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CO_2 as the Ultimate Degradation Product in the H_2O_2 Oxidation of 2,4,6-Trichlorophenol Catalyzed by Iron Tetrasulfophthalocyanine

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Chlorinated aromatic compounds such as 2,4,6-trichlorophenol (TCP) are well-known recalcitrant pollutants because of their slow biodegradation by microorganisms.[1−4] Efficient chemical catalysts are therefore needed to convert recalcitrant pollutants to more biodegradable molecules or to CO_2 and inorganics, mimicking a biomineralization process.

We recently reported the efficient oxidative dechlorination and aromatic cycle cleavage of TCP by H_2O_2 catalyzed by FePcS.[5] This molecule is one of the major chlorinated phenols produced by paper mills in the delignification of wood pulp by chlorine bleaching.[6] TCP was oxidized to a mixture of chloromaleic, chlorofumaric, maleic, and fumaric acids and also to oxidative coupling products. The number of Cl^- ions released in the TCP oxidation was found to be 2.1 Cl^- ions per converted molecule of TCP.[5] The major product of the oxidative aromatic cycle cleavage of TCP was chloromaleic acid (isolated yield = 24%). However, we found that the C_4-diacids were not the ultimate products of aromatic ring cleavage. Then the question arose: is this catalytic system able to perform the oxidative mineralization of TCP to carbon dioxide and inorganics? To answer this question without possible artifacts, we decided to investigate the oxidation of a (U-^{14}C)-TCP by FePcS−H_2O_2 in order to have a complete material balance of oxidation products including the putative formation of CO_2. (U-^{14}C)-TCP was obtained by oxidative chlorination of (U-^{14}C)phenol.[7] The specific activity was 62 mCi/mmol, and the radiochemical purity was 98.5%.

We performed the catalytic oxidation of (U-^{14}C)-TCP by FePcS−H_2O_2 (0.074 and 10 molar equivalents of FePcS and H_2O_2 versus TCP, respectively) in the experimental conditions indicated in ref 8. We checked by HPLC and TLC coupled with radiochemical detection that TCP was fully converted after 90 min at room temperature (in fact, TCP was converted in the early stage of the reaction, after 5 min). Chloride ion production determined by mercuric thiocyanate method[10] was 2.06 ± 0.06 Cl^- per converted TCP molecule.

Volatile products were displaced from the reaction flask (25 mL) by N_2 bubbling and were trapped by 0.1 M NaOH solution. Eleven percent of the initial radioactivity was recovered in this trap. This CO_2 formation was unambiguously evidenced by replacing the NaOH solution with a 0.1 M $BaCl_2$ solution. The ratioactive white precipitate of barium carbonate confirmed the evolution of carbon dioxide during the catalytic oxidation of TCP. When the $Ba^{14}CO_3$ precipitate was separated, no radioactivity was detected in the mother solution.

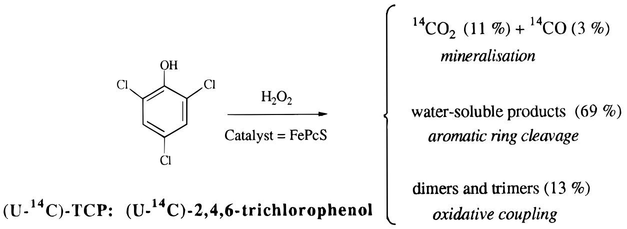

Figure 1. Recovered radioactivity in the oxidative degradation of (U-^{14}C)-TCP by FePcS−H_2O_2. See ref 5 and Figure 2 for the structures of water-soluble and oxidative coupling products.

Formaldehyde and carbon monoxide were two other possible volatile products formed in TCP oxidation. No formaldehyde was evidenced after the full conversion of TCP by using the Nash method[11] or by GC−MS detection of the formaldehyde−dimedone adduct.[12] Carbon monoxide was detected on a GC column filled with 5 Å molecular sieves. To quantify the formation of carbon monoxide, ^{14}CO was oxidized to $^{14}CO_2$ (see ref 8) and analyzed after trapping in a 0.1 M NaOH solution. The ^{14}CO yield was 3% of the starting TCP. Therefore, the total yield of carbon oxides was 14%. The addition of catalyst and oxidant in two portions or a decrease of TCP concentration had no significant influence on product distribution (see run 2 of Table 1 for a reaction at 2.5 mM TCP concentration instead of 5 mM).

After 90 min of reaction, the radioactivities corresponding to water-soluble products and organic compounds were quantified (see Figure 1). Sixty-nine percent of the TCP radioactivity was recovered 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. The degradation products of TCP have been previously identified (the lower ratio of coupling products obtained in these reaction conditions strongly suggests that they are also cleaved to water-soluble derivatives).[5] With the present study, we have now a complete overview of the oxidative degradation of TCP since 96% ±

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(8) A typical experiment consisted of 40 μmol of (U-^{14}C)-TCP (1 mL of a 40 mM stock solution in acetonitrile. Specific activity of TCP = 62 mCi/mmol), 2.96 μmol of FePcS catalyst (2 mL of 1.48 mM solution in water, FePcS was prepared according to ref 9), 1 mL of acetonitrile, and 4 mL of 0.5 M phosphate buffer, pH 7.0. The reaction was initiated by addition of 400 μmol of H_2O_2 (40 μL of 35% solution) and stirred at room temperature. A conversion of (U-^{14}C)-TCP was monitored by HPLC (Lichrosorb C18-5μ column, eluent of methanol−water 75:25, v/v, 35 °C, flow rate of 1.5 mL/min., radiochemical detection with Berthold LB 503) and thin layer chromatography (silica gel Merck 60 F254, hexane−ethyl acetate 90/10, v/v. Radiochemical detection: Berthold LB 2821). Cl^- release was determined at the end of reaction. Volatile products were displaced by a nitrogen bubbling starting 10 min after the beginning of the reaction. The flushing was continued for 80 min. $^{14}CO_2$ formed was trapped by placing the exit glass capillary in 3 mL of 0.1 M NaOH solution in a 25 mL two-neck flask, which, in turn, was connected with a carbon monoxide low-range detector tube (detecting limit 1 ppm, Gastec Corporation, Japan) to oxidize ^{14}CO to $^{14}CO_2$ by potassium disulfitopalladate(II): $CO + K_2Pd(SO_3)_2 \rightarrow CO_2 + Pd(0) + K_2SO_3 + SO_2$. $^{14}CO_2$ generated by ^{14}CO oxidation was trapped in a second trap containing 3 mL of a 0.1 M NaOH solution. Preliminary experiments with additional trapping flasks in series demonstrated that all radioactivity was retained in these traps after the 80 min nitrogen bubbling. Counting of radioactivity of the reaction mixture and both trapping solutions was performed with a Berthold Nuclear Spectrometer L 13 2040. Then the reaction mixture was separated after treatment with diethyl ether (3 × 20 mL) into aqueous and organic phases, containing water-soluble and organic-soluble products, respectively. Radioactivity of each phase was determined.

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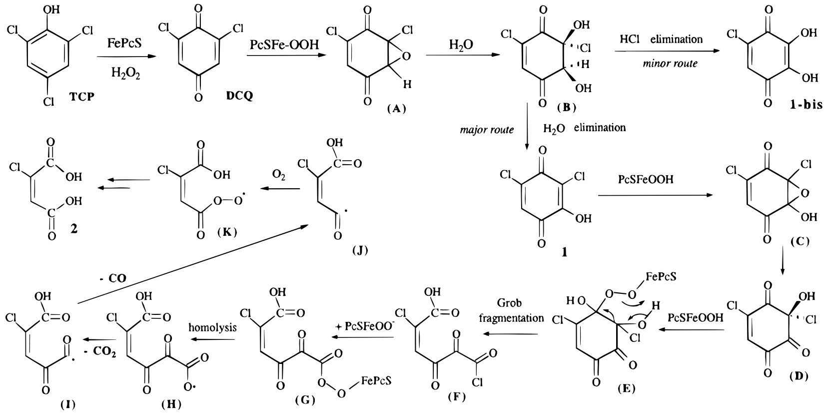

Figure 2. Presentation of some of the different possible pathways involved in the H_2O_2 degradation of TCP catalyzed by FePcS.

Table 1. Hydrogen Peroxide Oxidation of (U-^{14}C)-2,4,6-Trichlorophenol (TCP) Catalyzed by FePcS

		radioactivity (yield in %) recovered as			
run	TCP concentration (initial radioactivity)	water-soluble products	CO_2	CO	organic-phase products
1[a]	5 mM (2.1 mCi)	69 ± 2	11 ± 2	3 ± 1	13 ± 1
2[b]	2.5 mM (1.0 mCi)	74	10	4	11

[a] Run 1: total yield of recovered radioactivity = 96% ± 6% (experimental errors were obtained from three independent reactions). [b] Run 2: total yield (result of one experiment) = 99%.

6% of the initial radioactivity was recovered.[13] So, the FePcS−H_2O_2 catalytic system was able not only to cleave the TCP aromatic cycle but also to mineralize such a recalcitrant pollutant. A possible mechanism of formation of CO_2 and CO is depicted in Figure 2, taking into consideration intermediate products, previously identified (**DCQ** and **2**)[5] or described in the present work (**1, 1-bis**,[14] **CO_2**, and **CO**). PcSFeOOH acts as a nucleophilic oxidant able to epoxidize **DCQ** (2,6-dichloro-1,4-benzoquinone), leading to the formation of two violet quinones **1** (major intermediate) and **1-bis** (minor intermediate). A second epoxidation by PcSFeOOH provides **D** via **C** (see ref 15 for a recent report on the epoxidation of electron-deficient olefins by iron(III)−peroxo complexes). The C−C bond cleavage of **D** might be due to the nucleophilic attack of PcSFeOOH on one quinone carbonyl group giving rise to **F** as the result of a Grob fragmentation.[16] CO_2 might be formed after the homolytic cleavage of intermediate **G** produced by nucleophilic addition of PcSFeOOH to **F**. Other CO_2 might also be due to the oxidative degradation of any intermediates bearing a carboxylic acid function (the depicted pathway for CO_2 formation is one possibility among several others). After decarbonylation and O_2 incorporation, intermediate **K** would lead to chloromaleic acid **2**, the major C_4-diacid identified in the reaction mixture. The small amount of chlorofumaric acid which has also been identified in the TCP oxidation by FePcS/H_2O_2 might be produced by isomerization of intermediate **J**.

FePcS can be also used as a supported catalyst by impregnation of an ion-exchange resin like Amberlite IRA 900.[17] These supported catalysts (FePcS−Amb) can be recycled several times without significant loss of activity. Amberlite IRA 900 is a modified poly(vinylbenzene) resin with ammonium groups able not only to strongly interact with the sulfonato groups of the metallophthalocyanine catalyst by electrostatic interactions but also to retain C_4- and C_2-acid residues resulting from the oxidative degradation of TCP. In fact, we found that the yield of water-soluble products, organic products, and CO_2 were 4, 3, and 1%, respectively, and no CO was detected (we used 0.94 μmol of FePcS impregnated onto 222 mg of Amberlite corresponding to 4.7% of catalyst with respect to the substrate, 20 μmol). This low amount of released radioactivity in solution was compensated by a strong radioactivity detected on the resin itself, confirming that the ammonium groups of this catalyst support were able to fix the carboxylic acid residues generated during the TCP oxidation. This property of FePcS−Amb catalyst could be beneficial if pollutants should be removed from drinking water, both amberlite resins and hydrogen peroxide being acceptable chemicals in the treatment of drinking water.

The FePcS/H_2O_2 is complementary to the biodegradation of chlorinated phenols by white rot fungus *P. chrysosporium*,[18−20] since this chemical system would be less sensitive to experimental conditions. For example, the mineralization of ^{14}C-labeled pentachlorophenol (PCP) is dependent of the level of supplied nitrogen of fungus culture medium.[18,19] High nitrogen levels considerably lower the mineralization of chlorophenols. After a 36-day incubation approximately 61% of the 2,4,5-(U-^{14}C)-TCP was degraded to $^{14}CO_2$ in nitrogen-limited cultures while only 8% of the substrate was mineralized in nitrogen-sufficient conditions.[18] Furthermore, mineralization may not occur in the field to the extent found in laboratory studies.[4,21]

As concluding remark, the catalytic system FePcS−H_2O_2 might have a future in the oxidative removal of pollutants, providing more biodegradable material (C_4 unsaturated diacids), carbon dioxide, and chloride ions with an environmentally friendly oxidant and a cheap catalyst.

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Supporting Information Available: Details of the characterization of **1** and **1-bis** (1 page). See any current masthead page for ordering and Internet access instructions.

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(13) As pointed out by one of the referees, it must be noted that in the TCP oxidation two out of three Cl are recovered as chloride anion, and of the six carbons in TCP, approximately one ends up as carbon monoxide/carbon dioxide and one as organic material and four end up as water-soluble products.

(14) Details on characterization of **1** and **1-bis** are available as supporting information.

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