Rapid Total Destruction of Chlorophenols by Activated Hydrogen Peroxide

Sayam Sen Gupta,[1] Matthew Stadler,[1] Christopher A. Noser,[1]
Anindya Ghosh,[1] Bradley Steinhoff,[1] Dieter Lenoir,[2]*
Colin P. Horwitz,[1] Karl-Werner Schramm,[2] Terrence J. Collins[1]*

A practical, inexpensive, green chemical process for degrading environmental pollutants is greatly needed, especially for persistent chlorinated pollutants. Here we describe the activation of hydrogen peroxide by tetraamidomacrocylic ligand (TAML) iron catalysts, to destroy the priority pollutants pentachlorophenol (PCP) and 2,4,6-trichlorophenol (TCP). In water, in minutes, under ambient conditions of temperature and pressure, PCP and TCP are completely destroyed at catalyst:substrate ratios of 1:715 and 1:2000, respectively. The fate of about 90% of the carbon and about 99% of the chlorine has been determined in each case. Neither dioxins nor any other toxic compounds are detectable products, and the catalysts themselves show low toxicity.

Chlorophenols have found wide use in pesticides, disinfectants, wood preservatives, personal care formulations, and many other products, and they are substantial by-products of wood pulp bleaching with chlorine (*1*). However, growing knowledge about the toxicities and environmental fates of specific chlorophenols has caused governments to regulate these compounds. Five chlorophenols are listed by the U.S. Environmental Protection Agency as priority pollutants, including pentachlorophenol (PCP) and 2,4,6-trichlorophenol (TCP), which are present in the environment in significant quantities (*1*).

Biological methods for degrading TCP and PCP have been tested. These methods are prohibitively slow as well as ineffective at high concentrations, because of their toxicities to the organisms (*2–4*). More important, biological treatment leads to formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (*5*).

Several chemical degradation methods for TCP and PCP have been studied extensively (*6–13*). The most effective degradation method in homogeneous solution reported thus far is that of Meunier and co-workers (*10–12*). The process, which proceeds in a pH 7 solution containing 25% CH_3CN, uses H_2O_2 catalytically activated by water-soluble iron-phthalocyanines (*10–12*). With a catalyst/substrate molar ratio of 3.7%, Meunier's system converts TCP (5 mM) to CO_2 and CO (14%), chlorinated and nonchlorinated maleic and fumaric acids (29%), and several oxidatively coupled species (27%) containing multiple Cl atoms. Dichloromaleic anhydride is the major product identified from PCP oxidation, but oxidation of a 5 mM solution of PCP gives only 20% mineralization of chlorine and formation of multiple oxidatively coupled products (*11*). Here we show that micromolar concentrations of iron complexes of tetraamidomacrocyclic ligands—Fe-TAML activators (*14–16*)—activate H_2O_2 to rapidly convert more than 99% of millimolar solutions of PCP and TCP to nonhazardous products under ambient conditions in water without measurable dioxin production. The Fe-TAML activators and their degradation products tested to date appear not to present toxicity concerns.

Fe-TAML activators (Fig. 1) are an expanding family of macrocyclic iron complexes that have been developed during the past 20 years to be long-lived activators of H_2O_2 in water (*17*). These complexes are designed to be used under a variety of working conditions, including variable pH, temperature, and solvent composition. Fe-TAML activators, typically used at 0.1 to 10 μM concentrations, can perform rapid deep oxidation of commercial dyes in water (*14*) and colored effluent streams from pulp and paper mills (*18*).

Catalytic oxidation of PCP and TCP was carried out with the Fe-TAML activators $[Et_4N]$**1a** and Li_2**1b** (Fig. 1), at pH 10 and 25°C. A pH of 10 instead of 7 was chosen for this bulk study, both because $[Et_4N]$**1a** and Li_2**1b** work more rapidly at the higher pH (*19*) and because appreciable concentrations of PCP cannot be achieved at neutral pH. Fe-TAML–activated H_2O_2 also decomposes PCP at neutral pH (see below). In a typical TCP oxidation reaction, $[Et_4N]$**1a** or Li_2**1b** and H_2O_2 were added to a solution of 5 mM TCP in pH 10 buffer (1 ml, 0.1 M $NaHCO_3$/0.1 M Na_2CO_3) so that the final concentrations in solution were 2.5 μM (catalyst) and 0.5 M (H_2O_2). The catalyst/substrate molar ratio was 1:2000 (0.05%). The catalyst was added in two equal portions over 2 min, and the H_2O_2 was added in five equal portions over 4 min. This addition methodology was used to minimize H_2O_2 disproportionation (*20*), although Fe-TAML catalysts are known to decompose H_2O_2 unusually slowly (*19*). For specific details on the reaction conditions and product determination, see the supplementary information (*21*). Upon addition of the first aliquot of H_2O_2, the reaction mixture turned purple, suggesting rapid quinone formation as observed in Meunier's system (*11*). The purple color disappeared on further additions of H_2O_2. After the final H_2O_2 addition, the reaction was allowed to continue for 5 min (9 min in total) and was then quenched by addition of catalase (1.50 μL from *Aspergillus niger*, Sigma) to destroy unreacted H_2O_2. High-pressure liquid chromatography (HPLC) analysis of the resulting solution showed that more than 99.5% of the TCP had been degraded. A similar protocol was followed for the oxidative degradation of PCP by Li_2**1b**/H_2O_2. A 5 mM PCP solution (1 ml, pH 10 buffer) was treated with 7 μM Li_2**1b** and 0.5 M H_2O_2 for 9 min; catalyst/substrate ratio = 1:715 (0.14%). Again, essentially quantitive degradation was observed. Control experiments with Fe-TAML activators in the

Table 1. Mass balance after first-pass treatments of TCP and PCP with Fe-TAML-activated H_2O_2 (9 min).

Compound	TCP (mM)	TCP % C	TCP % Cl	PCP (mM)	PCP % C	PCP % Cl
CO + CO_2		35 ± 5			45 ± 3	
Cl^-			83 ± 2			87 ± 4
Oxalic acid	1.71 ± 0.04	11		3.4 ± 0.2	23 ± 1	
Formic acid	1.53 ± 0.14	5				
Chloromaleic acid	1.17 ± 0.02	16	8			
Dichloromaleic acid				1.27 ± 0.03	17 ± 1	10
Malonic acid	0.74	7.5				
Hydroxymalonic acid	0.45	6.5				
Chloromalonic acid	0.65	4.5	3	0.6	6	2
Chlorinated aromatics	0.07	2	1			
Total		87.5 ± 5%	95 ± 2%		91 ± 5%	99 ± 4%

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[1] Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, USA. [2] Institut für Ökologische Chemie, GSF-Forschungszentrum für Umwelt und Gesundheit, 85758 Neuherberg, Germany.

*To whom correspondence should be addressed.

absence of H_2O_2, or with H_2O_2 in the absence of Fe-TAML activators, or with catalase in the presence of H_2O_2, indicated no degradation of PCP or TCP under the above experimental conditions.

The extent of mineralization of PCP and TCP was quantified by determination of both the inorganic chloride released and the residual total organic carbon (TOC). Chloride ion was measured colorimetrically (*10*) and by ion chromatography (*21*). Chlorine mineralization was 87% in PCP and 83% in TCP. TOC measurements indicated that 45 ± 3% and 35 ± 5% of the carbon was mineralized for PCP and TCP, respectively (CO_2 and/or CO) (Table 1). Therefore, these analyses indicated that a substantial amount of the starting PCP or TCP was converted to other organic products.

The identification and quantification of measurable reaction products allowed for a virtually complete mass balance to be determined. Although no formaldehyde was detected (*22*) for either TCP or PCP, oxalate was a major product for TCP and PCP, whereas formate was detected for TCP only (Table 1).

Proton nuclear magnetic resonance (^{1}H-NMR) (at 300 and 600 MHz), electrospray ionization mass spectrometry, and gas chromatography–mass spectrometry (GC-MS) were used to identify other organic compounds in the reaction mixture. Samples were prepared by treating 50 ml of 5 mM chlorophenol solutions (pH 10) (*21*). The activator and H_2O_2 were added in aliquots as described above. During the reaction, the solution pH dropped to a final value of 9.5 for both TCP and PCP (H_2O_2 addition lowers the pH by 0.25 units). For TCP, four organic acids were identified by comparison with pure standards and were quantified (35% of total carbon) (*21*): chloromaleic acid **2**, malonic acid **3**, tartronic acid **4**, and chloromalonic acid **5** (Figs. 2 and 3). Mass spectrometry revealed three products with aromatic rings: 2,6-dichloro-4-hydroxybenzoic acid **6**, the aromatic ester **7** (*10*), and trace residual TCP (*21*) (Fig. 2). ^{1}H-NMR revealed four major products with intact aromatic rings, which accounted for approximately 2% of the total carbon (Fig. 3 and Table 1). A number of additional very small signals can be observed in the aromatic region at high sensitivity; the total carbon content integrating across the entire aromatic region [7.0 to 8.5 parts per million (ppm)] is approximately 2.5%. The resonances for TCP and **6** were assigned from standard compounds, whereas those at 8.4 and 7.6 ppm were not identified. The major products identified for PCP oxidation (with ^{1}H-NMR and GC-MS) were dichloromaleic acid **8** and chloromalonic acid **5** (*21*) (Fig. 2 and Table 1). The data in Table 1 clearly show that Fe-TAML activated H_2O_2 very rapidly and substantially mineralized PCP and TCP in pH 10 water under ambient conditions.

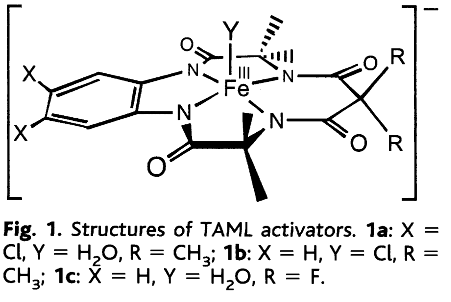

Fig. 1. Structures of TAML activators. **1a**: X = Cl, Y = H_2O, R = CH_3; **1b**: X = H, Y = Cl, R = CH_3; **1c**: X = H, Y = H_2O, R = F.

Residual H_2O_2 after 9 min of reaction was examined for both TCP and PCP oxidations (*21*). In the case of TCP, 10.5% of H_2O_2 was consumed, whereas 19% was consumed for PCP (11% is stoichiometric for complete mineralization of TCP, 9% for PCP). The greater extent of H_2O_2 consumption in PCP oxidation probably results from the higher concentration of Fe-TAML activator used.

The presence of trace coupling products for TCP and residual chlorinated organics prompted us to treat the TCP reaction solution a second time with another 1.25 μM aliquot of $[Et_4N]$**1a** or Li**1b** after adjusting the pH from 9.5 to 10.5 by means of concentrated NaOH to determine whether further degradation might be possible. This reaction mixture was stirred for 30 min, and the standard workup procedure was followed (*21*). The second treatment removed the four major aromatic compounds observed by ^{1}H-NMR remaining from the first treatment, with the exception of the resonance at 7.6 ppm (<1% of total carbon). GC-MS revealed the presence of **7**. Furthermore, the aliphatic acids, **2**, **3**, **4**, and **5** were recalcitrant for TCP, as was **8** for PCP. The maleic acids, **2** and **8**, are the major recalcitrant species.

Permanganate oxidation of various substituted maleic acids has been reported to show decreased reactivity in the order monoanion > acid > dianion (*23*). Thus, we reasoned that if the pH was lowered from 10 (predominant species, chloromaleate dianion) to pH 7 [1% chloromaleate monoanion; pK_a's (where K_a is the acid constant) of chloromaleic acid are 0.17 and 4.9], the rate of oxidation might increase. Oxidation of chloromaleic acid was performed at pH 7.0 (KH_2PO_4/$KHPO_4$ buffer) and 25°C using Li**1c**, the most active Fe-TAML activator at neutral pH, and H_2O_2 (*21*). Complete disappearance of chloromaleic acid was observed after 12 hours, with the simultaneous formation of oxalic acid, as determined by HPLC. Under the same conditions with $[Et_4N]$**1a** or Li_2**1b** in place of Li**1c**, 65% of the chloromaleic acid was degraded in the 12-hour time period. More than 99% of the recalcitrant

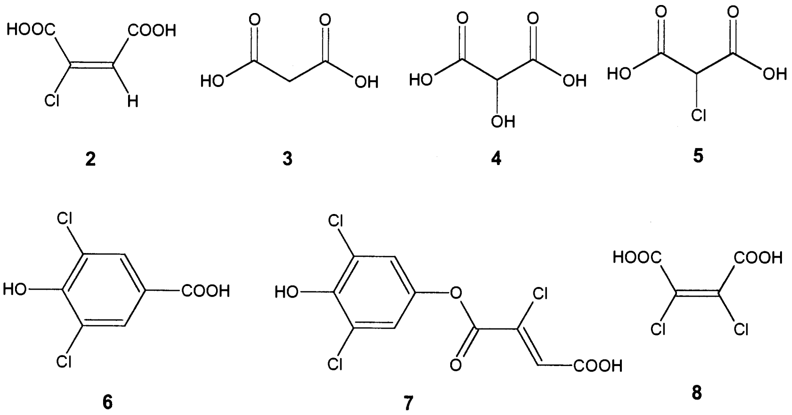

Fig. 2. Products formed after 9 min of TCP and PCP oxidation with $[Et_4N]$**1a**/Li_2**1b**.

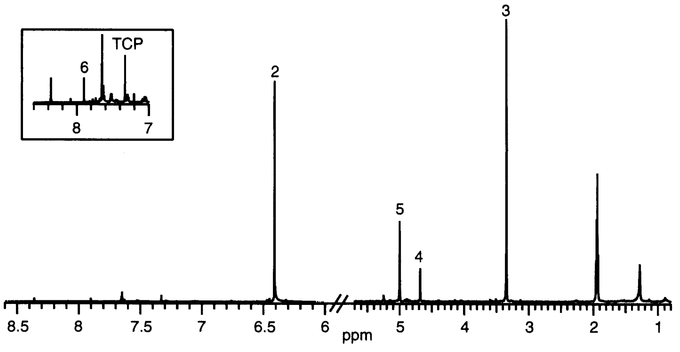

Fig. 3. ^{1}H-NMR spectrum of degraded TCP, >6 ppm at 600 MHz, <6 ppm at 300 MHz.

dichloromaleic acid from the PCP oxidation was observed by HPLC to be degraded after 12 hours, using Li**1c** and H_2O_2 at pH 7 and 25°C. Formation of oxalate was again observed. In short, three successive treatments under ambient conditions of 5 mM TCP with [Et$_4$N]**1a** or Li$_2$**1b** and Li**1c**, along with H_2O_2, converted virtually all of the starting TCP to a mixture of small biodegradable organic acids and CO, CO_2, and HCl. Two treatments of 5 mM PCP with Li$_2$**1b** and Li**1c** led, within experimental error, completely to a mixture of small biodegradable organic acids and CO, CO_2, and HCl.

Complete polychlorinated dibenzodioxin and furan (210 congeners) analyses were performed on the final PCP and TCP reaction mixtures as well as the commercial starting chlorophenols. Detection limits ranged from 120 fg for 2,3,7,8-TCDD to 240 fg for 1,2,3,4,6,7,8-HpCDD. Trace quantities of dioxins and furans already present in the starting commercial PCP and TCP were not increased by the TAML-activated H_2O_2 destruction process (*5*, *8*).

The aquatic toxicities of all three Fe-TAML activators used in this study were assayed with a luminescent bacteria test (*24*). The median effective concentration (EC_{50}) values for each activator, determined with 1 mM stock solutions, were 238 mg/liter for Li$_2$**1b**, whereas those for [Et$_4$N]**1a** and Li**1c** were too low to be determined with 1 mM stock solutions. The LONEC values (the highest observed concentrations of activator that show no bacterial death) for [Et$_4$N]**1a**, Li$_2$**1b**, and Li**1c** were found to be 80, 30, and 58 mg/liter, respectively; the total catalyst concentrations used in this study were approximately 3 mg/liter. The EC_{50} and LONEC values of toxic compounds are much lower than those observed for the three Fe-TAML activators (*24*, *25*). During the course of the reaction, the Fe-TAML activators are themselves oxidatively degraded where we have suggested ideas concerning the mechanism of action of the Fe-TAML activator/H_2O_2 system (*14*, *15*). The EC_{50} for the oxidation products of Li$_2$**1b** was lower than that of Li$_2$**1b** (*26*), and the LONEC value was higher, at 140 mg/liter (30 mg/liter for activator Li$_2$**1b**).

Because of the importance of PCP as a recalcitrant pollutant in ground water, its oxidation was also examined in pure water at pH 7 to approximate conditions in contaminated bodies of water in the environment. In this case, a ~75% saturated solution of PCP in water (1.5 mg/25 ml at 25°C) was prepared for treatment (pH adjusted to 7.0) (*21*), but full analysis was limited by the relatively low solubility of PCP in neutral water (4 mg/50 ml at 20°C compared with the 67 mg/50 ml used above). We found that 2 μM of Li**1c** in the presence of 5 mM H_2O_2 at 25°C was required to completely degrade the PCP from the above solution in 1 hour. Analysis for chloride showed that about 94% of the PCP chlorine was liberated as mineral chloride.

The Fe-TAML/H_2O_2 system efficiently oxidizes the recalcitrant micropollutants PCP and TCP into small biodegradable organic products with substantial mineralization and does so more rapidly than the biological and chemical systems that have been previously reported. The robust nature of the Fe-TAML activators under oxidizing conditions, together with their high inherent reactivity, lead to high catalytic turnover numbers in deep oxidations of chlorophenols over the pH range of 7 to 10.5. Dioxins are not produced by the treatments. With current concerns regarding the proliferation of environmental toxins, a green process for degrading pollutants is greatly needed; this is especially true for chlorinated pollutants. The Fe-TAML/H_2O_2 system shows considerable promise for providing such a technology, subject to favorable full ecotoxicological and toxicological examinations, including persistence and bioaccumulation. Fe-TAML activators are currently undergoing industrial scale-up syntheses in preparation for commercial applications.

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Organic Molecules Acting as Templates on Metal Surfaces

F. Rosei,[1] M. Schunack,[1] P. Jiang,[2] A. Gourdon,[2] E. Lægsgaard,[1]
I. Stensgaard,[1] C. Joachim,[2] F. Besenbacher[2]*

The electronic connection of single molecules to nanoelectrodes on a surface is a basic, unsolved problem in the emerging field of molecular nanoelectronics. By means of variable temperature scanning tunneling microscopy, we show that an organic molecule ($C_{90}H_{98}$), known as the Lander, can cause the rearrangement of atoms on a Cu(110) surface. These molecules act as templates accommodating metal atoms at the step edges of the copper substrate, forming metallic nanostructures (0.75 nanometers wide and 1.85 nanometers long) that are adapted to the dimensions of the molecule.

The adsorption of large functional molecules on surfaces plays a vital role for the emerging field of nanotechnology (*1*), in particular in areas such as molecular electronics (*2*), nanodevices (*3*), and molecular recognition (*4*). Molecular ordering is, in general, controlled by a detailed balance between intermolecular noncovalent binding forces and molecule-substrate interactions (*5*, *6*). It has been inferred that complex molecules such as hexa-*tert*-butyl decacyclene (*7*, *8*), C_{60} (*9*, *10*), and phthalocyanine (*11*) can induce restructuring of metal surfaces accompanied by long-range mass transport. The restructuring is often