Asian Journal of Chemistry Vol. 18, No. 4 (2006), 2969–2982

Synthesis, Mechanistic and Kinetic Study of 2,4,5-Trichloroaniline Phosphate Monoester

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Kinetic measurement of the hydrolysis of 2,4,5-trichloroaniline phosphate mono-ester has been made in acid (0.1–6.0 mol dm.^{3} HCl) solution at 97 ± 0.5°C supported the hypothesis that acid catalysis occurs only when electron attracting substituent is present in the aryl part. Pseudo first order rate coefficients have been calculated. Conjugate acid, neutral and mononegative species have been found to be reactive and contribute in the overall rates. The rate coefficients estimated are fairly in good agreement with the observed rates. Bond fission, molecularity and order of reaction have been supported by Arrhenius parameters, Zücker-Hammett hypothesis, concentration and solvent effect etc. Comparative isokinetic rate data of similarly substituted other amino phosphate mono-esters, supported P—N bond fission.

Key Words: Synthesis, Mechanism, Kinetic studies, Mono-2,4,5-trichloroaniline phosphate, Acid medium.

INTRODUCTION

The effect of substituents on the hydrolysis of aryl phosphate ester having C—N—P linkages[1–14] have been studied exhaustively by Mhala and co-workers[15–18] and established that substituents of graded polarity[19–21] not only affect the reaction rate but also alter the course of the reaction paths. This hypothesis was supported by different scientists[22–26]. It showed that the order of rates follows the order of electron attracting power of the substituents in the aryl part. The rate of hydrolysis of 3,4-dichloroaniline phosphate monoester[27] and 4-chloro-3-nitroaniline phosphate monoester[28] was shown to be the least in the series of other esters studied[29, 30]. The presence of acid catalysis was attributed to the +I effect of chlorine and by opposite inductive effect and hyperconjugative effect of the substituent in 2,4,5-trichloroaniline phosphate mono-ester are expected to favour acid catalysis with the greater rate of hydrolysis among the compounds studied. To test the hypothesis of abnormal acid catalysis[31, 32], a systematic ionic strength data shows the presence of acid catalysis and the order of rate values correlated well with the leaving abilities of the organic substituents with P—N bond fission. Moreover, hydrolysis in pH range has been found to differ from 5-chloro-2-methylaniline phosphate mono-ester[33].

EXPERIMENTAL

2,4,5-Trichloroaniline phosphate mono-ester has been prepared by the general

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method[34]. To the compound 2,4,5-trichloroaniline (19.65 g) dissolved in dry benzene (150 mL), phosphorus oxytrichloride (9.0 mL) was added slowly during 20 min with constant stirring. The reaction mixture was refluxed and distilled at reduced pressure. The second fraction distilled at b_{72} 136–156°C was dissolved in distilled water (100 mL), extracted with ether and recrystallised from absolute ethanol, m.p. 206°C (found: P, 12.02; C, 25.99; H, 1.85: Cl, 38.45; N, 5.10%; calculated for P, 11.21; C, 26.04; H, 1.81; Cl, 38.52; N, 5.06%) finally the structure was confirmed by IR spectrum. All the chemicals used belonged to BDH (AR) and Riedel quality. Hydrolysis of 2,4,5-trichloroaniline phosphate monoester (0.0005 M) was studied in distilled water and the inorganic phosphate was formed during the hydrolysis and estimated colorimetrically by Alien's modified method[35].

RESULTS AND DISCUSSION

Hydrolysis of 2,4,5-trichloroaniline phosphate monoester was kinetically studied in 0.1–6.0 mol dm^{-3} HCl at 97 ± 0.5°C. Pseudo first order rate coefficients have been summarized in Table-1 (Fig.1). From the results it may be concluded that the hydrolysis increases with increase in acid molarity.

TABLE-1
pH-log RATE PROFILE OF 2,4,5-TRICHLOROANILINE PHOSPHATE MONOESTER AT 97 ± 0.5°C

HCl (mol dm^{-3})	pH	$10^5.K_e$ (mol dm^{-3} min^{-1}) (Obsd.)	5 + log K_e
6.0	–0.778	46.93	1.67
5.0	–0.699	91.74	1.96
4.0	–0.602	170.64	2.23
3.5	–0.544	156.86	2.20
3.0	–0.477	149.35	2.17
2.5	–0.397	140.82	2.15
2.0	–0.300	127.36	2.11
1.5	–0.176	113.76	2.06
1.0	0.000	97.32	1.99
0.5	0.301	84.30	1.93
0.4	0.400	80.99	1.91
0.3	0.520	76.08	1.88
0.2	0.700	85.86	1.93
0.1	1.000	97.99	1.99
Buffers: Composition of buffers has been given in the experimental section	1.24	105.49	2.02
	2.20	133.12	2.12
	3.33	138.45	2.14
	4.17	147.86	2.17
	5.60	134.26	2.13
	6.43	115.36	2.06
	7.46	138.12	2.14

The rate maxima is at 4.0 mol dm^{-3} HCl and it gradually decreases with further increase in acid molarity. The rate maxima or bends of pH-log rate profile in acid region have also been found in some other cases. The decrease in rates from (> 4.0 mol dm^{-3} HCl) may be due to participation of water molecule, ionic strength effect or both. The decrease in rates with increase in acidity in the region 0.1–0.5 mol dm^{-3} may be attributed to the decrease in concentration of more reactive mononegative species and the incursion of less reactive neutral species. Further rise in rates in the region of 0.1–4.0 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 pH-log rate profile is due to ionic strength or water activity, could be determined by carrying out kinetic runs at constant ionic strength. The rate coefficients have been summarised in Table-2. Fig. 2 describes a plot between rate coefficients and acid molarity.

TABLE-2
HYDROLYSIS OF 2,4,5-TRICHLOROANILINE PHOSPHATE MONOESTER AT CONSTANT IONIC STRENGTH AT 97 ± 0.5°C

Ionic strength (μ) (mol dm^{-3})	Composition		$10^5 \cdot K_e$ (mol dm^{-3} min^{-1}) (Obsd.)
	HCl (mol dm^{-3})	kCl (mol dm^{-3})	
1.0	0.2	0.8	65.33
1.0	0.4	0.6	72.35
1.0	0.6	0.4	79.55
1.0	0.8	0.2	86.27
1.0	1.0	0.0	97.32
2.0	0.2	1.8	58.17
2.0	0.5	1.5	66.46
2.0	1.0	1.0	78.14
2.0	1.5	0.5	95.40
2.0	1.8	0.2	103.71
2.0	2.0	0.0	127.36
3.0	0.5	2.5	57.77
3.0	1.0	2.0	68.99
3.0	1.5	1.5	82.10
3.0	2.0	1.0	95.06
3.0	2.5	0.5	113.48
3.0	3.0	0.0	149.35

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

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

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.

The slope value K_{H^+} of linear curves of 2,4,5-trichloroaniline phosphate mono ester is subjected to specific acid catalysed rate, similar results were reported in the hydrolysis of 4-fluoroaniline phosphate [36], 5-chloro-2-methylaniline phosphate[41] mono-esters.

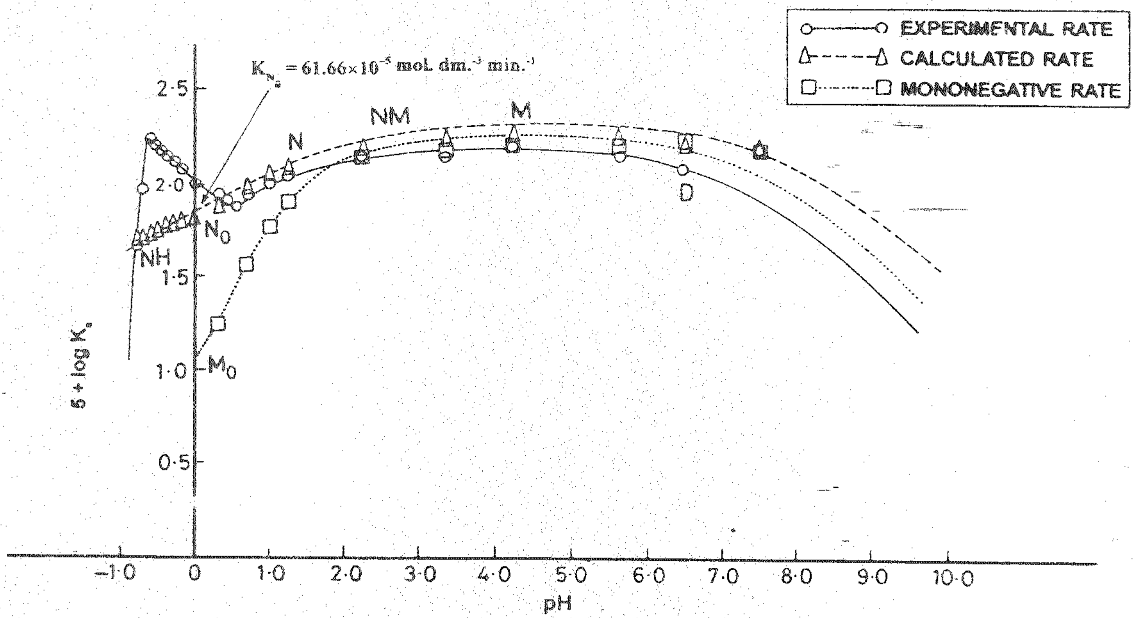


Fig. 1. pH-log rate profile of 2,4,5-trichloroaniline phosphate monoester at 97 ± 0.5°C

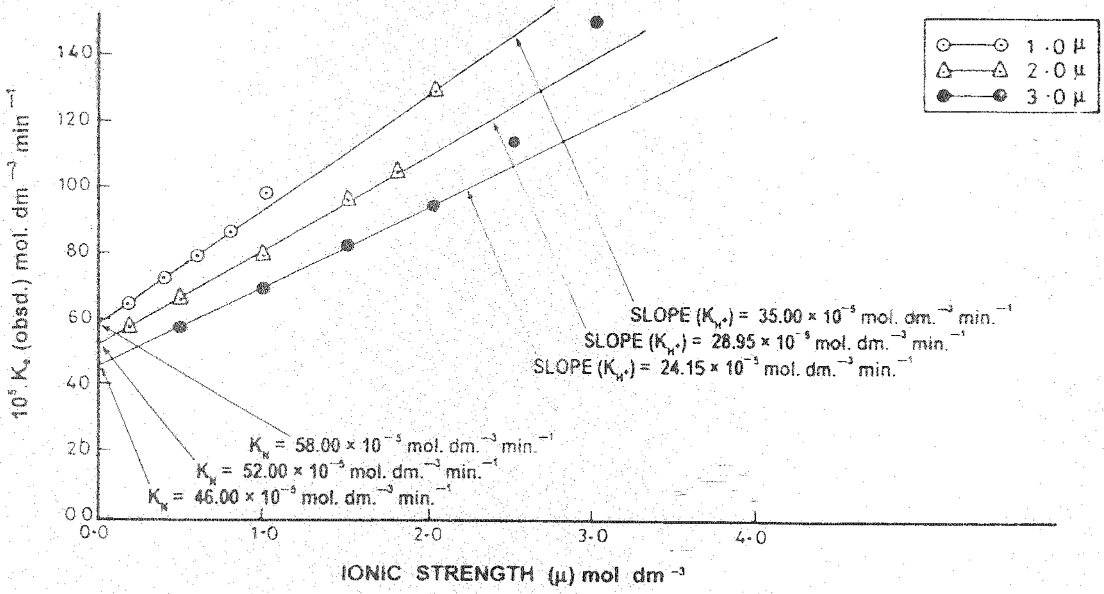


Fig. 2. Hydrolysis of 2,4,5-trichloroaniline phosphate monoester at constant ionic strength at 97 ± 0.5°C

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 strengths 1.0, 2.0 and 3.0 μ are 35.00×10^{-5}, 28.95×10^{-5} and 24.15×10^{-5} mol dm^3 min^{-1} respectively. Table-3 summarizes the log rate coefficients at the corresponding ionic strength.

A linear curve is obtained for specific acid catalysed rate (Fig. 3). The slope of this curve represents the constant b'_{H^+} and another linear curve is obtained for specific neutral rates (Fig. 4); the slope value of this curve represents the constant b'_{N^+} where $b' = b/2.303$. The intercepts on the rate axis represent specific acid catalysed rate $(5 + \log K_{H_0^+})$ and specific neutral rate $(5 + \log K_{N_0})$ at zero ionic strength.

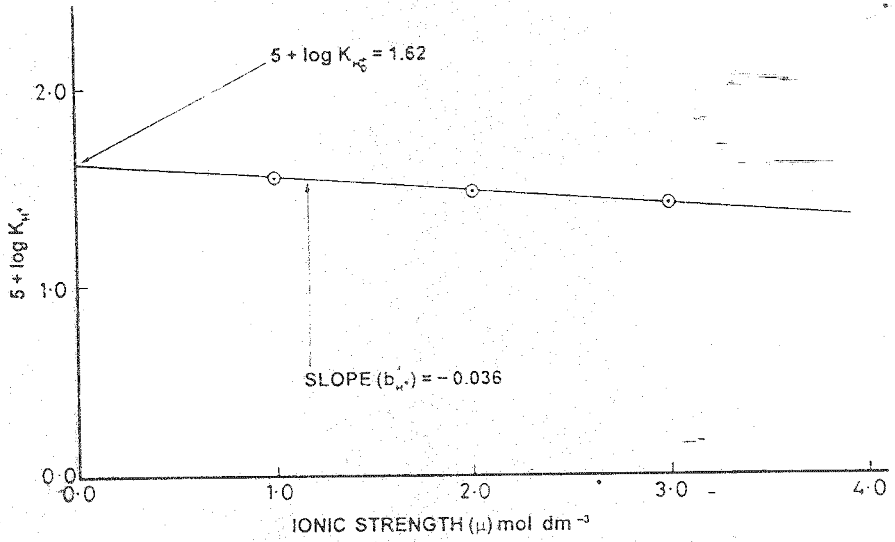


Fig. 3. Hydrolysis of 2,4,5-trichloroaniline phosphate monoester at 97 ± 0.5°C (log-specific acid catalyzed rate *vs.* ionic strength)

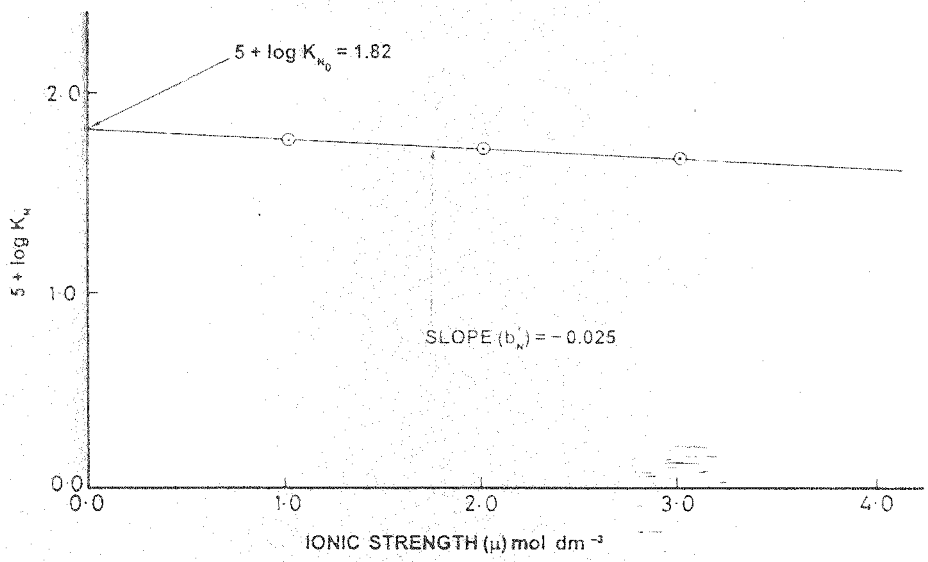


Fig. 4. Hydrolysis of 2,4,5-trichloroaniline phosphate monoester at 97 ± 0.5°C (log-specific neutral rate *vs.* ionic strength)

TABLE-3

SPECIFIC ACID CATALYSED AND SPECIFIC NEUTRAL RATES FOR THE HYDROLYSIS OF 2,4,5-TRICHLOROANILINE PHOSPHATE MONOESTER AT DIFFERENT IONIC STRENGTHS AT 97 ± 0.5°C

Ionic strength (μ)	$10^5 \cdot K_{H^+}$ (mol dm^{-3} min^{-1})	$5 + \log K_{H^+}$	$10^5 \cdot K_N$ (mol dm^{-3} min^{-1})	$5 + \log K_N$
1.0	35.00	1.54	58.00	1.76
2.0	28.95	1.46	52.00	1.72
3.0	24.15	1.38	46.00	1.66

Table-4 summarises the log rate coefficients of specific acid catalysed and specific neutral rate at zero ionic strength with their corresponding b'_{H^+} and b'_{N^+}.

TABLE-4
SPECIFIC ACID CATALYSED [K_{Ho^+}] AND SPECIFIC NEUTRAL [K_{No}]
RATES FOR THE HYDROLYSIS OF 2,4,5-TRICHLOROANILINE
PHOSPHATE MONO ESTER AT ZERO IONIC STRENGTH AT 97 ± 0.5°C.

$10^5 \cdot K_{H_0^+}$ (mol dm^{-3} min^{-1})	$5 + \log K_{H_0^+}$	b'_{H^+}	$10^5 \cdot K_{N_0}$ (mol dm^{-3} min^{-1})	$5 + \log K_{N_0}$	b'_N
41.69	1.62	–0.036	66.07	1.82	–0.025

The linearity of the curves of Figs. 3 and 4 show the following relation of rate constant with ionic strength. This is an empirical form of Debye-Hückel equation[37].

$$K_e = K_0 \exp b \cdot \mu \tag{2}$$

The specific acid catalysed rate may be shown as:

$$K_{H^+} = K_{H_0^+} \cdot \exp b_{H^+} \cdot \mu \tag{3}$$

and the acid rates can be shown as follows:

$$K_{H^+} \cdot C_{H^+} = K_{H_0^+} \cdot C_{H^+} \cdot \exp b_{H^+} \cdot \mu \tag{4}$$

or, its logarithmic form can be shown as:

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

where K_{H^+}, $K_{H_0^+}$, b'_{H^+} and μ are the specific acid catalyzed rates at that ionic strength, at zero ionic strength, a constant and ionic strength respectively.

Similarly, the specific neutral rates may be represented as follows:

$$K_N = K_{N_0} \cdot \exp b_N \cdot \mu \tag{6}$$

and its logarithmic form may be shown as:

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

where K_N, b'_N and μ are the specific neutral rate, a constant and the ionic strength respectively.

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

Therefore, the total rate of hydrolysis of 2,4,5-trichloroaniline phosphate monoester can be represented by the following equation:

$$K_e = K_{H^+} \cdot C_{H^+} + K_N \tag{8}$$

$$5 + \log K_e = 5 + \log K_{H_0^+} + \log C_{H^+} + b'_{H^+} \cdot \mu + 5 + \log K_{N_0} + b'_N \cdot \mu \tag{9}$$

$$5 + \log K_e = 1.62 + \log C_{H^+} + (-0.036) \cdot \mu + 1.82 + (-0.025) \cdot \mu \tag{10}$$

The rate constants calculated from the equation have been summarised in Table-5.

It is clear from the results that there is fairly good agreement between the calculated and experimentally observed rates up to 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 has been sought by introducing water activity parameter. In this way, both acid catalysed and neutral rates have been calculated by the modified form of eqns. (5) and (7) suggested by Bronsted and Bjerrum[38, 39].

$$5 + \log K_{H^+} \cdot C_{H^+} = 5 + \log K_{H_0^-} + \log C_{H^+} b'_{H^+} \cdot \mu + n \log(a_{H_2O}) \qquad (11)$$

and neutral rates at higher concentration can be shown as:

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

where (a_{H_2O}) represents the water activity.

TABLE-5

CALCULATED AND OBSERVED RATES FOR THE HYDROLYSIS OF 2,4,5-TRICHLOROANILINE PHOSPHATE MONO ESTER AT 97 ± 0.5°C

HCl (mol dm^{-3})	pH	$10^5 \cdot K_N$ (mol dm^{-3} min^{-1})	5 + log K_N	$10^5 \cdot K_{H^+} \cdot C_{H^+}$ (mol dm^{-3} min^{-1})	$10^5 K_{H^+} \cdot C_{H^+}$ (mol dm^{-3} min^{-1})	$10^5 \cdot K_N$ (mol dm^{-3} min^{-1})	$10^5 \cdot K_e$ (mol dm–^{3} min–^{1}) (Calcd.)	$10^5 \cdot K_e$ (mol dm^{-3} min^{-1}) (Obsd.)
1.0	0.000	62.37	1.79	38.37	–	–	100.74	97.32
1.5	–0.176	60.60	1.78	55.21	–	–	115.81	113.76
2.0	–0.300	58.88	1.77	70.47	–	–	129.35	127.36
2.5	–0.397	57.21	1.75	84.53	–	–	141.74	140.82
3.0	–0.477	55.59	1.74	97.50	–	–	153.09	149.35
3.5	–0.544	54.01	1.73	109.14	–	–	163.15	156.86
4.0	–0.602	52.48	1.72	119.67	–	–	172.15	170.64
5.0	–0.699	49.55	1.69	137.72	67.45*	24.27*	91.72	91.74
6.0	–0.778	46.77	1.67	152.05	35.40*	10.89*	46.29	46.93

n = 0 for 1.0–4.0 mol dm^{-3} HCl and n* 2 and 3 respectively for 5.0 and 6.0 mol dm^{-3} HCl.

Molecularity

The various correlation plots like Hammett plot[40] (0.235), Zucker-Hammett plot[41] (0.714), Bunnett-plot[42] ($\omega = 11.43$ and $\omega^* = 5.65$) and Bunnett-Olsen plot[43] ($\phi = 1.68$) postulate a bimolecular rate of hydrolysis, that is, the involvement of water molecule as second reaction partner in the slow reaction step. The slopes of Figs. 5–9 and Tables 6–8 show the bimolecularity of the reaction.

TABLE-6

HAMMETT PLOT DATA FOR THE RATE OF HYDROLYSIS OF 2,4,5-TRICHLOROANILINE PHOSPHATE MONO ESTER AT 97 ± 0.5°C

HCl (mol dm^{-3})	$10^5 \cdot K_e$ (mol dm^{-3} min^{-1}) (obsd.)	5 + log K_e	$-H_0$	$-\log (a_{H_2O})$
1.0	97.32	1.99	0.20	0.017
1.5	113.76	2.06	0.47	0.027
2.0	127.36	2.11	0.69	0.039
2.5	140.82	2.15	0.87	0.053
3.0	149.35	2.17	1.05	0.070
3.5	156.86	2.20	1.23	0.087
4.0	170.64	2.23	1.40	0.107
5.0	91.74	1.96	1.76	0.155
6.0	46.93	1.67	2.12	0.211

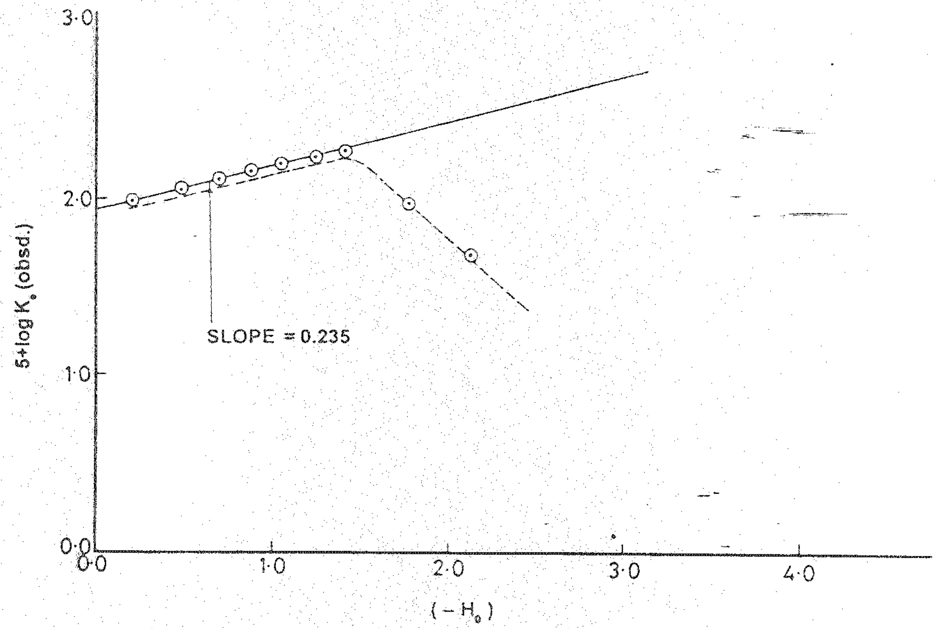


Fig. 5. Hammett plot for the hydrolysis of 2,4,5-trichloroaniline phosphate monoester at 97 ± 0.5°C

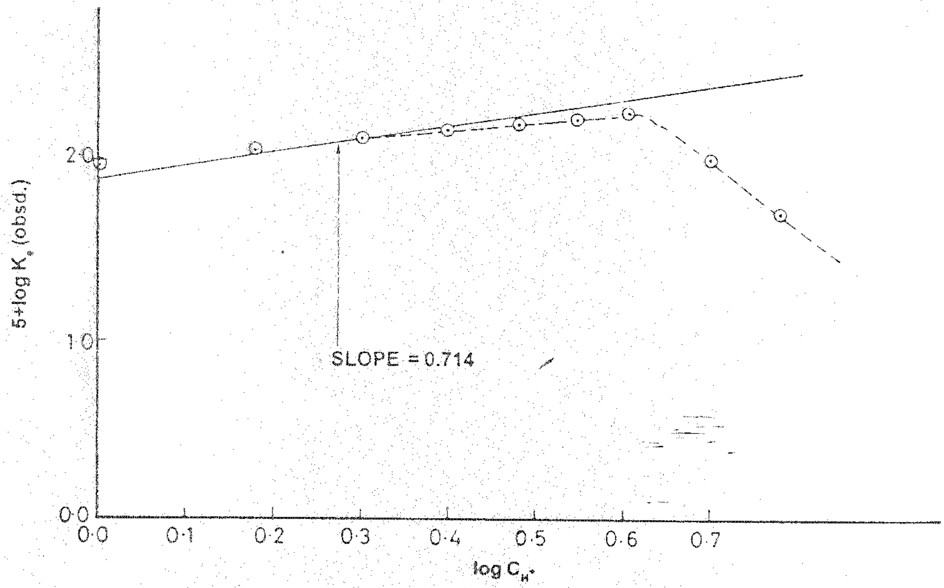


Fig. 6. Zücker-Hammett plot for the hydrolysis of 2,4,5-trichloroaniline phosphate monoester at 97 ± 0.5°C.

The Arrhenius parameters[44] at 3.0 mol dm^{-3} HCl, $\Delta E = 21.05$ kcal $mol^{-}1$, frequency factor $A = 6.74 \times 10^7$ sec^{-1}, $\Delta S^{\#} = -25.14$ e.u. and at 5.0 mol dm^{-3} HCl $\Delta E = 21.97$ kcal mol^{-1}, $A = 14.3 \times 10^7$ sec^{-1}, $\Delta S^{\#} = -23.63$ e.u.

The above Arrhenius parameters[44] at 3.0 and 5.0 mol-dm^{-3} HCl show the bimolecular mode of hydrolysis with P—N bond fission and by isokinetic relationship[45]. Table-9 and Fig. 10 represent the conjugate acid species hydrolyses with P—N bond fission.

Solvent effect[46] and concentration effect also show the reaction to be of bimolecular nature of hydrolysis.

TABLE-7

ZÜCKER-HAMMETT PLOT DATA FOR THE RATE OF HYDROLYSIS OF 2,4,5-TRICHLOROANILINE PHOSPHATE MONO ESTER AT 97 ± 0.5°C.

HCl (mol dm^{-3})	log C_{H^+}	$10^5 \cdot K_e$ (mol dm^{-3} min^{-1}) (obsd.)	5 + log K_e
1.0	0.000	97.32	1.99
1.5	0.176	113.76	2.06
2.0	0.300	127.36	2.11
2.5	0.397	140.82	2.15
3.0	0.477	149.35	2.17
3.5	0.544	156.86	2.20
4.0	0.602	170.64	2.23
5.0	0.699	91.74	1.96
6.0	0.778	46.93	1.67

TABLE-8

OLD-BUNNETT AND BUNNETT-OLSEN PLOT DATA FOR THE RATE OF HYDROLYSIS OF 2,4,5-TRICHLOROANILINE PHOSPHATE MONO ESTER AT 97 ± 0.5°C.

HCl (mol dm^{-3})	log C_{H^+} (a)	$10^5 \cdot K_e$ (mol dm^{-3} min^{-1}) (Obsd.)	5 + logK_e (b)	$-H_o$ (c)	5 + log K_e − log C_{H^+} (b − a)	5 + log K_e + H_0 (b − c)	−(−log C_{H^+} + H_o) (c-a)	−log (a_{H_2O})
1.0	0.000	97.32	1.99	0.20	1.990	1.79	0.200	0.017
1.5	0.176	113.76	2.06	0.47	1.884	1.59	0.294	0.027
2.0	0.300	127.36	2.11	0.69	1.810	1.42	0.390	0.039
2.5	0.397	140.82	2.15	0.87	1.753	1.28	0.473	0.053
3.0	0.477	149.35	2.17	1.05	1.693	1.12	0.573	0.070
3.5	0.544	156.86	2.20	1.23	1.656	0.97	0.686	0.087
4.0	0.602	170.64	2.23	1.40	1.628	0.83	0.798	0.107
5.0	0.699	91.74	1.96	1.76	1.261	0.20	1.061	0.155
6.0	0.778	46.93	1.67	2.12	0.892	−0.45	1.342	0.211

TABLE-9

COMPARATIVE ISOKINETIC RATE DATA FOR THE HYDROLYSIS OF SOME PHOSPHATE MONO-ESTERS *VIA* THEIR CONJUGATE ACID SPECIES

S. No.	Phosphate Mono-ester	Temp. (°C)	Medium	E (kcal/mol)	−ΔS* (e.u.)	Bond fission	Ref.
1.	Cyclohexylamine	50	3.0	26.65	−0.77	P—N	47
2.	$H_3N^+COO^-$	37	–	26.00	12.23	P—N	24
3.	2,5-Dimethoxyaniline	97	3.0	2333	19.03	P—N	48
			5.0	22.88	21.08	P—N	
4.	4-Chloro-3-nitroaniline	97	3.0	21.50	23.93	P—N	12
			5.0	21.96	23.56	P—N	
5.	*m*-Nitroaniline	98	3.0	21.05	25.57	P—N	49
6.	4-Fluoroaniline	97	3.0	19.67	28.00	P—N	36
			5.0	20.59	27.34	P—N	
7.	*p*-Propoxyaniline	97	3.0	19.68	29.28	P—N	11
8.	N-2-Carboxyphenyl-N-(2-hydroxy-3-nitrophenyl)amine	97	3.0	18.30	32.84	P—N	50
9.	3,4-Dichloroaniline	97	3.0	17.61	34.53	P—N	27
10.	3-Chloroaniline	97	3.0	16.93	36.39	P—N	51
11.	*p*-Naphthylamine	98	3.0	14.56	39.46	P—N	52
12.	*o*-Toluidine	50	–	15.05	40.40	P—N	53

S. No.	Phosphate Mono-ester	Temp. (°C)	Medium	E (kcal/mol)	–ΔS* (e.u.)	Bond fission	Ref.
13.	2,4-Dinitroaniline	98	3.0	12.10	45.10	P—N	54
14.	1-Nitro-2-naphthylamine	98	5.0	10.49	49.76	P—N	55
15.	3-Nitro-p-toluidine	–	3.0	8.28	52.87	P—N	56
16.	Diethylamine	40	3.0	5.72	60.65	P—N	57
17.	2,4,5-trichloroaniline	97	3.0	21.05	25.14	P—N*	Present
			5.0	21.97	23.63	P—N*	work

*Bond fission assumed

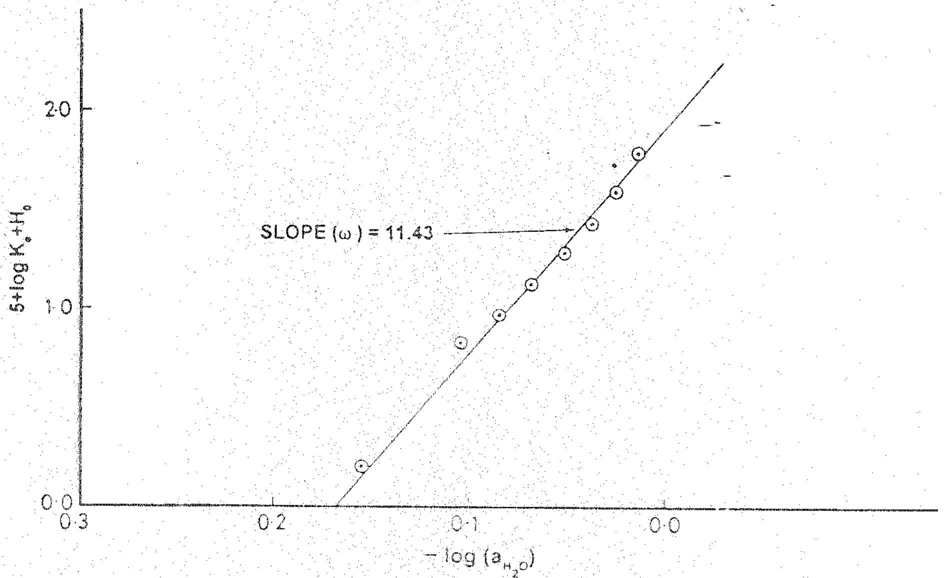


Fig. 7. Bunnett plot for the hydrolysis of 2,4,5-trichloroaniline phosphate monester at 97 ± 0.5°C.

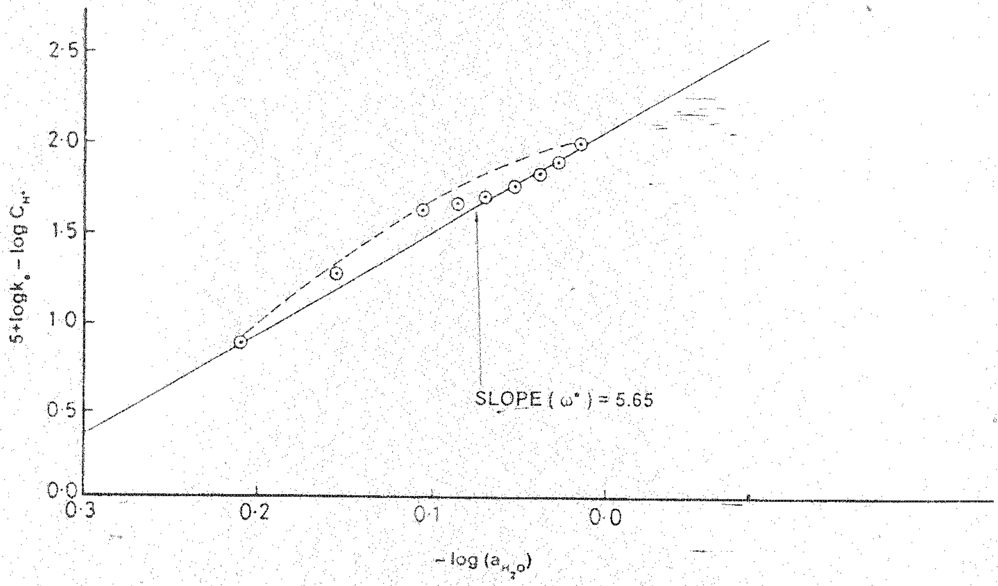


Fig. 8. Old-Bunnett plot for the hydrolysis of 2,4,5-trichloroaniline phosphate monoester at 97 ± 0.5°C.

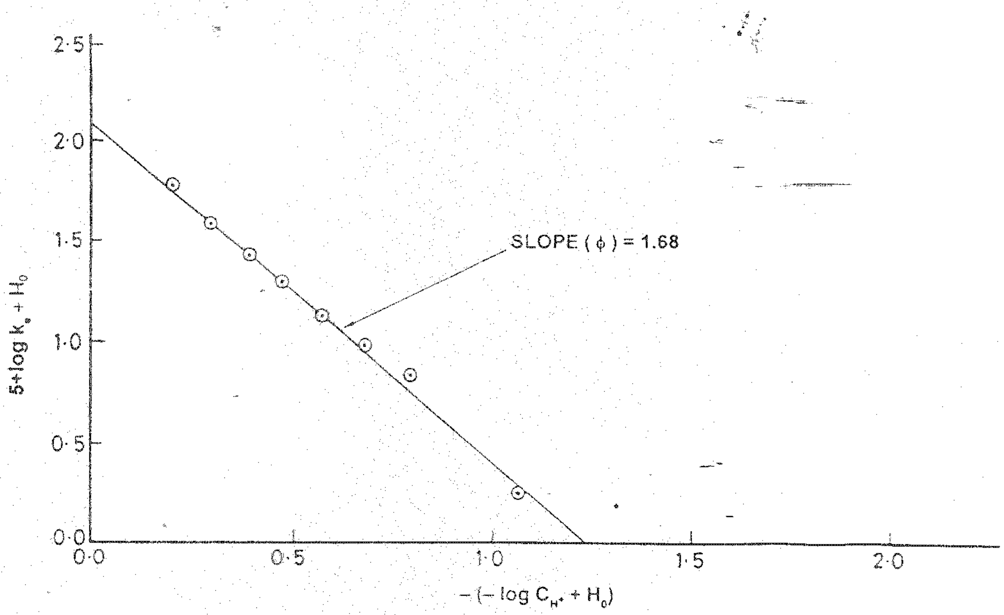


Fig. 9. Bunnett and Olsen plot for the hydrolysis of 2,4,5-trichloroaniline phosphate monoester at 97 ± 0.5°C.

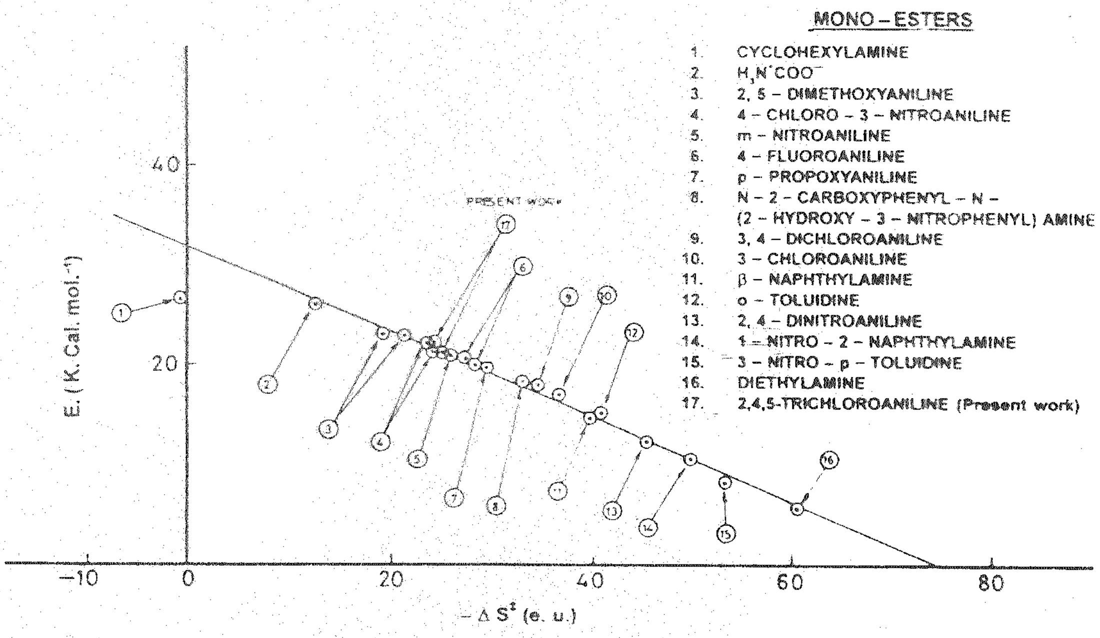
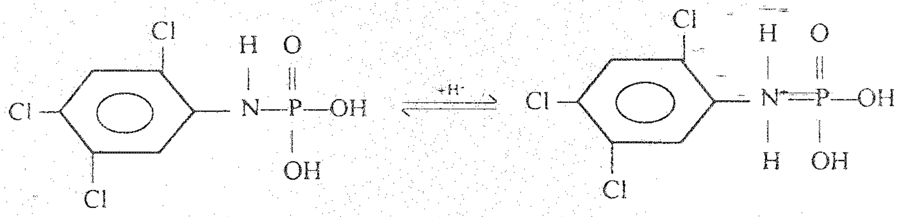


Fig. 10 Isokinetic relationship plot for the hydrolysis of some phosphate monoesters *via* their conjugate acid species

Mechanism

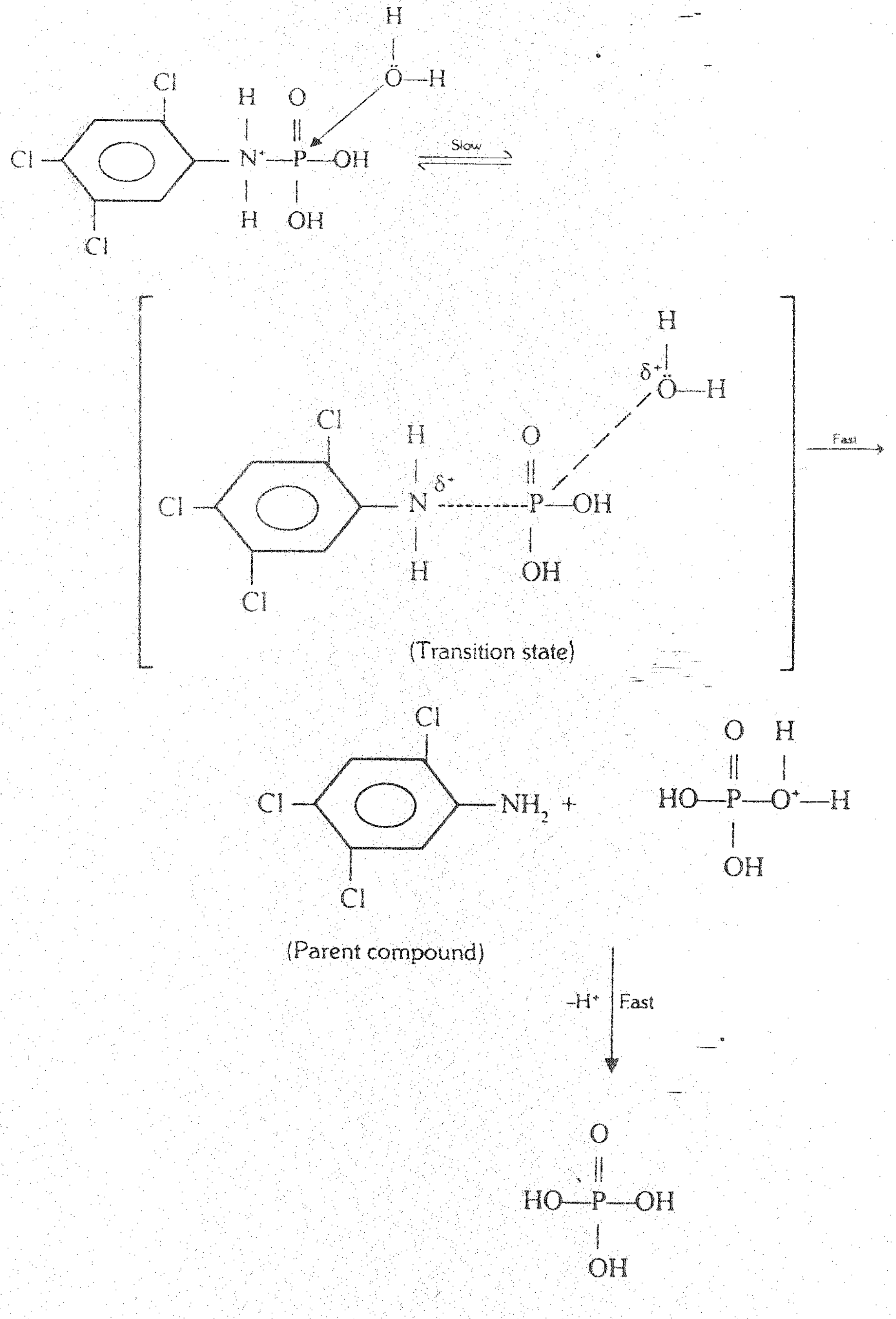
Taking into account all the observed rate data, the most probable reaction pathway *via* conjugate acid species may be formulated as follows:

(a) Formation of conjugate acid species by fast pre-equilibrium proton transfer from the undissociated mono-ester:



(Neutral species) (Conjugate acid species)

(b) Bimolecular nucleophilic attack of water on phosphorus of the conjugate acid species of the mono-ester involving P—N bond fission S_N^2(P):



(Transition state)

(Parent compound)

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(*Received*: 17 October 2005; *Accepted*: 2 May 2006) AJC-4829