Effect of Position of Chloro Substituent on the Rate of Acidic Hydrolysis of Mono Ester of Phenyl Phosphate Esters at 2, 4 and 2, 5 Positions

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Abstract: *The rate of hydrolysis of mono 2,4 dichlorophenyl phosphate and mono 2,5-dichlorophenyl phosphate have been investigated over a wide range of acidities in HCl (0.1mol dm^{-3} to 6.0 mol dm^{-3}) at 98°. Both the esters were found reactive through their neutral and conjugate acid species, in the acid region. Ionic strength, temperature, solvent concentration effect have been probed to identify the reactive species and molecularity of the hydrolytic reaction. Molecularity and Bond-fission are also discussed in term of Zucker-Hammett hypothesis, Hammett acidity function, Bunnett Hypothesis, Bunnett-olsen parameter and isokinetic relationship. Arrhenius parameters and kinetic data also support the Bimolecular nucleophilic attack of water on tetrahedral phosphorus atom of the conjugate acid species of mono-2,4-dichlorophenyl phosphate and 2,5-dichlorophenyl phosphate.*

Keywords: *Acidic hydrolysis, phosphate ester, conjugate acid species, mechanism.*

1. INTRODUCTION

The chemistry of phosphate esters continue to attract the attention of chemists due to their versatile applications in the different field like Agriculture[1-8], Industrial9[-12], Medicinal[13-17] and Engineering fields. Organophosphates having C-O-P linkages are very important compound in the field of crop protection and Biochemistry. There is scanty information about the complete mechanistic investigations of hydrolysis of orthophosphate esters. Some chloro substituted aryl esters show acid catalysis, the effectiveness of which follows the position of electron attracting group. The effectiveness of the chloro substitutent in aryl phosphate is expected to be slightly less in 2, 4 position of benzene ring than 2,5 position of benzene ring. This paper describes the results of acidic-hydrolysis of 2, 4 & 2, 5 dichlorophenyl phosphate. The rate of hydrolytic reaction of both esters follow the following order.

2. 2,4 DICHLOROPHENYL PHOSPHATE < 2,5 DICHLOROPHENYL PHOSPHATE

2.1. Materials & Method

Mono 2, 4 dichlorophenyl phosphate and mono 2, 5-dichlorophenyl phosphate were synthesized by Auger & Dupis[18] method using 2, 4 dichlorophenol & 2, 5 dichlorophenol as parent compound and POCl$_3$ as phosphorylating agent, in the ratio of 1:1. Both esters A (2, 4-dichlorophenyl phosphate) and B (2, 5-dichlorophenyl phosphate) were identified by their spectral and elemental analysis.

Table1. *IR. Spectral data of 2, 4-dichlorophenyl phosphate & 2, 5 dichlorophenyl phosphate*

S.No.	Phenyl Phosphate	IRν Cm^{-1} P=O stretching	IR ν cm^{-1} C=0 stretching	IR ν Cm^{-1} C-H adj.) stretching	IR ν Cm^{-1} C-H(ISO) stretching	IR ν Cm^{-1} C-Cl stretching
1	Mono 2,4-dichlorophenyl phosphate	1090	1240	810-830	870	600-720
2	Mono 2,5-dichlorophenyl phosphate	1069.68	1258.80	-	891.75	579.34

Investigation of the hydrolytic reaction of compound A & B have been made in the region 0.6 to 6.0 mol. dm^{-3} HCl at 98º in 20% and 10% (V/V) dioxan-water media respectively. Kinetic measurements were made by spectrophotometric method employing an spectronic 20^{+} spectrophotometer. The concentration of monoester A & B in all the kinetic runs were kept 5.0×10^{-4}mol. dm^{-3} respectively (unless otherwise specified).The rate of hydrolysis was determined by the rate of appearance of inorganic phosphate by Allen's modified method[19].

3. RESULT AND DISCUSSION

Table2. *Rate Coefficients of hydrolysis of mono-2, 4 dichloro and 2, 5-dichlorophenyl phosphate at 98°*

HCl mol dm^{-3}	Ke x 10^3 min^{-1} mono-2,4-dichlorophenyl phosphate		Ke x 10^3 min^{-1} Mono 2,5 dichlorophenyl phosphate	
	Experimental	Estimated	Experimental	Estimated
0.5	8.28	8.73	9.18	9.52
1.0	10.77	10.75	16.14	15.41
1.5	13.60	13.74	23.02	22.11
2.0	18.10	18.05	29.12	29.73
2.5	18.62	28.92	39.29	30.40
3.0	19.87	20.18	a 48.94 b. 50.16 c= 52.29 60.14	48.25 59.45
4.0	a 22.58 b. 18.80 c. 16.49	22.75	72.65	72.11
4.5	13.76	13.81	61.25	63.81 57.02
5.0	9.40	9.32	54.86	47.29
5.5	5.65	5.50	47.12	42.11
6.0	4.38	4.29	40.59	
6.5	3.26	3.16	-	
7.0	1.18	1.17	-	
a	0.00% dioxan		a= 0.00% dioxan	
b	10.0% dioxan		b= 5.0% dioxan	
c	30.0% dioxan		c=10.0% dioxan	

The data in table No. 02 for rate of hydrolysis of mono 2,4-dichlarophenyl phosphate and mono 2,5-dichlorophenyl phosphase show that the log of observed first order rate constants versus acidity profiles go through maximum at the pH 4.0 mol dm^{-3} HCl .

It is found that the rate of hydrolysis of monoesters A & B increase linearly with the increase in acidities upto 4.0 mol. dm^{-3} .At this characterstic and molarity (4.0 mol dm^{-3} HCl) they exhibit maximum rate which may be ascribed to the presence of increased percentage of singly protonated form of the monoester. Further rise in acidities decrease the rate constant due to decrease in the concentration of the nucleophile and variation in water activity.

4. KINETIC SALF EFFECT

In order to determine whether or not there is any effect of ionic strength or the percentage of acid catalysis, kinetic runs were made at three different ionic strength (1.0μ, 2.0μ and 3.0μ) for both monoesters A and B, which were maintained by adequate mixture of NaCl and HCl. Hydrolysis of each ionic strength is represented by a linear curve (Fig. not shown) in case of monoester. A the slope of straight line increases with increase in ionic strength clearly indicating positive salt effect and acid catalyzed nature of the reaction. All the three lines have common intercept (7.39x10^{-3}min^{-1}) on the rate axis indicating the constant contribution of other reactive species (neutral species) to the over all rate of hydrolysis. In case of monoester B, each linear curve (fig. not shown) makes a positive slope with the acid axis indicating the presence of acid catalysis, these curves make three different intercepts indicating the presence of side reaction of the neutral species which is the specific neutral rate of solvolytic reaction (K_N) and the contribution of the neutral species is varying to the over all hydrolysis in this acid region. From the study of ionic strength effect the total rates contributed by conjugated acid species and neutral species can be calculated by the following second empirical term of Debyel-Huckel equation.

$$Ke=K_H^{+}C_H^{+} + K_N \qquad \text{(i)}$$

Here,

Ke = observed rate constant

K_H^+ = specific acid catalyzed rate

K_N = specific neutral rate

The lowering in rate in 4.5 to 6.0 mol dm^{-3} can be explained by considering water activity[20-22] as an additional parameter. The hydrolysis of monoester A and B in the 4.5 mol dm^{-3} to 6.0mol dm^{-3} HCl may be represented by

$$Ke = K_H^+ C_H^+ + \mu(\alpha + H_2O)^n + K_N \qquad \text{(ii)}$$

Where $\mu(\alpha + H_2O)^n$ is water activity and n is an integer.

5. RATE CORRELATION

The bimolecular nature of hydrolytic reaction of monoester A and B are supported by Hammett acidity function[23] and Zucker-Hammett hypothesis[24]. Bunnett parameters[25] ω and ω^* and Bunnett-Olsen parameter[26] (ϕ) were carried out on the basis of data given in table no. 04. The results of analysis of the kinetic data in terms of various criteria are shown in table. No. 03 for both monoester A and B the value of ω fall into the range normally associated with water acting as a nucleophile for which a bimolecular mechanism was proposed. The value of ϕ lies in the range 1.0-1.5, such values are said to be characteristic of water acting as a proton transfer agent. It is interesting to note that the values of both ω and ϕ were consistently high and consistent with water playing as an additional role beyond that of a nucleophile.

Table3. *Summary of rate correlations*

S.No.	Correlation	Slope Value for mono 2,4-dichloropheynl phosphate	Slope value for mono 2,5-dichlorophenyl phosphate
1	Hammet-slope	0.33	0.444
2	Zucker Hammet slope	1.15	1.25
3	Bunnett slope ω	9.74	4.801
4	Bunnett slope ω^*	3.33	2.272
5	Bunnett olsen slope ϕ	1.52	1.000

6. ARRHENIUS PARAMETERS

The magnitude of Arrhenius parameters[27] for hydrolytic reaction at 3.0 and 5.0 mol dm^{-3} HCl are indicative of bimolecular nature of hydrolysis of monoesters A and B, values for Arrhenius parameters are given in table No.04.

Table4. *Arrhenius parameters for the hydrolysis of 2,4-dichlorophenyl phosphate & 2,5-dichlorophenyl phosphate in acid media.*

| S.No.	Acid	Parameters		
	Mol dm^{-3}	Activation Energy of 'E' K. cal. mol^{-1}	Frequency factor 'A' Sec^{-1}	Anthalpy of Activation $\neq \Delta s$ e.u.
Compound 'A'	3.0	16.9	2.0×10^8	31.3
	5.0	17.5	3.4×10^8	30.3
Compound 'B'	3.0	11.80	0.82×10^{-3}	61.33
	5.0	9.88	0.92×10^{-3}	61.11

7. KINETIC SOVENT EFFECT

Solvent effect studies (Table No. 02) show a significant rise in rates in case of compound B by a change over from solvent mixture of less to more dioxan content which has a better proton donating nature than pure water. In case of compound A the rate constants decrease with increase in dioxan which may be due to decrease in solubility of reactive species.
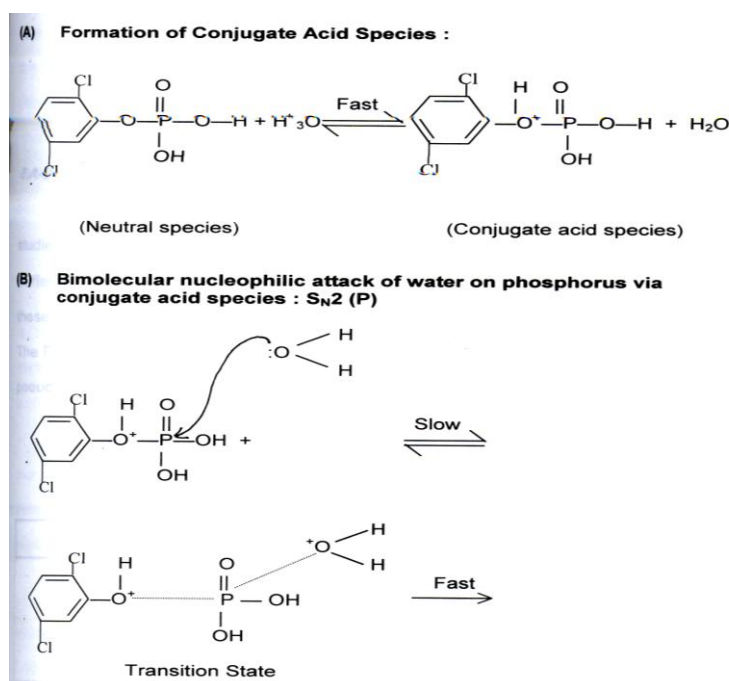
8. ISOKINETIC RELATIONSHIP

A comparative kinetic rate data[28] of other monoester support P-O Bond fission.

9. CONCLUSION

Having applied several mechanistic criteria in relation to the present study, we can now evaluate the results of these treatments. The Bunnett, Bunnett-Olsen plot, temperature effect, solvent effect and isokinetic relationship data support the SN^2 type mechanism, for the hydrolysis of both monoester A and B (see scheme 1 and 2 respectively) In this mechanism, the electron donating substituent accelerates the protonation (step-1) and electron withdrawing substituent facilitates the attack of water molecules on the protonated species (step-2). Acid hydrolysis of these monoesters may, therefore, be suggested to involve bimolecular attack of water on phosphorus atom of conjugate acid species formed by fast pre-equilibrium proton transfer (mechanism shown in scheme 1 and 2)
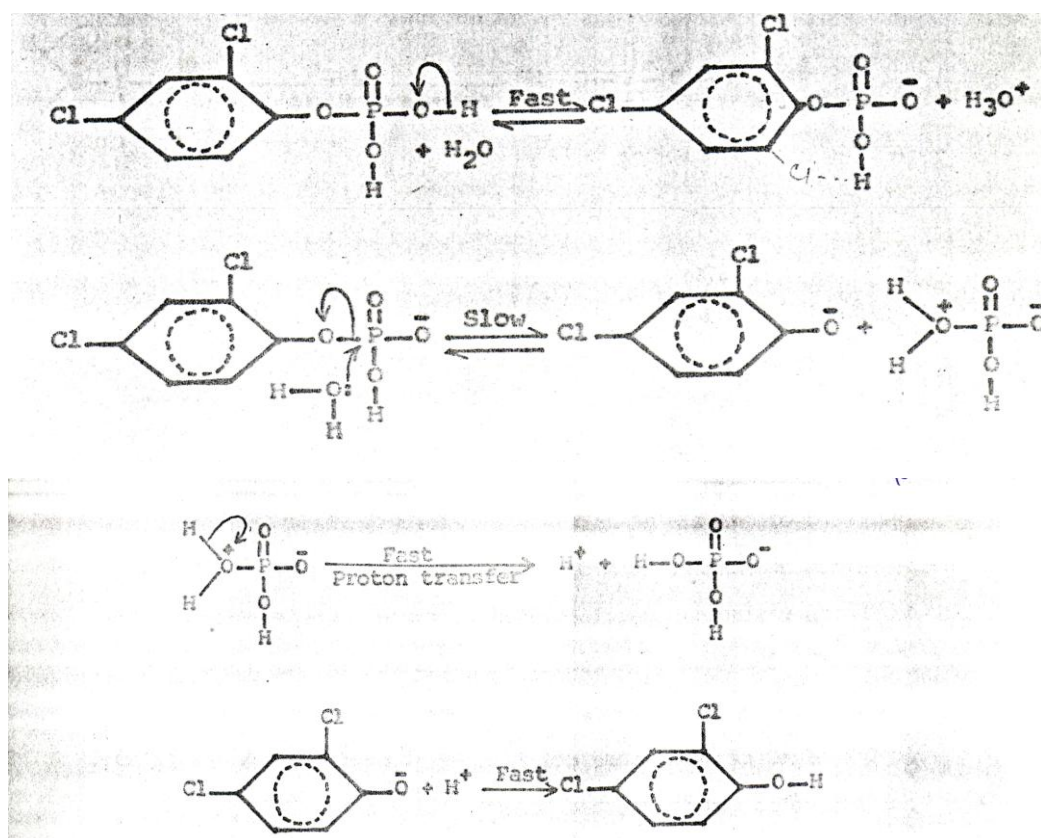
Scheme1. *Acid hydrolysis of mono 2, 4-dichlorophenyl phosphate via their conjugate acid species.*
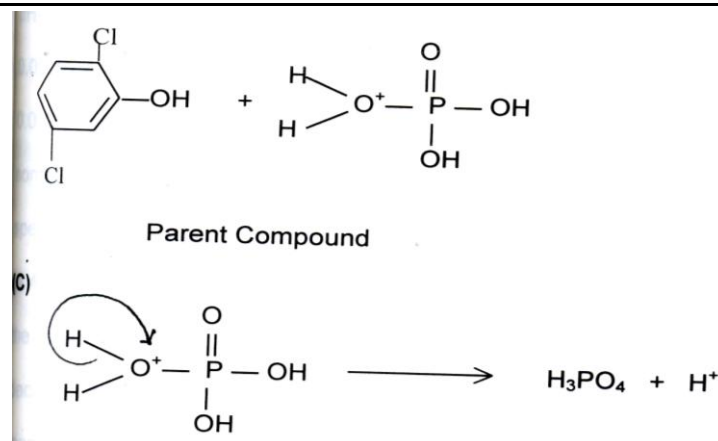
Scheme2. *Acid catalysed hydrolysis of mono 2, 5- dichlorophenyl phosphate via their conjugate acid species.*

REFERENCES

[1] Matingly, G.E.G. and Failibudeen, O, "Topics in phosphorus chemistry", 4, 157 (1967).

[2] Grapov, A.F., and melnikov N.N., Russ chem. Revs. 42, 772 (1973).

[3] Ashton, F.M. and Crafts A.S., "mode of Action of Herbicides," wiley inter science, New York. (1973).

[4] Knipling, E.F., J. Econ Entomol., 53, 415 (1960)

[5] Knipling, E.F., ibid, 55, 782 (1962).

[6] Knipling, E.F., Agr. Res. 14(9), 3(1966)

[7] Scheinpflue, of H., Jung, H.F. and schrader, G., Farben Fabriken Bayes Ag. Belg, p655. 301 (1964/1965)

[8] Schrader, G. and Lorenz, W, Farben Fabriken Bayer AG D.B.P., 947 369 (1955/1956)

[9] Granzow, A, Accounts chem. Res., 11, 177 (1978).

[10] Goss, M.F., Jr. J. Chem. Ed., 18, 3 (1941)

[11] Fisher, J. and Van wazer (1961)

[12] Tonaka, Y. kano, S. and odwarag, K., Nippon soda Co. Ltd., D.O.S. 2416, 178 (1974/1975)

[13] Holmstedl. et al (1978)

[14] Schrader, G., Farben Fabriken Bayer AG. D.B.P. 814, 152, (1984/1951)

[15] Topley, B., Chem. Ind. London 859 (1950)

[16] koellc, 1970, Connors 1974 and Holmstedt et at (1978)

[17] Njida, T., Inove, Sh., Tsuruoka, T., Kawasaki, Sh. Et. Al, Mejji seika kaisha Ltd.,D.A.S. 2,236, 599 (1973/1974)

[18] Auger, V. & Dupis, P., C.R. Lebd., Seanc. Acad. Sci., Paris, 146, 1152 (1908)

[19] Allen R.J.L., J. Biochem, 34, 858 (1940)

[20] Lefler, J.E. and Grunwald, E., The rates and Equilibiria of organic Reactions, "John wiley and sons, Inc., New-York, pp 177, 286 (1963).

[21] Hughes, E.D. and Ingold, C.K., J.chem. Soc., 224 (1933)

[22] Barnard, P.W.C.,Vernon, C.A.and Welch, V.A., J. chem. Soc., 227, 229 (1966).

[23] Hammet, L.P., Physical organic chemistry; Mc Graw Hills Book Comp., London, p 335-273 (1940).

[24] Gillion R.D., Introduction to physical organic chemistry 'Addition-west'ey pub., PP 167, 169 (1970).

[25] Bunnet. J.F., J. Am. Chem. Soc., 83, p 4968, 4973 and 4978 (1981).

[26] Bunnett, J.F. and Olsen, F.F., Can. J. Chem. 44, 1917 (1966).

[27] Arrhenius S.C.Z., phy. chem. 4, 226 (1989).

[28] Gillion, R.D., "Introduction to physical organic chemistry", Addision-wesley Fub. Co., London, 167-169 (1970).