

# A SIMPLE CATALYTIC HYDROLYSIS OF ORGANOPHOSPHORUS COMPOUND BY METAL CATIONS

**Dr. Vaishali Ayachit, Dr. Maya Shukla, Mrs. Preeti Gupta**  
**Asstt. Professor, Department of Chemistry**

Mata Gujri Mahila Mahavidhyalaya, Jabalpur 482001, India

E-mail- [drvaishali.ayachit@gmail.com](mailto:drvaishali.ayachit@gmail.com)

Mobile no. - 9827093316

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**Abstract -:** The effect of tetravalent and bivalent metal ions on the hydrolysis of organophosphorus compound have been studied and the rate maxima observed were at around pH 2.0 and 6.0. Since the metal aquo complexes are known to exist in equilibrium with deprotonated species and therefore, metal bound OH<sup>-</sup> nucleophile might be available abundantly even in acidic aqueous solutions. Thus, an interaction of Sulphur of P=S group with metal cation followed by an intramolecular nucleophilic attack of hydroxy anion at the ester phosphorus atom would results in cleavage of P-O bond.

Key words – organophosphorus compound, deprotonated, catalyst, hydrolysis

## INTRODUCTION

Earlier reports include the development of new methods for accelerating hydrolysis of organophosphorus esters under the mild acidic conditions is an important area of industrial and academic research (Klinkel et al., 2006). Phosphorus triesters (e.g. Paraoxon etc.) are accepted as suitable mimics of G-type nerve agents (eg. Sarin, Soman etc) (Yang et al., 1992, 1999). These compounds are not only highly toxic but also highly persistent in the environment. A significant body of information on the effect of divalent (Morrow et al., 1988, Fife et al., 1988, Moss et al., 2002) and trivalent (Komiyama et al., 1992, Takasaki et al., 1994, Moss et al., 1995, Braken et al., 1997) ions on the hydrolysis of diesters like DNA and RNA has already been reported. Recent work has demonstrated extraordinary catalytic effect of tetravalent (Zang et al., 1997, Morales et al., 2001, Sumaoka et al., 1994, Raghunathan., 1998) cations on the hydrolysis of phosphate diester as well as nucleotides. Ethyl-cyanophos, being an important insecticide could control rice stem

borer, cotton ball worm, cabbage worm and aphids. (Eto., 1974). Moreover, ECP is highly toxic to mammals; the oral LD<sub>50</sub> for rats is about 43 mg/kg (FAO. 1980) and besides toxicities. Although, it is detoxified quickly in alkaline solutions, but persist under neutral and slightly acidic conditions, typical in surface water, soil etc. In order to avoid accidental exposure to birds, animals and humans from the spillage and used containers etc. all these sources of contamination must be decontaminated by economically viable methods. This study includes hydrolysis of ethylcyanophos, catalyzed by Cu (II) in mild acidic aqueous solutions.

## **EXPERIMENTAL METHOD**

PCP (5 gm, 0.036 M) was dissolved in acetone (50 ml) by stirring in a 250 ml round bottom flask. To the stirred solution dicyclohexyl amine (0.036 M) was added. A slight exothermic reaction occurred. This stirred mixture was boiled for about 30 min and rapidly cooled by keeping RBF in ice water mixture for about 1 hr (till crystallization ceased). The crystals were filtered and washed 2-3 times with acetone. Excess solvent was removed under reduced pressure. White crystals of PCP-DCHA salt obtained were stored in air tight container in a desiccator.

A solution of dicyclohexylammonium salt of cyanophenol (5.5 g, 20 mM) in benzene (25 ml) was slowly added to a stirring solution of diethyl thiophosphoryl chloride (4.2 g, 20 mM) in benzene (25 ml) maintained at reflux temperature. The reaction mixture was kept under reflux and stirred further for 3 hrs. It was then cooled, filtered and solvent was removed along with unreacted chloride under vacuum. The residue on distillation at 150-152°C (0.01 mm Hg) gave a colorless oily liquid.

Yield =85% (3.2 gms)

Ethyl cyanophos obtained from above process was subjected to TLC (Adsorbent: Silica Gel-G, Eluent: Chloroform, Developing Agent: Iodine vapors). The TLC showed two spots, one

at higher level of suspected compound and one at lower level of PCP-DCHA salt. The compound was then purified by column. A column of height 30 cm was made by filling Silica-G (mesh size: 60-120) as a slurry in chloroform. About 1.0 ml of ethyl-cyanophos was dropped in column with the help of pipette and column was allowed to run. The fraction of 10 ml each was collected and monitored by TLC. Fraction no 3, 4 and 5 contained compound. These fractions were mixed and the solvent was removed first by distillation on a water bath under reduced pressure. The left pure compound, as seen by single spot in TLC, was then collected in sample holder, properly stoppered with the help of PTFE tape and kept in refrigerator.

### **Spectral analysis**

The compound thus obtained was then subjected to UV, FT-IR and GC-MS analysis. UV:  $\lambda_{\max} = 232 \text{ nm}$ ,  $\epsilon = 40000$ , IR (Neat) = 2983, 2229, 1602, 1498, 1224, 1166, 1022, 923, 846, 553, GC: Single peak, Mass  $M^+$  ( $m/z$ ) = 271( $M^+$ ), 196, 166, 137, 135, 119 (Base Peak), 109, 97, 90.

The spectral data were in good agreement with reported values which confirmed the structure of the compound as O, O-diethyl, O-p-cyanophenyl phosphorothioate (ethyl-cyanophos).

### **Kinetic Measurements**

Stock solution of ethyl-cyanophos ( $5 \times 10^{-3} \text{ M}$ ) in dioxan was prepared by dissolving 0.068gm in minimum quantity of dioxan in 50 ml amber colored VF. The solution was then made up to mark by further addition of dioxan. The solution was mixed well, stoppered with the help of PTFE tape and stored in refrigerator.

A typical kinetic run was made by adding KCl (0.037g, 10mM),  $\text{CuCl}_2$  (0.004g,  $3 \times 10^{-4} \text{ M}$ ) in water in 50ml flask to which approximately 40-45 ml water was added. The pH of the medium was adjusted by using 0.1 N HCl or 0.1 N KOH. HEPES buffer (0.122, 10mM) was used to maintain  $\text{pH} \geq 6.0$ . The solution was chilled and 0.15 ml of solution of ethyl-cyanophos in dioxan ( $5 \times 10^{-3}$

*M*) was added to it. It was made upto mark with chilled water, mixed well and equal volume of this was then quickly transferred to separate test tubes for the convenience of our measurements. The properly stoppered test tubes were placed in a digital water bath maintained at 83<sup>0</sup>C (±0.5<sup>0</sup>C), such that the temperature inside the test tubes were at 80<sup>0</sup>C. The test tubes were withdrawn one by one at definite time intervals and the measurement of liberated p-cyanophenol was made as p-cyanophenolate anion as described earlier. All other runs (i.e., pH 1.0-5.0) were carried out in unbuffered aqueous solutions, as metal salt solutions acts as self-buffers (Kramer et al., 1998). Similar kinetic runs were performed for varied [Substrate/Metal] ratio e.g., 1:30, 1:15, 1:10, 1:5 and 1:1 at pH value 2.0.

## **RESULTS AND DISCUSSION**

All reactions were observed for more than three half-lives and plots of  $\log A_{\infty}-A_o / A_{\infty}-A_t$ , (where  $A_o$ ,  $A_t$  and  $A_{\infty}$  are absorbance of p-cyanophenolate anion at time zero, t and infinity respectively) versus time were linear indicating that the hydrolysis occurs via first order kinetics with respect to the parent compound. All runs were performed in duplicate and found reproducible within ±5% (max.) and the mean value of pseudo-first order rate constant obtained. Our experiments showed that all the metals require at least 20 fold excess over [substrate] for showing maximum catalysis. In contrast to this, Cu catalyzed hydrolysis rate maxima has been found at pH 6.0, which is indicative of catalytically active species of copper being present around this pH . A ~ 5640 fold increase in rates with respect to metal free hydrolysis at pH 6.0, clearly shows superior catalytic ability of Cu around neutral pH. However, below pH 6.0, the rate decreases which might be due to the decrease in the concentration of active copper hydroxo species. Above pH 6.0, the decrease

in rates seems to be possible as evident by the precipitation of copper as its hydroxide (Zang et al., 1998).

The rate equation for ester hydrolysis including metal catalysis may be given by the Eq. 1

$$d [p\text{-cp}]/dt = ( k_a [ H^+ ] + k_n [H_2O] + k_b [OH^-] + k_m [Metal hydroxo species]) [Parent ] \text{ ----- (1)}$$

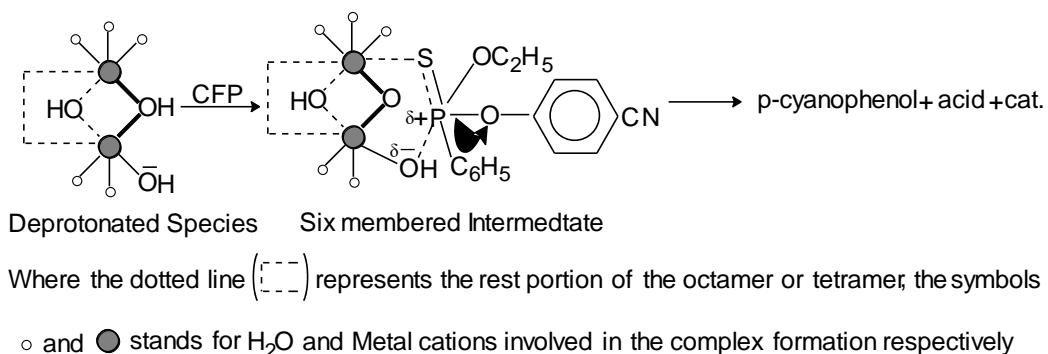
Where  $k_a$ ,  $k_n$ ,  $k_b$  and  $k_m$  are the rate constants for the hydrolysis of ethyl-cyanophos by acid, water, base and the metal ion present as hydroxo complex, respectively. Moreover the hydroxide ion  $[OH^-]$  is stronger nucleophile, but its concentration in neutral and acidic solutions being low, have negligible contribution to the reaction rates and at the same time the reaction rate at around pH 6.5-7.0 are very small , therefore  $k_n$  &  $k_b$  terms can be dropped out from the equation 1 .

Again we found that metal catalyzed reaction rates are much greater than the acid catalyzed rates, thus, contribution of  $k_a[H^+]$  term appears to be negligible and hence the final form of the rate equation may be written as equation 2.

$$\text{Rate} = k_m [Metal hydroxo complex] [Parent] \text{ ----- (2)}$$

From the magnitude of  $K_M$  and  $pK_a$  values, it became evident that hydroxo species formed from  $Cu^{2+}$  would bind more efficiently to esters molecules than those with other metal ions and additionally might facilitate intramolecular nucleophilic attack by metal bound hydroxide ion at phosphorus atom initiating the formation of a six membered ring intermediate. Thus, the reaction appears to follow a push-pull mechanism (Singhal et al., 1996, Rojas et al., 2004, Algiwale et al., 2007, Burgess et al., 1978) as described in the case of bivalent metal ion catalyzed hydrolysis of phosphorus compounds (Smolen et al 1997, Sutton et al., 1987, Acc. Chem. Res.,1992, Morrow et al., 1989, Gellman et al., 1989). Therefore, considering the above facts it has been proposed

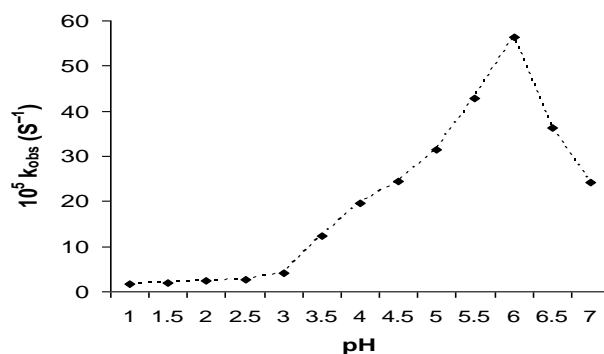
that, electrons of sulfur atom of the P=S bond binds with complexed metal ions making phosphorus an electron deficient centre, which subsequently being attacked by OH<sup>-</sup> ion of the adjacent metal ion to liberate the cyanophenol as shown by the Scheme -1.



**Scheme-1**

**Effect of pH on metal catalyzed hydrolysis of ethyl-cyanophos kept at concentration**

**1.5 × 10<sup>-5</sup> M at 80<sup>o</sup> C**



## REFERENCES

1. Klinkel., Kiemele., Gin and Hagadron (2006), Rapid phosphorus triester hydrolysis catalyzed by bimetallic tetrabenzimidazole complexes., *Chem. Comm.* 2919-2921.
2. Y. C. Yang, J. A. Baker, J. R. Ward (1992), Decontamination of chemical warfare agents., *Chem. Rev.* 92, 1729.
3. Y. C. Yang (1999), A novel catalytic approach to the chemical detoxification of P-ester nerve agents., *Acc. Chem. Res.* 32, 109.
4. J. R. Morrow, C. William (1988), Hydrolysis of phosphate diesters with copper (II) catalysts *J. Inorg. Chem.* 27, 3387.
5. T. H. Fife, P. Pujari (1988), Divalent metal ion catalysis in the hydrolysis of phosphomonoesters. Hydrolysis of 2-(1,10-phenanthrolyl) phosphate., *J. Am. Chem. Soc.* 103, 7790.
6. R. A. Moss, P. K. Gong, H. Morlas-Rojas (2002), catalysts for the hydrolysis of thiophosphate triesters., *Org. Lett.* 4 (2002) 1835.
7. M. Komiyama, K. Matsumura, Y. Matsumoto (1992), *J. Chem. Soc. Chem. Comm.* 640.
8. B. K. Takasaki, J. Chin (1994), *J. Am. Chem. Soc.* 116, 1121.
9. R. A. Moss, B. D. Park, P. Scrimin, G. Ghirlanda (1995), *J. Chem. Soc. Chem. Comm.* 640.
10. R. A. Moss, K. Braken, J. Zang (1997), *Chem. Comm.* 563.
11. R. A. Moss, J. Zang, K. Braken (1997), *Chem. Comm.* 1639.
12. R. A. Moss, H. Morales-Rojas (2001) *J. Am. Chem. Soc.* 123, 7457.
13. J. Sumaoka, S. Miyama, M. Komiyama (1994), *J. Chem. Soc., Chem. Comm.* 1639.
14. R. A. Moss, K. G. Ragunathan (1998), *Chem. Comm.* 1871.

15. M. Eto, *Organophosphorus Pesticides Organic and Biological Chemistry*, CRS Press Inc, Cleveland, 1974.
16. Joint meeting on FAO Panel of Experts on Pesticides Residues in Food and Environment and the WHO Expert Group Pesticides Residues Rome, October (1980) 6.
17. R. Kramer, R Ott, *Angew (1999), Chem. Int. Ed. Eng.* 37, 1958.
18. R. A. Moss, J. Zang, K. G. Ragunathan (1998), *Tet. Letts.* 39, 1529.
19. A. Singhal, L. M. Toth, J. S. Lin, K. Affholter (1996), *J. Am. Chem. Soc.* 118, 11529.
20. R. A. Moss, H. M. Rojas, S. Vijayraghavan, J. Tian (2004), *J. Am. Chem. Soc.* 126, 10923.
21. T. A. Algiwale, C. P. Shinde, Purnanand (2007), *I. J. Chem.* 46A, 269.
22. J. Burgess, "Metal Ions in Solutions", Halsted Press, New York (1978) 267.
23. J. M. Smolen, A. T. Stone (1997), *Environ. Sci. Technol.* 31, 1664.
24. P. A. Sutton, D. A. Buckingham (1987), *Acc. Chem. Res.* 20, 357.
25. J. Chin (1992), *Acc. Chem Res.* 25, 273.
26. J. R. Morrow, W. C. Trogler (1989), *Inorg. Chem.* 28, 2330.
27. S. H. Gellman, R. Peter, R Breslow (1986), *J. Am. Chem. Soc.* 108, 2388.