Molecularity, Bond-Fission and Reaction Mechanism in the Acid Hydrolysis of *p*-Propoxy Aniline Phosphate Diester Via Conjugate Acid Species

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Abstract: *Kinetic study of the hydrolysis of p-propoxy aniline phosphate diester has been carried out from 0.1 to 6.0 mol dm^{-3} HCl at 97 ± 0.5 $^{\circ}$C in 20 % aqueous dioxin mixture. The diester has been found to be reactive via conjugate acid, neutral and mononegative species, but in this discussion only conjugate acid species are given. The rate of hydrolysis of inorganic phosphate obtained has been estimated by Allen's modified method [1]. The concentration of the diester in all kinetic runs was maintained at 5.0 × 10^{-4} mol. dm^{-3}. The pseudo first order rate coefficients have been calculated by using Debye - Huckle equation [2]. $Ke = K_H^+ . C_H^+ . \exp.\mu$*

Factors such as hydrogen ion concentration, ionic-strength, temperature, substrate concentration etc. have been studied to find out the participation of water molecule, bond-fission and molecularity of the reaction. Ionic strength data and pK values were used to estimate theoretical rates in various zones of pH - log rate profile of the reactive species: Molecularity of the reaction has been discussed in terms of concepts such as Hammett acidity function [3,4], Zucker - Hammett hypothesis [5] and Bunnett parameters [6]. Kinetic rate data and isokinetic relationship [7,8] has been employed to suggest bond - fission of the reaction.

Keywords: phosphate diester, Molecularity

1. Introduction

The recent development in the field of diesters having C-N-P linkage [9-22] reflects the current emphasis on acid hydrolysis of present work. At present due to the efforts and studies of the scientists we are familiar with the inventions of organophosphates in the pure and applied field of Chemistry [23]. Today many organophosphates esters are artificially produced for the practical use in the field of agriculture as pesticides, insecticides, rodenticides and plant hormones etc. In industry they are used as plasticizers, lubricants, surfactants, wetting agent and oil-additives. Phosphate esters also play a significant role in the field of insecticidal activities, radioactive tracer technique and antiviral activities (medicine). In addition, the phosphate esters have also been used as polymeric substance, synthetic lubricants, hydraulic break fluids and also in textile industry as fire retardant.

2. Preparation of DI-p-Propoxy Aniline Phosphate Ester

The method of preparation of diester of p-propoxy aniline has been carried out by the general methods proposed by P. Rudert [24-26]. The residue left after removing p-propoxy aniline phosphate monoester, at b_{50} 180°C was washed several times with hot distilled water and 0.1 N NaOH solution to remove p-propoxy aniline phosphate monoester, unreacted $POCl_3$ and the aryl amine. It was finally digested in 5.0 N NaOH solution (to separate diester from triester of p-propoxy aniline phosphate). It was then filtered off and the filtrate was acidified with dilute HCl using phenolphthalein as an indicator. A white precipitate so obtained was separated by filtration and made free from hydroxyl ions with repeated washings with hot distilled water. It was then dried at room temperature and recrystallised with absolute ethyl alcohol to give a white crystalline solid which was identified to be di-p-propoxy aniline phosphate with the following physical properties.

(i) Melting point (observed) = 285°C
(ii) Theoretical percentage of 'P' = 8.51
(iii) Observed percentage of 'P' = 8.42

3. Result and Discussion

The kinetic study of the hydrolysis of di-p-propoxy aniline phosphate has been performed from 0.1 to 6.0 mol. dm^{-3} HCl at 97± 0.5^{0}C in 20 % aqueous dioxan mixture. Table–1 summarises pseudo first order rate constant and Fig. I describes the pH - log rate profile. Results show that the rate of hydrolysis increases with the increase in acid concentration upto 4.0 mol dm^{-3} HCl and futher increase in acidity decreases the rate of hydrolysis. This bend may be due to ionic strength effect or variation of water molecule activity [27, 28] or simultaneous action of both.

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FIG. I pH – log RATE PROFILE OF DI-p-PROPOXY ANILINE PHOSPHATE AT 97°C

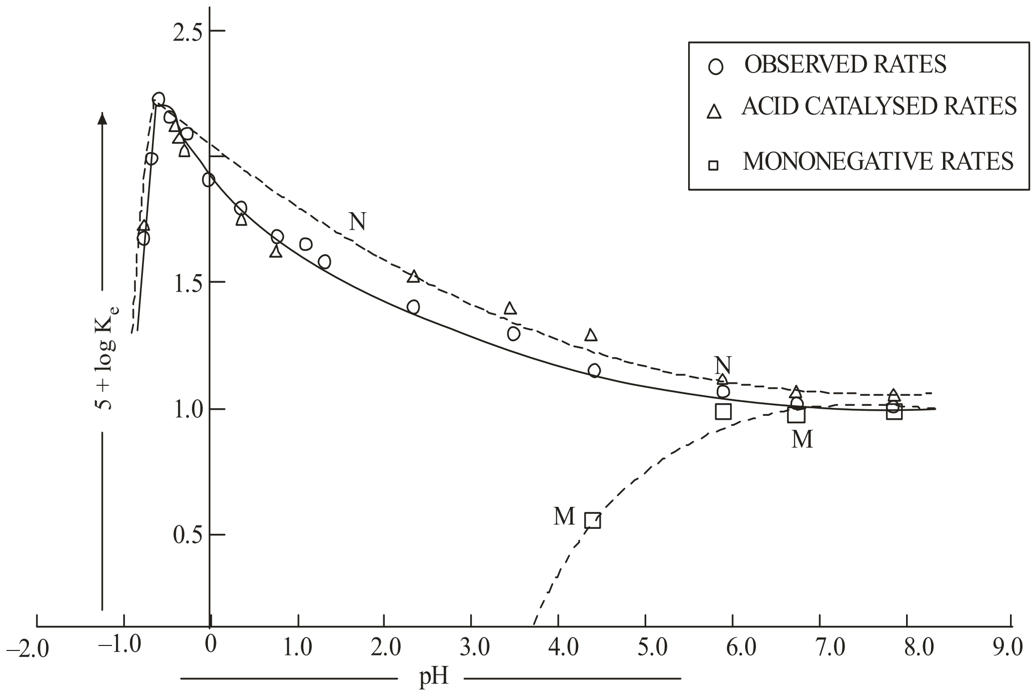

Table 1: pH - log Rate Profile of D1-p-Propoxy Aniline Phosphate at 97°C

HCl (mol.dm.$^{-3}$)	pH	$K_e.10^5$ (mol.dm.$^{-3}$ min^{-1})	5+log K_e
6.0	-0.778	42.77	1.63
5.0	-0.699	90.48	1.96
4.0	-0.602	160.92	2.20
3.0	-0.477	130.96	2.12
2.5	-0.400	122.12	2.08
2.0	-0.300	114.84	2.06
1.0	0.000	70.51	1.85
0.5	0.301	56.32	1.75
0.2	0.700	49.69	1.63
0.1	1.000	38.72	1.59
Buffers:-			
Composition of buffers have been given in experimental section	1.24	32.70	1.51
	2.20	21.62	1.33
	3.30	16.28	1.21
	4.17	12.22	1.08
	5.60	9.46	0.97
	6.43	8.48	0.93
	7.46	8.28	0.92

Effect of Ionic Strength :- The ionic strength effect was examined by carrying out kinetic runs at constant ionic strengths ie. 1.0 μ, 2.0 μ and 3.0 μ, which were obtained by making various compositions of appropriate mixture of KCl and HCl acid. Table - 2 summarises rate coefficients and

Fig. II describes a plot between rate coefficients and acid molarities.

Table 2: Hydrolysis of DI-p-Propoxy Aniline Phosphate at Constant Ionic Strength at 97°C

Composition		Ionic strength (μ)	$k_e.10^5$ (mol.dm.$^{-3}$min^{-1})
HCl (mol.dm.$^{-3}$)	KCl (mol.dm.$^{-3}$)		
0.2	0.8	1.0	31.28
0.4	0.6	1.0	43.04
0.6	0.4	1.0	47.42
0.8	0.2	1.0	58.86
1.0	0.0	1.0	71.70
0.2	1.8	2.0	23.45
0.5	1.5	2.0	36.20
1.0	1.0	2.0	53.50
1.5	0.5	2.0	70.87
1.8	0.2	2.0	81.92
2.0	0.0	2.0	110.66
0.5	2.5	3.0	30.12
1.5	1.5	3.0	58.24
2.0	1.0	3.0	72.58
2.5	0.5	3.0	84.21
3.0	0.0	3.0	142.17

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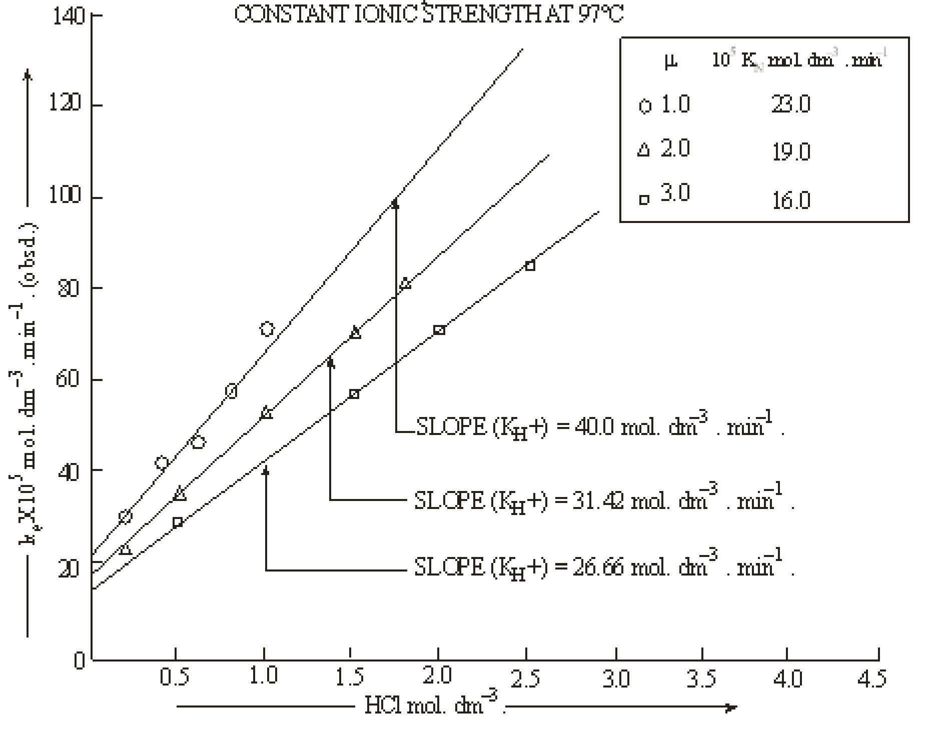
FIG. II HYDROLYSIS OF DI-p-PROPOXY ANILINE PHOSPHATE ESTER AT CONSTANT IONIC STRENGTH AT 97°C



In the plot three linear curves were obtained for each ionic strength indicating the presence of acid catalysis. The slope of the curve are the specific acid catalysed rates at that ionic strength. Different intercepts on the rate axis represents the specific neutral rates at the corresponding ionic strength.

Table 3 summarises both the observed and calculated rates of hydrolysis of di-p-propoxy aniline phosphate at 97°C for the acid region from 1.0 to 6.0 mol. dm^{-3} HCl. Result show that both the calculated and experimentally observed rates are fairly in good agreement upto 4.0 mol. dm^{-3} HCl but beyond 4.0 mol. dm^{-3} there is steep fall in the rates. This has been presumed due to participation of water molecule as a second reaction partner in the nucleophilic substitution reaction. Thus acid catalysed and neutral rates have been calculated by the modified form suggested by Bronsted - Bjerrum [29, 30]. Acid catalysed rates at higher concentration.

$$K_{H^+} C_{H^+} = K_{H^+} . \exp. b_{H^+} . \mu \; (a_{H_2O})^n \quad ...(1)$$

and its logarithmic form can be showed as :

$$5 + \mathrm{Log}\, K_{H^+} C_{H^+} = 5 + \log K_{H_0^+} + \log C_{H^+} + b'_{H^+} . \mu + n \log \; (a_{H_2O})^n \quad ...(2)$$

whereas neutral rates at higher concentrations are as follows :

$$K_N = K_{N_0} . \exp. b'_N . \mu \; (a_{H_2O})^n \quad ...(3)$$

and its logarithmic form can be showed as :

$$5 \log K_N = 5 + \log K_{N_0} + b'_N . \mu + n \log \; (a_{H_2O})^n \quad ...(4)$$

where $(a_{H_2O})^n$ is water activity and n is an integer value.

Table 3: Calculated and Observed Rates for the Hydrolysis of DI -p- Propoxy Aniline Phosphate at 97^0 C

HCl (mol.dm.$^{-3}$)	10^5K_N (mol.dm.$^{-3}$ min.$^{-1}$)	$10^5K_H^+ C_H^+$ (mol.dm.$^{-3}$ min.$^{-1}$)	$10^5K_H^+C_H^+$ (mol.dm.$^{-3}$ min.$^{-1}$) from eq (2)	10^5K_N (mol.dm.$^{-3}$ min.$^{-1}$) from eq (4)	10^5K_e (mol.dm.$^{-3}$ min.$^{-1}$) (Calcd.)	5+log K_e (Calcd.)	K_e10^5 (mol.dm.$^{-3}$ min.$^{-1}$) (Obsd.)
0.1	27.31	4.96	-	-	32.27	1.51	38.72
0.2	27.09	9.80	-	-	36.89	1.57	42.69
0.5	26.42	23.90	-	-	50.32	1.70	56.32
1.0	25.35	45.40	-	-	70.75	1.85	70.51
2.0	23.34	82.04	-	-	105.38	2.02	114.84
2.5	22.38	98.29	-	-	120.67	2.08	122.12
3.0	21.48	111.68	-	-	133.16	2.12	130.96
4.0	19.77	134.90	-	-	154.67	2.19	160.92
5.0	18.20	152.76	74.82*	12.74*	87.56	1.94	90.48
6.0	16.75	165.96	38.64*	6.34*	44.98	1.65	42.77

* n = 2,3 for 5.0 and 6.0 mol.dm.$^{-3}$ HCl (for acid rates)

n = 1,2 for 5.0 and 6.0 mol.dm.$^{-3}$ HCl (for neutral rates)

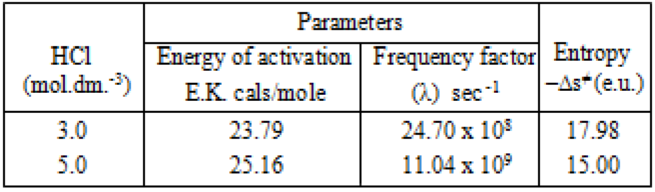
Molecularity: The molecularity of a solvolytic reaction of acid catalysed hydrolysis of di-p-propoxy aniline phosphate have been decided by using number of co-relation plots [figures not shown]. The various co-relation plots are :

(i) Hammet plot [4] (slope value =0.334).
(ii) Zucker Hammett plot [5] (slope value = 0.667).
(iii) Bunnett - plot [6] (slope value ω and ω* =10 and 5).
(iv) Bunnett - olsen plot [31] (slope value ϕ□= 1.71).

All the above parameters of various co-relation plots proves that the acid catalysed hydrolysis of p-propoxy aniline phosphate diester in the entire range may be taken to be bimolecular, in which water molecule participates as a second reaction partner.

Table - 4 summarises Arrhenius parameters [32] of diester at 3.0 and 5.0 mol.dm^{-3} HCl. The magnitude of parameter falls is the range of bimolecular reaction. The value of activation energy (E) is very low (< 25 kcal/mole), the frequency factor(λ) has the power less than 12 and the value of entropy of activation is negative value. Hence the reaction via conjugate acid species shows bimolecular nature of hydrolysis.

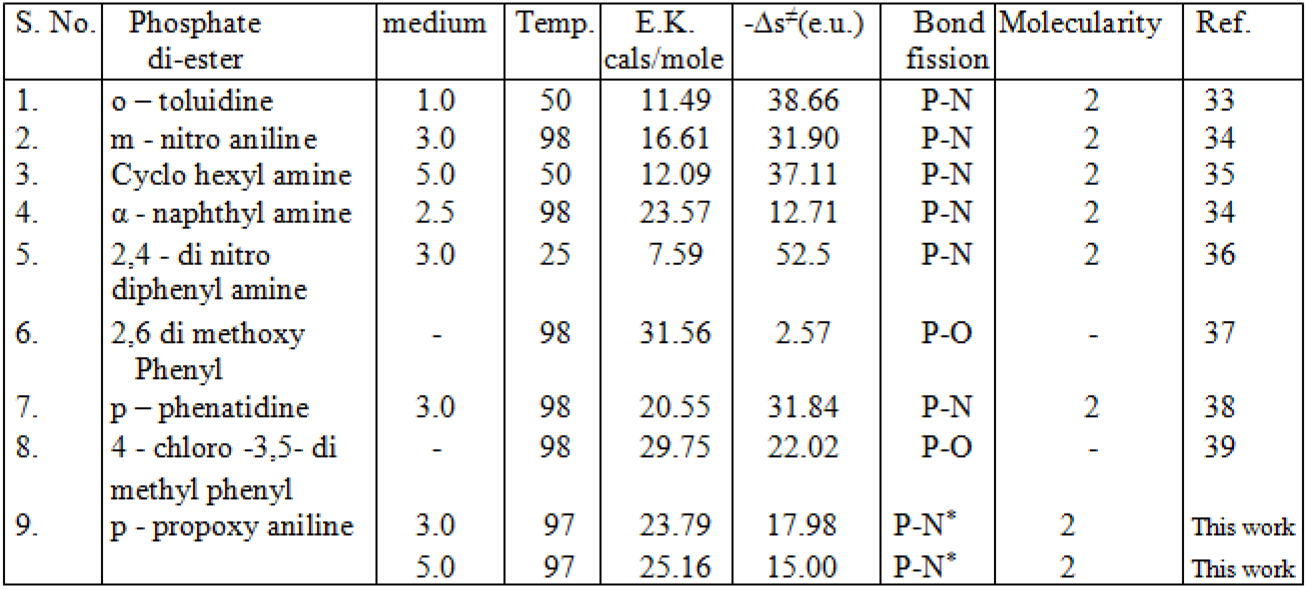
Table 4: Arrhenius Parameters For The Hydrolysis of DI -p-Propoxy Aniline Phosphate AT 97^{0}C



HCl (mol.dm.$^{-3}$)	Parameters		Entropy $-\Delta s^{\neq}$(e.u.)
	Energy of activation E.K. cals/mole	Frequency factor (λ) sec^{-1}	
3.0	23.79	24.70 x 10^8	17.98
5.0	25.16	11.04 x 10^9	15.00

Bond Fission: The hydrolysis of p-propoxy aniline phosphate diester may involve P-N bond fission in the transition state, formed due to bimolecular nueleophilic attack of water molecule. Table 5 summarises the comparative kinetic data for the hydrolysis of other phosphate diesters, which supports P-N bond fission for this diester.

Table 5: Comparative Kinetic Rate Data for the Hydrolysis Of Some Phosphate Diesters Via Their Conjugate Acid Species



S. No.	Phosphate di-ester	medium	Temp.	E.K. cals/mole	$-\Delta s^{\neq}$(e.u.)	Bond fission	Molecularity	Ref.
1.	o – toluidine	1.0	50	11.49	38.66	P-N	2	33
2.	m - nitro aniline	3.0	98	16.61	31.90	P-N	2	34
3.	Cyclo hexyl amine	5.0	50	12.09	37.11	P-N	2	35
4.	α - naphthyl amine	2.5	98	23.57	12.71	P-N	2	34
5.	2,4 - di nitro diphenyl amine	3.0	25	7.59	52.5	P-N	2	36
6.	2,6 di methoxy Phenyl	-	98	31.56	2.57	P-O	-	37
7.	p – phenatidine	3.0	98	20.55	31.84	P-N	2	38
8.	4 - chloro -3,5- di methyl phenyl	-	98	29.75	22.02	P-O	-	39
9.	p - propoxy aniline	3.0	97	23.79	17.98	P-N*	2	This work
		5.0	97	25.16	15.00	P-N*	2	This work

Fig III describes the isokinetic relationship of p-propoxy aniline phosphate diester with some other phosphate diesters. The linearity of the curve exhibit similarity in the mechanism of hydrolysis the present diester with the other diesters of known mechanism, since the data obtained for p-propoxy aniline phosphate diester lies on the same isokinetic line where all the other phosphate diester lies. Thus, p-propoxy aniline phosphate diester undergo bimolecular hydrolysis with P-N bond fission.

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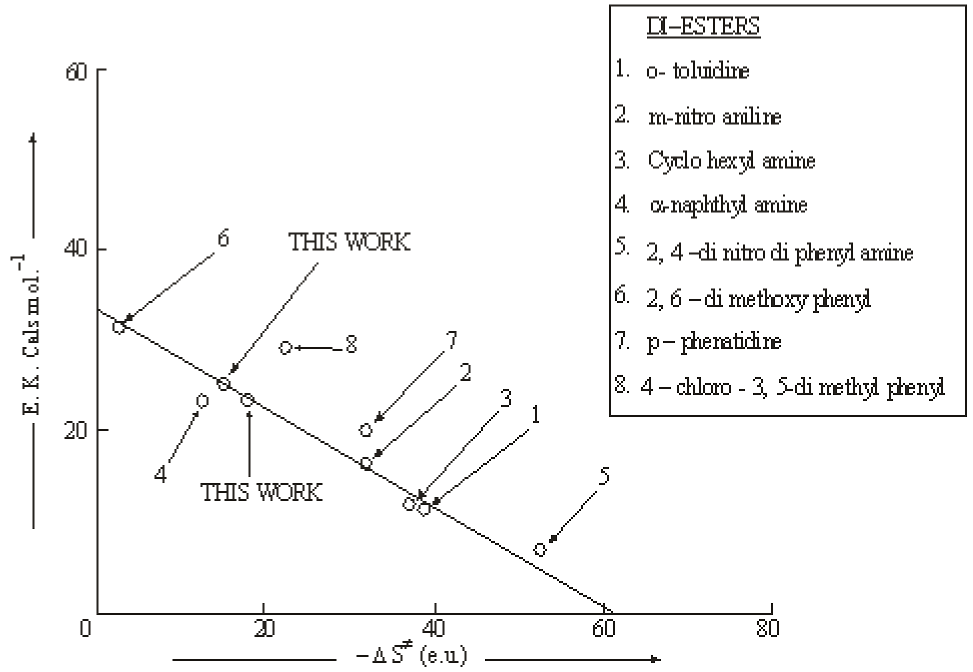
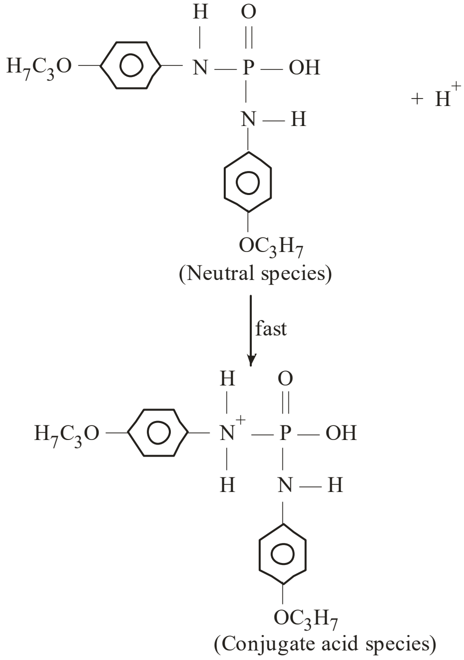
FIG. III COMPARATIVE KINETIC RATE DATA FOR THE HYDROLYSIS OF SOME PHOSPHATE DI-ESTERS VIA THEIR CONJUGATE ACID SPECIES



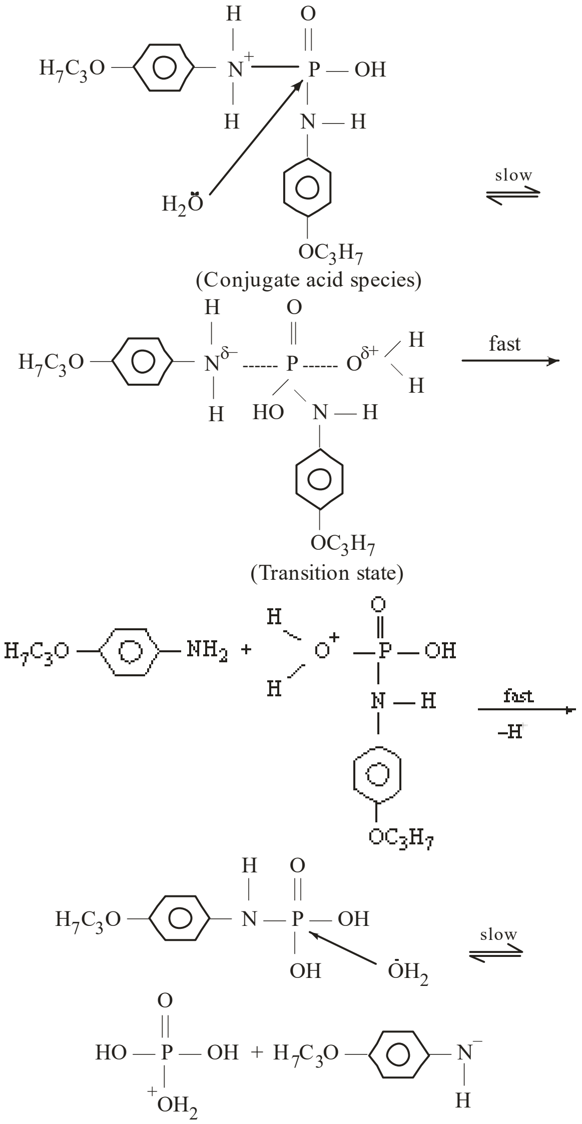
4. Mechanism

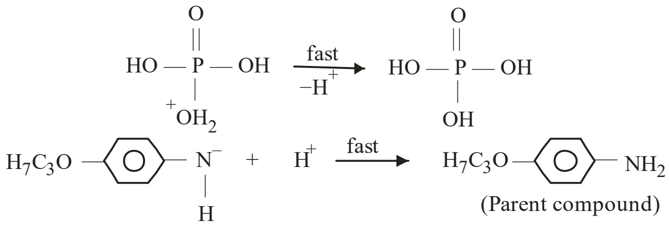
On the basis of all the experimental and theoretical evidences, mechanism of the acid catalysed hydrolysis of p-propoxy aniline phosphate diester via conjugate acid species may be as follows :

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



(b) Bimolecular heterolysis of the conjugate acid species $S_N^2(P)$:





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