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Oxidation of Pollutants Catalyzed by Metallophthalocyanines

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The range of chemical products is larger every year, and these products make an invaluable contribution to different manufacturing industries and, in the end, to our current standard of living. However, chemical production also leads to millions of tons of unwanted byproducts, and the elimination of these wastes is now a key factor for the development of the "green" chemical industry.[1] Efficient catalytic processes should be introduced in fine chemical syntheses ("atom economy" concept to maximize the number of atoms of raw material that end up in the final product).[2] However, before reaching the hypothetical zero-waste level, it is necessary to develop efficient methods to facilitate the degradation of chemical wastes before release into the environment. This is a challenging goal not only for microbiology, since we are used to hoping that microorganisms will do the cleaning job for all chemical wastes, but also for chemistry when wastes, like polychlorinated aromatics, are persistent in the environment because of their resistance to oxidation under aerobic conditions.[3,4] The accumulation of these recalcitrant molecules in the biosphere is also usually associated with biomagnification processes in mammals through the food chain of living systems.

The present Account will be a short survey of the different possible methods of degradation of chemical wastes and a report on our recent results on a new bioinspired catalytic oxidation of chlorinated phenols,[5−7] after a short presentation on the current state of chemicals elimination, with particular attention to chlorinated compounds (see ref 8 for an overview of their industrial utilization).

1. Some Aspects on Current Methods of Waste Elimination

1.1. Incineration. Incineration is a widely used technique for the destruction of chlorinated aromatics. High temperatures and long residence times are usually sufficient to destroy chlorinated aromatics PCB (polychlorinated biphenyls), DDT (1,1-bis(4-chlorophenyl)-1,1,1-trichloroethane), and polychlorobenzodioxins in high-temperature incinerators or cement kilns.

1.2. Supercritical Water Oxidation (SCWO). Above its critical point ($T_c = 374$ °C and $P_c = 221$ bar), water becomes a unique reaction medium where hydrocarbons and molecular oxygen have an infinite solubility. The density of SCW is 0.128 (instead of 0.998 for ambient liquid water), and its viscosity is 0.029 cP (instead of 0.890). With such properties, SCW is attractive for the oxidation of various organic molecules including chlorophenols and PCBs.[1,9−11] Several pilot-scale SCWO systems are operating in the U.S. and Germany. After a few minutes within the reactor, most of the organic molecules are oxidized with a yield of over 99.9%.

Oxidation reactions in SCW involve free-radical mechanisms that also operate in wet air oxidation (WAO). Hydroxyl radicals are produced in SCWOs by direct homolysis of H_2O_2, which is usually added with the compounds to be oxidized (eq 1). Hydroperoxyl radical, a key species in SCWO, results from the attack of a hydrogen atom on dioxygen (eq 2) and is able to abstract a hydrogen atom from water (eq 3).[11]

$$\mathrm{H_2O_2} \rightarrow 2\mathrm{HO}^{\bullet} \tag{1}$$

$$\mathrm{H}^{\bullet} + \mathrm{O_2} \rightarrow \mathrm{HO_2}^{\bullet} \tag{2}$$

$$\mathrm{HO_2}^{\bullet} + \mathrm{H_2O} \rightarrow \mathrm{H_2O_2} + \mathrm{HO}^{\bullet} \tag{3}$$

Acetic acid, alcohols, carbon oxides, and inorganic residues are the main oxidation products of SCWOs of organic pollutants. Benzofurans and dibenzodioxins have been detected in SCW phenol oxidations.[12] To overcome the incomplete oxidation of chlorinated phenols, catalysts have been added to boost SCWO systems.[9,13] Copper and manganese salts are less efficient catalysts in SCWOs of chlorophenols than V_2O_5/Al_2O_3, MnO_2/CeO_2, or TiO_2. One advantage of catalytic SWCO is the absence of coking and poisoning of the catalyst. Coke precursors are soluble in SCW and are further oxidized before deposition. The main drawbacks of SCWOs are the requirement of high temperatures (450−500 °C), high pressures (240−300 atm),

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and pure O_2, as well as severe corrosion problems, all these facts resulting in a high-cost technology.

1.3. Wet Air Oxidation (WAO). Organic compounds can also be oxidized by oxygen from air at pressures and temperatures lower than the critical pressure and temperature of water. This process is known as wet air oxidation. A typical plant operates at 200 °C and 100 bar, and the residence time within the reactor is 1 h. The advantage compared to SCWO is the cheaper cost, but the oxidation is not complete and should be associated with a biodegradation process.

1.4. Chemical Dechlorination. Chemical dechlorination is a rather expensive alternative to thermal treatment used to detoxify PCB-contaminated transformers. The PCB residues are treated with alkali metal poly(ethylene glycolate) and produce low chlorine-containing PCB conjugated to poly(ethylene glycol).[14] A titanium catalyst and borohydride can be an alternative method for reductive dechlorination.[15] The mineralization of chlorofluorocarbons has been recently obtained by heating these CFCs with sodium oxalate at 270−290 °C.[17]

1.5. Electrochemical Treatment of Chlorinated Wastes. The electrochemical degradation of PCBs can be improved when using a surfactant, to favor mass transport of molecules and ions, in combination with a mediator like zinc phthalocyanine. The electrochemical generation of strong oxidants such as cerium(IV) and silver(II) salts in PCB-containing solutions is also effective. Modified PbO_2-film electrodes are promising in the electrochemical degradation of chloroaromatics.[18]

1.6. Photochemical Treatment of Wastes. Many different photochemical techniques have been developed for treating wastewaters. Two major review articles are available.[19,20]

1.6.1. Degradation of Pollutants by UV. Chlorinated aromatics can be degraded by UV irradiation. For example, a 70 μM water solution of 1,2,4-trichlorobenzene was transformed by UV-C photolysis (200−280 nm) with a high yield (90%) within 2 h at room temperature.[21] When an aqueous solution of pentachlorophenol is exposed to sunlight, one chlorine is removed and the resulting tetrachlorohydroquinone is then air-oxidized to chloranil, which is further oxidized to dichloromaleic acid, CO_2, and HCl within 4−5 days.[22] However, such photolysis processes are less efficient than a photodegradation in the presence of an oxidant like H_2O_2 or O_3.

1.6.2. Degradation of Pollutants by H_2O_2/UV. Hydroxyl radical $HO^\bullet$, the active species of the Fenton reaction (Fe^{II}/H_2O_2), is a strong electrophilic oxidant able to abstract a hydrogen atom from all different types of C−H bonds and to add to unsaturated molecules at diffusion rate.[23] However, it must be noted that $HO^\bullet$ generated in diluted water solutions of pollutants are also reacting very quickly with carbonate to produce an inactive carbonate radical anion (eq 4). Chlorophenols are converted by H_2O_2/UV to quinones with elimination of HCl.[19]

$$HO^\bullet + CO_3^{\ 2-} \rightarrow HO^- + CO_3^{\ \bullet-} \qquad k = 2 \times 10^8\ M^{-1}\ s^{-1} \tag{4}$$

1.6.3. Degradation of Pollutants by O_3/UV. The irradiation of aqueous solution of ozone generates $HO^\bullet$ radicals via the homolysis of O_3 and the interaction of excited atomic oxygen with water (eqs 5 and 6).[24,25]

$$O_3 + h\nu < 310\ nm \rightarrow O_2 + O(^1D) \tag{5}$$

$$O(^1D) + H_2O \rightarrow 2HO^\bullet \tag{6}$$

A second route for the production of $HO^\bullet$ involves the formation of H_2O_2 (eq 7).

$$O_3 + H_2O + h\nu < 310\ nm \rightarrow H_2O_2 + O_2 \tag{7}$$

The resulting H_2O_2 is then a source of $HO^\bullet$ radicals via a photohomolysis. Pentachlorophenol (widely used as a pesticide and wood preservative) and lindane (1α,2α,3β,4α,5α,6β-hexachlorocyclohexane) are efficiently degraded by O_3/UV at low concentrations (50−60 μg/L) within 1 h of irradiation with a mercury lamp.[19] A more promising industrial method is the combination of O_3/H_2O_2 and UV irradiation. However, 1,1-dichloroethane or 1,1,1-trichloroethane are not oxidized under these conditions.[19]

1.6.4. Degradation of Pollutants by TiO_2/UV. Over the last two decades, the application of the semiconductor photocatalysis to the degradation of organic pollutants has been largely developed.[20,26] The main degradation products of chlorinated aromatic oxidations mediated by TiO_2/UV are CO_2, HCl, and H_2O. TiO_2 can be excited in different domains of UV light, compatible with sunlight activation. Electronically excited TiO_2 exhibits the strong oxidation potential of an electron-depleted valence band (eq 8) (h^+_{vb} is a valence-band hole and e^-_{cb} a conduction-band electron). Two oxidation reactions have been experimentally observed: (i) an electron transfer from adsorbed substrate RX generating a radical cation (eq 9) and (ii) an electron transfer from adsorbed water molecules producing hydroxyl radicals (eq 10).[20]

$$TiO_2 + h\nu \rightarrow h^+_{\ vb} + e^-_{\ cb} \tag{8}$$

$$TiO_2\ h^+_{\ vb} + RX \rightarrow TiO_2 + RX^{\bullet +}_{\ ad} \tag{9}$$

$$TiO_2\ h^+_{\ vb} + H_2O \rightarrow TiO_2 + HO^\bullet_{\ ad} + H^+ \tag{10}$$

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The balance between these two oxidation pathways is dependent on the nature of the substrate.[27] The competition between the transfer of electrons from adsorbed molecules and electrons of the conduction band is dependent on the nature of the TiO_2 material. The main drawbacks of the TiO_2/UV process are (i) the relatively low quantum yield ($\Phi < 0.05$) and (ii) the limited irradiation zone in a scattering and adsorbing heterogeneous medium. In addition, the recovery of microparticules of TiO_2 from treated water is not an easy process, which suggests finding methods for catalyst immobilization.

1.7. Degradation of Pollutants by Sonochemistry. The ultrasonic activation of water solutions is able to break the hydrogen bond network between water molecules and produces at the microscopic level the heat necessary for the thermal homolytic splitting of H_2O-generating hydroxyl radicals and hydrogen atoms. These two reactive species produce a rather exotic mixture of oxidative and reductive chemistry. This method has been used to oxidize chlorinated solvents and pentachlorophenol.[28] Large-scale reactors are now commercially available.[29]

1.8. Biological Degradation of Pollutants. Microorganisms able to utilize many different chemicals as sources of carbon atoms are obvious candidates for clean degradation methods of pollutants. In addition, the fast adaptation of microorganisms to a new source of feeding allows a selection of new strains suitable for pollutant degradation.[30,31] Dehalogenating enzymes can be classified according to three different mechanisms: (i) hydrolytic dehalogenation, (ii) reductive dehalogenation, and (iii) oxidative dehalogenation.[4,32,33]

1.8.1. Hydrolytic Dehalogenation. Halogenated alkanes such as 1,2-dichloroethane can be hydrolyzed by an enzyme produced by *Xanthobacter autotrophicus*. The structure of this hydrolytic enzyme reveals that the Cl atom is displaced by the nucleophilic attack of Asp 124.[34] The active site residues of 4-chlorobenzoyl-coenzyme A dehalogenase have also been identified.[35] An aspartic residue (Asp 145) is also responsible for the nucleophilic displacement of the chlorine atom as chloride ion.

1.8.2. Reductive Dehalogenation. Reductive dehalogenation involves an initial electron-transfer reaction to produce $RX^{\bullet-}$ and the release of halides within the active site of the enzyme. The reduced form of the enzyme can be the iron(II) center of a cytochrome P-450 enzyme or a glutathion-dependent enzyme.[33,36,37] Such bioreductive dehalogenation has been mimicked with low-valent transition metal complexes.[38] However, it should be noted that these bioreductive dehalogenation processes involve the accumulation of hydrophobic halogenated aromatics within cell membranes to be available for the reduction by intracellular or membrane-associated enzymes. During the enzymatic transformation of these pollutants, produced intermediates might be toxic to the microorganism (this remark is also true for oxidative dehalogenations). Pentachlorophenol and tetrachlorophenol are biotransformed to trichlorophenol by reduction, but this latter is not further reduced by microorganisms.

1.8.3. Oxidative Dehalogenation. Polychloroaromatics are reluctant to oxidative degradation because of (i) their high redox potentials, making difficult the generation of a radical cation by peroxidases, and (ii) the weak reactivity of aromatic C−H bonds in hydroxylations mediated by monooxygenases. Very few enzymes are able to catalyze the oxidation of polychlorophenols. Among monooxygenases, PCP 4-hydroxylase from *Flavobacterium sp.* strain ATCC 39723 catalyzes the formation of tetrachlorohydroquinone, and ^{18}O labeling studies indicate that one oxygen atom from O_2 is incorporated into the product.[39] A cytochrome P-450 of *Rhodococcus chlorophenolicus* PCP-1 is also able to produce the same tetrachloroquinone, but the oxidative dechlorination is very slow with activity expressed in nanomoles per milligram of protein per hour.[40] A PCB-degrading strain of *Pseudomonas cepacia* catalyzes the oxidation of 2-chlorobenzoate to catechol with a flavin-dependent oxygenase based on a [2Fe−2S] cluster.[41]

Trichlorophenols are among the most resistant substrates to biodegradation by aerobic and anaerobic microorganisms, and they are difficult to reduce and oxidize. These pollutants, produced by paper mills using chlorine-based oxidants,[42] are obvious paradigms for studies on biological or chemical oxidations.

Chlorophenols are metabolized by the lignin-degrading fungus *Phanerochaete chrysosporium* via successive oxidation and reduction steps.[43−45] Several companies are trying to develop soil remediation by using this fungus.[46] One of the extracellular peroxidases secreted by *Phanerochaete c.* is a heme-peroxidase having a high-redox-potential compound I (LiP-I) able to oxidize substrates reluctant to horseradish peroxidase oxidations. The structure of ligninase has been solved,[47] but the origin of the high oxidative capacity of Lip-I is still a matter of debate.[48] The weak point of ligninase, limiting its use, is the formation of Lip-III*, a compound III form of LiP which

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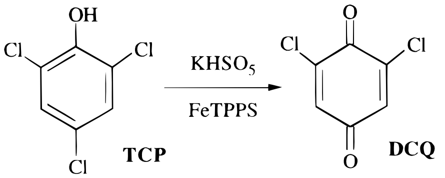

FIGURE 1. Oxidation of 2,4,6-trichlorophenol (TCP) to 2,6-dichloro-1,4-benzoquinone (DCQ) by the FeTPPS/KHSO$_5$ system.

reacts with H_2O_2 to give rise to the bleaching of the prosthetic group, at peroxide concentrations above 10–20 μM.[49] For these reasons, we decided to develop chemical models able to oxidize recalcitrant molecules such as trichlorophenols.

2. A Bioinspired Oxidation of Chlorophenols Using Hydrogen Peroxide and an Iron Tetrasulfophthalocyanine Catalyst.

We developed chemical models of ligninase with water-soluble iron and manganese sulfonated porphyrins (M^{III}TPPS, TPPS = dianion of *meso*-tetrakis(4-sulfonatophenyl)porphyrin) using H_2O_2 or KHSO$_5$ as oxidants.[50–52] We also found that these biomimetic complexes were able to catalyze very efficiently the oxidation of 2,4,6-trichlorophenol (TCP) to the corresponding 2,6-dichloro-1,4-benzoquinone (DCQ) (Figure 1).[53] At low catalyst/substrate molar ratios (0.1–0.3%), turnover rates were as high as 10–20 cycles/s with KHSO$_5$. However, the limits of this catalytic reaction are a lower catalytic activity with H_2O_2, the cost of metalloporphyrins, and the absence of deep oxidation of the generated quinone.

For all of these reasons, we looked for a catalytic system able to degrade trichlorophenols according to the following criteria: the catalyst should be cheap and readily available, the oxidant should be H_2O_2 (the "clean" oxidant, water being the only byproduct after oxidation), and the oxidation of TCP should provide ring cleavage products and CO_2 like in a biomineralization process.

We recently found that iron(III) tetrasulfonatophthalocyanine (FePcS, see Figure 2 for structure) was able to catalyze the H_2O_2 oxidation of TCP in the reaction conditions listed above.[5–7] Since phthalocyanines are industrial dyes, metallophthalocyanines are an attractive alternative as readily available biomimetic (in fact "bioinspired") oxidation catalysts. CuPcS and CoPcS are already manufactured as dye and catalyst for the oxidation of mercaptans in gasoline fractions,[54] respectively. Up to now, iron and manganese phthalocyanine catalysts were found to be less active in oxidation reactions than metalloporphyrins.[55,56] FePcS can be prepared in high yield (65–70%) in a one-step reaction by improving the Weber–Busch method.[57,58] The analysis is consistent with a μ-oxo $Fe^{III}-O-Fe^{III}$ dimer structure with an intense visible band at 632 nm.[7,58]

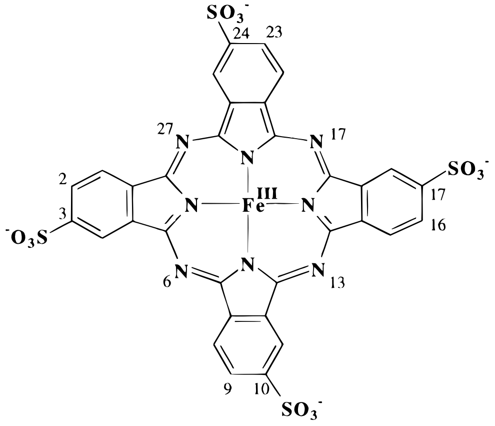

FIGURE 2. Structure of iron(III) tetrasulfonatophthalocyanine (FePcS). Only one of the four possible regioisomers is depicted (the 3,10,17,24 isomer). FePcS should be a mixture of four isomers: Fe(3,10,17,24-tetrasulfonato-Pc), Fe(3,9,17,23-tetrasulfonato-Pc), Fe(3,9,16,24-tetrasulfonato-Pc), and Fe(3,9,16,23-tetrasulfo-Pc) with a statistical distribution of 1/1/2/4. For the formation of dimers via μ-oxo bridges, see the text.

2.1. Analysis of the Oxidation Products of 2,4,6-Trichlorophenol by FePcS/H_2O_2. When 3.7 mol % of FePcS and 5 equiv of H_2O_2 with respect to the substrate in a mixture of acetonitrile/buffered water (1/3, v/v) at pH 7 were used, TCP was quantitatively converted at room temperature within a few minutes (TCP concentration = 2000 ppm).[5] The transient formation of DCQ and the release of two Cl^- ions per consumed TCP molecule strongly suggested that TCP was converted to ring-cleavage products. The final products were identified and quantified by GC–MS and NMR analyses and fell in two categories: five products corresponding to aromatic ring cleavage and four resulting from oxidative coupling of TCP (Figure 3).[5,7] The total yield of identified products was 60–70% after 60 min of reaction at room temperature.

The major TCP cleavage product was chloromaleic acid **1** (yield = 24%). Chlorofumaric **2**, maleic **3,** and fumaric **4** acids were only minor products. Oxalic acid **5** was among the products of TCP oxidation.[7] This C_2 diacid is an expected partner with chloro-C_4 diacids as signature of the oxidative TCP ring cleavage. Four TCP coupling products (**6**–**9** of Figure 3) have been identified by mass spectrometry.[5,7] These coupling products are probably generated via the radical form of TCP produced by the one-electron oxidation of the TCP phenolate. The product distribution profiles of FePcS-catalyzed TCP oxidations are dependent on the initial concentration of TCP and on the substrate/catalyst ratio.[5,6]

2.2. Oxidation of TCP by FePcS/H_2O_2 in the Presence of $H_2{}^{18}O$ or $^{18}O_2$. GC–MS analyses of TCP oxidation products generated by FePcS/H_2O_2 in $H_2{}^{18}O$ suggested that the main source of oxygen atom in chloromaleic acid was not water but H_2O_2, since only one labeled oxygen atom was detected on one of its carboxylic functions.[7] After 10 min of reaction under $^{18}O_2$, only 11% of chloromaleic acid was labeled with one ^{18}O atom, indicating that incorpora-

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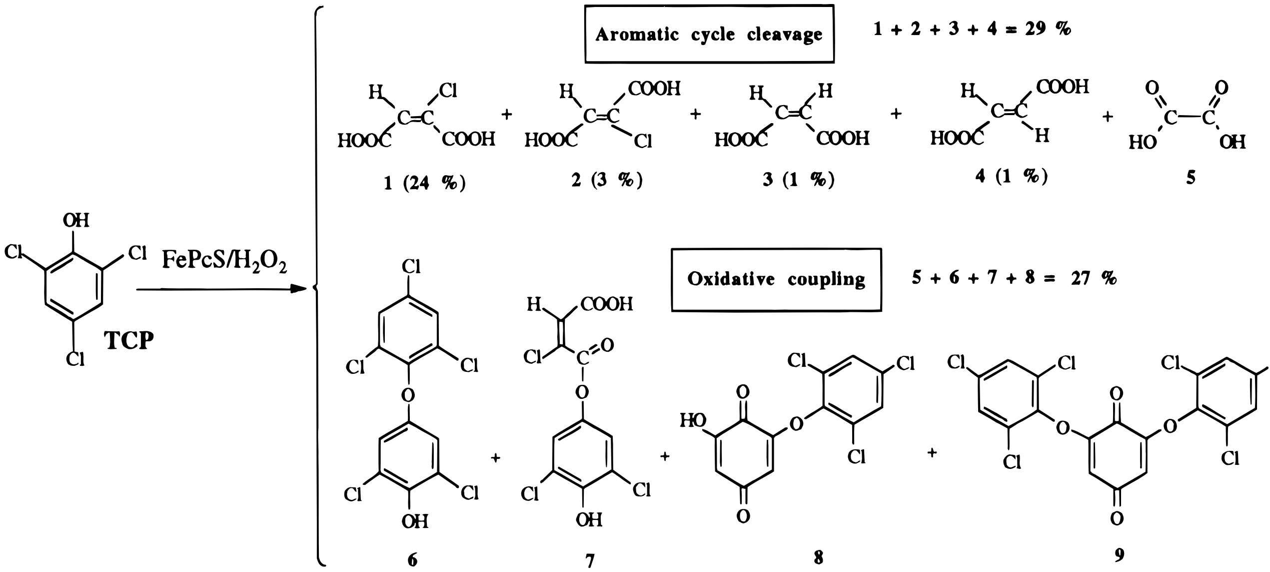

FIGURE 3. Main characterized products in the H_2O_2 oxidation of 2,4,6-trichlorophenol (TCP) catalyzed by FePcS.

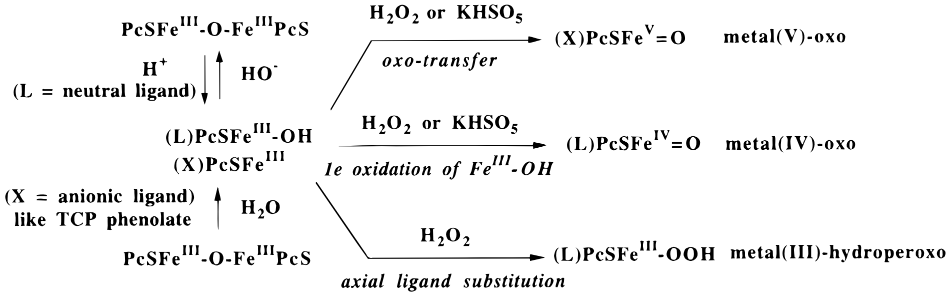

FIGURE 4. Generation of iron−oxo and iron−peroxo species by activation of FePcS with hydrogen peroxide or potassium monopersulfate.

tion of oxygen atoms from dioxygen was low compared to that arising from H_2O_2 or H_2O.[7] All of these oxygen labeling experiments strongly suggested that the oxygen atom sources in TCP ring cleavage products were, in decreasing order, hydrogen peroxide, water, and then dioxygen.

2.3. CO_2 Formation in the TCP Oxidation by FePcS/H_2O_2. The major products of ring cleavage in the TCP oxidation by FePcS/H_2O_2 are C_4-diacids such as chloromaleic acid. But we found that these diacids can also be degraded by the catalytic system. Consequently, to avoid any possible artifact, we decided to investigate the formation of CO_2 from TCP by monitoring the release of labeled CO_2 during the oxidation of a (U-^{14}C)-TCP by FePcS/H_2O_2 to have a complete material balance of oxidation products.[6] The specific activity of labeled TCP was 62 mCi/mmol with a radiochemical purity of 98.5%.[59]

The catalytic oxidation of (U-^{14}C)-TCP by FePcS/H_2O_2 was performed with 0.074 and 10 mol equiv of FePcS and H_2O_2 versus TCP, respectively, at room temperature, and products were analyzed after 90 min of reaction. Eleven percent of the initial radioactivity was recovered as CO_2. The ^{14}CO yield was 3% of the starting TCP, increasing the total yield of carbon oxides to 14%. Sixty-nine percent of the initial TCP radioactivity was detected in the aqueous phase, as expected for intermediate C_4-diacids resulting from TCP ring cleavage. Only 13% of the TCP radioactivity was recovered as hydrophobic organic products resulting from oxidative coupling reactions, suggesting that these TCP dimers were cleaved to water-soluble derivatives. This study with radiolabeled TCP gave a complete overview of the oxidative degradation of TCP since 96 ± 6% of the initial radioactivity was recovered. The FePcS/H_2O_2 catalytic system was able not only to cleave the TCP aromatic cycle but also to mineralize such pollutants to CO_2 and inorganics.

2.4. Proposed Mechanism for TCP Oxidation by FePcS/H_2O_2. 2.4.1. Nature of the Active Metal−Oxygen Species. Control experiments showed no influence of the presence of hydroxyl radical traps on TCP oxidation, indicating that TCP oxidation was not mediated by $HO^\bullet$ radicals generated by a possible metal-assisted homolysis of the weak peroxidic bond of H_2O_2. The initial step before the formation of active metal−oxygen species in oxidation reactions catalyzed by FePcS is the cleavage of the μ-oxo dimer to an iron(III) monomer (see Figure 4). The monomer formation is favored at acidic pH or by the presence of a strong anionic ligand (like TCP phenolate) or by a dissociating solvent. Then the oxidation of FePcS might generate three different iron-centered oxidizing species (Figure 4) depending on the oxidant. When the oxidant is an efficient oxygen atom donor like $KHSO_5$, it might be able to produce an iron(V)−oxo species as with metalloporphyrin precursors.[51,60] Depending on the nature of the axial ligand and the macrocycle, the formal oxidation state of the iron center might be IV with a radical cation on the macrocycle or on the axial ligand. For an

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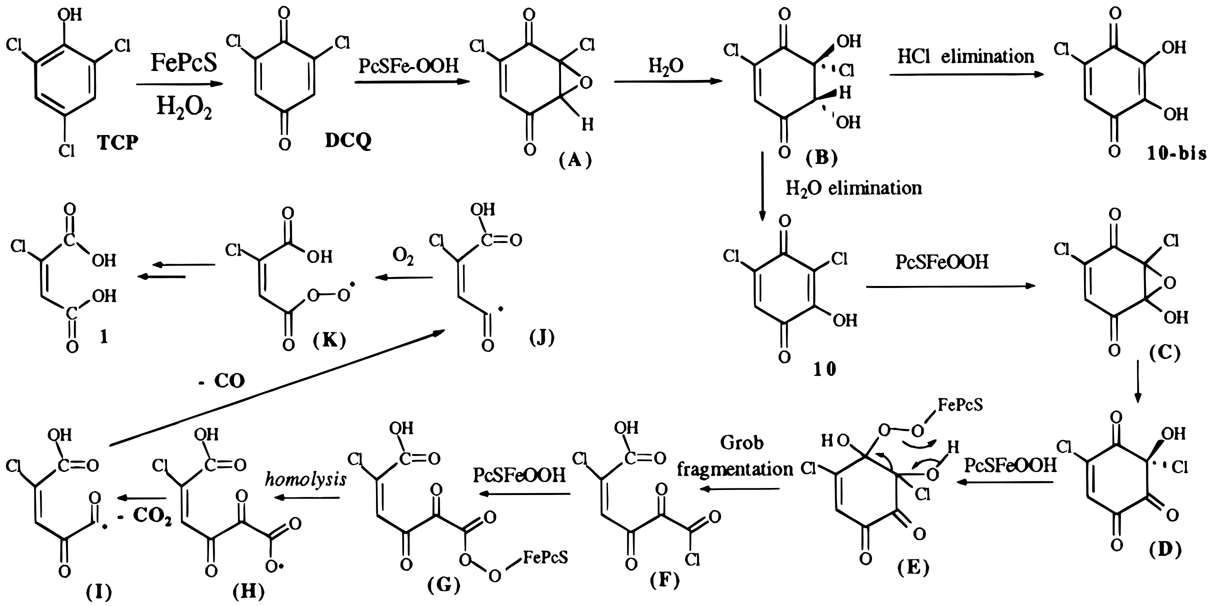

FIGURE 5. Proposed mechanism for the aromatic ring cleavage of TCP by FeTPPS/H_2O_2. Compounds indicated by a capital letter (A−K) have not been identified and must be considered as possible intermediates of a current working hypothesis on the catalytic degradation of TCP. Isomerization of J would lead to chlorofumaric acid. I might also be trapped by dioxygen, giving rise to a second possible route for CO_2 evolution.

efficient oxygen atom transfer high-valent iron−oxo entities should be two redox equivalents above the iron(III) state (see refs 61−63 for recent data on oxygen atom transfers catalyzed by water-soluble metalloporphyrins). Since FePcS is unable to catalyze the epoxidation of electron-rich olefins with H_2O_2 or $KHSO_5$ at pH 7, such species, namely iron(V)−oxo, are probably not present in the reaction mixture (water-soluble metalloporphyrins are able to catalyze the epoxidation of olefins in aqueous solutions with $KHSO_5$[61]). Another species able to abstract electrons from TCP will be the iron(IV)−oxo complex resulting from the one-electron oxidation of an iron(III)−OH entity with departure of one proton. When $KHSO_5$ was used as the oxidant, TCP was quickly oxidized to DCQ, but this quinone was then oxidized at a lower rate compared to the initial rate of TCP conversion. The fast degradation of quinones with FePcS/H_2O_2 suggested the presence of a nucleophilic oxidizing species rather than an electrophilic metal−oxo complex like (X)PcSFe^{V}=O or (L)PcSFe^{IV}=O. With H_2O_2, a third activation mode of the metal center is possible and corresponds to the substitution of an axial anionic ligand by H_2O_2 to generate a metal−hydroperoxo (L)PcSFe^{III}−OOH, which is probably deprotonated at pH 7. Such Fe(III)−OOH entities are able to oxidize quinone derivatives by nucleophilic addition.[7,64] Such complexes cannot be produced by $KHSO_5$, explaining why the FePcS/$KHSO_5$ system was unable to quickly oxidize DCQ after the two-electron oxidation of TCP.

2.4.2. Working Hypothesis on the Mechanism of the TCP Oxidation by FePcS/H_2O_2. DCQ formation results from the one-electron oxidation of the phenolate form of TCP at pH 7 by (L)PcSFe^{III}−OOH or (L)PcSFe^{IV}=O. Then the phenoxy radical is oxidized to an aromatic carbocation which reacts with water to give rise to the corresponding DCQ with the release of one Cl^- ion.[7] Besides the formation of DCQ, radical intermediates might be trapped by O_2 and cationic or radical species can react with an excess of TCP, leading to dimers or trimers.

The relatively fast oxidation of DCQ (the key step in the biomimetic mineralization of TCP) is probably mediated by PcSFeOOH acting as a nucleophilic oxidant able to produce the two violet quinones **10** and **10-bis** (see Figure 5 for the present state of our current working hypotheses on the FePcS-catalyzed oxidation of TCP). These two quinones have been isolated after a reaction time of 4 min. A second epoxidation by PcSFeOOH provides **D** via **C**. The C−C bond cleavage of **D** might be due to the nucleophilic attack of PcSFeOOH on one quinone carbonyl group, leading to **F** via a Grob fragmentation.[65] CO_2 might be formed after the homolytic cleavage of **G** produced by the nucleophilic addition of PcSFeOOH onto **F**. After decarbonylation and dioxygen incorporation, intermediate **K** would lead to chloromaleic acid **I**, the major C4-diacid identified in the reaction mixture. All of the key steps of the deep oxidation of the different chlorinated quinones by FePcS/H_2O_2 involve only one active metal−peroxo species, PcSFeOOH, which might be considered as a unique feature of this new catalytic mode of degradation of chlorinated aromatics. The initial addition of the nucleophilic Fe−OOH entity provides the formation of hydroxyquinones, and then the same intermediate can attack a carbonyl adjacent to a hydroxyl substituent to generate a −CX(OH)−C(OH)−OOFePcS entity allowing the fragmentation of a C−C bond of the original aromatic cycle.

2.5. Pentachlorophenol Oxidation. Pentachlorophenol (PCP) is also highly recalcitrant to aerobic biodegradation.[22] For example, *Rhodococcus chlorophenolicus* PCP-

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1, a strain known to dechlorinate aerobically several polyhalogenated phenols via an oxidative process catalyzed by a cytochrome P-450, is poorly able to mediate PCP degradation. PCP is converted by the purified enzyme at a turnover rate of 2.26 nmol of PCP/mg of protein/h, e.g. few catalytic cycles per hour.[40] We found that FePcS was a rather efficient catalyst of PCP oxidation with H_2O_2 (96% of conversion within 5 min with 1% of catalyst/PCP).[7] Dechlorination of PCP ranged from 0.34 to 1.43 Cl^- released per converted PCP molecule depending on initial PCP concentration. This rather low level of dechlorination is mainly due to the presence of a dimer compound still containing 10 Cl atoms.[7] Dichloromaleic anhydride was the only identified product resulting from the oxidative cleavage of PCP. The poor solubility of PCP oxidative coupling products allowed an easy recovery by filtration. Seven coupling products have been detected (three dimers and four trimers).[7] Chlorodibenzodioxins and chlorodibenzofurans were not detected in the oxidations of PCP and TCP. Peroxidase-mediated formations of chlorinated dibenzodioxins and dibenzofurans have been published for trichlorophenol biological oxidations.[66]

Concluding Remarks

These findings indicate that a recalcitrant pollutant like 2,4,6-trichlorophenol can be deeply oxidized to CO_2 by H_2O_2 and an iron sulfophthalocyanine catalyst in aqueous solutions. The FePcS/H_2O_2 is an alternative method to the biodegradation of chlorinated phenols by white rot fungus *Phanerochaete chrysosporium*[45,67] or by environmental bacterial strains[68] since this chemical system would be less sensitive to experimental conditions used in waste treatment. For example, the mineralization process is dependent on the level of supplied nitrogen of fungus culture medium.[45] Sixty-one percent of 2,4,5-(U-^{14}C)-TCP was degraded to $^{14}CO_2$ in nitrogen-limited cultures after a 36-day incubation, while only 8% of the substrate was mineralized under nitrogen-sufficient conditions.[45] In conclusion, the catalytic system FePcS/H_2O_2, which is easy to handle, might have a future in the oxidative removal of pollutants, especially in the treatment of large amounts of concentrated pollutants of process waters still containing organic solvents,[58] i.e. in conditions making difficult an efficient use of microorganisms.

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