

Kinetics and mechanism of the acid hydrolysis of mono-5- chloro, 2-methylaniline phosphate ester

Amit Chaudhary

Chemistry Department D.S. College, Aligarh

Abstract

The acid hydrolysis of mono-5-chloro, 2- methylaniline phosphate in the acid range 0.1 to 6.0 M HCl at 80 ± 0.5 °C has been performed in water. The concentration of monoester in all kinetic runs used was 5.0×10^{-4} moldm⁻³. The inorganic phosphate obtained in overall hydrolysis has been estimated colorimetrically by Allen’s modified method. The first order rate coefficients have been calculated using integrated form of the corresponding rate equation.

$$K_e = K_H^+ \cdot C_{H^+} \cdot \exp. \mu$$

Conjugate acid, neutral, mononegative and dinegative species have been found to be reactive and contribute to the overall rates, but in this discussion only conjugate acid and neutral species are given. The rate coefficients estimated by above equation are fairly in good agreement with the experimentally observed rates. Factors such as hydrogen ion concentration, ionic strength, temperature, solvent, substrate concentration effects etc., have been studied to find the participation of water molecules, bond fission and molecularity of the reaction. Probable mechanism of the acid hydrolysis of mono-5-chloro,2-methyl aniline phosphate via different reactive species has been suggested on the basis of kinetic rate data and iso kinetic relationship.

Keywords: Customer Satisfaction, Two-Wheeler Motor Bikes, Descriptive Analysis

1. Introduction

The effects of substituent on the hydrolysis of aryl phosphate esters having C-O-P linkage [1,2] have been studied exhaustively by Mhala and his co-workers [3-5] and established that the effect of substituent of graded property [6-12] not only effect the reaction rates but also alter the course of the reaction paths, the substituent having positive inductive effect (+I) and tautomeric effect (+T) increase the electron density at the oxygen of the ester linkage.

Consequently conjugate acid species is readily formed, which enhances the reaction rate, on the other hand substituent having (-I and -T) reduced the basicity of the ester oxygen, consequently, the formation of conjugate acid species is restricted and the reaction rates are reduced. In view of the above mono-5- chloro, 2-methylaniline phosphate ester having C-N-P linkage [13-24] is taken to study the effect of substituent on the reaction rates. The nitrogen atom in the ester linkage alone is sufficient to form the conjugate acid species due to the presence of lone pair of electron whether or not the substituent chlorine atom at para position having (-I and +M) effect would bring about any change in the reaction rates and the formation of reaction species is the purpose of the present study.

Experimental:- The Mono-ester has been synthesized by P. Rudert [25-27] method. Both, the present aniline in benzene and POCl₃ (3:1 ratio w/w) were stirred at 65°C for about 40 hours and distilled at reduced pressure. The first fraction distilled at b₅₀, 150 °C was rejected and second fraction which sublimed at 150^o – 170^oC was found to be dichloridate of monoester. It was dissolved in 100 ml of ice cooled water and kept at low temperature overnight. The 5-chloro, 2-methylaniline phosphoro-di-chloridate converted into 5-chloro, 2-Methylaniline di-hydrogen phosphate, was extracted with solvent ether. After removing the solvent ether a light brown

coloured crystalline solid was obtained which on recrystallisation with absolute ethyl alcohol gave a white crystalline solid and it was identified to be 5 chloro, 2-methylaniline phosphate M.P. 210°C (found P.13.94 required theoretically P.14.0) and finally the structure was confirmed by I.R. spectrum. All the chemicals used belonged to BDH (A.R) and riedel qualities.

Results and Discussion

Table 1 summarises pseudo first order rate coefficients of the hydrolysis of 5-chloro, 2-methylaniline phosphate mono-ester at 80 ± 0.5 °C in 0.1 to 6.0 MHCl. In the region 0.1 to 1.0 MHCl the rate falls with increase in acidity due to the incursion of less reactive neutral species, while rise in rates with increase in acidity from 1.0 to 4.0 MHCl is due to ionic acceleration. Plot of log- rate constants Vs acid molarity (Fig. 1) gives three linear curves indicating the presence of acid catalysis. Different intercepts on the rate axis are neutral rates at the corresponding ionic strength. Variations of acid catalysed rates and neutral rates with the ionic strength are governed by the following kinetic equations.

$$\log K_{H^+} \cdot C_{H^+} = \log K_{H_0^+} + \log C_{H^+} + b'_{H^+} \cdot \mu \quad \dots\dots\dots 1$$

$$\log K_N = \log K_{N_0} + b'_N \cdot \mu \quad \dots\dots\dots 2$$

Where 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 and b'_{H^+} , b'_N are the constants. The equations (1) and (2) may be used to compute the acid catalysed

and neutral rates at each experimental acid molarity. Thus, both acid catalysed and neutral rates may represent the total rates in acid medium as

$$K_e = K_{H^+} \cdot C_{H^+} + K_N \quad \dots\dots 3$$

The rates estimated by the equations (1) and (2) are in fair agreement with the observed rates in the region 1.0 to 4.0 MHCl, deviation in the very strong acid medium (from 5.0 to

6.0 MHCl) is removed when water activity parameter is included in the above relation (eq-1 and 2) as

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

and $\dots\dots 4$

$$\log K_N = \log K_{N_0^+} + b'_{N_0^+} \cdot \mu + n \log a_{H_2O} \quad \dots\dots 5$$

The rates estimated by equation (4) and (5) agree well with the experimental rates observed at 5.0 and 6.0 MHCl.

Table 1: Calculated And Observed Rates For The Hydrolysis Of Mono-5-Chloro, 2-Methyl Aniline Phosphate At 80°C.

HCl (mol dm ⁻³)	10 ⁵ . K _N (mol dm ⁻³ min ⁻¹) from eq 2	5+ log K _N	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 4}	10 ⁵ K _N (mol dm ⁻³ min ⁻¹) from eq 5	K _e 10 ⁵ (mol dm ⁻³ min ⁻¹) calcd. from eq 3	10 ⁵ . K _e (mol dm ⁻³ min ⁻¹) obsd.
1.0	59.56	1.77	37.06	-	-	96.62	95.87
2.0	56.23	1.75	68.86	-	-	125.09	125.38
2.5	54.63	1.73	83.65	-	-	138.28	139.89
3.0	53.08	1.72	96.38	-	-	149.46	148.48
4.0	50.11	1.70	119.67	-	-	169.78	169.77
5.0	47.31	1.67	139.31	19.49*	33.11*	52.60	52.42
6.0	44.66	1.65	155.59	9.81*	16.90*	26.71	28.17

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

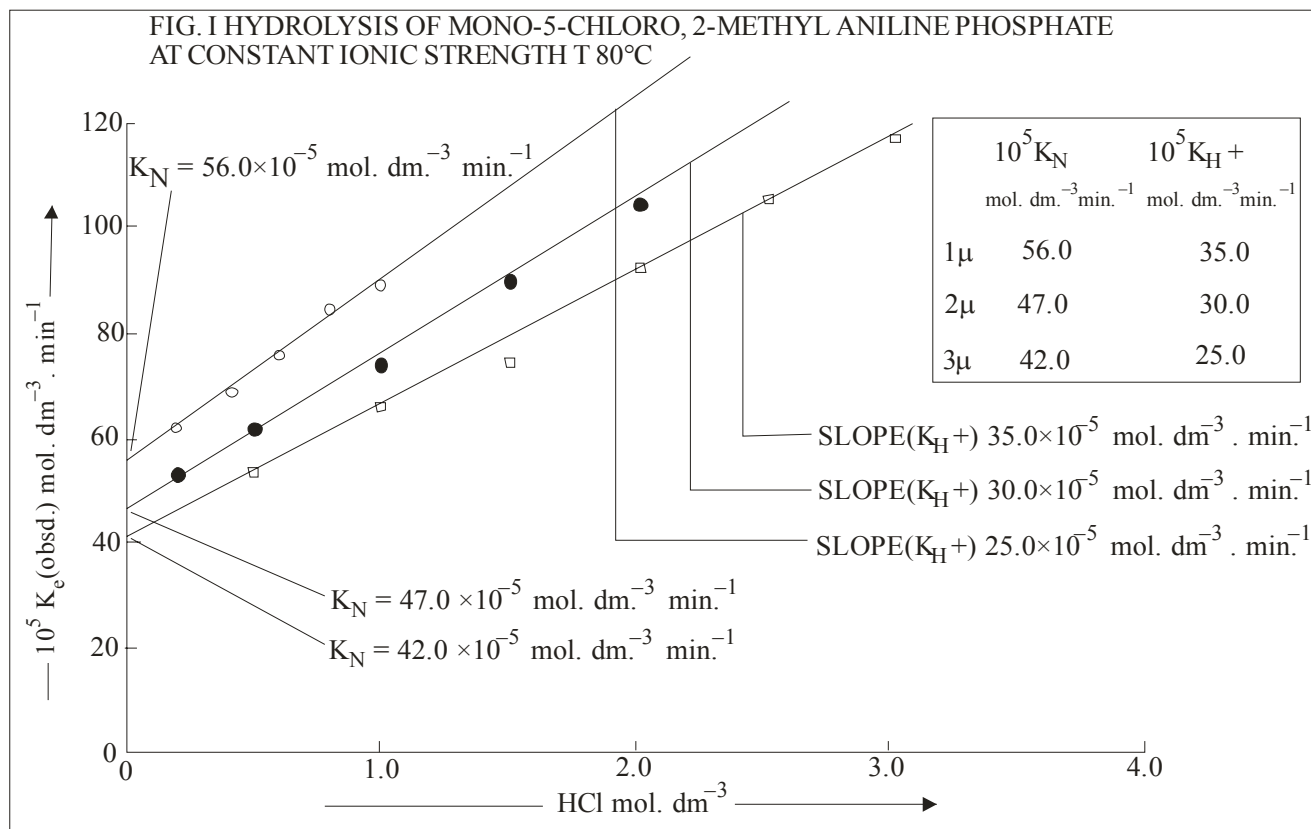


Table -2 summarises Arrhenius parameters [23] for the hydrolysis of 5-chloro, 2-methyl aniline phosphate monoester in 3.0 and 5.0 m HCl. The values show the similarity of mechanism at these acidities and also indicate bimolecular nature of hydrolysis, since according to Arrhenius parameters,

if the value of ΔE is < 25.0 kcal mol⁻¹, the value of ΔS‡ is negative and the value of frequency factor (λ) has power less than twelve on the base ten (ie λ < 10¹²), then the reaction in general will be bimolecular. Thus from table-2 it is clear that the parameters fall in the range of bimolecular reaction.

Table 2: Arrhenius Parameters for the Hydrolysis of 5-Chloro, 2- Methyl Aniline Phosphate Monoester.

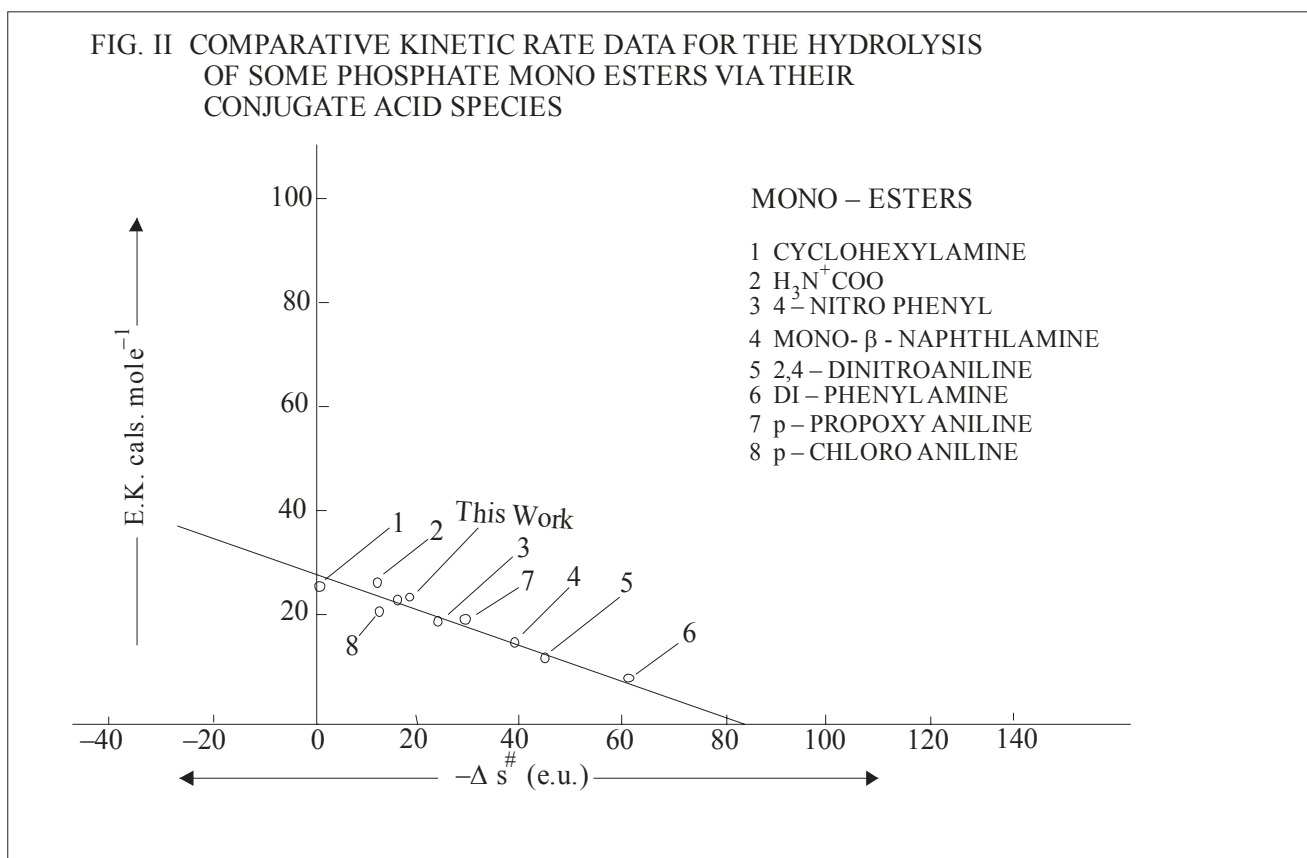
HCl (mol. dm ⁻³)	Parameters		Entropy $-\Delta S^\ddagger$ (e.u.)
	Energy of activation E.K.cals/mole	Frequency factors λ . Sec ⁻¹	
3.0	22.42	18.81×10^8	18.42
5.0	23.33	24.45×10^8	17.89

Table -3 summarises comparative isokinetic data of some other phosphate monoesters, the bond fission and molecularity of which are known. Fig II describes a relationship between some other phosphate monoesters and the present monoester. Linearity of the curve show similarity of mechanism since the

point of mono-5-chloro, 2-methyl aniline phosphate lies on the same line of other monoesters that undergo bimolecular hydrolysis with P-N bond fission for the acid catalysed hydrolysis.

Table 3: Comparative Kinetic Rate Data for the Hydrolysis of Some Phosphate Monoesters via Their Conjugate Acid Species.

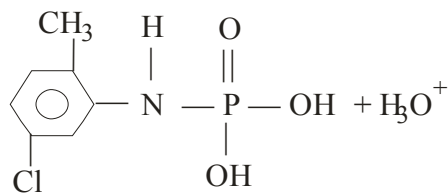
S. No.	Phosphate Mono Ester	Temp °c	Medium	E.K. (Cals./Mol.)	$-\Delta S^\ddagger$ (E.U.)	Fission	References
1	Cyclohexylamine	50	3.0	26.65	0.77	P-N	14
2	H ₃ N ⁺ COO	37	-	26.00	12.23	P-N	29
3	4-Nitrophenyl	-	-	18.70	24.0	P-O	30
4	Mono-B-naphthyl amine	98	3.0	14.56	39.46	P-N	31
5	2,4- dinitroaniline	98	3.0	12.10	45.10	P-N	32
6	Di- phenylamine	98	3.0	8.32	60.43	P-N	33
7	p-propoxyaniline	97	3.0	19.68	29.28	P-N	34
8	p-chloroaniline	20	-	20.4	12.60	P-N	35
9	5- chloro,2 methylaniline	80	3.0 5.0	22.42 23.33	18.42 17.89	P-N* P-N*	36

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

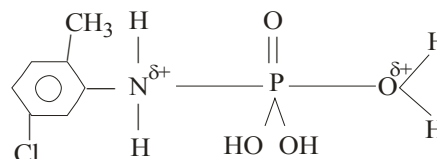
Mechanism: The mechanism of hydrolysis of 5-chloro, 2-methyl aniline phosphate monoester in the acid region involved the bimolecular nucleophilic attack of water on phosphorus of conjugate acid and neutral species, passing through a transition state in which the developed charges cause P-N bond fission

and then liberate a proton by fast step giving the parent amine and phosphoric acid.

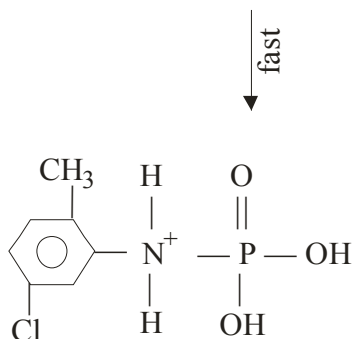
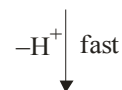
I. Formation of conjugate acid species by fast pre-equilibrium proton transfer.



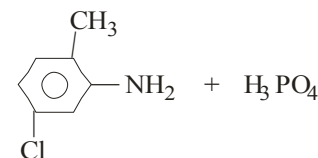
(Neutral species)



(Transition state)

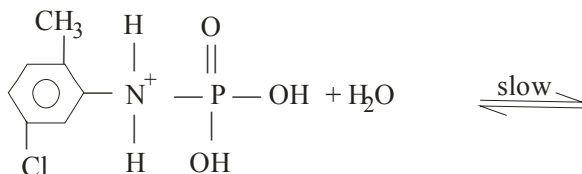


(Conjugate acid species)



(Parent compound)

II Bimolecular nucleophilic attack of water on phosphorus of conjugate acid species involving P-N bond fission $\text{S}_{\text{N}}^2(\text{P})$



Hydrolysis Via Neutral Species

Hydrolysis in the Region 0.1 to 1.0 M HCl and PH 4.24 to 7.46 : Table 4 summarises pseudo first order rate constant for the hydrolysis of 5-chloro, 2-methylaniline phosphate mono-ester via neutral and mononegative species at 80°C Results show that the rate rises with the rise in pH value passing through maxima at 4.17 pH further rise in pH decreases the rate. Dissociation of neutral into mono negative species increases with the increase in pH and is almost complete at pH 4.17. Thus, the observed maximum is the specific mononegative rates (K_{M_0}). The increase in pH brings about the dissociation of monoanion into dianion and a proton. $\text{p}K_1$ and $\text{p}K_2$ values together with the fractions of the various species at different pH values were determined.

Table 4: Hydrolysis of Mono-5-Chloro, 2-Methyl Aniline Phosphate Via Neutral And Mononegative Species At 80°C

pH	M/M + N	N/N + M	$K_{\text{M}} \cdot 10^5$ (mol. dm ⁻³ min. ⁻¹)	$K_{\text{N}} \cdot 10^5$ (mol. dm ⁻³ min. ⁻¹)	$K_{\text{e}} \cdot 10^5$ (mol. dm ⁻³ min. ⁻¹) (calcd.)	$K_{\text{e}} \cdot 10^5$ (mol. dm ⁻³ min. ⁻¹) (obsd.)	5 + log K_{e} (calcd.)	5 + log K_{M} (calcd.)
0.30	0.117	0.883	17.91	55.70	73.61	76.01	1.86	1.25
0.70	0.251	0.749	38.42	47.25	85.67	86.25	1.93	1.58
1.00	0.400	0.600	61.23	37.85	99.08	97.61	1.99	1.78
1.24	0.537	0.463	82.20	29.21	111.41	108.01	2.03	1.91
2.20	0.914	0.860	139.92	5.42	145.34	143.75	2.16	2.14
3.30	0.992	0.008	151.86	0.50	152.36	152.05	2.18	2.18
4.17	0.999	0.001	152.93	0.06	152.99	153.38	2.18	2.18

Theoretical rates were computed from the following relation.
(a) Region 0.1 to 1.0 MHCl and 0.0 to 4.17

$$K_{\text{e}} = K_{\text{M}} + K_{\text{N}}$$

$$K_{\text{e}} = 63.42 \times 10^{-5} \times \frac{N}{N + M} \text{ mol. dm}^{-3} \cdot \text{min}^{-1} + 153.38 \times 10^{-5} \times \frac{M}{M + N} \text{ mol. dm}^{-3} \cdot \text{min}^{-1}$$

Where K_{e} , K_{N} and K_{M} are the rate constant of total hydrolysis, rate constant of neutral hydrolysis and rate constant of mononegative hydrolysis $\frac{N}{N + M}$ and $\frac{M}{M + N}$ are the

fraction of neutral and mononegative species and $K_{\text{N}_0} = 63.09 \times 10^{-5} \text{ min}^{-1}$, $K_{\text{M}_0} = 153.09 \times 10^{-5} \text{ min}^{-1}$ respectively are the specific neutral and specific mononegative rates. Table 5 summarises Arrhenius parameters for the hydrolysis of 5-chloro, 2-methyl aniline phosphate ester via neutral species

Table 5: Arrhenius Parameters For The Hydrolysis Of 5-Chloro,2-Methyl Aniline Phosphate Ester Via Neutral Species

HCl (mol.dm ⁻³)	Parameters		Entropy(-Δs [‡]) (e.u.)
	Energy of activation E.K. cal./mol.	Frequency factor (λ) sec ⁻¹	
0.2	22.69	16.16 × 10 ⁸	18.72

The reaction via neutral species have been found to hydrolyse bimolecularly, since the entropy of the reaction fall in the range of bimolecular hydrolysis. *ie.* Frequency factor (λ) is $< 10^{12}$, entropy of activation (ΔS^\ddagger) is negative value and energy of activation (E) is < 25 Kcal mol⁻¹. Hence the reaction via neutral species shows bimolecular nature of hydrolysis.

The neutral species of the monoester hydrolyse bimolecularly with P-N bond fission since in the isokinetic relationship plot (Fig III), the point of 5-chloro, 2-methyl aniline phosphate monoester lies on the same line of other phosphate monoesters. Table-6 summarises the range of isokinetic data for the hydrolysis of some phosphate monoesters supporting P-N bond fission.

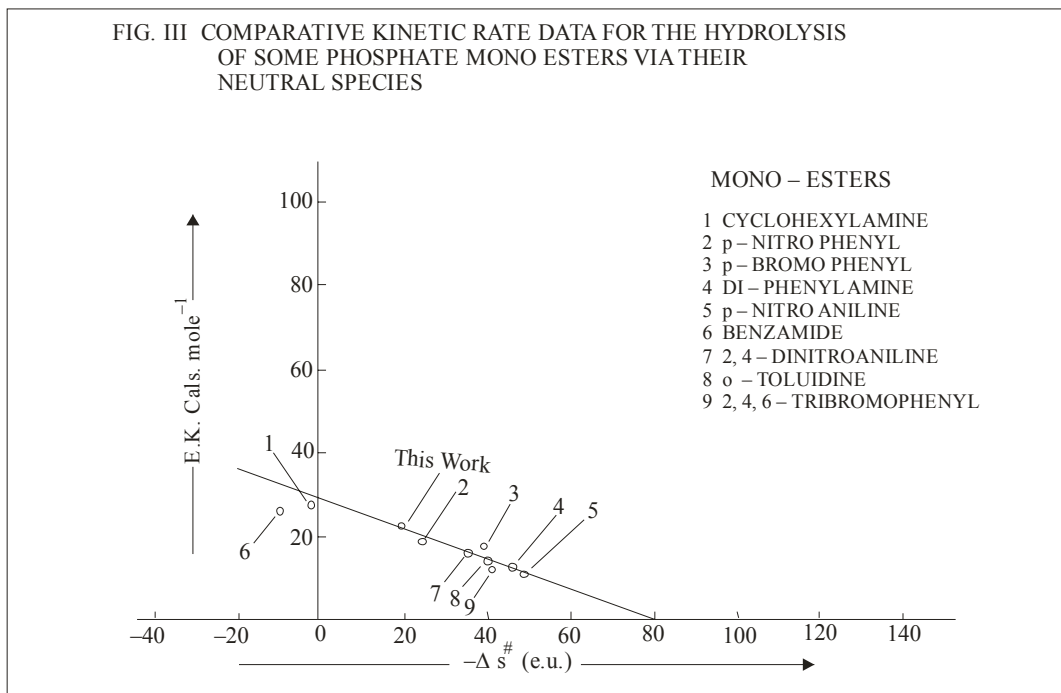


Table 6: Isokinetic Relationship Plot Data for the Hydrolysis of Some Phosphate Monoesters via Their Neutral Species.

S. No.	Phosphate Mono (Ester)	Medium	Temp °c	E.K (cals./mol.)	$-\Delta S^\ddagger$ (e.u.)	Fission	Ref.
1	Cyclohexylamine	1.24	50	27.40	-2.52	P-N	14
2	p-nitrophenyl	-	-	18.70	24.00	P-O	37
3	p-bromophenyl	1.00	98	17.40	38.94	P-O	38
4	Di- phenylamine	1.24	98	13.08	46.68	P-N	33
5	p-nitroaniline	1.20	40	11.44	48.82	P-N	39
6	Benzamide	-	37	26.40	10.00	P-N	40
7	2,4- dinitroaniline	1.24	98	16.57	35.80	P-N	40
8	o-toluidine	1.20	-	14.14	39.98	P-N	41
9	2,4,6- tribromophenyl	-	98	13.73	41.48	P-O	7
10	5-Chloro 2- methylaniline	0.70	80	22.69	18.72	P-N*	This work

*Bond Fission Assumed.

Bond Fission and Molecularity

Molecularity of the hydrolysis of the monoester under investigation. as decided by the slopes of Bunnett plot(42) (slope value $w=12.22$ and $w^* 6.66$). Olsen plots (43) (slope value $\phi = 2.14$) which fall in the range of bimolecular reaction (fig not shown). It is further supported by the involvement of water molecule as a second reaction partner, since there is a dependence of the rates in the participation of the water molecule. The bimolecular nature has also been supported by Arrhenius parameters [28] and solvent effect, particularly high negative value of entropy of the reaction. Hence, the hydrolysis may be taken to be bimolecular.

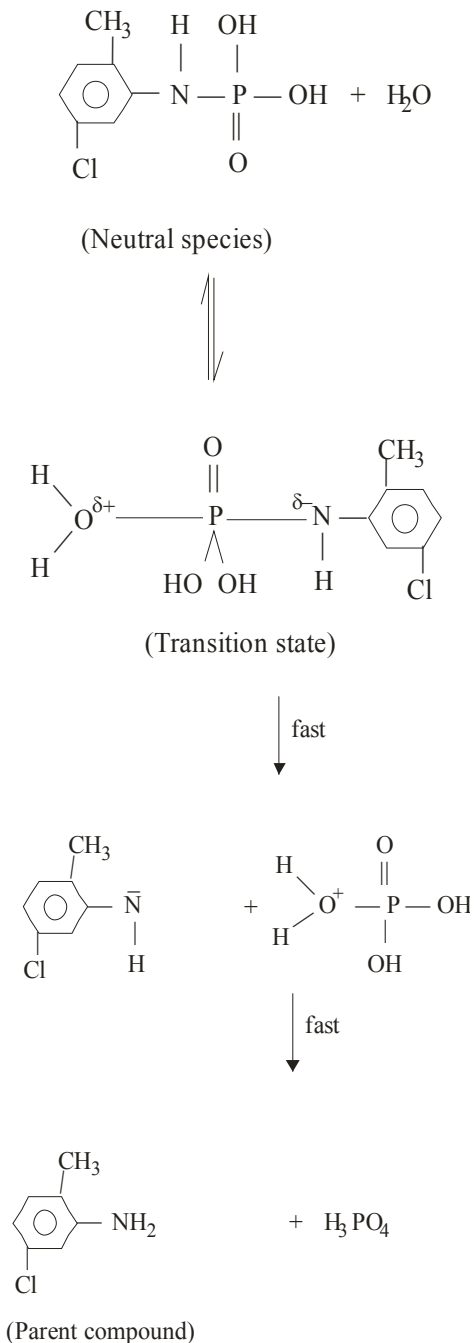
Bond fission may be examined by isokinetic relationship which has been performed by the Arrhenius parameters [28] of similarly substituted phosphate monoesters which used to hydrolyse with

similar mechanism have been taken under similar experimental conditions.

Bimolecular hydrolysis of mono-5-chloro, 2-methylaniline phosphate may involve P-N and C-N bond fission. The isokinetic relationship plot of some mono-esters as represented by the linear curves show similarities of mechanism of acid catalysed hydrolysis. Since the other mono-ester have been found to undergo hydrolysis with P-N bond fission. The hydrolysis of 5-chloro, 2-methylaniline phosphate monoester has also been presumed to undergo with P-N bond fission

Mechanism: from the above results and discussion the hydrolysis of 5-chloro, 2-methyl aniline phosphate monoester via neutral species involved P-N bond fission with bimolecular nucleophilic attack of water on phosphorus atom. The reaction paths may be formulated as;

Bimolecular nucleophilic attack of mono-ester on phosphorus of neutral species involving P-N bond fission $S_N^2(P)$:



References

- Mhala MM, Patwardhan MD, Mrs. G Kasturi. *Ind. J Chem.* 1969; 7:149.
- Barnard PWC, Bunton CA, Killerman D, Mhala MM, Silver B, Vernon CA et al. *J Chem Soc. sec* 1966; B:227.
- Mhala MM, Patwardhan MD, Mrs. G. Kasturi. *Ind. J Chem.* 1969, 149.
- Mhala MM, Killerdar AV. *J Ind Chem Soc.* 1976; LIII:476-479.
- Mhala MM, partwardhan MD. *J Ind Chem.* 1968; 6(12):704-707.
- James R. Cox (Jr.) and O.B. Ramsay, *Chem. Rev.*, 1964; 64:317.

- Chaudhary S. Hydrolysis of organic phosphates, hydrolysis of tri-bromo phenyl phosphates, Ph.D. thesis, Jiwaji Univ, Gwalior, 1974.
- Shinde CP. Kinetic study of the reaction of some ester of tri-basic acids, Ph.D. Thesis, Jiwaji Univ, Gwalior, 1977.
- Kushwaha RS. Ph.D. Thesis, Jiwaji Univ., Gwalior, 1980.
- Sharma R, Studies on organic phosphate esters, Ph.D. Thesis, Jiwaji Univ., Gwalior, 1981.
- Tiwari BK. Ph.D. Thesis, Agra Univ., Agra, 1985.
- Patwardhan MD. Hydrolysis of organic phosphates, Ph.D. Thesis, Jiwaji Univ., Gwalior, 1967.
- Chaudhary Amit, *IJETA*, 2015; 6:39-50.
- Abanish Kumar. *Pak.j. Sci. ind. Res. Ser. A : Phys. Sci* 2015; 58(3):117-121.
- Bhoite AK. Kinetic study of hydrolysis of compounds Containing C, N and P (C-N-P) linkage, 1977.
- Kushwaha RS, Tiwari BK, Singh P. *Acta Ciencia. Indica*, 1986; XIIC(4):207.
- Patel Anil. Ph.D. Thesis, Dr. B.R. Ambedkar Univ., Agra, 2012.
- Verma Devdutt. Ph.D. Thesis, Dr. B.R. Ambedkar Univ., Agra, 2013.
- Chaudhary Gaurav. Ph.D. Thesis, Dr. B.R. Ambedkar Univ., Agra, 2013.
- Kumar Abanish. Ph.D. Thesis, Dr. B.R. Ambedkar Univ., Agra, 2013.
- Kumar Raman. Ph.D. Thesis, Dr. B.R. Ambedkar Univ., Agra, 2013.
- Singh Sanchita. Ph.D. Thesis, Dr. B.R. Ambedkar Univ., Agra, 2014.
- Singh Pratap, kumar Abanish. *J. of Indian Council of Chemists*, 2011; 28(1):56-69.
- Saxena Amrita. Ph.D. Thesis, Dr. B.R. Ambedkar Univ., Agra, 2014.
- Rudert P. *Ber.*, 1893; 26:565.
- Rudert P. *J Chem Soc. Ai*, 1893, 323-324.
- Paul Otto., *ber.*, 1895; 28:816.
- Arrhenius SZ. *Physik-Chem.*, 1893, 4-226.
- Halmann M, Lapidot A, Samuel D. *J Chem. Soc.* 1944, 1962.
- Purnanand, Ph.D., Thesis, Jiwaji Univ., Gwalior, 1984.
- Samadhiya Anju, Ph.D., Thesis, Jiwaji Univ., Gwalior, 1984.
- Raje, S.R., Ph.D., Thesis, Jiwaji Univ., Gwalior, 1984.
- Singh, Pratap, Ph.D. Thesis, Dr. B.R. Ambedkar Univ., Agra, 1990.
- Chadhary Amit. Ph.D. Thesis, Dr. B.R. Ambedkar Univ., Agra, 1998.
- Chanles. J.D. and Feageson, E., *Ibid*, 1958; 80:2686.
- Chaturvedi Kumud. Ph. D. Thesis, Dr. B.R. Ambedkar Univ., Agra, 2000.
- Glasstone S, Laidler KJ, Eyring H. *The theory of rate processes*, Mcgraw Hill, New York, Chap, 1941, 3.
- Kasturi (Mrs.) G, Ph. D. Thesis, Jiwaji Univ., Gwalior, 1969.
- Jain P. Ph. D. Thesis, Jiwaji Univ., Gwalior, 1974.
- Chanley JD. *Feaqson EJ. Am. Chem., Soc.* 1953; 77:4002.
- Sagne AN. Ph. D. Thesis, Jiwaji Univ., Gwalior, 1972.
- Bunnett JF. *J Am Chem Soc.* 1961; 83., 4956, 4968, 4973, 4978,
- Bunnett JF, Olsen FF. *Canadian Journal of Chemistry.* 1966; 44:1917.