate should remain constant but it further decreases with the increase of acid molarity. The decrease may be attributed to the lowering of concentration of attacking nucleophile taking part in a reaction. Although, it appears, that there is no similarity in rate maxima, with amides as it is not possible due to complete protonation because there is a small variation in temperature coefficient before and after rate maxima and it may be taken as an indication for the absence of maximum protonation.

#### IV. EFFECT OF IONIC STRENGTH

In order to investigate the cause of rise in the hydrolysis rate in acid medium, kinetic runs at constant ionic strength was maintained using appropriate mixture of KCl and HCl at 97°C. The rate coefficients were obtained at three ionic strength. Plot of rate constant vs acid molarity (Fig 2) and Table 2 gives three linear curves indicating the presence of acid catalysis.

TABLE 2 : HYDROLYSIS OF MONO-p-PROPOXY ANILINE PHOSPHATE AT CONSTANT IONIC STRENGTH AT 97°C

Ionic strength ( $\mu$ ) (mol dm <sup>-3</sup> )	Composition		Ke 10 <sup>5</sup> (mol dm <sup>-3</sup> min <sup>-1</sup> ) (obsd.)
	HCl (mol dm <sup>-3</sup> )	KCl(mol dm <sup>-3</sup> )	
1.0	0.2	0.8	60.1
1.0	0.4	0.6	68.6
1.0	0.6	0.4	76.2
1.0	0.8	0.2	77.9
1.0	1.0	0.0	84.4
2.0	0.2	1.8	54.0
2.0	0.5	1.5	62.5
2.0	1.0	1.0	72.3
2.0	1.5	0.5	87.5
2.0	2.0	0.0	90.3
3.0	0.5	2.5	56.4
3.0	1.0	2.0	65.2
3.0	1.5	1.5	67.8
3.0	2.0	1.0	82.3
3.0	2.5	0.5	90.2
3.0	3.0	0.0	115.6



A plot of straight line is obtained in case of mono-p-propoxy aniline phosphate and it is clear from the plot that :

(1) Linear curves represent the rate of hydrolysis at that ionic strength by the following equation :

$$K_e = K_{H^+} \cdot C_{H^+} \tag{1}$$

Where  $K_e$ , and are experimental rate constant, specific acid catalysed rate at that ionic strength and hydrogen ion concentration respectively.

(2) Plot of mono-p-propoxy aniline phosphate shows that the three lines are intersecting the rate axis at different points Hence this indicates the presence of some other species in addition to conjugate acid species. Since the mono-negative species cannot be reactive at higher acidities ( $> 1.0 \text{ mol dm}^{-3}$ ) so the neutral species participation may be expected together with conjugate acid species. As it is evident that straight lines are intersecting the rate axis at different points, which show that contribution of neutral species at different acid concentrations is varying definitely.

(3) is the slope of linear curve and its value decreases with the increase in ionic strength. It is the ionic retarding effect which is indicating that mono-p-propoxy aniline phosphate ester undergoes acid catalysed hydrolysis with negative effect of ionic strength.

Fig. III and Table 3 describes the relation between log rate coefficients and ionic strength.

TABLE-3

SPECIFIC ACID CATALYSED  $[K_{H^+}]$  AND SPECIFIC NEUTRAL  $[K_{NO}]$  RATES FOR THE HYDROLYSIS OF p-PROPOXY ANILINE PHOSPHATE MONO ESTER AT DIFFRENT IONIC STRENGTH AT 97°C

Ionic strength	$10^5 K_{H^+}$ (mol.dm. <sup>-3</sup> min. <sup>-1</sup> )	$10^5 K_N$ (mol.dm. <sup>-3</sup> min. <sup>-1</sup> )	$5 + \log K_{H^+}$	$5 + \log K_N$	$5 + \log K_{NO}$
1.0	25.0	55.0	1.39	1.74	
2.0	2.0	20.0	50.0	1.30	1.69 1.78
3.0	16.7	47.0	1.22	1.67	

Two linear curves are obtained, the slopes of these curves represents the constants  $b'_{H^+}$  and  $b'_N$ , where ( $b' = b/2.303$ ) and the intercepts on the rate axis represents the specific acid catalysed rates ( $\log K_{H_0^+}$ ) and specific neutral rates ( $\log K_{N_0}$ ) at zero ionic strength. Table - 4 summarises the log rate coefficients of specific acid catalysed and specific neutral rates at zero ionic strength with their corresponding constants ( $b'_{H^+}$  and  $b'_N$ )

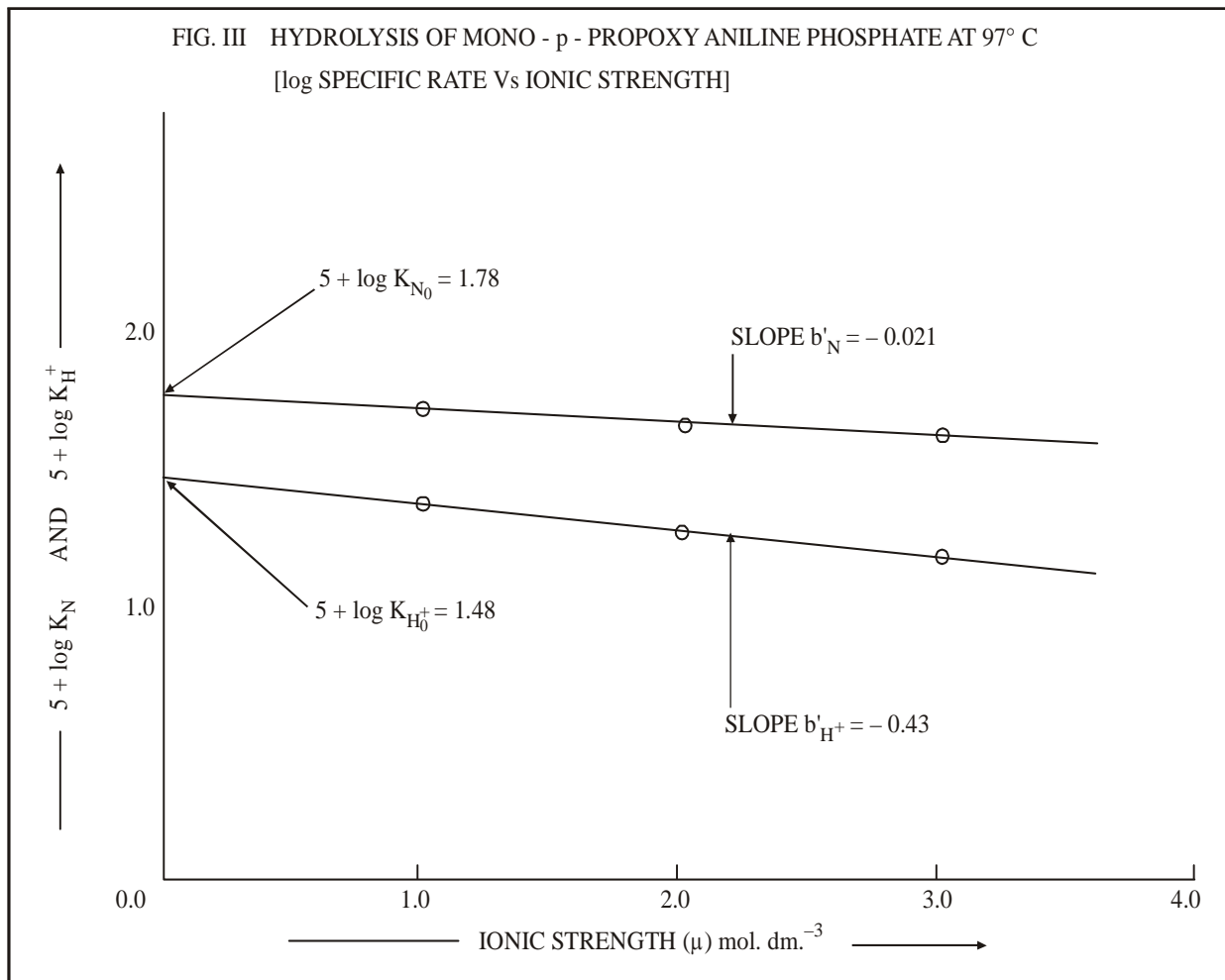


TABLE-4  
 SPECIFIC ACID CATALYSED [ $K_{H_0^+}$ ] AND SPECIFIC NEUTRAL [ $K_{N_0}$ ] RATES FOR THE HYDROLYSIS OF MONO -p-PROPOXY ANILINE PHOSPHATE AT ZERO IONIC STRENGTH 97°C

$10^5 K_{H_0^+}$	$5 + \log K_{H_0^+}$	$b'_{H^+}$	$10^5 K_{N_0}$	$10^5 + \log K_{N_0}$	$b'_{N}$
30.20	1.48	-0.043	60.26	1.78	-0.021

The linearity of the curves of Fig. III shows the following relation of rate constant with ionic strength. This is an empirical term of Debye – Huckle equation [32, 35]

$$K = K_0 \cdot \exp. b \cdot \mu \dots\dots(2)$$

The specific acid catalysed rates may be represented as :

$$K_{H^+} = K_{H_0^+} \cdot \exp. b_{H^+} \cdot \mu \dots\dots(3)$$

and the acid rates as :

$$K_{H^+} \cdot C_{H^+} = K_{H_0^+} \cdot C_{H^+} \exp. b_{H^+} \cdot \mu \dots\dots(4)$$

which may be improved logarithmically by the following equation :

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

Similarly the specific neutral rates may be represented as :

$$K_N = K_{N_0} \cdot \exp. b_N \cdot \mu \dots\dots(6)$$

and its logarithmic form may be represented as :

$$5 + \log K_N = 5 + \log K_{N_0} + b'_N \cdot \mu \dots\dots(7)$$

$$\text{Where } b'_n = \frac{b}{2.303}$$

The equation (5) & (7) may be used to compute the acid-catalysed and the neutral rates at each experimental acid molarity. Thus, the total rates in acid region may be represented by both acid catalysed and the neutral rates as :

$$K_e = K_{H^+} \cdot C_{H^+} + K_N \dots\dots(8)$$

In the above equation the terms  $K_{H^+}$ ,  $K_N$  are the specific acid catalysed rates and specific neutral rates at that ionic strength. While  $K_{H_0^+}$  and  $K_{N_0}$  are the specific acid catalysed and specific neutral rates at zero ionic strength respectively.

The values of specific acid catalysed rates  $K_{H_0^+} = 1.48$  and specific neutral rates  $K_{N_0} = 1.78$  can be obtained from the intercept on the rate axis while  $b'_{H^+} = -0.043$  and  $b'_N = -0.021$  can be obtained from the slopes of Fig. II. Equation (5), (7) and (8) have been used to calculate the theoretical rates.

TABLE-5  
CALCULATED AND OBSERVED RATES FOR THE HYDROLYSIS OF MONO-p-PROPOXY ANILINE PHOSPHATE AT 97°C

HCl (mol. dm. <sup>-3</sup> )	10 <sup>5</sup> . K <sub>N</sub> (mol.dm <sup>-3</sup> min. <sup>-1</sup> ) from eq.(7)	5 + log K <sub>N</sub>	10 <sup>5</sup> .K <sub>H</sub> <sup>+</sup> .C <sub>H</sub> <sup>+</sup> (mol.dm <sup>-3</sup> min. <sup>-1</sup> ) from eq.(5)	10 <sup>5</sup> K <sub>H</sub> <sup>+</sup> C <sub>H</sub> <sup>+</sup> (mol.dm <sup>-3</sup> min. <sup>-1</sup> ) from eq.(10)	10 <sup>5</sup> .K <sub>N</sub> (mol.dm <sup>-3</sup> min. <sup>-1</sup> ) from eq.(12) from eq.(8)	K <sub>e</sub> . 10 <sup>5</sup> (mol.dm <sup>-3</sup> min. <sup>-1</sup> ) (calcd)	10 <sup>5</sup> . K <sub>e</sub> (mol.dm <sup>-3</sup> min. <sup>-1</sup> ) (obsd)
1.0	57.41	1.76	27.35	–	–	84.76	83.42
2.0	54.70	1.74	49.43	–	–	104.13	103.21
2.5	53.39	1.73	59.22	–	–	112.61	112.30
3.0	52.12	1.72	67.29	–	–	119.41	120.31
4.0	49.66	1.70	81.28	–	–	130.94	129.22
5.0	47.32	1.68	92.04	12.89*	33.11*	46.00	50.23
6.0	45.08	1.65	102.32	6.31*	17.06*	23.37	24.92

n = 0 for 1.0 to 4.0 mol.dm.<sup>-3</sup> HCl and n\* = 1, 2 respectively for 5.0 and 6.0 mol. dm.<sup>-3</sup> HCL

Table – 5 summarises both the observed and calculated rates of hydrolysis for the acid region from 1.0 to 6.0 mol. dm.<sup>-3</sup> HCl. It is clear from the results that there is fairly good agreement between calculated and experimentally observed rates upto 4.0 mol.dm<sup>-3</sup> HCl. but beyond 4.0 mol.dm.<sup>-3</sup> HCl, 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.

Thus water activity can be represented the following equation :

$$K_{H^+} \cdot C_{H^+} = K_{H_0^+} \cdot C_{H_0^+} \cdot \exp. b_{H^+} \cdot \mu(a_{H_2O})^n \quad \text{.....(9)}$$

$$5 + \log K_{H^+} \cdot C_{H^+} = 5 + \log K_{H_0^+} + \log C_{H_0^+} + b'_{H^+} \cdot \mu + n \log(a_{H_2O}) \quad \text{.....(10)}$$

And neutral rates at higher concentration are as follows :

$$K_N = K_{N_0} \cdot \exp. b_N \cdot \mu(a_{H_2O})^n \quad \text{.....(11)}$$

$$5 + \log K_N = 5 + \log K_{N_0} + b'_N \cdot \mu + n \log(a_{H_2O}) \quad \text{.....(12)}$$

where (a<sub>H2O</sub>)<sup>n</sup> is water activity and n is an integer, which increases with increase in acidity.

Thus, the fall in the rates in higher acid medium is caused due to both water activity and negative effect of ionic strength. Higher is the acidity, higher is the value of n, indicating the hydrolysis to be bimolecular.

#### V. MOLECULARITY :

The various correlation plots (figures not shown) like Hammett plot [3] (Slope value = 0.167), Zucker-Hammett plot [4] (Slope value = 0.34), Bunnett plot [5] (Slope value ω and ω\* = 12.5 and 6.67) and Bunnett-olsen plot [36] (slope value (φ) = 2) proves a bimolecular rate of hydrolysis with the involvement of water molecule as a second reaction partner.

Solvent effect has been studied for both the reactive forms at 3.0 and 4.0 mol dm<sup>-3</sup> HCl. The results are shown in Table 6.



TABLE-6  
EFFECT OF SOLVENT FOR THE HYDROLYSIS OF -p- PROPOXY ANILINE  
PHOSPHATE MONO -ESTER

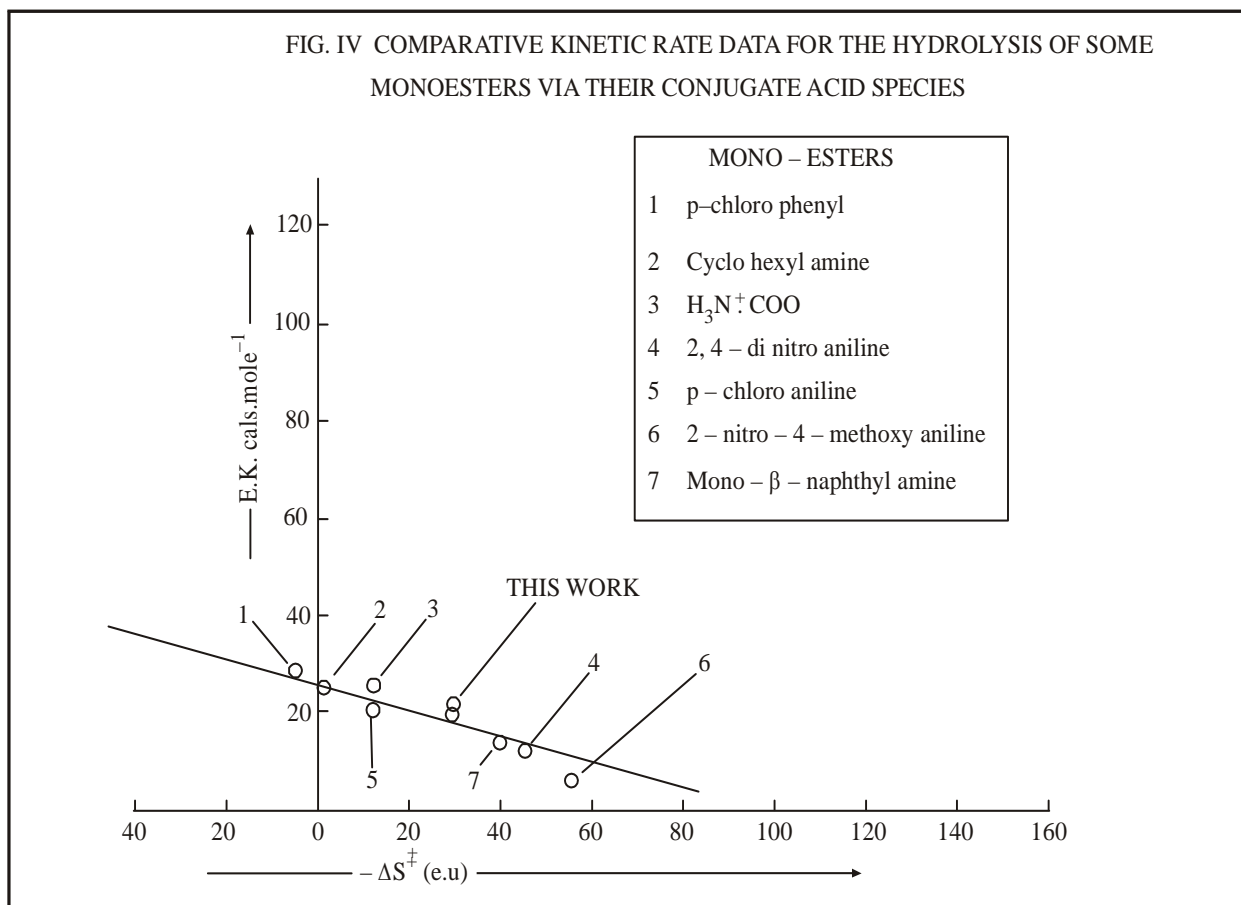
HCl (mol.dm. <sup>-3</sup> )	Water percentage (%v)	Dioxan percentage (%v)	Ke.10 <sup>5</sup> (mol.dm. <sup>-3</sup> min. <sup>-1</sup> ) (obsd.)
3.0	100.0	0.0	120.31
3.0	60.0	40.0	62.92
4.0	100.0	0.0	129.22
4.0	60.0	40.0	90.63
4.0	50.0	50.0	73.49

Reaction between two neutral molecules should form a transition state in which charges are created. Since there is an equilibrium in between transition state and reactants, the rate of reaction or the rate of formation of transition state should increase by a change over from less to more polar than pure water. A change over from pure water to aqueous dioxan mixture as a reaction medium should decrease the rate. Chanley [37] obtained similar results in acidified dioxan mixture.

**Table – 7** summarises the Arrhenius parameters of different substituted phosphate monoesters with their corresponding Arrhenius parameter and Fig. IV describes the isokinetic relationship plot. The linearity of the plot shows similarity of the mechanism of acid catalysed hydrolysis of monoester. On this basis it is worth while to consider the present monoester to hydrolyse bimolecularly with P–N bond fission.

TABLE-7  
COMPARATIVE KINETIC RATE DATA FOR THE HYDROLYSIS OF SOME PHOSPHATE MONOESTERS VIA THEIR CONJUGATE  
ACID SPECIES

S.No.	Phosphate mono ester	Temp °C	Medium	E.K. (cals/ mol.)	-Δs ≠ (e.u.)	Fission	Ref.
1.	p-chloro phenyl	80	–	28.46	-5.57	P–O	24
2.	Cyclo hexyl amine	50	3.0	26.65	0.77	P–N	38
3.	H <sub>3</sub> N <sup>+</sup> COO	37	–	26.00	12.23	P–N	39
4.	2,4 – dinitro aniline	98	3.0	12.10	45.10	P–N	40
5.	p-chloro aniline	20	–	20.4	12.6	P–N	41
6.	2-nitro –4-methoxy aniline	60	4.0	6.61	54.84	P–N	42
7.	Mono-β-napathy amine	98	3.0	14.56	39.46	P–N	43
8.	p- propoxy aniline	97	3.0	19.68	29.28	P–N*	This work
			5.0	20.14	29.77	P–N*	This work



#### VI. MECHANISM OF THE HYDROLYSIS :

Thus, the mechanism of hydrolysis of p-propoxy aniline monoester in the acid region involves a bimolecular nucleophilic attack of water on phosphorus of neutral and conjugate acid species, passing through a transition state in which the developed charges cause P-N bond fission and then liberate a proton by fast step giving the amine and phosphorus acid.

Chart (a) : Formation of conjugate acid species by fast pre-equilibrium proton transfer :

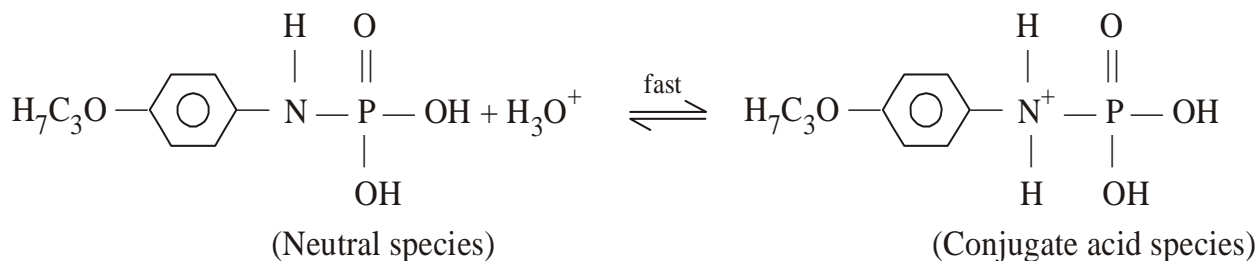
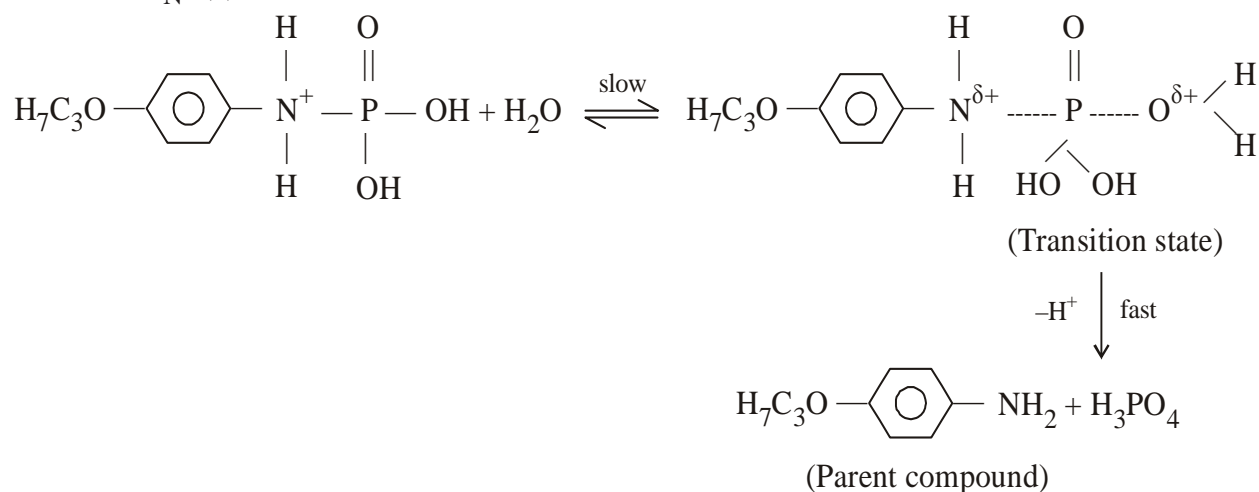


Chart (b) : Bimolecular nucleophilic attack of water on phosphorus of conjugate acid species involving P–N bond fission  $S_N2(P)$  :



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