Kinetic Study Regarding Molecularity, Bond–Fission and Reaction Mechanism In The Acid Hydrolysis of 5–Chloro, 2–Methyl Aniline Phosphate Triester

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Abstract: ***Kinetic study of the hydrolysis of 5–chloro, 2–methyl aniline triester has been done in 0.1 to 6.0 mol. dm^{-3} HCl and pH 1.24 to 7.46 at 80 ± 0.5°C in aqueous dioxan (v/v) mixture. The rate of hydrolysis was determined by measuring the rate of appearance of inorganic phosphates by Allen's modified colorimetric method [1]. The concentration of triester in all kinetic runs was maintained at 5.0×10^{-4} mol dm^{-3}. Conjugate acid and neutral species of the triester have been found to be reactive, but this discussion is based only on conjugate acid species. Effects of variable factors such as temperature, pH, ionic strength, concentrations etc. on the rate of hydrolysis of the triester have been studied in detail. Concepts such as Hammett acidity function [2], Bunnett parameters [3,4], Zucker-Hammett hypothesis [5], isokinetic relationship [6] together with Arrhenius parameters [7] and comparative isokinetic data of other triesters of known mechanism were considered for deciding the molecularity, bond-fission and probable mechanism of the hydrolysis of the triester.***

Keywords: Kinetic study, hydrolysis, molecularity, bond-fission and Reaction mechanism

1. Introduction

Organic compounds of phosphate esters play a significant role in the maintenance of life. Since, organophosphates esters have significant chemical, physical and biological properties thus they have wide range of application in the field of antiviral activities [8] insecticidal activities [9,10] and tracer techniques [11]. They are artificially synthesised for their practical use as lubricants [12], oil-additives, plasticizers [13] and pesticides [14]. Some organophosphates are also used as polymeric substances [15] hydraulic break fluids [16], fuel additives for explosion control and flame resistant [17]. Also, the survival of human body on the earth is the result of sugar phosphates and its compound which constitutes the metabolic activities of the human body. Thus, the importance of phosphate esters can be studied in various fields of biological, industrial and academics etc.

The recent interest in the field of esters having C–O–P & C–N–P linkage [18–32] reflects the current emphasis on acid hydrolysis of 5–chloro, 2–methyl aniline phosphate triester.

2. Experimental Investigation

The triester has been synthesised by P. Rudert [33, 34] method. The present aniline in dry benzene and $POCl_3$ (3 : 1 ratio w/w) were stirred and the mixture was refluxed for about 40 hours on the soxhlet heater at constant temperature 65°C and then distilled at reduced pressure. The first fraction of benzene and unreacted $POCl_3$ was rejected by distillation at b_{50} 150°C. The second fraction which sublimed at b_{50} 150–170°C found to dichloridate of 5–chloro, 2–methyl aniline phosphate. The residue left in the round bottom flask was treated with hot 5.0 mol dm^{-3} NaOH solution and washed several times with boiling distilled water. It was then dried and recrystallised with absolute ethyl alcohol to give a white crystalline solid, which was indentified to be tri–5–chloro, 2–methyl aniline phosphate with the following physical properties:

(i) Melting point (observed) = 294°C
(ii) Theoretical percentage of 'P' = 6.64
(iii) Observed percentage of 'P' = 6.52

3. Result and Discussion

Kinetic study to examine the effect of ionic strength on the rate of hydrolysis of 5–chloro, 2–methyl aniline phosphate triester were performed at three different ionic strengths ie 1.0µ, 2.0µ and 3.0µ and it was maintained by using appropriate mixtures of KCl and HCl acid. The calculation of specific acid catalysed and specific neutral rates for the hydrolysis of 5–chloro, 2–methyl aniline phosphate triester has been done on the basis of Debye–Huckel equation [ ]

Acid Rates:

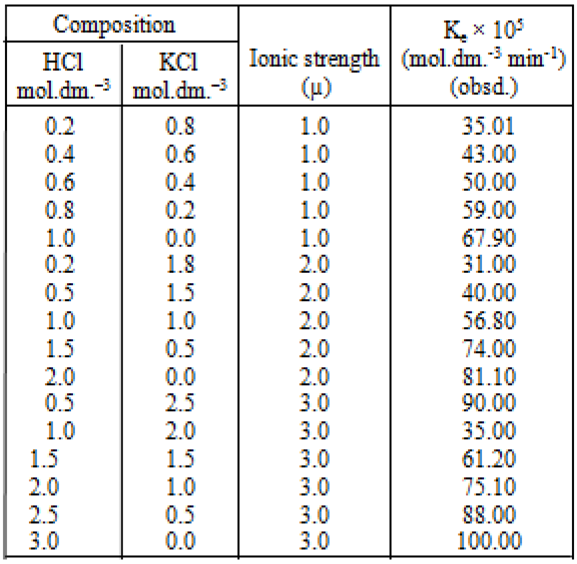
$$\log K_{H^+}.C_{H^+} = \log K_{H_0^+} + \log C_{H^+} + b_{H^+}.\mu \quad \ldots (1)$$

Neutral Rates

$$\log K_N = \log K_{N_O} + b'_H.\mu \quad \ldots(2)$$

Kinetic runs have been summarised in Table 1. A plot between rate coefficients and acid molarity describes in the Figure I.

Table 1: Hydrolysis of Tri–5–Chloro, 2–Methylaniline Phosphate at Constant Ionic Strength



Composition		Ionic strength (μ)	$K_e \times 10^5$ (mol.dm.$^{-3}$ min^{-1}) (obsd.)
HCl mol.dm.$^{-3}$	KCl mol.dm.$^{-3}$		
0.2	0.8	1.0	35.01
0.4	0.6	1.0	43.00
0.6	0.4	1.0	50.00
0.8	0.2	1.0	59.00
1.0	0.0	1.0	67.90
0.2	1.8	2.0	31.00
0.5	1.5	2.0	40.00
1.0	1.0	2.0	56.80
1.5	0.5	2.0	74.00
2.0	0.0	2.0	81.10
0.5	2.5	3.0	90.00
1.0	2.0	3.0	35.00
1.5	1.5	3.0	61.20
2.0	1.0	3.0	75.10
2.5	0.5	3.0	88.00
3.0	0.0	3.0	100.00

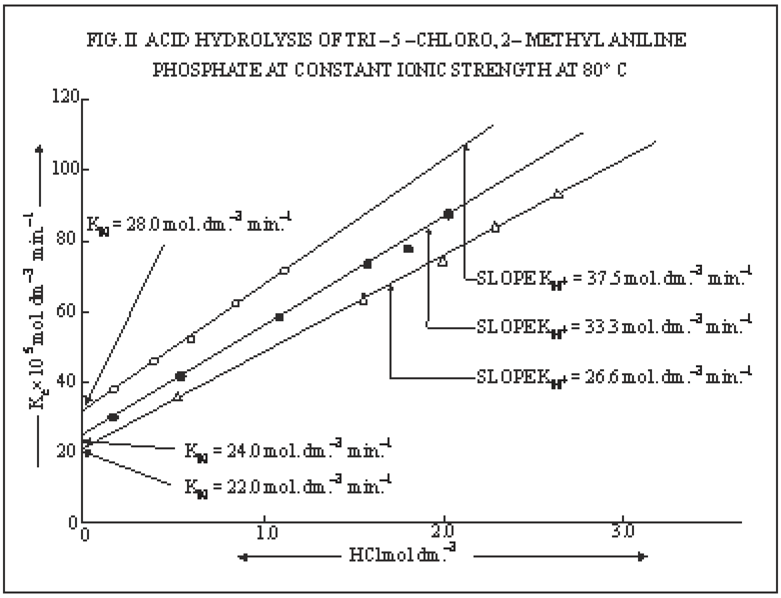


FIG. II ACID HYDROLYSIS OF TRI – 5 – CHLORO, 2 – METHYL ANILINE PHOSPHATE AT CONSTANT IONIC STRENGTH AT 80° C

As clear from the plot, three linear curves are obtained for the hydrolysis of triester. The slope of the linear plot indicates the presence of acid catalysed hydrolysis. At each ionic strengths hydrolysis may be represented as

$$K_e = K_{H^+}.C_{H^+} \qquad \text{.......... (3)}$$

Where K_e is observed rate constant, K_{H^+} is specific acid catalysed rate constant and C_{H^+} is concentration of hydrogen ion.

Different intercepts on the rate axis are the neutral rate at the corresponding ionic strength. Variation of the neutral rates with the ionic strength is governed by the kinetic rate expression. Thus both acid catalysed and the neutral rates may be represented as

$$K_e = K_{H^+}.C_{H^+} + K_N \qquad \text{.......... (4)}$$

There values are summarised in Table–2

Table 2: Calculated and Observed Rates for the Hydrolysis of Tri -5-Chloro, 2–Methyl Aniline Phosphate at 80^0 C

HCl (mol.dm.$^{-3}$)	$10^5 K_{H}^{+} C_{H}^{+}$ (mol.dm.$^{-3}$ min.$^{-1}$) from eq (1)	$10^5 K_{H}^{+} C_{H}^{+}$ (mol.dm.$^{-3}$ min.$^{-1}$) from eq(5)	$10^5 K_N$ (mol.dm.$^{-3}$ min.$^{-1}$) from eq (2)	$10^5 K_N$ (mol.dm.$^{-3}$ min.$^{-1}$) from eq (6)	$K_e\, 10^5$ (mol.dm.$^{-3}$ min.$^{-1}$) (calcd.)	$10^5 K_e$ (mol.dm.$^{-3}$ min.$^{-1}$) (obsd.)
0.1	4.53	–	33.67	–	38.20	37.19
0.2	7.90	–	33.46	–	41.36	42.49
0.5	22.10	–	32.84	–	54.94	53.87
1.0	42.55	–	31.84	–	74.39	74.04
2.0	79.06	–	29.92	–	108.98	107.16
2.5	96.05	–	29.00	–	125.05	125.25
3.0	110.66	–	28.11	–	138.77	138.05
4.0	137.40	–	26.42	–	163.82	162.59
5.0	159.95	22.38*	24.83	17.37*	39.75	38.97
6.0	178.64	11.27*	23.33	8.83*	20.10	21.12

n = 0 for 1.0 to 4.0 mol dm^{-3} HCl.
n* = 1,2 respectively for 5.0 and 6.0 mol dm^{-3} HCl.

From the results, it is clear that there is close agreement between observed and estimated rates up to 4.0 × 10^{-5} mol dm^{-3} HCl. The observed deviation in acid solutions (5.0 and 6.0 mol dm^{-3} HCl) can be removed by introducing water activity parameters in the above equations which can be shown as :

Acid Rates

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

Neutral Rates

$$\log K_N = \log K_{N_0} + b'_N.\mu + n\log(a_{H_2O}) \quad ..... (6)$$

Where (a_{H_2O}) represents water activity term.

4. Molecularity

The molecularity of the acid catalysed hydrolysis of 5–chloro, 2–methyl aniline phosphate triester has been determined by the concepts such as Hammett relationship, Zucker–Hammett hypothesis, Bunnett parameters and Bunnett–Olsen parameters. The values of various co-relation plots (figs. not shown) are.

(i) Hammet relationship [2] (slope value = 0.33).
(ii) Zucker Hammett plot [5] (slope value = 0.57).
(iii) Bunnett - plot [3,4] (slope value ω and ω* = 6.25 and 10.71).
(iv) Bunnett - Olsen plot [35] (slope value ϕ□ = 1.45).

All the above value of various correlation plots supports biomolecular mechanism of 5–chloro, 2–methyl aniline phosphate triester in the entire range of hydrolysis, in which rates depend on acidity and water activity.

Bimolecular mechanism of 5–chloro, 2–methyl aniline phosphate triester has also been supported by Arrhenius parameters. Table–3 summarises Arrhenius parameters of hydrolysis of triester at 3.0 and 5.0 mol dm^{-3} HCl. The magnitude of Arrhenius parameters fall in the range of bimolecular reaction since the value of energy of activation (E) is very low *i.e.* 25 k cal mole^{-1}, the value of frequency factor (λ) has the power less than 12 and the value of entropy of activation ($-\Delta s^{\pm}$) is negative value. Hence, the hydrolysis proceeds bimolecularly via conjugate acid species.

Table 3: Arrhenius Parameters For The Hydrolysis of TRI -2- CHLORO, 2-Methylaniline Phosphate

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	21.50	4.59×10^8	21.22
5.0	19.67	9.85×10^6	28.85

5. Bond–Fission

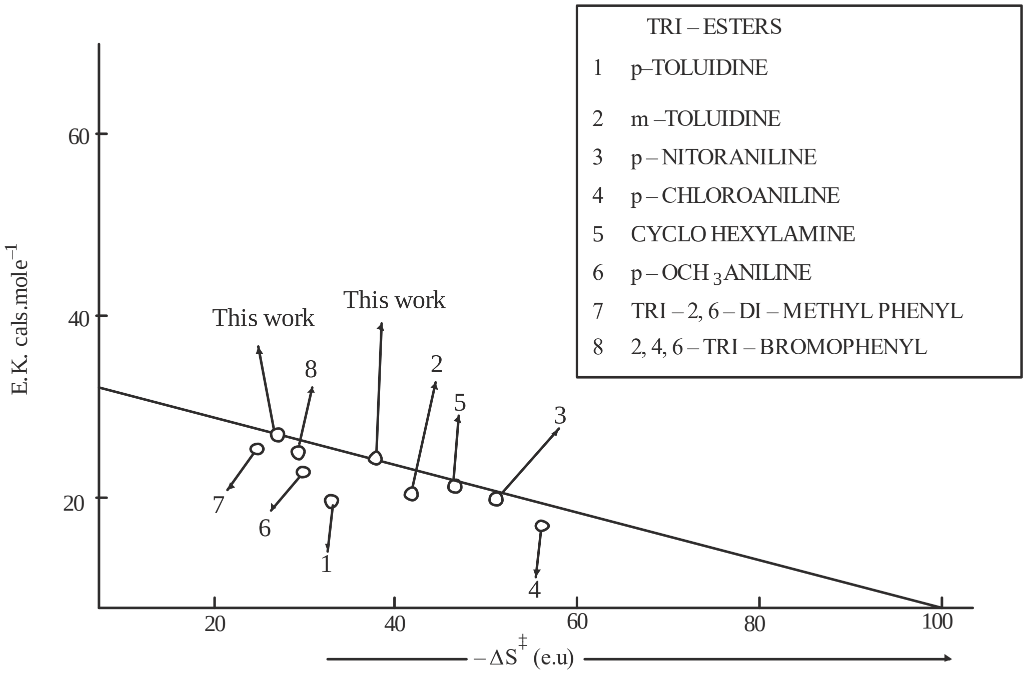
The bimolecular hydrolysis of triester as determined from various correlation plots and Arrhenius parameters may involve either P-N or C-N bond fission. The Probability of former seems to be more because of the stability of intermediate formed during the progress of the reaction. In this fission amine molecule formed as an intermediate will be stabilised to a large extent by mesomeric effect. The probability of P–N bond fission is also supported by comparative iso-kinetic data of other triester (the bond-fission and molecularity of which are known) which have been summarised in Table–4.

Table 4: Comparative Kinetic Rate Data for the Hydrolysis of Some Phosphate triesters Via Their Conjugate Acid Species

S. No	Phosphate tri-ester	Temp. °C	Medium.	E. k cals/mole	$-\Delta s^{\neq}$(e.u.)	Bond fission	Molecularity	Ref.
1.	p – toluidine	80	4.0	15.08	25.85	P-N	2	18
2.	m – toludine	80	4.0	14.62	32.92	P-N	2	18
3.	p – nitroaniline	98	3.0	15.25	42.71	P-O	2	36
4.	p – cholroaniline	98	4.0	11.44	46.68	P-N	2	37
5.	Cyclohexyamine	50	1.0	15.96	37.47	P-N	2	38
6.	p – OCH_3 aniline	65	–	18.67	22.70	P-N	2	39
7.	tri, 2,6–dimethyl phenyl	98	–	21.59	19.19	P-O	–	40
8.	2,4,6- tri bromo phenyl	98	–	20.59	22.28	P-O	–	41
9.	5–chloro, 2–methyl Aniline	80	3.0 5.0	21.50 19.67	21.22 28.85	P-N* P-N*	2 2	This work This work

Thus, conjugate acid species of the triester have been invariably found to undergo P-N bond fission. It has also been supported by isokinetic relationship of 5–chloro, 2–methyl aniline phosphate triester with some other phosphate triesters. Fig. II describes a plot between activation energy (E) and entropy of activation ($-\Delta s^{\neq}$). The plot is linear covering almost all the point of similar phosphate triester, hence the linearity of the curve shows similarity of mechanism of present triester with other triesters of known mechanism. Thus, 5–chloro, 2–methyl aniline phosphate triester undergo bimolecular hydrolysis via P–N bond fission.

FIG. II COMPARATIVE KINETIC RATE DATA FOR THE HYDROLYSIS OF SOME TRI-ESTERS VIA THEIR CONJUGATE ACID SPECIES



6. Mechanism

Taking into account all the above experimental evidences and discussions, the most probable reaction path via conjugate acid species of 5–chloro, 2–methyl aniline phosphate triester may be formulated as :

Chart I: Formation of conjugate acid species by fast pre-equilibrium proton transfer.

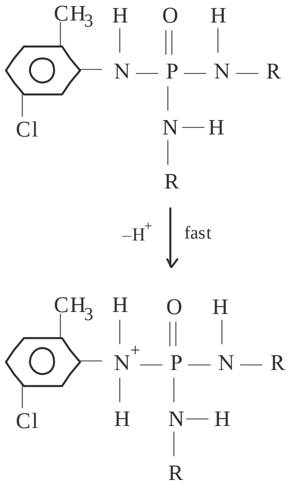
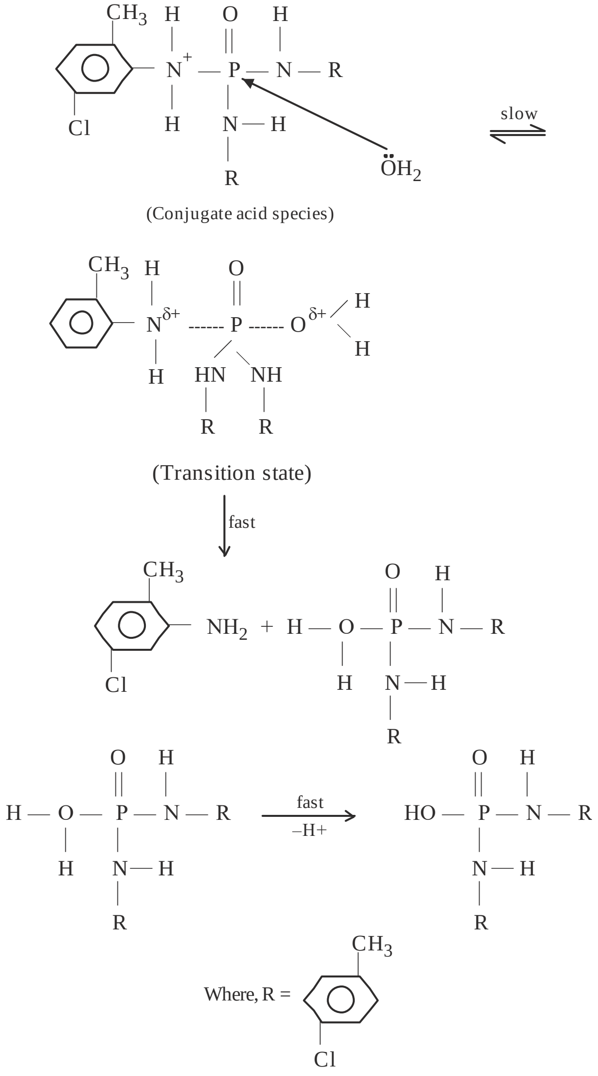


Chart II : Bimolecular nucleophilic attack of water on phosphorus $S_N^2(P)$—



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