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

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Organophosphorus (OP) triesters constitute the largest group of crop protectants. Their widespread use in agriculture is linked to environmental concerns associated with cholinergic toxicity and, in some cases, delayed neuropathy. Some thiophosphate pesticides are associated with endocrine disruption. Disposal of obsolete pesticides and remediation of associated contaminated sites are of worldwide concern. The available approaches for degradation and/or detoxification of OP pesticides are currently inadequate. Chemical and enzyme-mediated hydrolyses have been the most commonly employed detoxification methods; however, these often produce hydrolysates that have mild to acute toxicity. Metal complex catalyzed hydrolysates can contribute their own additional toxicity to the final wastes. For example, Fenton oxidations have been commonly used, but these operate at strongly acidic pH values (pH 1–4) and use a large excess of iron salts. Immobilized enzymes, genetically modified bacteria, modified Fenton processes, and phytoremediation 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). Their abilities to degrade chlorinated phenols—the iron-containing sludge produced in wastewaters can lead to the proliferation of algae. Some thiophosphate pesticides and remediation of associated contaminated sites are of worldwide concern. The approach described here is technically straightforward and flexible, would work rapidly under ambient conditions at environmental pHs, and would not leave toxic residues.

Fe-TAML (1a, 40 μM or 1b, 10 μM)/H₂O₂ (2.0 M, 0.3 M suffices at pH 12 (see later)) treatment of 2 (1 mM) at pH 8.0 (0.1 M KH₂PO₄/KOH, 10% 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/H₂O₂ 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 LD₅₀ rat: 3.3 mg/kg) is unacceptable. Moreover, while 2 and 3 were easily destroyed by 1/H₂O₂ 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.

Phosphate esters undergo more facile base hydrolysis than their thio phosphate analogues. The strongly nucleophilic hydroperoxide ion (HO₂⁻), which forms at elevated pH (pK_a of H₂O₂ ≈ 11.5), can lead to accelerated hydrolysis in a process called perhydrolysis. 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/H₂O₂ system attains maximum oxidative efficiency near pH 10.0. Therefore, we studied the degradation of 2 at pH 10.0. The treatment of 2 with 1/H₂O₂ at pH 10.0 (water/10% 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. In a control experiment, at pH 10.0, H₂O₂ 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 H₂O₂ to oxidize 3 clearly underscored that activation of H₂O₂ by 1 was critical in achieving the total degradation of 2. By raising the pH to 12.0, the H₂O₂ concentration could be reduced to 0.3 M as the increased concentration of HO₂⁻ accelerated the hydrolysis of 4.

The degradation products of 2 after treatment with 1b/H₂O₂ 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...
identified as the major reaction products and total organic carbon (TOC) analysis showed 10 ± 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 BuOH cosolvent (see Supporting Information, Table S1). In an application, surfactants would probably be used in place of BuOH to solubilize the pesticides.

Treatment with 1/H₂O₂ also led to facile degradation of other widely used OP pesticides, parathion and chlorpyriphos methyl, the oxidation of 1 by H₂O₂ through oxidative desulfuration, forming trichloropyridin-2-ol. Degradation of parathion and chlorpyriphos methyl, widely used OP pesticides, parathion and chlorpyriphos methyl, with release of CO₂ and NO₂⁻ (methyl maleic acid 5, maleic acid 2, oxalic acid 23, Dimethyl phosphate was the sole phosphorus containing product identified percentage 36% (of total C) 72% (of total N) 100% (of total P) 31 P NMR 2% mineralization. An aquatic toxicity study 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.

References
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(17) The addition of 1 in multiple aliquots mimics its catalase-like activity with H₂O₂ as well as its self-degradation processes in the presence of excess H₂O₂. For pH 10.0 reaction, I was added in two aliquots in an hour interval. For pH 12.0 reaction, I was added in smaller aliquots.