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Total Degradation of Fenitrothion and Other Organophosphorus Pesticides by Catalytic Oxidation Employing Fe-TAML Peroxide Activators

Arani Chanda, Sushil K. Khetan, Deboshri Banerjee, Anindya Ghosh, and Terrence J. Collins*

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Received June 7, 2006; E-mail: tc1u@andrew.cmu.edu

Organophosphorus (OP) triesters constitute the largest group of crop protectants.[1] Their widespread use in agriculture is linked to environmental concerns associated with cholinergic toxicity and, in some cases, delayed neuropathy.[2] Some thiophosphate pesticides are associated with endocrine disruption.[3] Disposal of obsolete pesticides and remediation of associated contaminated sites are of worldwide concern.[4] The available approaches for degradation and/or detoxification of OP pesticides are currently inadequate. Chemical[5] and enzyme-mediated hydrolysis[6] have been the most commonly employed detoxification methods; however, these often produce hydrolysates that have mild to acute toxicity.[7] Metal complex catalyzed hydrolyses[5,8] can contribute their own additional toxicity to the final wastes.[9] For example, Fenton oxidations have been commonly used, but these operate at strongly acidic pH values and use a large excess of iron salts[10]—the iron-containing sludge produced in wastewaters can lead to the proliferation of algae.[11] Immobilized enzymes,[12a] genetically modified bacteria,[12b] photocatalytic,[12c] modified Fenton processes,[12c−e] and phytoremediation[12f] are some of the other approaches for OP pesticide decontamination. An ideal decontamination process would be inexpensive, technically straightforward and flexible, would work rapidly under ambient conditions at environmental pHs, and would not leave toxic residues.

Here we describe an approach for the total degradation of OP pesticides using Fe-TAML activators (**1**, TAML: tetraamido macrocyclic ligands, Figure 1A), water-soluble peroxide-activating catalysts that function effectively in low parts-per-million concentrations at room temperature over a wide pH range (~3 to 14).[13] Their abilities to degrade chlorinated phenols[14a] and deactivate bacterial spores have been reported.[14b] We have studied degradation of three OP pesticides with **1**/H_2O_2, fenitrothion (**2**), parathion, and chlorpyriphos methyl (Figure 1B), and report here a detailed study for **2**. Fenitrothion has low adult mammalian toxicity (oral LD_{50} rat: 330−800 mg/kg).[15a] However, it is a known endocrine disrupting chemical (EDC).[3a] Moreover, its common hydrolysis product, 3-methyl-4-nitrophenol (**3**), is also an EPA priority pollutant[7a] and an EDC.[7b] Therefore, this work also demonstrates a facile method for destroying EDCs to environmentally acceptable endpoints.

Fe-TAML (**1a**, 40 μM or **1b**, 10 μM)/H_2O_2 (2.0 M, 0.3 M suffices at pH 12 (see later)) treatment of **2** (1 mM) at pH 8.0 (0.1 M KH_2PO_4/KOH, 10% ^{t}BuOH cosolvent) led to the immediate formation of a yellow color (UV−vis, λ_{max} = 396 nm) characteristic of **3**. This absorbance began diminishing immediately to nearly disappear (2 h, >95% degradation, Figure 1C). Treatment of **3** with **1**/H_2O_2 under these conditions led to similar UV−vis observations. The reaction kinetics followed by UV−vis spectroscopy revealed that the rate of formation of **3** (from **2**) is considerably faster than its subsequent degradation. HPLC analysis confirmed the generation of **3** as the major initial product (~90%) and its concomitant degradation. At this pH of 8, the formation of fenitrooxon (**4**) as a minor product (~10%) was also observed. However, the presence of even small amounts of highly mammalian toxic (oral LD_{50} rat: 3.3 mg/kg)[15b] **4** is unacceptable. Moreover, while **2** and **3** were easily destroyed by **1**/H_2O_2 under the above reaction conditions, it had no observable effect on **4** after 2 h. Therefore, we have adapted the reaction conditions to obviate formation of and/or degrade **4** also, which has been achieved easily by working at higher pH levels.

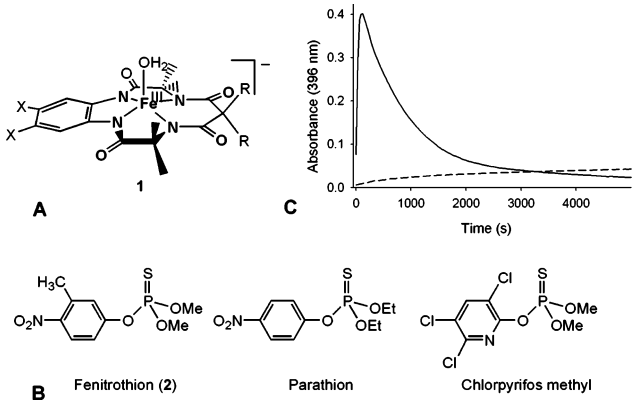

Figure 1. (A) Fe-TAML activators used in this study (**1a**, R=F and X=H and **1b**, R=F, X=Cl); (B) three OP pesticides degraded on treatment with **1**/H_2O_2; (C) UV−vis spectrophotometric study of the degradation of fenitrothion (**2**) by **1a**/H_2O_2. The absorbance change at 396 nm results from formation of 3-methyl-4-nitrophenol (**3**) from **2**, followed by its decay: solid line, **1a**/H_2O_2; dotted line, H_2O_2-only treatment.

Phosphate esters undergo more facile base hydrolysis than their thiophosphate analogues.[16] The strongly nucleophilic hydroperoxide ion (HO_2^-), which forms at elevated pH (pK_a of H_2O_2 ≈ 11.5), can lead to accelerated hydrolysis in a process called perhydrolysis.[16] The hydrolysis rate of **4** increases by almost 2 orders of magnitude upon raising the pH from 8.0 through 12.0. Separate kinetic studies revealed that the **1**/H_2O_2 system attains maximum oxidative efficiency near pH 10.0.[17] Therefore, we studied the degradation of **2** at pH 10.0. The treatment of **2** with **1**/H_2O_2 at pH 10.0 (water/10% ^{t}BuOH) under ambient conditions initially led to complete conversion to **3** and **4**, followed by 95−98% degradation of **3** with no residual **4** after 2 h (Scheme 1) as determined by HPLC and GC−MS.[18] In a control experiment, at pH 10.0, H_2O_2 alone led to 85−90% hydrolysis of **2**, producing **3** in 2 h with no formation of **4**. However, in this case, **3** is not degraded. The inability of H_2O_2 to oxidize **3** clearly underscored that activation of H_2O_2 by **1** was critical in achieving the total degradation of **2**. By raising the pH to 12.0, the H_2O_2 concentration could be reduced to 0.3 M as the increased concentration of HO_2^- accelerated the hydrolysis of **4**.

The degradation products of **2** after treatment with **1b**/H_2O_2 were identified and quantified using a variety of analytical techniques achieving ca. 98% mass balance as shown in Table 1. Four small aliphatic acids—formic, oxalic, maleic, and methyl maleic—were

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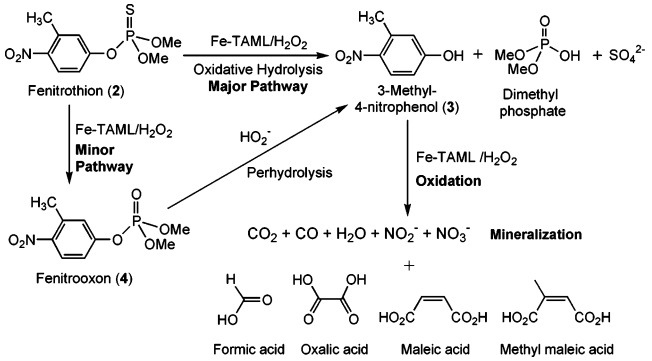
Scheme 1. Fenitrothion Degradation by **1**/H_2O_2[a]



[a] Degradation products and their quantitation are listed in Table 1.

Table 1. Degradation Products of Fe-TAML/H_2O_2 Treatment of **2**

products identified	percentage	analytical techniques used
$CO + CO_2$	$10 \pm 2\%$ (of total C)	TOC
methyl maleic acid maleic acid	$5 \pm 1\%$ (of total C) $2 \pm 1\%$ (of total C)	HPLC
SO_4^{2-} $NO_2^- + NO_3^-$ $HCOO^-$	100% (of total S) 72% (of total N) 36% (of total C)	ion chromatography
dimethyl phosphate[a]	100% (of total P) 22% (of total C)	^{31}P NMR
oxalic acid	$23 \pm 4\%$ (of total C)	oxalate kit (Sigma)

[a] Dimethyl phosphate was the sole phosphorus containing product observed in ^{31}P NMR; amounts of P and C for dimethyl phosphate were calculated theoretically.

identified as the major reaction products and total organic carbon (TOC) analysis showed $10 \pm 2\%$ mineralization. An aquatic toxicity study of the postdegradation mixture of **2** was conducted by Microtox assay. There was a 10-fold reduction in toxicity of the reaction mixture as compared to untreated **2** in solution. Microtox assays of different components of the reaction mixture showed that all residual toxicity in the degradation of **2** could be attributed to the ^{t}BuOH cosolvent (see Supporting Information, Table S1). In an application, surfactants would probably be used in place of ^{t}BuOH to solubilize the pesticides.

Treatment with **1**/H_2O_2 also led to facile degradation of other widely used OP pesticides, parathion and chlorpyriphos methyl, including their hydrolysate components, 4-nitrophenol and 3,5,6-trichloropyridin-2-ol. Degradation of parathion and chlorpyriphos methyl yielded maleic acid and chloromaleic acid, respectively. Oxalic acid and formic acid were degradation products with each.

Cytochrome P-450 co-enzymes have been reported to catalyze the oxidation of **2** by H_2O_2 through oxidative desulfuration, forming **4** with release of **3**.[19] The formation of similar initial products upon treatment of **2** with **1**/H_2O_2 suggests that the reactions follow similar pathways. Nevertheless, **1**/H_2O_2 provides a much more complete treatment, as **4** is totally eliminated and **3** is oxidized to nonhazardous products. In P-450 mediated reactions, the enzyme is inactivated upon formation of **3**.[20]

These studies establish that complete degradation of a series of widely used OP pesticides can be achieved using **1**/H_2O_2 in a controlled, rapid, versatile, and environmentally friendly manner (on the basis of aquatic toxicity assays). Both **1a** and **1b** contain CF_2 groups with potential for persistent residuals mandating careful toxicity studies prior to commercial use.[14a] This catalytic oxidation approach could potentially be adopted for the safe and environmentally benign disposal/remediation of OP pesticides and their hydrolysates, including environmentally problematic nitrophenols and other hydroxyaromatics.

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Supporting Information Available: Materials and methods, experimental and toxicity studies (Table S1), complete references 2a and 11. This material is available free of charge via the Internet at http://pubs.acs.org

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