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Tetravalent metalion mediated hydrolysis of cyanofenphos and their oxon in mild acidic condition

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Abstract: Hydrolytic cleavage of both thionate and oxonate esters of insecticidal nature using divalent, trivalent and tetravalent catalyst in mild and weak acidic condition. The hydrolysis study was monitered measuring phenolate product concentrations during the hydrolysis reaction by UV spectroscopy.

Key words: Tetravalent metalion, cyanofenphos and their oxon, Tetravalent metalion mediated hydrolysis.

Introduction

Organophosphorus compounds are widely used as pesticides and as petroleum additives, although their main application is to play a very important role in the life processes[1] of all plants[2] and animals[3]. While phosphate esters have been and continue to be extremely useful in agricultural pest control. Although these compounds can be beneficial, they need to be used with care as they have the ability to harm the environment by affecting non-target organisms through application to non-target areas by spray drift during application or in water run-off, including human. These phosphate esters have therefore been the subject of a large number of studies. The majority of organophosphorus pesticides are neutral esters or amides derived from phosphoric acid anhydride, or sulphur analogs. Hydrolysis is a major degradation pathway for phosphate esters. Therefore hydrolysis of organophosphorus pesticides and their metabolites are of great importance, because the hydrolysis results in detoxification of pesticides. Many thionate and oxonate esters hydrolyze quickly in alkaline solutions[4-6], but persist under the neutral and slightly acidic conditions typical of surface water, soils and aquifer sediments. Therefore hydrolysis of both thionate and oxonate esters of insecticidal nature using divalent, trivalent and tetravalent catalyst in mild and weak acidic condition is reported in the present communication.

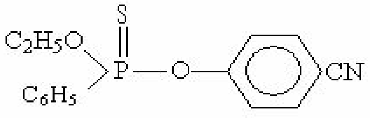
Material and Method

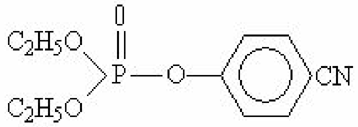
2.1 Chemicals:

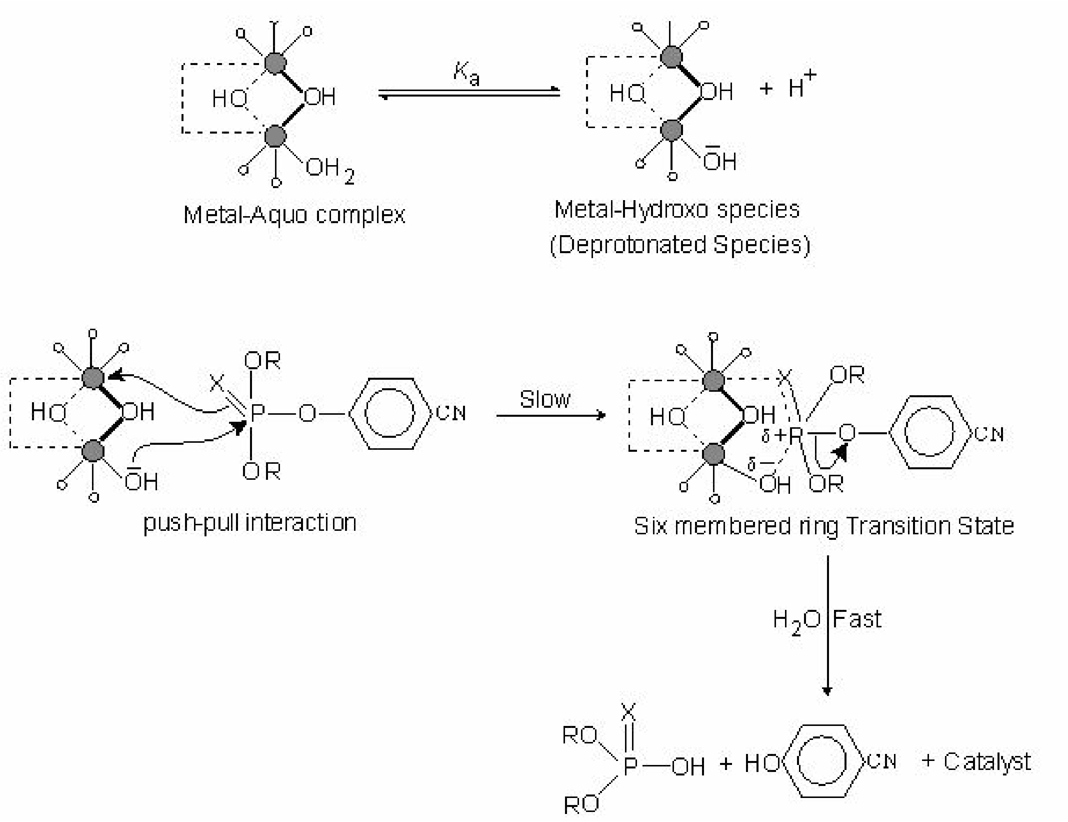
Commercial grade cyanofenphos was obtained from India Pesticides Ltd. and were of (> 98% pure) technical grade and its degradation product was supplied by Aldrich (Sigma-Aldrich chemie, Germany). The metal salts, copper (II) chloride, Zirconium (IV) chloride, Hafnium (IV) chloride and HEPES buffer were also obtained from Aldrich. KCl was used AR grade and was obtained from central drug house (P) Ltd. Mumbai.

2.2 Synthesis

The Cyanofenphos and diethylcyanofenphos-oxon compounds of the following configuration will be synthesized according to the standard procedure[19].







The dotted line (⬚) represents the octameric or dimeric structure of the metal aquo-complex, the symbols o and ● stands for H_2O and metal cations involved in the complex formation respectively; R= CH_3 or C_2H_5 and X = S or O.

Scheme-1

2.3 Kinetic Measurement

A typical kinetic run of [CPP]/[Zr^{4+}] (1:20) was prepared by dissolving KCl (.037g 1mM), $ZrCl_4$ (500 µl, 0.01M) in water in a 50 mL flask. The desired pH was then adjusted by using 0.1N HCl or 0.1N KOH. The solution at 6.0 pH was buffered by HEPES (0.122g, 1mM), prior to pH adjustment. All other runs performed at pH 1.0-5.0 were carried out in unbuffered aqueous solutions, because metal salt solutions themselves have sufficient buffer capacity.

3.1 Result and discussion

Measurements of phenolate product concentrations during the hydrolysis reaction can provide valuable information regarding mechanism. If the phenolate product is less than the amount of parent lost, then a significant fraction of the triester hydrolysis must occur through the alcoholate leaving group. If the phenolate product is equal to the amount of parent lost, triester hydrolysis occurs exclusively via the departure of the phenolate leaving group. The work embodies is a part of a broader study that seeks to (i) identify thionate ester pesticides subject to metal catalysis (ii) compare the susceptibility of thionate esters and oxonate ester toward catalysis (iii) examine how catalysis depends upon the properties of metal catalysis, and (iv) examine how pH affects catalysis.

It has been observed from this work that the oxonate ester hydrolyses more rapidly than the corresponding thionate ester in the absence of metal catalysts. Replacing the thionate sulphur with the more electronegative oxygen resulted in an increased protonation of hard base; oxonate oxygen, by hard acid (H^+) and consequently an overall increase in the hydrolysis rates were observed. It was noticed in case of tetravalent metal cation catalyzed hydrolysis that the values of k_{obs} are 2-3 fold higher in case of oxonate esters than corresponding thionate esters for example the k_{obs} value of ethyl cyanophos oxon is 13.4×10^{-5} but that of ethyl cyanophos is 4.5×10^{-5} (Table 1.1 & 1.2) shows 3 fold higher values.

The larger values of rate constant for tetravalent metal catalyzed hydrolysis of triester in the pH range from pH 2.0 to 3.5 indicated that the formation of active hydroxo species takes place in the pH range. During the experimental tenure, it was observed that the tetravalent metal salts when added to water reduces the pH (between 2.0-3.5 depending upon the type of metal salt and its concentration), probably due to the formation of metal hydroxo (deprotonated metal–aquo) complex, which might have resulted in an increased acidity of the solution. According to the literature, in the pH region 2.0 to 3.5 the metal hydroxo species predominates, whose geometry has been reported to be octameric for Zr (IV) and Hf (IV) and dimeric for Ce (IV) and Th (IV) Section (1.4). Therefore, it could be concluded that the catalytically active form of hydroxo species may be octameric and dimeric in nature. The decrease in k_{obs} values for tetravalent metal catalyzed hydrolysis of triesters with increasing pH, suggested a reduction in the concentration of catalytically active metal hydroxo species, and which might happens due to the precipitation of the metal ion as their hydroxides above pH 5.0. In contrast to these observations, in the case of Cu (II) mediated hydrolysis, the k_{obs} values increase with increasing the pH of the medium, showing the maxima at pH 6.0. This might be due to the increased concentration of active Cu (II) hydroxo species, as has already been reported for the Cu (II) catalyzed hydrolysis of triesters.

During course of investigations, it was observed that phosphonate ester (cyanofenphos) is hydrolyzed at slower rate (k_{obs}= 0.21*10^{-5} Sec^{-1}) than phosphate ester (k_{obs}=0.24*10^{-5} Sec^{-1}) under metal free (acidic conditions) as reported. In alkylphosphonates, there is no pπ-dπ contribution to P-C bond because the carbon atom has no free lone pair of electrons. Therefore, despite the fact that carbon atom has lower electro negativity than oxygen atom, the phosphorus atom of phosphonates is more electrophilic than that of corresponding phosphate esters, in which lone pair of electrons possessed by oxygen can be donated to phosphorus by pπ-dπ overlap. Thus, phosphonate esters are usually more susceptible to alkaline hydrolysis than phosphate esters[7]. However, in the case of metal catalyzed hydrolysis, cyanofenphos hydrolyzes ~2 times faster than cyanophos with k_{obs} in case of Zr(IV) catalyzed reactions being 10.4*$10^{-5}$$Sec^{-1}$ and 4.5*$10^{-5}$$sec^{-1}$ respt. for cyanofenphos and cynophos. Thus, it could be concluded that even in acidic conditions, the alkaline (hydroxide catalyzed) hydrolysis occurs, the source of hydroxide ions being metal-bound OH^- from metal-hydroxo complex.

Apart from these observations it was noticed that the hydrolysis of triesters is poorly catalyzed than diesters by the tetravalent metal cations. The high affinity of hard acids (tetravalent cations) towards hard base (hydroxide ion generated by deprotonation of metal bound water) restricts intramolecular attack of hydroxyl ion on phosphorus atom. The diesters like BNPP, HENPP and phosphonoformate, under similar conditions, remain in their anionic form[8-11]. The anionic oxygen provides an additional site for metals to bind. Thus, the interaction of metal ions with phosphoryl oxygen as well as anionic oxygen decreases positive charge density on the metal species to a greater extent, which results in decrease in hydroxide-metal interaction and subsequent increased attack of hydroxide ion upon the phosphorus atom. However, in case of the neutral triesters, the second anionic site being absent, the positive charge density of metal ion is neutralized up to a smaller extent, resulting in hydroxide ion to bind strongly with metal ion causing a decrease in the nucleophilic attack. Moreover, triesters are more sterically hindered which could also cause obstacle on the way of OH^- for nucleophilic attack. These reasons might explain for only marginal catalysis *viz.*~100-400 fold catalysis of triesters compared to ~10^9 fold catalysis of diesters reported by tetravalent metals[8-11].

However, Cu being a softer base reported to be less interacted with hydroxide, which makes hydroxide ion to attack phosphorus atom with more ease. Moreover, copper forms less sterically hindered monomeric species which might provide hydroxide ion more free space to attack.

The above discussion indicates that, in the metal catalyzed hydrolysis of OP triesters, the metal ion forms aqua-complex which remains in equilibrium with its deprotonated (hydroxide) form. From the *pKa* values of the metal bound water, it is clear that deprotonated metal bound hydroxide ion is much poorer nucleophile for the direct attack at the phosphoryl center of the ester. On the other hand tetravalent metal cations may simultaneously coordinate both hydroxide ion and the ester molecule. If the sulfur of the P=S (or oxygen of P=O) is bound to the metal ion of the aqua-complex, then the phosphorus atom becomes a susceptible electrophilic center and the metal bound hydroxide ion attack will be possible. Although, metal bound hydroxide is a rather weak nucleophile than hydroxide ion itself, the phosphorus is so activated, that facilitates intramolecular nucleophilic attack. If the site is bound to the metal ion via the ester linkage, then metal bound hydroxide, which may serve as nucleophile could possibly attack the phosphorus center, forming a six membered ring transition state. The decomposition of the six membered ring transition state would give rise to product. Such **push-pull mechanism** (i.e. the attraction of electron density of phosphorus by metal ion through interaction with phosphoryl oxygen or thiophosphoryl sulfur and subsequent attack of hydroxide nucleophile on electrophilic phosphorus being simultaneous process) are also reported in case of bivalent metal catalyzed hydrolysis of organophosphorus esters[12-15, 18]. (Scheme- 1)

Because of the lower *pK*a value of the PCP(7.95) than the alcohols (C_2H_5 = 15.9), the P-O-

Ar bond being weaker than the P-O-R bond and the resulting phenolate anion is far more stable in the solution than the alcoholate anions[16], which resulted in the liberation of PNP than the alcohols.

The values of Arrehenius parameters for both uncatalyzed and metal catalyzed reactions, suggest bimolecular nature of the reactions for all substrates[17]. The pKa values of leaving group may also effect the hydrolysis rates On comparing the rates of parathion with ethyl cyanophos with pKa of leaving group of p-nitrophenol in parathion is 7.14 and that of p-cyanophenol is 7.95, it was found that ethyl cyanophos with higher *pKa* values hydrolyses slower than parathion. These results are consistent with the results obtained by Stone *et al.*(Scheme-1**)**

4.1 Conclusion

Conclusively, the observations obtained by the present investigation for metal catalyzed hydrolytic cleavages of phosphorus triesters of insecticidal nature in weak and mild acidic solutions, suggest that:

1. In case of metal free solutions, as the *p*H of the solution was decreased, the formation of protonated species increased, as visualized by increase in the hydrolysis rates.
2. The metal salts when were added to water, reduces the *p*H, owing to the formation of either dimeric or octameric aqua complexes, which subsequently undergoes deprotonation by virtue of their lower *pK*a values.
3. The rate of deprotonation depends on the acidity of metal bound water which is reported to be greater in case of Zr(IV) relative to other tetravalent cations. Consequently, the larger numbers of OH^- nucleophiles are produced which attack intramolecularly on ester molecule, resulting in increased rates of hydrolysis.
4. The oxonate esters hydrolyze two to three times faster as compared to thionate esters in the absence as well as in the presence of tetravalent cations. This might be due to the increased electrophilicity at phosphorus by more electronegative oxygen of P=O.
5. The methyl ester hydrolyzes more rapidly in the absence as well as in the presence of metal ions because of the larger +I effect of the ethyl group which cause reduction in the electrophilicity at phosphorus atom and lowers the nucleophilic attack on it. Also, the steric hindrance provided by ethyl group may also be considered as one of the factors contributing for reduction in the rates.
6. Above *p*H 5.0, decrease in the hydrolysis rate was observed, which might be due to the disappearance of catalytically active species.
7. In case of Cu(II) catalyzed reactions, the hydrolysis rates increased with increasing *p*H of the solution, showing maxima at *p*H 6.0 which might be due to the formation of its hexaaquo complex. The *pK*a of water coordinated in this species, is lower than that of water itself so that, at given *p*H hydroxide nucleophiles are abundantly available for nucleophilic attack.
8. The thionates hydrolyzed faster than oxonates in the presence of Cu (II), which might be due to the greater interaction of the soft acid copper with soft base sulfur.
9. The extraordinary catalysis was shown by Cu (II), which might be due to the nucleophilicity of copper bound hydroxide ions being greater than those of tetravalent metal bound hydroxide ions. The hard acids, tetravalent cations are strongly bonded with hard base hydroxide ion resulting poor availability of OH^- for a nucleophilic attack on phosphorus atom. Contrary to this, copper being softer acid binds OH^- relatively loosely and allowed its smooth attack on the phosphorus atom. Additionally, the large size of tetravalent cations and presence of their bulky hydroxo species might cause hindrance in the nucleophilic attack.

These results are quite encouraging for using copper as a powerful decontaminating agent for phosphorothionate ester pesticides at around neutral to slightly acidic *p*H range i.e. by water from any available source. Current studies in this lab have been directed mainly towards finding the solutions to problems of detoxification of insecticidal OP compounds under neutral and mild acidic condition.

Table 1.1 – *p*H-dependence of pseudo-first order rate constants (k_{obs}) for the metal free and metal catalyzed hydrolysis of Cyanofenphoss metal cations at 80 ^{0}C; [Substrate] = 1.5 × 10^{-5} *M* and [M^{n+}] = 3 × 10^{-4} *M*

			$10^5 k_{obs}$			
***p*H**	**Zr^{4+}**	**Ce^{4+}**	**Hf^{4+}**	**Th^{4+}**	**Cu^{2+}**	**Metal Free**
1.0	2.7	2.5	1.9	1.7	1.6	0.23
1.5	3.2	3.1	2.7	2.5	1.9	0.22
2.0	4.5	3.7	3.1	2.7	2.4	0.24
2.5	3.6	3.4	2.6	2.4	2.7	0.22
3.0	3.1	2.7	2.1	1.9	4.1	0.21
3.5	2.7	2.2	1.7	1.6	12.4	0.19
4.0	1.9	1.8	1.2	1.1	19.7	0.18
4.5	1.2	1.1	0.9	0.8	24.5	0.15
5.0	0.92	0.7	0.8	0.6	31.4	0.14
5.5	0.63	0.6	0.6	0.5	42.9	0.11
6.0	0.42	0.3	0.4	0.3	56.4	0.07
6.5	0.17	0.2	0.2	0.1	36.2	0.04
7.0	0.12	0.1	0.1	0.1	24.1	0.01

Table 1.2 – *p*H-dependence of pseudo-first order rate constants (k_{obs}) for the metal free and metal catalyzed hydrolysis of ethyl cyanophos-oxon with various metal cations at 80 ^{0}C; [Substrate] = 1.5 × 10^{-5} *M* and [M^{n+}] = 3 × 10^{-4} *M*

			$10^5 k_{obs}$			
***p*H**	**Zr^{4+}**	**Ce^{4+}**	**Hf^{4+}**	**Th^{4+}**	**Cu^{2+}**	**Metal Free**
1	2.8	1.9	1.8	1.5	0.2	0.27
1.5	3.2	2.9	2.7	2.4	0.4	0.25
2	2.6	3	2.9	2.6	0.7	0.21
2.5	6.4	5.2	4.8	5.1	2	0.2
3	9.4	7.5	7.9	6.9	3	0.15
3.5	13.4	10.2	9.2	8.5	4	0.1
4	9.6	7.1	5.7	4.6	4.2	0.06
4.5	5.7	4.6	3.6	3.1	4.9	0.05
5	3.8	2.7	1.8	1.2	6.2	0.03
5.5	2.9	2	1.7	1.1	7.4	0.02
6	2.5	1.9	1.2	0.9	10.9	0.02
6.5	1.9	1.5	0.9	0.7	7.1	0.01
7	1.7	1.2	0.7	0.5	5.2	0.01

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