

# DEGRADATION OF ORGANOPHOSPHORUS COMPOUNDS BY HYDROLYSIS IN PRESENCE OF METAL CATIONS

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## ABSTRACT

*Hydrolysis of Ethyl-cyanophos (organophosphorus compounds) has been studied in acidic medium with catalysts such as Zr<sup>4+</sup>, Ce<sup>4+</sup>, Hf<sup>4+</sup> and Th<sup>4+</sup> cations and the rate maxima observed were at around pH 2.0. Since the metal aquo complexes are known to exist in equilibrium with deprotonated species and therefore, metal bound OH 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.*

**Keywords:** organophosphorus, hydrolysis, tetravalent, metal cations

## I. INTRODUCTION

*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<sup>[1]</sup>. Phosphorus triesters (e.g. Paraoxon etc.) are accepted as suitable mimics of G-type nerve agents (eg. Sarin, Soman etc) <sup>[2,3]</sup>. These compounds are not only highly toxic but also highly persistent in the environment. A significant body of information on the effect of divalent<sup>[4-6]</sup> and trivalent<sup>[7-10]</sup> ions on the hydrolysis of diesters like DNA and RNA has already been reported. Recent work has demonstrated extraordinary catalytic effect of tetravalent<sup>[11-14]</sup> 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<sup>[15]</sup>. Moreover ECP is highly toxic to mammals; the oral LD<sub>50</sub> for rats is about 43 mg/kg <sup>[16]</sup> 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 ethyl-cyanophos, catalyzed by Zr (IV), Ce(IV), Hf (IV) and Th(IV) in mild acidic aqueous solutions.*

## II. EXAMINATION

(a) Synthesis of PCP-DCHA salt: 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.

#### (b) Synthesis of crude ethyl - cyanophos

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)

(c) Purification of ethyl cyanophos 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.

#### (d) Spectral data of ethyl-cyanophos

The compound thus obtained was then subjected to UV, FT-IR and GC-MS analysis.

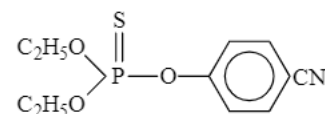
UV :  $\lambda_{\max} - 232 \text{ nm}$ ,  $\epsilon = 40000$

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).



Ethyl cyanophos

Fig.1- ethyl-cyanophos

(e) Preparation of stock solution of ethyl - cyanophos Stock solution of ethyl-cyanophos ( $5 \times 10^{-3}$  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), ZrCl<sub>4</sub> (0.004g, 3×10<sup>-4</sup> 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 pH ≥6.0. The solution was chilled and 0.15 ml of solution of ethyl- cyanophos in dioxan (5×10<sup>-3</sup> 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<sup>[17]</sup>. 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.

### III. 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 has been given in Table-1. Our experiments showed that all the metals require at least 20 fold excess over [substrate] for showing maximum catalysis. All the metal cations showed rate maxima at pH 2.0 which indicates the presence of catalytically more active species around this pH. The Rate constants for Zr(IV), Ce(IV), Hf(IV) and Th(IV) at pH 2.0 were  $10.4 \times 10^{-5} \text{ sec}^{-1}$ ,  $7.6 \times 10^{-5} \text{ sec}^{-1}$ ,  $5.5 \times 10^{-5} \text{ sec}^{-1}$  and  $4.9 \times 10^{-5} \text{ sec}^{-1}$  respectively showed the enhancement of 43, 31, 22 and 20 fold compared to those of uncatalyzed reactions. The decreases in  $k_{\text{obs}}$  values with increasing pH, suggested a reduction in the concentration of catalytically active species, and which might happens due to the precipitation of the metal ion as their hydroxide above pH 5.0<sup>[18]</sup>. The literature reports indicated that at around pH 2.0, Zr(IV) exists as coordination complex of water {e.g. Zr<sub>8</sub> (OH)<sub>20</sub>(H<sub>2</sub>O)<sub>24</sub>Cl<sub>12</sub>}, whose geometry has been determined to be octameric<sup>[19]</sup>, and under similar conditions Hf(IV) has been reported to exhibit a similar chemistry<sup>[18]</sup>. These octameric species may be formed by bridging of two tetramers via four single OH<sup>-</sup> bridges and each metal cations of the octamer would bind to three H<sub>2</sub>O molecules. Ce(IV) at pH 2.0 exists as dimeric Ce(IV) - hydroxo

species  $\{\text{Ce}_2(\text{OH})_4(\text{H}_2\text{O})_2\}^{4+}$ , which has been found to be a more reactive entity<sup>[20]</sup>. However, the geometry of aquo complex of Th(IV) has been proposed to be more or less similar to that of Ce(IV)<sup>20</sup>. The rate equation for ester hydrolysis including metal catalysis may be given by the Eq. 1

$$d[\text{p-cp}]/dt = (k_a [\text{H}^+] + k_n [\text{H}_2\text{O}] + k_b [\text{OH}^-] + k_m [\text{Metal hydroxo species}]) [\text{Parent}] \text{----- (1)}$$

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  $[\text{OH}^-]$  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 (table-1), 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  $k_a[\text{H}^+]$  term appears to be negligible and hence the final form of the rate equation may be written as equation 2.

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

In all our reactions metal hydroxo species being present in large excess; hence the rate is governed by first order kinetics. It has been reported that, because of increasing Lewis acid strength and deprotonation ability of metal bound water

molecule, due to increasing positive charge on metal cation, the tetravalent metal cations like  $\text{Zr}^{4+}$ ,  $\text{Ce}^{4+}$ ,  $\text{Hf}^{4+}$  and  $\text{Th}^{4+}$  are found to be highly reactive towards activated phosphodiester like bis(p-nitrophenyl phosphate)<sup>[11,18]</sup>, dimethyl phosphate<sup>[14]</sup>, hydroxyethyl p-nitrophenyl phosphate<sup>[18]</sup> etc. and neutral triesters like methyl parathion.<sup>[21]</sup> The metal ester binding constant  $K_M$  obtained, dividing intercept by the slope of the linear plots between  $1/k_{\text{obs}}$  vs.  $1/[\text{M}^{4+}]$  are  $4.1 \times 10^{-3}$ ,  $3.8 \times 10^{-3}$ ,  $3.5 \times 10^{-3}$  and  $2.6 \times 10^{-3}$  for  $\text{Zr}^{4+}$ ,  $\text{Ce}^{4+}$ ,  $\text{Hf}^{4+}$  and  $\text{Th}^{4+}$  respectively. Since, the  $pK_a$  values of the metal bound water molecule for  $\text{Zr}^{4+}$ ,  $\text{Ce}^{4+}$ ,  $\text{Hf}^{4+}$  and  $\text{Th}^{4+}$  are found to be around  $\sim 0.6$ <sup>[22]</sup>,  $\sim 0.7$ <sup>[22]</sup>,  $\sim 1.1$ <sup>[22]</sup> and  $\sim 2.3$ <sup>[11]</sup> respectively which explains that deprotonation of  $\text{H}_2\text{O}$  molecule attached to  $\text{Zr}^{4+}$  and  $\text{Ce}^{4+}$  occurs faster than  $\text{H}_2\text{O}$  molecules linked to  $\text{Hf}^{4+}$  and  $\text{Th}^{4+}$  in acidic solutions. From the magnitude of  $K_M$  and  $pK_a$  values, it became evident that hydroxo species formed from  $\text{Zr}^{4+}$  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 as described in the case of bivalent metal ion catalyzed hydrolysis of phosphorus compounds<sup>[22,23-27]</sup>. 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  $\text{OH}^-$

ion of the adjacent metal ion to liberate the cyanophenol as shown by the Scheme -1.

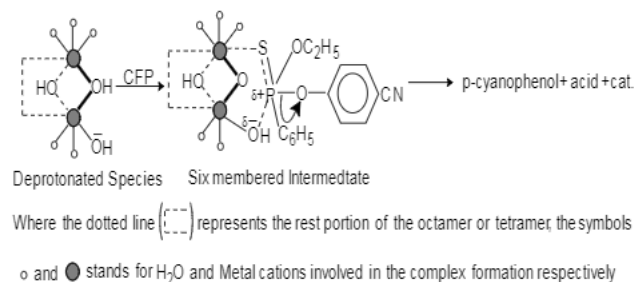


Fig.2

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