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Bivalent Metal Ion Catalyzed Hydrolysis of Organ Phosphorus Compounds in Mild Acidic Conditions

***Vaishali Naik**
****Dr. C. P. Shinde**
*MGMM, Japalpur, (M.P.) India
**Jiwaji University, Gwalior (M.P.) India

ABSTRACT

Hydrolysis of O, O-diethyl, O-p -cyanophenyl phosphate (organophosphorus compound) has been studied in acidic medium with catalyst Cu^{++} *cation and the rate maxima observed were at around pH 6.0. 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.*

Key Words- organophosphorus, hydrolysis, bivalent, metal cation

I. INTRODUCTION

Synthetic organophosphorus compounds are used extensively as agricultural and domestic pesticides including insecticides, fungicides and herbicides[1]. Due to environmental concerns associated with the accumulation of these pesticides in food products and water supplies, there is a great need to develop safe, convenient and economically feasible methods for pesticides detoxification[2,3]. The organophosphorus pesticides of major commercial and toxicological interest are esters or thiols derived from phosphoric, phosphonic, phosphinic or phosphoramidic acid. The OPs exert their main toxicological effects through non-reversible phosphorylation of esterases in the central nervous system (Aldridge and Reiner, 1972; WHO, 1986 b). The acute toxic effects are related to inhibition of acetyl cholinesterase (AChE) (WHO, 1986 b). The inhibition of this enzyme causes over stimulation of nicotine and muscarinic acethylcholine receptors. The POs exert other toxic effect on the central and peripheral nervous system. This toxic effect is called 'organophosphorous induced delayed neuropathy[4,5]. The POs are mainly detoxified through oxidation and hydrolysis[6-9]. The detoxification of phosphorus (v) pesticides and nerve agents is a challenging problem in catalytic hydrolytic chemistry. Metal ions are required in most enzyme catalyzed nucleophilic displacement reactions at phosphorus (V) and therefore a logical choice in the search for catalysts to promote hydrolysis of man made phosphorus (V) toxins[7-10]. The role of metal ions has been considered to be Lewis acid catalysis through coordination of the metal ion to substrate, rendering the later more susceptible to nucleophilic attack. Substrate ligation to metal ion may also assist the departure of the incipient leaving group[11,12]. In, addition, a metal ion ligated to substrate may act as a carrier of nucleophilic hydroxide ion. The pka of the water ligated to metal ion is considerably lower than that of water itself, so that at a given pH, a higher concentration of hydroxide ion can be obtained in the presence of metal ion[13-16]. This study includes hydrolysis of O, O-diethyl, O-p -cyanophenyl phosphate, catalyzed by Cu(II) in mild acidic aqueous solutions.

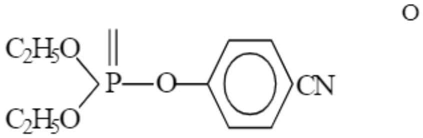
II. EXPERIMENTAL

(a) **Synthesis of crude compound:**- PCP (3.50g, 0.03 M), water (25 ml), carbon tetrachloride (70 ml), NaOH (4.8g, 0.12 M) and TBAB (1.0g, 3.0 M) was taken in a 500 ml RBF and stirred for 15 min. To this stirred solution, diethyl phosphite (16.6g, 0.12 M) in CCl_4 (30 ml) was added drop wise in 10 min A slight exothermic reaction took place, which was controlled with the help of cold water bath. The mixture was stirred for one hour. The mixture was then filtered and organic layer separated. The organic layer was washed three times with ice cold water till free from alkaline impurity. It was then dried with fused $CaCl_2$; solvent first removed by distillation on a water bath and then under reduced pressure. The crude compound so obtained was distilled under vacuum (78 %) Yield

(b) **Purification of compound:**- The crude compound was subjected to TLC (absorbent: silica G, eluent – hexane: acetone 4:1) analysis; showed two spots, one corresponding PCP and another to that of the compound, slightly lower level. In order to remove PCP, the extraction of the crude material was done with n-hexane, till TLC showed single spot. After evaporation of n-hexane the residue was redistilled. The pure compound, was transferred to a sample tube, properly stoppered with the help of PTFE tape and stored in a refrigerator.

(c) **Spectral data:**- The compound thus obtained was then subjected to UV, FT-IR and GC-MS.
UV: ▼ max – 232 nm,
GC-MS M+ (m/z): Single peak

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



O, O-diethyl, O-p -cyanophenyl phosphate

(d) Preparation of stock solution:- Stock solution of compound (5×10^{-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 , 10m*M*), $CuCl_2$ (0.004g, 3×10^{-4} *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, 10m*M*) was used to maintain pH $\geq$6.0. The solution was chilled and 0.15 ml of solution of compound in dioxan (5×10^{-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^{0}C (±0.5^{0}C), such that the temperature inside the test tubes were at 80^{0}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 [17]. 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 DISCUSSON

The reactions were observed for more than three half lives and plots of log A_∞-A_o / A_∞-A_t, (where A_o, A_t and A_∞ 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. 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 (Chapter-1). 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[18].

From the magnitude of *pK*$_a$ value, 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 as described in the case of bivalent metal ion catalyzed hydrolysis of phosphorus compounds [19-22, 23-27]. 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^- ion of the adjacent metal ion to liberate the cyanophenol.

Effect of pH on metal catalyzed hydrolysis of O, O-diethyl, O-p -cyanophenyl phosphate kept at concentration 1.5×10^{-5} *M* at 80^0 C

Table 1

*p*H	Cu^{2+}	Metal Free
1.0	0.2	0.27
1.5	0.4	0.25
2.0	0.7	0.21
2.5	2.0	0.20
3.0	3.0	0.15
3.5	4.0	0.10
4.0	4.2	0.06
4.5	4.9	0.05
5.0	6.2	0.03
5.5	7.4	0.02
6.0	10.9	0.02
6.5	7.1	0.01
7.0	5.2	0.01

Effect of pH on metal catalyzed hydrolysis of O, O-diethyl, O-p -cyanophenyl phosphate kept at concentration 1.5×10^{-5} *M* at 80^0 C

Table 2

*p*H	Cu^{2+}	Metal Free
1.0	0.2	0.27
1.5	0.4	0.25
2.0	0.7	0.21
2.5	2.0	0.20
3.0	3.0	0.15
3.5	4.0	0.10
4.0	4.2	0.06
4.5	4.9	0.05
5.0	6.2	0.03
5.5	7.4	0.02
6.0	10.9	0.02
6.5	7.1	0.01
7.0	5.2	0.01

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