Oxidative Degradation of Polychlorinated Phenols Catalyzed by Metallosulfophthalocyanines

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Abstract: 2,4,6-trichlorophenol (TCP) is oxidized by potassium monopersulfate or hydrogen peroxide in the presence of iron or manganese tetrasulfonatophthalocyanines (FePcS or MnPcS) to yield not only the corresponding 2,6-dichloro-1,4-benzoquinone but also ring-cleavage products. Catalytic oxidation of the TCP ring by hydrogen peroxide is more efficient than by potassium monopersulfate, despite a slower substrate conversion, suggesting that different mechanisms are involved for these two catalytic systems: a metal–oxo mechanism for FePcS/$KHSO_5$ and a metal–peroxo mechanism for FePcS/H_2O_2. Eight different final oxidation products and four quinone intermediates have been identified in the oxidation of TCP by the FePcS/H_2O_2 catalytic system. Chloromaleic acid is the main product of the oxidative ring cleavage. An iron–peroxo complex PcS-FeOOH is probably the active species responsible for the epoxidation of 2,6-dichloro-1,4-benzoquinone and the C–C bond cleavage of 3,5-dichloro-2-hydroxy-1,4-benzoquinone ring, both intermediates generated during the catalytic TCP degradation. The oxidation of pentachlorophenol (PCP) is also catalyzed by FePcS or MnPcS with $KHSO_5$ or H_2O_2.

Keywords
chlorophenols · iron complexes · manganese complexes · phthalocyanines · pollutant degradation

Introduction

The diminution of the production of nonbiodegradable chemical wastes is a major goal in the move to "clean chemistry", but when zero-waste chemical methods are not available, the release of biotransformable wastes can be considered as an acceptable alternative. Many potential pollutants can be converted into easily degradable compounds by hydrolysis, reduction, and/or oxidation pathways by microorganisms that utilize intra- and extracellular enzymes.[1, 2] However, some substances, like polychlorinated aromatics, are extremely persistent in the environment because of their resistance to oxidation under aerobic conditions. Polychlorinated phenols (produced by paper mills when wood pulp is delignified by chlorine bleaching[3]) are environmental contaminants.[4] Their biodegradation is slow, and can occur by a reductive dehalogenation route in anaerobic conditions[5] or by an oxidative pathway catalyzed by ligninase[6] or a cytochrome P-450 of *Rhodococcus chlorophenolians*.[7] Obviously, there is a need for efficient chemical catalysts for the oxidative degradation of these recalcitrant compounds, especially in the case of industrial effluents where large amounts of pollutants in high concentrations make an efficient use of microorganisms impossible. Chemical systems based on an environmentally friendly oxidant like hydrogen peroxide (water is the only residue after the oxidation) might be useful to transform chlorinated aromatics to more biodegradable compounds. We recently published preliminary reports on an efficient H_2O_2 ring cleavage of 2,4,6-trichlorophenol (TCP, a typical example of a recalcitrant pollutant) catalyzed by iron tetrasulfophthalocyanine (FePcS, Fig. 1).[8]

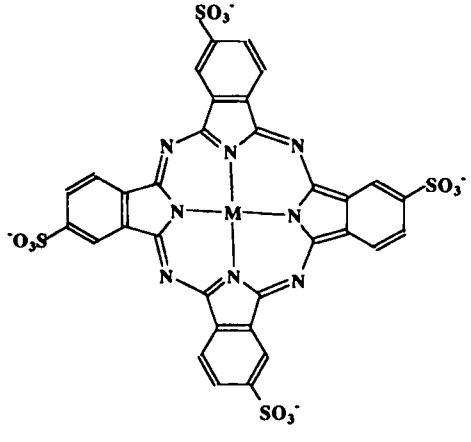

Fig. 1. Structure of sulfonated metallophthalocyanines MPcS (M = Fe or Mn).

Metal derivatives of phthalocyanines are important industrial dye products (worldwide output of 45000 tons in 1987 according to ref. [9]), so they can be considered as attractive possibilities as cheap and readily available catalysts for oxidation of pollutants. We previously used metalloporphyrins as catalysts in the oxidation of TCP, but we only obtained 2,6-dichlorobenzoquinone as a product without ring cleavage.[10] Here we report a detailed mechanistic study of the H_2O_2 oxidation of 2,4,6-trichlorophenol and pentachlorophenol catalyzed by iron and

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0947-6539/96/0210-1308 $ 15.00+.25/0

manganese complexes of tetrasulfophthalocyanine, based on chlorine release quantification, identification of quinone intermediates and aromatic ring-cleavage products, and oxygen labeling experiments.

Results

Typical catalytic oxidations of these two chlorinated phenols were performed with a 10^{-2} M substrate solution (corresponding to 2000 and 2600 ppm of TCP or PCP, respectively), 3.7×10^{-4}, 10^{-4}, 10^{-5}, or 10^{-6} M catalyst concentration (for a catalyst/substrate ratio of 3.7, 1, 0.1, or 0.01%, respectively) in a mixture of acetonitrile–water (1:3 for TCP and 1:1 for PCP oxidations) and 5×10^{-2} M of oxidant (5 equivalents of $KHSO_5$ or H_2O_2 with respect to the substrate). Acetonitrile was used as cosolvent to solubilize the hydrophobic chlorinated phenols. However, in the case of lower concentrations of TCP (10^{-4} or 10^{-5} M, 20 or 2 ppm, respectively), there was no need to add an organic solvent; consequently the catalytic oxidation of pollutants can simply be performed in buffered water (pH 7).

We first checked the catalytic activities of different soluble metallophthalocyanines in the oxidation of TCP with potassium monopersulfate or hydrogen peroxide (Table 1). NiPcS was completely inactive. There was no conversion of TCP after 1 hour of reaction with $KHSO_5$ or H_2O_2. CoPcS was inactive with H_2O_2, whereas some catalytic activity was observed with $KHSO_5$ (run 12, Table 1). Both FePcS and MnPcS are highly efficient catalysts of the $KHSO_5$ oxidation of TCP at pH 7. Full substrate conversion was observed within a few minutes even with a 0.1 mol% ratio of catalyst:TCP (runs 1 and 6 of Table 1; turnover rate 16 cycles per second). FePcS was the better catalyst with $KHSO_5$ at pH 7 as well as at pH 2 (runs 1 and 2 compared with runs 4 and 5). This latter pH value corresponds to a nonbuffered aqueous solution of potassium monopersulfate.[11] The catalytic activity of MnPcS with $KHSO_5$ is similar to that observed for FePcS at pH 7 (runs 6–8 compared with runs 1–3). The only time catalytic activity of MnPcS was lower than that of FePcS was at pH 2 for very low catalyst loading (run 10 compared with run 5). High catalytic activities were attained with these two catalysts and $KHSO_5$ as oxidant, but it should be noted that efficient oxidation of TCP was also achieved with the environment-compatible oxidant H_2O_2 (runs 13 to 15). In terms of oxidation rates, the catalytic activities of Fe- or MnPcS/H_2O_2 were below those observed with Fe- or MnPcS/$KHSO_5$ in homogeneous conditions, but we recently reported that fixation of FePcS and MnPcS onto an insoluble support such as a cationic ion-exchange resin resulted not only in the improvement of the catalyst stability but also in an increase of catalytic activity when H_2O_2 is used as the oxidant.[8b] The catalytic activity of the supported catalyst FePcS–amberlite was better with H_2O_2 than with $KHSO_5$, and it could be recycled without significant loss of catalytic activity.

Table 1. Oxidation of 2,4,6-trichlorophenol and pentachlorophenol by $KHSO_5$ or H_2O_2, catalyzed by an iron or manganese sulfonated phthalocyanine complex FePcS or MnPcS.

Run	Catalyst	% Cat./ substrate	pH	Oxidant	Conversion (%) 1 min	5 min	Initial rate cycles s^{-1} [a]
Trichlorophenol oxidation							
1	FePcS	0.1	7	$KHSO_5$	97	98	16
2	FePcS	0.01	7	$KHSO_5$	43	56	72
3	FePcS	1	2	$KHSO_5$	100	–	n.d.
4	FePcS	0.1	2	$KHSO_5$	96	100	16
5	FePcS	0.01	2	$KHSO_5$	58	70	97
6	MnPcS	0.1	7	$KHSO_5$	100	–	n.d.
7	MnPcS	0.01	7	$KHSO_5$	58	73	97
8	MnPcS	1	2	$KHSO_5$	83	100	1.4
9	MnPcS	0.1	2	$KHSO_5$	45	62	7.5
10	MnPcS	0.01	2	$KHSO_5$	10	10	17
11	MnPcS	1	3	$KHSO_5$	100	–	n.d.
12	CoPcS	1	7	$KHSO_5$	30	56	0.5
13	FePcS	1	7	H_2O_2	6	38	0.1
14	FePcS	3.7 [b]	7	H_2O_2	68	100	0.3
15	MnPcS	1	8.5	H_2O_2	8	25	0.1
Pentachlorophenol oxidation [c]							
16	FePcS	1	2	$KHSO_5$	100	–	n.d.
17	FePcS	0.1	2	$KHSO_5$	100	–	n.d.
18	FePcS	1	7	$KHSO_5$	94	98	1.6
19	FePcS	3.7 [b]	7	H_2O_2	49	100	0.2
20	FePcS	1	7	H_2O_2	46	96	0.8
21	MnPcS	0.1	2	$KHSO_5$	46	55	7.7

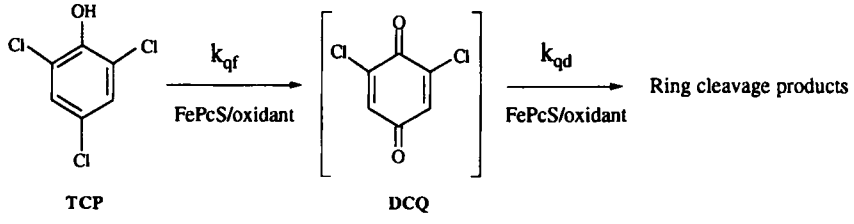
[a] Based on 1 min reaction time. For very fast reactions (full conversion within one minute), initial rates cannot be accurately determined by HPLC methods (n.d.). [b] In this case, 740 nmol of FePcS were used (500 µL of a 1.48 mM stock solution). [c] Because of the low solubility of PCP in a 1/3 mixture of MeCN/H_2O, reactions were performed in a 1/1 mixture of MeCN/H_2O.

In transition-metal-complex-mediated oxidations with peroxides, especially with H_2O_2 as an oxidant, there is always the possibility of forming hydroxyl radicals by metal-mediated homolysis of the weak O–O bond. The addition of HO$^{\bullet}$ radicals to aromatics is controlled by diffusion.[12] In order to examine the hypothesis that hydroxyl radicals are responsible for TCP oxidation by the FePcS/H_2O_2 system, we carried out oxidation experiments by replacing acetonitrile by a better HO$^{\bullet}$ trap. The reaction rate of ethanol with HO$^{\bullet}$ being 350 times that of acetonitrile, ethanol is an effective trapping agent with which to inhibit oxidation reactions mediated by hydroxyl radicals.[13] A large excess of EtOH should therefore prevent or significantly diminish TCP oxidation by FePcS/H_2O_2. This was not the case, even with a reaction mixture containing 25 vol% of ethanol. In fact, TCP oxidation by FePcS/H_2O_2 at pH 7 was slightly more efficient in the presence of EtOH, indicating that hydroxyl radicals were not the key active species in this catalytic oxidation of TCP. In addition, oxidations of TCP by FePcS/H_2O_2 and FePcS/$KHSO_5$ were performed under nitrogen. We found that the catalytic TCP oxidations were not significantly modified by performance under an inert atmosphere compared with air. Consequently, the reaction of free organic radical species with molecular oxygen cannot be a determining step in TCP oxidation. The absence of influence of O_2 and of HO$^{\bullet}$ traps on TCP oxidation indicates alternative oxidative pathways other than an autoxidation or an oxidation by hydroxy radicals; the results suggest that TCP oxidation is mediated by a metal-centered active species, possibly a high-valent metal–oxo species or a metal–peroxo entity generated by the primary oxidant, H_2O_2 or $KHSO_5$.

Spectrophotometric titration of a 2×10^{-5} M aqueous solution of FePcS with 10 aliquots of 10 molar excess of TCP revealed a decrease of the band at 632 nm and the appearance of a new absorbance at 670 nm with isosbestic points at 552, 650, and 714 nm, suggesting the cleavage of the Fe^{III}PcS–O–Fe^{III}PcS μ-oxo dimer and the formation of an Fe^{III}PcS–TCP complex with TCP acting as axial ligand, rather than a reduction of Fe^{III}PcS by TCP. Fe^{II}PcS is characterized by a strong band at 668 nm and a weaker band at 435 nm (see ref. [14] for recent UV/vis data). We can also exclude the possibility of oxidation of the coordinated TCP by the opposite high-valent iron–oxo or -peroxo species, since the axial tyrosine ligand of catalase is not oxidized during the efficient catalytic dismutation of hydrogen peroxide by catalase.[15]

We compared the catalytic activity of $FePcS/H_2O_2$ and $FePcS/KHSO_5$ systems in the oxidation of olefins. Only 32% of styrene was converted by $FePcS/KHSO_5$ after 1 h at room temperature; benzaldehyde (6% yield) and traces of epoxide (<1%) were the only products detected by GC analysis. Cyclohexene was oxidized by $FePcS/H_2O_2$ and $FePcS/KHSO_5$ systems with 46 and 44% conversion after 1 h, respectively, but no cyclohexene oxide was detected in either case. This absence of epoxide suggests that the active species in these two catalytic systems is not a high-valent metal-oxo complex like $LFe^{V}=O$ or $L^{+}\cdot Fe^{IV}=O$ analogous to that responsible for epoxidation or hydroxylation reactions catalyzed by cytochrome P-450 or related models.[10b]

Product analysis in TCP oxidation catalyzed by FePcS: With both oxidants, $KHSO_5$ and H_2O_2, the initial oxidation product of TCP was the 2,6-dichloro-1,4-benzoquinone (DCQ). But this quinone was only detected in the first few minutes of the catalytic reaction with both catalytic systems at pH 7, and then it underwent further catalytic transformations. However, the kinetic behavior of these catalytic oxidations is dependent on the oxidant used (Scheme 1). With $KHSO_5$ at pH 7, the formation



Scheme 1. Formation and degradation of 2,6-dichloro-1,4-benzoquinone (DCQ) during TCP oxidation. k_{qf} = rate constant for quinone formation; k_{qd} = rate constant for quinone degradation ($k_{qf} > k_{qd}$ when oxidant = $KHSO_5$ and $k_{qf} < k_{qd}$ when oxidant = H_2O_2).

of the quinone was sufficiently fast to allow its detection by HPLC before its further degradation ($k_{qf} > k_{qd}$). This phenomenon is enhanced at low pH values. At pH 2 with monopersulfate, DCQ was formed in 60% yield and was very slowly degraded. In the case of hydrogen peroxide, the rate of TCP oxidation was slower than with monopersulfate, but only traces of quinone DCQ were detected during the conversion of TCP to ring cleavage products ($k_{qf} < k_{qd}$). During the first minute after the addition of H_2O_2 the reaction mixture became violet, suggesting the formation of a new product, which was detected by HPLC. The maximum concentration of this violet product was obtained after 4 min at room temperature, and then it was gradually oxidized to further degradation products. We isolated and purified the violet product from a large-scale preparation and identified it as 3,5-dichloro-2-hydroxy-1,4-benzoquinone (**12**, Scheme 6) and also its reduced acetylated derivative 1,2,4-triacetoxy-3,5-dichlorobenzene by UV/vis, MS, ^1H NMR, and ^{13}C NMR techniques (see Experimental Section). A similar product was also detected in the oxidation of tetrachlorohydroquinone by *Pseudomonas cepacia* AC1100 and was identified as being 3,5,6-trichloro-2-hydroxy-1,4-benzoquinone.[16] We also checked that 2,6-dichloro-1,4-benzoquinone was oxidized by $FePcS/H_2O_2$ to this violet quinone derivative **12**.

We determined the number of Cl^- ions released per TCP molecule consumed (Table 2).[8a] With H_2O_2 as oxidant, about 2 Cl^- ions per TCP molecule were liberated during TCP oxidation, with an increase in dechlorination at low substrate concentrations. But only 1 Cl^- ion was released with $KHSO_5$ as oxidant, suggesting that dichlorobenzoquinone was degraded by a nondechlorination process (e.g., polymerization), rather than by ring cleavage, in other words, that the mechanism for oxidation of DCQ to degradation products is different for these two catalytic systems.

Table 2. Determination of Cl^- release in the oxidation of 2,4,6-trichlorophenol or pentachlorophenol catalyzed by FePcS [a].

Run	Substrate conc. (mM)	Cl^-/converted TCP [b]	Cl^-/converted PCP
H_2O_2 as oxidant			
1	2.5	2.12±0.14	1.43±0.17
2	5.0	1.96±0.04	0.97 [c]
3	7.5	1.73 [c]	0.59 [c]
4	10	1.74±0.13	0.34±0.02
$KHSO_5$ as oxidant [d]			
5	5.0	1.06±0.04	
6	10		0.20 [c]

[a] Reaction conditions for H_2O_2 oxidations were identical to those of runs 14 and 19 of Table 1 for TCP and PCP, respectively, with 50 mM H_2O_2. The FePcS concentration was 0.37 mM. Determinations of Cl^- release were carried out after 1 h of reaction. [b] Molar ratio. [c] One experiment. [d] Reaction performed at pH 7 with 3.7% of FePcS/substrate.

The final products of TCP oxidation by $FePcS/H_2O_2$ (performed under the conditions of run 2 of Table 2) were identified and quantified by GC-MS and NMR analyses.[8a] TCP oxidation products can be divided into two categories: products resulting from the oxidative coupling of TCP and those resulting from aromatic ring cleavage (Fig. 2).

The total yield of identified products was 56% after 60 min of reaction at room temperature (quantified by ^1H NMR spectroscopy, see ref. [8a] for detailed method). This total yield was underestimated because of the extraction method before NMR analysis. Taking this parameter into consideration, the material balance for the TCP oxidation by $FePcS/H_2O_2$ was close to 70%.[8a] Furthermore, the TCP ring cleavage products were susceptible to further oxidative degradation.

The major TCP cleavage product was chloromaleic acid (**1**) (yield = 24%). Chlorofumaric (**2**), maleic (**3**), and fumaric (**4**) acids were only minor products. We also detected oxalic acid among the products of TCP oxidation by GC-MS; however, this ring-cleavage product cannot be quantified by the ^1H NMR method used. This C_2 diacid is expected in the company of chloro-C_4 diacids as a signature of the oxidative TCP ring cleavage in which 2 Cl^- are released.

The TCP coupling products were identified by EI-MS after extraction of the reaction mixture with dichloromethane.[8a] Two phenolic dimers (**5** and **6**) and two quinone oligomers (**7** and **8**) were identified (see Fig. 2 for structures). These coupling products are probably generated by reaction of the radical form of TCP with the excess of TCP followed by one-electron oxidation. No coupling products were detected in the oxidation of 2,6-dichlorobenzoquinone by $FePcS/H_2O_2$. Lower ratios of coupling products with respect to cleavage products were observed at low TCP concentration.

Oxidation of TCP by $FePcS/H_2O_2$ in the presence of $H_2{}^{18}O$: The oxygen atoms in the products of TCP oxidation can originate from water, hydrogen peroxide, or molecular oxygen. We performed TCP oxidation by the $FePcS/H_2O_2$ system in $H_2{}^{18}O$ (97% enrichment). GC-MS analyses of reaction products were

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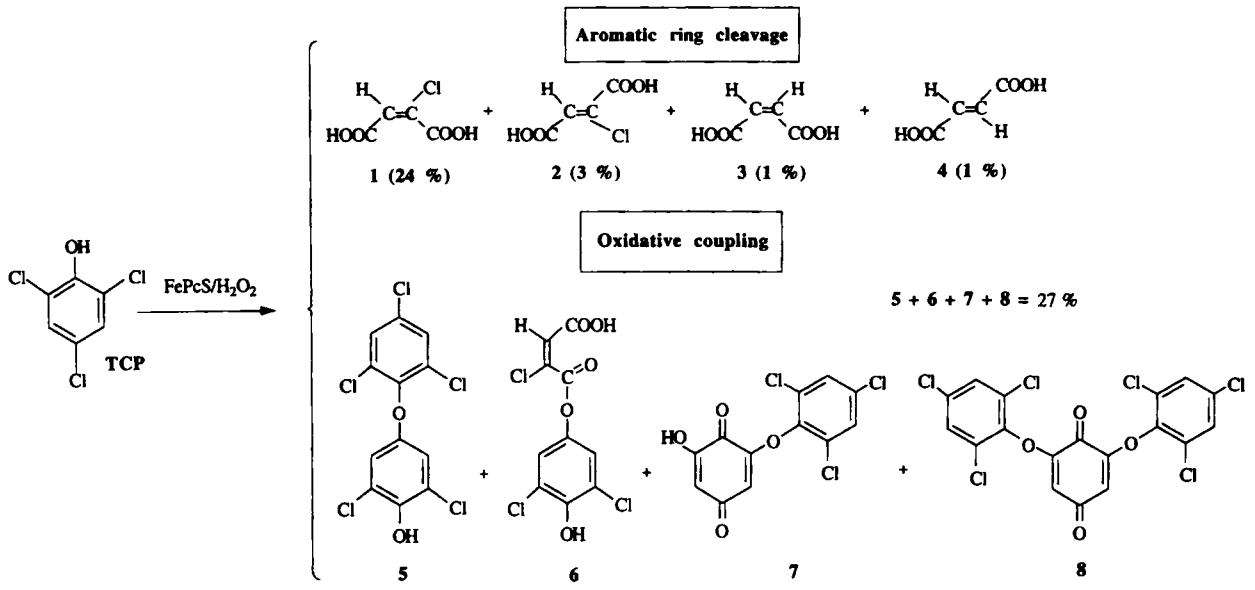


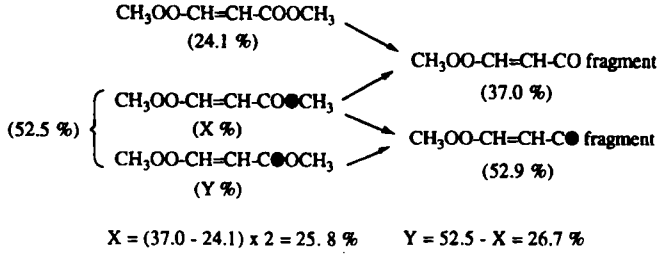
Fig. 2. Product distribution of the H_2O_2 oxidation of TCP catalyzed by FePcS.

Table 3. Incorporation of ^{18}O from $H_2{}^{18}O$ into products of TCP ring cleavage by the FePcS/H_2O_2 system after a reaction time of 10 min or 1 h. GC-MS analysis of TCP ring cleavage products (all C_4 diacids were analyzed as dimethyl esters after in situ treatment with trimethylsulfonium hydroxide; all reported data correspond to MS peak ratios).

Product containing:	Reaction time (min)	Chloromaleic acid M^+	Chloromaleic acid $(M-OCH_3)^+$	Chlorofumaric acid $(M-OCH_3)^+$	Maleic acid $(M-OCH_3)^+$	Fumaric acid $(M-OCH_3)^+$
no ^{18}O	10	24.1±2.2	37.0±0.8	30.0±0.9	27.4±0.5	28.3±1.8
	60	15.9±0.9	30.0±0.7			
one ^{18}O atom	10	52.5±1.4	49.6±0.9	46.5±2.3	50.3±2.3	50.3±1.5
	60	50.5±1.8	52.9±0.3			
two ^{18}O atoms	10	23.4±1.9	13.4±0.8	23.5±1.8	22.3±2.5	21.4±1.7
	60	33.6±1.5	17.1±0.4			

performed after reaction for 10 and 60 min at room temperature. The resulting isotopic contents of the products are listed in Table 3. The main product of TCP oxidation, chloromaleic acid, was converted to its dimethyl ester by trimethylsulfonium hydroxide for GC-MS analyses. The diester of **1** showed an intense molecular peak at 178/180 Da. ^{18}O contents were calculated after correction for natural ^{37}Cl abundance (32.4% relative to ^{35}Cl) (Table 3). After 10 min of reaction at room temperature, the percentages of chloromaleic diester without, with one, and with two ^{18}O atoms were 24.1, 52.5, and 23.4%, respectively. These data suggest that the main source of the oxygen atom in chloromaleic acid is not water. After 60 min, the ^{18}O content of chloromaleic acid became more significant: 15.9%, 50.5%, and 33.6% for products without, with one, and with two ^{18}O atoms, respectively, indicating the oxygen atom exchange of chloromaleic acid with water was rather slow in these conditions. Peaks of maleic, fumaric, and chlorofumaric dimethyl esters were small compared with the fragment peaks $(M-OCH_3)^+$, making a detailed study of the isotope composition of these products by GC-MS difficult. However, data obtained on $(M-OCH_3)^+$ peaks of dimethylesters of **1**–**4** indicated that all C_4 diacids had the same ^{18}O atom content and consequently were probably generated according to the same reaction pathway.

Comparison of the ^{18}O percentages of the molecular and $(M-OCH_3)^+$ peaks for chloromaleic acid allowed calculation of the ^{18}O distribution between the hydroxyl and the carbonyl



Scheme 2. Mass-spectrometric analysis of the oxygen contents and calculation of the ^{18}O distribution in chloromaleic acid obtained in the oxidation of TCP by FePcS/H_2O_2 system in the presence of $H_2{}^{18}O$ (● = ^{18}O).

group in chloromaleic acid containing one ^{18}O atom (Scheme 2). Fragmentation analysis allowed us to determine the ratio of chloromaleic acid with one labeled oxygen atom on the carbonyl (Y) or on the hydroxyl group (X). X and Y are equal within experimental error, indicating an equal distribution of labeled oxygen between the hydroxyl and carbonyl groups of chloromaleic acid.

Traces of TCP were found in samples analyzed after the catalytic oxidation in labeled water. Inspection of molecular cluster peaks of methylated TCP showed the expected typical 3 Cl-containing molecule pattern and indicated also that no oxygen exchange occurred on the phenolic function of TCP during the

catalytic reaction. The same observation was made for the coupling product **5**: no ^{18}O from water was incorporated. Product **6**, which might be generated by oxidative cleavage of one ring of **5**, consisted of $47.3 \pm 1.5\%$ of material without ^{18}O, $29.2 \pm 0.9\%$ with one ^{18}O, and $23.4 \pm 2.4\%$ of material with two ^{18}O (data obtained after 10 min of reaction).

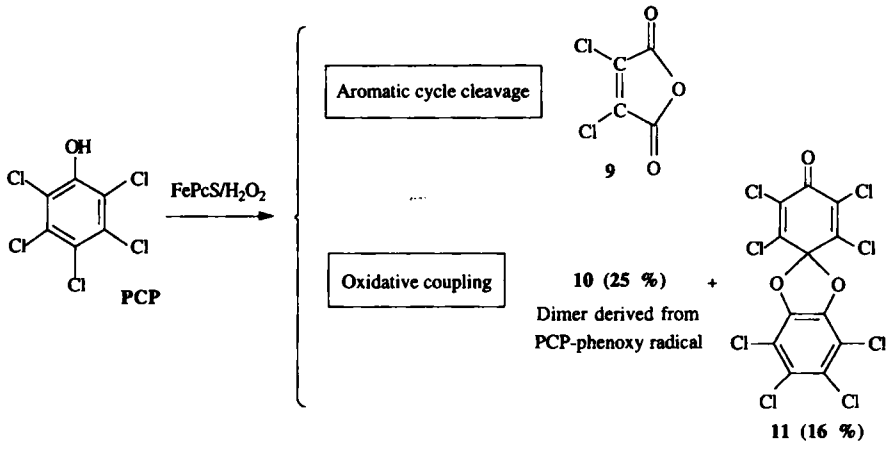
We also decided to investigate the possible incorporation of oxygen atoms from molecular oxygen during the oxidative ring cleavage of TCP.

TCP oxidation by FePcS/H_2O_2 in the presence of $^{18}O_2$: After 10 min of reaction under $^{18}O_2$ (98% enrichment), product samples for GC-MS analysis were prepared as described in the Experimental Section. The isotopic composition of the dimethylester of chloromaleic acid was as follows: $10.9 \pm 3.7\%$ of material with one ^{18}O atom and $89.1 \pm 3.7\%$ of unlabeled material, indicating that incorporation of oxygen atom from dioxygen was small compared with that arising from hydrogen peroxide or water. Analysis of the $(M - OCH_3)^+$ fragment indicated that $5.5 \pm 0.9\%$ of the material contained one atom of ^{18}O. Thus, labeled oxygen from molecular $^{18}O_2$ was mainly located on the hydroxyl groups of chloromaleic acid.

All these oxygen labeling experiments strongly suggest that the oxygen atom sources in TCP ring-cleavage products are, in decreasing order, hydrogen peroxide, water, and then dioxygen.

Pentachlorophenol oxidation: Pentachlorophenol (PCP) belongs to the group of chloroaromatics which are highly resistant to aerobic biodegradation. For example, *Rhodococcus chlorophenolians* PCP-1, a strain known to dechlorinate several polyhalogenated phenols aerobically by an oxidative process catalyzed by a cytochrome P-450, is only poorly able to mediate PCP degradation. PCP is converted by the purified enzyme at a turnover rate of 2.26 nmol of PCP per mg of protein per hour, that is, few catalytic cycles per hour.[7] We found that both FePcS and MnPcS are efficient catalysts of PCP oxidation (Table 1). PCP was quickly oxidized by $KHSO_5$ or H_2O_2 in the presence of only 1% of FePcS (runs 16, 18, and 20), whereas the corresponding manganese complex is slightly less active (run 21 compared with run 17). Comparison of TCP and PCP oxidations by FePcS/H_2O_2 system (Table 1, runs 13 and 20) indicated that the PCP conversion was slightly faster than that of TCP in these catalytic conditions. Conversions were 46% and 6% after 1 min and 96% and 38% after 5 min for PCP and TCP, respectively. Data on Cl^- release accompanying PCP oxidation are reported in Table 2. Dechlorination of PCP also depends on substrate concentration: it ranges from 0.34 to 1.43 Cl^- released per converted PCP molecule, low substrate concentration corresponding to higher dechlorination. However, PCP dechlorination was low compared with that of TCP under the same experimental conditions, as expected for a compound much more recalcitrant to oxidative degradation. Products resulting from PCP oxidation by FePcS/H_2O_2 were analyzed by GC-MS after an isolation procedure similar to that used for TCP oxidation products. $Me_3S^+OH^-$ or CH_2N_2 were used for derivatization. Dichloromaleic anhydride (**9**) was the only identified product resulting from the oxidative cleavage of PCP. No dimethylester of **9** was detected by GC-MS.

The poor solubility of PCP oxidative coupling products (yellow precipitate) permitted easy product recovery by simple filtration of the reaction mixture. No traces of chlorinated aromatics in the solution could be detected by HPLC. After a work-up (see the Experimental Section), seven coupling products were detected: three dimers and four trimers. Only two products, **10** (25% yield) and **11** (16% yield), were fully characterized by ^{13}C NMR spectroscopy, negative desorption chemical ionization ((−)DCI) MS, and IR (see Scheme 3).



Scheme 3. Products of the H_2O_2 oxidation of PCP catalyzed by FePcS.

The MS data currently to hand rule out the formation of chlorodibenzodioxins and chlorodibenzofurans in the oxidation of PCP as well as TCP. Peroxidase-mediated formation of chlorinated dibenzodioxins and dibenzofurans have been published for 3,4,5 and 2,4,5-trichlorophenol oxidations.[17]

When tetrachloro-1,4-benzoquinone (2.5 mM) was used as substrate with FePcS/H_2O_2, 100% conversion was observed within 60 min with high dechlorination: 2.4 Cl^- ions per converted tetrachlorobenzoquinone molecule. Again, dichloromaleic anhydride was detected by GC-MS as a product of ring cleavage, but no coupling products were detected. These results evidenced the ability of FePcS/H_2O_2 system to cleave the aromatic ring of PCP and suggested that tetrachlorobenzoquinone was only an intermediate in the ring cleavage of pentachlorophenol.

Discussion

The main interest of these catalytic oxidations of pollutants is the possibility of utilization of an environmentally friendly oxidant like hydrogen peroxide and readily available complexes (FePcS and MnPcS) as catalysts. Iron and manganese sulfophthalocyanines are metal(III) complexes when prepared according to the Weber–Busch method and all available data suggest that these complexes are probably a mixture of the μ-oxo dimer and monomers with different spin states.[18] Magnetic moments of FePcS (1.9–2.5 μ_B) correspond to low spin d^5 species, suggesting different iron(III) complexes with an axial ligand (possibly a hydroxo or the oxygen of a μ-oxo—for data on μ-oxo dimers, see ref. [19]). UV/visible spectral data suggest that TCP interacts with FePcS and probably cleaves FePcS–O–FePcS to a monomer with TCP as axial ligand. Since the pK_a value of TCP is 6.2 (4.7 for PCP),[20] the TCP anion is potentially a good anionic ligand.

These metallophthalocyanine-catalyzed oxidations of TCP and PCP are not related to classical phenol autoxidations. They

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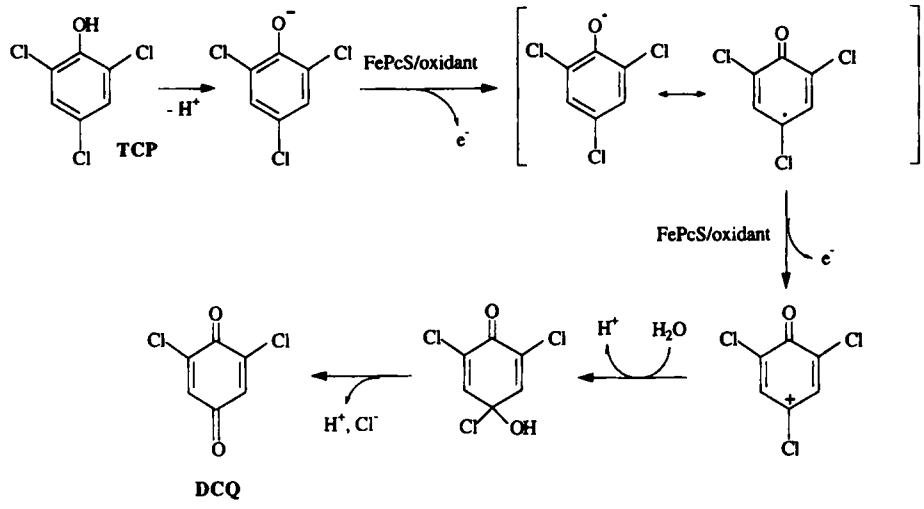
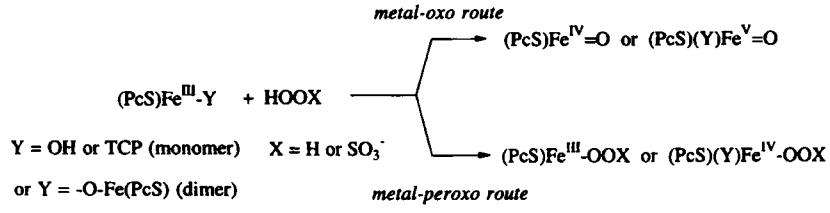
are performed at room temperature and conversions of these poorly oxidizable substrates are the same when performed in air or under inert atmosphere, indicating molecular oxygen is not involved in the rate-determining step of the oxidation of TCP or PCP.

When potassium monopersulfate is used as the oxidant, TCP is quickly oxidized to the corresponding *para*-quinone (see below), and this two-electron oxidation product of TCP is then oxidized further at a slower rate compared with the rate of TCP conversion. The first step resembles what was already observed in the TCP oxidation with $KHSO_5$ and iron and manganese complexes of sulfonated porphyrins.[10] So we can propose that activation of potassium monopersulfate by FePcS (or MnPcS) leads to the formation of a $Fe^{IV}=O$ (or a $Mn^{IV}=O$) species that is able to abstract electrons from TCP, but unable to transfer an oxygen atom to an electron-deficient olefin (see the metal–oxo route formation in Scheme 4).



Scheme 5. Generation of radical and cationic intermediates on the route to 2,6-dichloro-1,4-benzoquinone (DCQ) in the oxidation of TCP by $FePcS/H_2O_2$ or $FePcS/KHSO_5$.



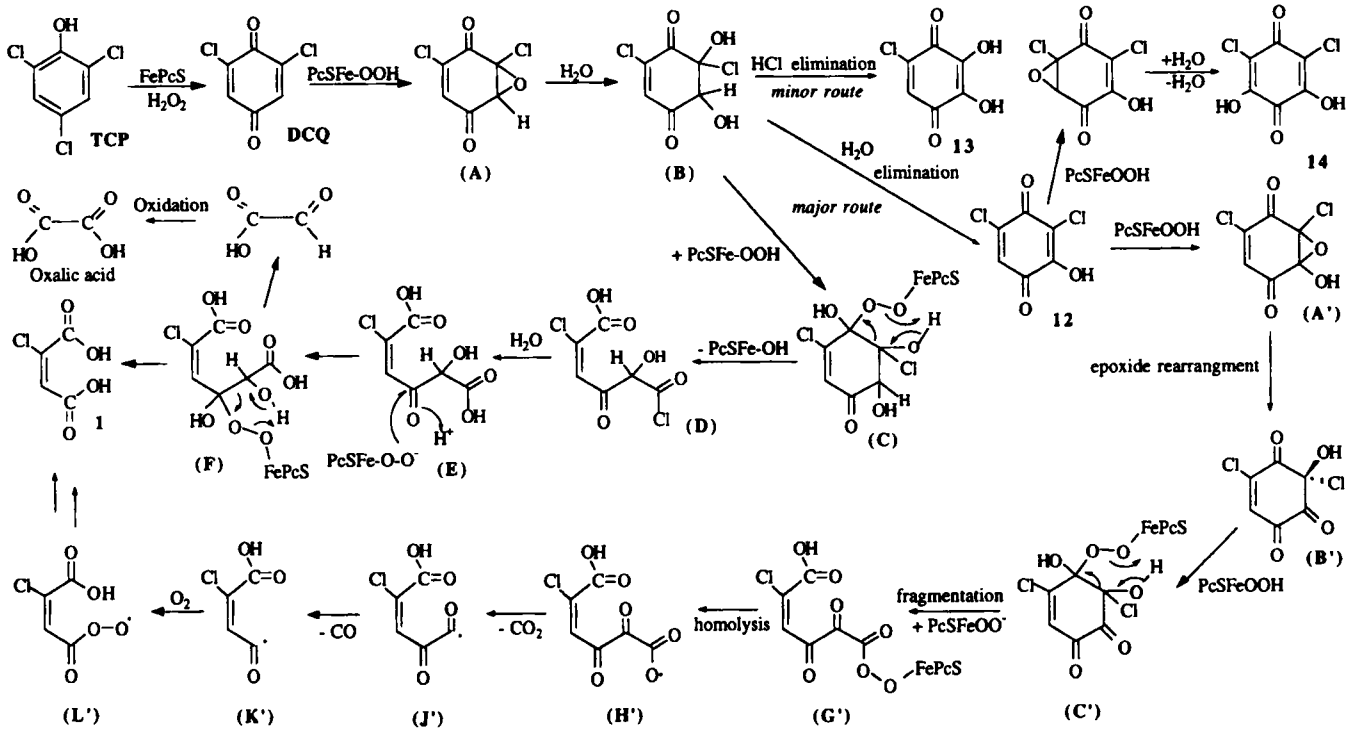
Scheme 4. Different possible modes of activation of FePcS by H_2O_2 or $KHSO_5$.

The formation of a phthalocyanine–Fe^V–oxo species may be excluded, since no epoxide was detected in the cyclohexene oxidation by $FePcS/KHSO_5$, and the corresponding hydrophobic iron or manganese phthalocyanines FePc and MnPc are poor epoxidation catalysts with potassium monopersulfate.[21] These data suggest that the formal iron(v) oxidation state is not reached in the $FePcS/KHSO_5$ catalytic system. For an efficient oxygen-atom transfer, high-valent iron–oxo entities should be two redox equivalents above the iron(III) state (see ref. [22] for recent data on oxygen-atom transfer catalyzed by water-soluble metalloporphyrins).

Several facts strongly suggest that no high-valent metal–oxo species are involved in the mechanism of TCP (or PCP) oxidation by $FePcS/H_2O_2$. Substrate conversion is slower with $FePcS/H_2O_2$ than with $FePcS/KHSO_5$, deep dechlorination is observed, only a very low level of 2,6-dichlorobenzoquinone is detected, and oxygen atoms from hydrogen peroxide are incorporated on a large scale. In addition, styrene is poorly oxidized by $FePcS/H_2O_2$ without formation of epoxide. With this catalytic system, the metal–peroxo route is probably favored, as opposed to the metal–oxo route, leading to Fe^{III}- or Fe^{IV}–OOH entities able to generate quinone derivatives (Scheme 5). The 2,6-dichlorobenzoquinone formation is a result of the one-electron oxidation of the phenolate form of TCP (or PCP) at pH 7 (their respective pK_a values are given above). Then the phenoxy radical is oxidized to the aromatic carbocation form, which reacts with water to give rise to the corresponding chlorobenzoquinone with the release of one Cl^- ion. Besides the formation of 2,6-dichlorobenzoquinone, radical intermediates may be trapped by molecular oxygen and cationic species by the excess of TCP, leading to dimers or trimers. The formation of coupling products depends on the TCP (or PCP) concentration. As expected, low ratios of coupling products were observed at low phenol concentrations. Cl^- release was also greater at low TCP concentrations. When the TCP concentration was decreased from 10 to 2.5 mM, Cl^- release increased from 1.7 to 2.1 (Table 2). This trend is more pronounced in the case of PCP: for the same concentration change, Cl^- release increased from 0.3 to 1.4. The tendency to form coupling products is much higher for PCP as compared with TCP, resulting in a greater dechlorination dependence on PCP concentration. PCP oxidation products are insoluble in the reaction mixture and the precipitate is thus not available for further oxidation, while soluble TCP coupling products can be further degraded. For example, product **6** corresponds to a ring cleavage of **5**. The difference between TCP and PCP dechlorinations can be explained by the fact that PCP oxidation intermediates are more difficult to oxidize than the corresponding TCP intermediates.

In order to explain the facile degradation of 2,6-dichlorobenzoquinone by $FePcS/H_2O_2$, we can assume that this electrophilic quinone is epoxidized by a nucleophilic metal–peroxo complex, leading to intermediate **A** (Scheme 6).[23] Epoxide **A** can be hydrolyzed to diol **B**. This intermediate **B** can undergo H_2O or HCl elimination to generate a quinone structure. The major product is the violet 3,5-dichloro-2-hydroxy-1,4-benzoquinone (**12**) from H_2O elimination, and the minor product 5-chloro-2,3-dihydroxy-1,4-benzoquinone (**13**) results from HCl elimination. However, **12** might be directly obtained from the intermediate **A** by a NIH shift mechanism, as proposed for cytochrome P-450-mediated oxidations of aromatics (the same applies for the formation of **14**).[24] The quinone **12** was isolated from the reaction mixture when the oxidation was stopped after 4 min and **13** was only identified by GC-MS as a minor product. This finding strongly supports the intermediate formation of epoxide **A** and its hydrolysis to diol **B**, which eliminates water to form **12** as a major degradation intermediate.

Degradation of such hydroxyquinone compounds might involve nucleophilic attack by an iron–peroxo complex. In the absence of data concerning the pK_a value of a [Fe]–OOH com-



Scheme 6. Proposed mechanism for aromatic ring cleavage of TCP by $FePcS/H_2O_2$ (formation of chloromaleic and oxalic acids). Compounds indicated by numbers have been identified whereas derivatives assigned capital letters are only putative intermediates.

plex in water, we can assume the acidity is higher than that of hydrogen peroxide itself (first pK_a of $H_2O_2 = 11.8$, see ref. [25]) because of orbital interactions with the metal in the β-position to the terminal OH bond. Such an [Fe]–OOH species is certainly a strong nucleophile, as expected for an electron-rich d complex (for a review article on metal–peroxo complexes, see ref. [26]). It is therefore reasonable to assume that **12** can be epoxidized by the nucleophilic addition of a nucleophilic peroxide ($PcSFe-OO^-$) on one or the other side of the quinone to give the 3,5-dichloro-2,6-dihydroxy-1,4-benzoquinone (**14**) (susceptible to degradation by oxidative pathways similar to those involved in the oxidation of **12**, see below) or the intermediate **A'**, which would easily rearrange to **B'**. Intermediate **14** was identified by GC-MS after reduction and acetylation (see Experimental Part). Then one carbonyl group of the intermediates **B** or **B'** can be attacked by $PcSFe-OO^-$ to give rise to compounds **C** or **C'**, which would undergo a C–C bond ring cleavage by a Grob-type fragmentation. Simple Hückel calculations indicated that the coefficient of the LUMO of **B** with an α-chlorine is slightly higher than that of the opposite carbonyl carbon (steric effects might be able to reverse the order of PcSFe–OOH additions). A similar attack of PcSFeOOH on the intermediate **D** would perform the second C–C bond cleavage (via **E**) required finally to produce chloromaleic acid **1** and the acid chloride of glyoxalic acid, which is quickly hydrolyzed and oxidized to oxalic acid with release of a Cl^- ion. On the other pathway, the addition of $PcSFe-OO^-$ to intermediate **B'** as described above would lead via **C'** to **D'** (this acyl chloride derivative is not indicated in Scheme 6). Intermediates **D** or **D'**, with highly electrophilic acyl chloride functions, can also be attacked by $PcSFe-OO^-$; the homolysis of the peroxidic O–O bond would result in the carboxylic radical **H'**, which would then undergo a fast decarboxylation step (this route from compound **D** is not depicted in Scheme 6). Preliminary experiments showed $^{14}CO_2$ and ^{14}CO formation in the catalytic oxidation of (U-^{14}C)-**TCP**.[27] Intermediate **J'** can release carbon monoxide and **K** can react with molecular oxygen to finally produce chloromaleic acid (**1**).

Data obtained on the isotopic composition of chloromaleic acid formed in $H_2{}^{18}O$ (Table 3) or $^{18}O_2$ experiments are compatible with the different degradation steps of **TCP** proposed in Scheme 6. The small amount of labeled oxygen (11% of chloromaleic acid has only one ^{18}O-hydroxyl group) in TCP oxidation under $^{18}O_2$ suggests that this amount of labeled oxygen is probably not incorporated in the early steps of TCP oxidation, namely during 2,6-dichlorobenzoquinone formation (for the incorporation of an oxygen atom from water in quinoneimine catalyzed by a peroxidase, see ref. [28]). Another reasonable possibility is the reaction of intermediate **K** with $^{18}O_2$ to give rise (via a radical peroxide) to chloromaleic acid **1**. This hypothesis is supported by the fact that most of the labeled oxygen from $^{18}O_2$ was mainly located on the hydroxyl groups of chloromaleic acid **1**.

When generated in $H_2{}^{18}O$, chloromaleic acid is only partially labeled. Four oxygen atoms can be labeled if water is the only source of oxygen. In fact, 24% of the diacid was without ^{18}O atoms, 53% contained only one ^{18}O atom, and 23% had two ^{18}O atoms (Table 3). Since one carbonyl oxygen of 2,6-dichlorobenzoquinone is labeled by the nucleophilic attack of water on the cationic intermediate resulting from the two-electron oxidation of TCP (Scheme 5), the other three oxygen atoms should originate from hydrogen peroxide. This general trend is certainly tuned by additional exchange processes that might occur at different stages of this multistep catalytic oxidation of TCP, but collection of such data is far beyond the present study.

Finally, we believe that two main reactions are responsible for the deep oxidative cleavage of 2,6-dichloro-1,4-benzoquinone, the first intermediate product of TCP oxidation: firstly, nucleophilic addition of an iron(III) peroxo complex, $PcSFeOO^-$,

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able to epoxidize the double bond of electron-deficient intermediate quinones to provide, after hydrolysis, derivatives with a hydroxy group adjacent to a carbonyl group (intermediates **B** and **B'**). Secondly, the same nucleophilic peroxo complex can attack the carbonyl group of the different quinone intermediates, leading to ring cleavage by a Grob fragmentation. Similar nucleophilic metal–peroxo complexes might be involved in biodegradation of polychlorinated aromatic compounds by monooxygenases.

Conclusion

To our knowledge, the present data comprise the first report on the mechanism of the oxidative ring cleavage of 2,4,6-trichlorophenol, not an easily oxidizable aromatic phenol, by a catalytic system involving the environmentally friendly oxidant hydrogen peroxide and easily accessible catalysts, FePcS and MnPcS, the iron and manganese complexes of tetrasulfonatophthalocyanine. We propose a nucleophilic iron(III) peroxo complex, PcSFeOOH, as the active species responsible for the epoxidation of electron-deficient double bond of the different intermediate quinones[23] and of the C–C bond cleavage leading to the product acids. It has been proposed that similar peroxo complexes are involved in acyl-carbon cleavage catalyzed by cytochrome P-450$_{17\alpha}$[29] and in cytochrome-P-450-mediated oxidative deformylation of aldehydes.[30] We are currently working on the development of the FePcS/H_2O_2 system for the oxidation of other nonbiodegradable molecules. This catalytic method might have a real future in the treatment and purification of waste waters.

Experimental Procedure

Instrumentation: Gas chromatography–mass spectrometry data (GC-MS) were obtained with a Hewlett–Packard 5890 instrument by electron-impact ionization at 70 eV. The carrier gas for GC-MS was He, and a 12 m × 0.2 mm HL-1 (crosslinked methylsilicone) capillary column was used. Gas chromatography analyses were performed with an Intersmat IGC 120 DFL chromatograph equipped with a flame ionization detector and a 30 m × 0.25 mm capillary column Superox II from Altech (N_2 was the carrier gas). 1,2-Dichlorobenzene was used as internal standard in GC analyses. High performance liquid chromatography (HPLC) analyses were performed on a Varian 5000 liquid chromatograph equipped with a μ-Bondapak C18 column with a CH_3OH/H_2O mixture (1/1, v/v) as eluent at 1 mL min^{-1} and detection at 280 nm. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WM 250 MHz spectrometer (working at 62.9 MHz for ^{13}C).

Materials: All chemicals used were of reagent grade. Potassium monopersulfate, the triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, was a gift from Interox (Curox™). Hydrogen peroxide was obtained from Janssen as a 35 wt.% aqueous solution. $H_2{}^{18}O$ (97 atom%) and $^{18}O_2$ (98 atom%) were supplied by Eurisotop (Gif-sur-Yvette, France). Nickel tetrasulfophthalocyanine (Ni^{II}PcS) was purchased from Aldrich. Iron, manganese, and cobalt complexes of tetrasulfophthalocyanine (Fe^{III}PcS, Mn^{III}PcS and Co^{II}PcS, respectively) were prepared according to the method of Weber and Busch [20a]. All the available data on Fe^{III}PcS and Mn^{III}PcS (elemental analyses, magnetic and Mössbauer data) suggest that iron and manganese phthalocyanine derivatives are irreversibly oxidized to the oxidation state III in aqueous solutions when prepared according to the Busch method [20b–d]. Magnetic moments of FePcS are in the low-spin d^5 region (1.9–2.5 μ_B), suggesting an iron(III) complex with an axial ligand (possibly a hydroxo or a μ-oxo of a FePcS–O–FePcS dimer).

General analytical procedures: The concentrations of Cl^- were determined by the mercuric thiocyanate method [31]. Trimethylsulfonium hydroxide solution was used to obtain volatile methyl esters of compounds containing phenolic and carboxylic acid functions in situ during GC-MS analyses [32]. Diazomethane was also used as an alternative methylating agent for the crude reaction mixture and was freshly prepared from *N*-methyl-*N'*-nitro-*N*-nitrosoguanidine according to the safe method of ref. [33].

General catalytic procedures for TCP oxidation: Typical procedure: 20 μmol of 2,4,6-trichlorophenol (500 μL of a 40 mM stock solution), a catalyst solution (200, 20, or 2 nmol of FePcS or MnPcS for 1, 0.1, or 0.01% catalyst/substrate ratio; i.e., 500, 50, or 5 μL of a 0.4 mM solution in water, respectively), and a buffered solution of the oxidant (100 μmol of oxidant in 500 μL of buffer; i.e., 30.7 mg of $KHSO_5$ or 10 μL of a 35 wt% H_2O_2 solution in water). The reaction medium was adjusted to a final volume of 2 mL with water ($MeCN/H_2O$ = 1/3, v/v) and stirred at 20 °C. Reactions were monitored by HPLC. Phosphate (pH 7.0, 0.5 M for the stock solution), citrate (pH 3.0, 0.1 M), or borate (pH 8.5, 0.05 M) buffers were used.

Characterization of TCP oxidation products: The products of TCP oxidation were isolated and characterized as decribed in ref. [8a]. Oxalic acid was identified by GC-MS after methylation with an excess of trimethylsulfonium hydroxide. MS (70 eV, EI): *m/z* (%) = 118 (5) [M^+], 59 (100) [$(M - COOCH_3)^+$].

Isolation and characterization of 3,5-dichloro-2-hydroxy-1,4-benzoquinone (12): TCP (84 mg) was dissolved in acetonitrile (10 mL), and an FePcS aqueous stock solution (1.48 mM, 10 mL), water (10 mL), and 0.5 M phosphate buffer (10 mL), pH 7.0, were added. H_2O_2 (35%, 200 μL) was added, and the reaction mixture was stirred for 4 min. The violet reaction mixture was acidified to pH 2 with 1 M HCl saturated with NaCl and extracted with diethylether (3 × 40 mL). The dark yellow ether solution was dried over Na_2SO_4 and evaporated to dryness. 63 mg of crude product were recovered. The crude residue was purified by preparative TLC (Merck Kieselgel 60 F_{254}, 2 mm, ethylacetate/methanol = 9/1, v/v). 20 mg of violet product were recovered. UV/vis (phosphate buffer pH 7.0): λ = 282, 518 nm (broad); ^{13}C NMR (62.9 MHz, D_2O, 298 K): δ = 130.98 (C_6–H), 131.90 (C_3–Cl), 150.80 (C_5–Cl), 169.5 (C_2–O), 175.46 (C_4=O), 186.38 (C_1=O).

Since MS data could not be obtained because of the instability of **12** under MS analysis conditions (EI, 70 eV or DCI NH_3), we further characterized this quinone as the reduced and acetylated derivative, 3,5-dichloro-1,2,4-triacetoxybenzene. 10 mg of **12** were treated for 5 min with 1 mL of acetic anhydride in the presence of a small amount of zinc and sodium acetate at 100 °C [16]. 1 mL of water was added to the cooled reaction mixture and the aqueous solution was treated with diethylether (3 × 2 mL). The combined ether phases were washed with aqueous $NaHCO_3$ solution, dried over Na_2SO_4, and evaporated to dryness. 5 mg of a yellow-brown oil material was recovered after drying for 1 h under vacuum. GS-MS (70 eV, EI): *m/z* = 322 (0.8) [$(M+2)^+$], 320 (1.2) [M^+], 280 (14.7) [$(M+2 - CH_2CO)^+$], 278 (22.3) [$(M - CH_2CO)^+$], 238 (23.2) [$(M+2 - 2CH_2CO)^+$], 236 (34.2) [$(M - 2CH_2CO)^+$], 196 (63.5) [$(M+2 - 3CH_2CO)^+$], 194 (100) [$(M - 3CH_2CO)^+$]; ^{1}H NMR (250 MHz, $CDCl_3$, 298 K): δ = 2.28 (s, 3H), 2.34 (s, 3H), 2.38 (s, 3H), 7.28 (s, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 298 K): δ = 20.14 (2 × CH_3), 20.55 (CH_3), 122.54 (C_6–H), 125.73 (C_3–Cl), 129.27 (C_5–Cl), 139.07 (C_2–O), 141.20 (C_1–O), 142.51 (C_4–O), 166.68 (C=O), 166.83 (C=O), 167.46 (C=O). The ^{13}C shifts were attributed by comparison with those of 1-acetoxy-2,4,6-trichlorobenzene and 1,4-diacetoxy-2,6-dichlorobenzene prepared according to above procedure from 2,4,6-trichlorophenol and 2,6-dichloro-1,4-benzoquinone, respectively. ^{13}C NMR of 1-acetoxy-2,4,6-trichlorobenzene (62.9 MHz, $CDCl_3$, 298 K): δ = 20.11 (CH_3), 128.55 (C_3–H), 129.52 (C_2–Cl), 131.96 (C_4–Cl), 142.95 (C_1–O), 167.02 (C=O); ^{13}C NMR of 1,4-diacetoxy-2,6-dichlorobenzene (62.9 MHz, $CDCl_3$, 298 K): δ = 20.14 (CH_3), 20.86 (CH_3), 122.13 (C_3–H), 128.92 (C_2–Cl), 141.79 (C_1–O), 147.96 (C_4–O), 167.33 (C=O), 168.59 (C=O).

Identification of 5-chloro-2,3-dihydroxy-1,4-benzoquinone (13) and 3,5-dichloro-2,6-dihydroxy-1,4-benzoquinone (14): A large-scale TCP oxidation was performed, and the crude products were isolated as described in the previous paragraph. TLC indicated several minor products, but the yields were not sufficient to isolate and to fully characterize all of them. These products could not be directly characterized by GC-MS because of their instability during this analysis. The crude products were therefore reduced and acetylated as described above and these derivatives analyzed by GC-MS. MS data for 5-chloro-1,2,3,4-tetraacetoxybenzene: 346 (0.9) [$(M+2)^+$], 344 (2.8) [M^+], 304 (10.9) [$(M+2 - CH_2CO)^+$], 302 (31.6) [$(M - CH_2CO)^+$], 262 (19.4) [$(M+2 - 2CH_2CO)^+$], 260 (56.6) [$(M - 2CH_2CO)^+$], 220 (19.6) [$(M+2 - 3CH_2CO)^+$], 218 (54.4) [$(M - 3CH_2CO)^+$], 178 (34.8) [$(M+2 - 4CH_2CO)^+$], 176 (100) [$(M - 4CH_2CO)^+$]. MS data for 3,5-dichloro-1,2,4,6-tetraacetoxybenzene: 380 (1.2) [$(M+2)^+$], 378 (2.0) [M^+], 338 (20.7) [$(M+2 - CH_2CO)^+$], 336 (30.5) [$(M - CH_2CO)^+$], 296 (42.3) [$(M+2 - 2CH_2CO)^+$], 294 (67.9) [$(M - 2CH_2CO)^+$], 254 (53.1) [$(M+2 - 3CH_2CO)^+$], 252 (81.0) [$(M - 3CH_2CO)^+$], 212 (65.7) [$(M+2 - 4CH_2CO)^+$], 210 (100) [$(M - 4CH_2CO)^+$]. These acetylated compounds derived from **13** and **14**, respectively.

Oxidation of olefins: Olefin oxidations were performed in a MeCN/phosphate pH 7 buffer (7/3, v/v). Final concentrations of FePcS, substrate (styrene or cyclohexene), and oxidant ($KHSO_5$ or H_2O_2) were 0.2 mM, 20 mM and 100 mM, respectively. Reactions were monitored by GC.

TCP oxidation in the presence of $H_2{}^{18}O$: A mixture of phosphate buffer (pH 7.0, 500 μL) and FePcS stock solution (1.48 mM, 500 μL) was dried under vacuum. The dry residue was then dissolved in 97% $H_2{}^{18}O$ (1 mL) and a TCP stock solution in MeCN (40 mM, 250 μL), followed by addition of MeCN (250 μL). The final volume was 1.5 mL ($MeCN/H_2O$ = 1/2, v/v). Final concentrations of FePcS, H_2O_2, and TCP were 0.49 mM, 33.3 mM, and 6.7 mM, respectively. The substrate conversion was monitored by HPLC (97% conversion after 10 min). Under these conditions, we checked that Cl^- release was 2.2 Cl^- per TCP molecule. After 10 min (or 60 min for

some experiments, see Table 3) the reaction mixture was dried under vacuum, and $Me_3S^+OH^-$ methanolic solution (0.1 M, 400 μL) was added. The resulting mixture was concentrated to 50 μL before GC-MS analysis.

TCP oxidation in the presence of $^{18}O_2$: A mixture of FePcS stock solution (1.48 mM, 1 mL), phosphate buffer (pH 7.0, 1 mL), water (1 mL), TCP stock solution (40 mM, 0.5 mL), and MeCN (0.5 mL) was submitted to three freeze–pump–thaw cycles to remove $^{16}O_2$ originating from the air. Then the system was filled with $^{18}O_2$ (98%). H_2O_2 (35%, 20 μL) was added, and the reaction mixture was stirred for 10 or 60 min. The solvent was removed under vacuum and the dry residue was extracted with MeOH (3 × 2 mL). The resulting solution was dried and $Me_3S^+OH^-$ methanolic solution (0.1 M, 750 μL) was added. GC-MS analysis was performed after sample concentration to 50 μL.

PCP oxidation: The same conditions were used as those for TCP oxidation, except the reaction mixture consisted of a 1/1 (v/v) MeCN/H_2O mixture. Water-soluble products of PCP oxidation from a reaction performed under the conditions used for run 1 of Table 2 were analyzed. The reaction mixture was acidified to pH 2 with 1 M HCl saturated with NaCl, and the volume of resulting mixture was reduced under vacuum. The products were extracted with diethyl ether (3 × 2 mL). The organic layer was dried and treated with CH_2N_2 solution in diethyl ether. Dichloromaleic anhydride was identified by comparison of its GC-MS behavior (retention time and mass spectrum) with those of an authentic sample. MS (70 eV, EI): m/z = 168 (37) $[(M+2)^+]$, 166 (56) $[M^+]$, 126 (9) $[(M+4-CO_2)^+]$, 124 (49) $[(M+2-CO_2)^+]$, 122 (74) $[(M-CO_2)^+]$, 98 (11) $[(M+4-CO_2-CO)^+]$, 96 (66) $[(M+2-CO_2-CO)^+]$, 94 (100) $[(M-CO_2-CO)^+]$. Coupling PCP oxidation products from a reaction performed in the conditions of run 19 of Table 1 were analyzed: 331 mg of the yellow precipitate resulting from the catalytic oxidation of 418 mg of PCP after 1 h at room temperature were recovered by filtration. Seven products were separated by dry column chromatography (SiO_2, elution first with MeOH, then with a pentane/CH_2Cl_2 mixture, 1/2, v/v). Products were characterized by NH_3 negative DCI-MS, ^{13}C NMR and IR spectra. The principal products were a dimer of the PCP phenoxy radical **10** (isolated yield = 25%) and 2,3,5,6,3′,4′,5′6′-octachloro-1′2′-dioxaspiro[cyclohexa-2,5-diene-1,2′-indan]-4-one (**11**) (isolated yield = 16%).

Product 10: MS ((−)DCI): m/z = 535 (2.5) $[(M+8-H)^-]$, 533 (4.8) $[(M+6-H)^-]$, 531 (5.5) $[(M+4-H)^-]$, 529 (3.6) $[(M+2-H)^-]$, 527 (0.9) $[(M-H)^-]$, 497 (1.2) $[(M+4-Cl)^-]$, 460 (1.3) $[(M+2-2Cl)^-]$, 426 (0.9) $[(M+4-2Cl-HCl)^-]$, 267 (67), 265 (100), 263 (70), 230 (19); the molecular ion cluster corresponded to a 10 Cl-containing molecule (calculated and experimental molecular ion cluster spectra for compounds **10** and **11** are illustrated in Fig. 3). ^{13}C NMR (62.9 MHz, CD_3OD, 298 K): δ = 118.0, 123.6, 133.9, 158; IR (KBr): $\tilde{\nu}$ = 1631 (s), 1540 (s), 1416 (s), 1380 (s), 1278 (m), 1192 (m) cm^{-1}. The structure of **10** is not shown in Scheme 3 because of its structural ambiguity.

2,3,5,6,3′,4′,5′,6′-Octachloro-1′,2′-dioxaspiro[cyclohexa-2,5-diene-1,2′-indan]-4-one (11): MS ((−)DCI): m/z = 478 (61.6) $[(M+6)^-]$, 476 (100) $[(M+4)^-]$, 474 (94.8) $[(M+2)^-]$, 472 (28) $[M^-]$, 248 (33.5), 246 (56.2), 244 (38.7), molecular ion cluster corresponds to an 8 Cl-containing molecule; ^{13}C NMR (62.9 MHz, [D$_6$]DMSO, 298 K): δ = 124.7, 128.6, 131.3, 131.9, 147.3, 150.4, 189.9; IR (KBr): $\tilde{\nu}$ = 1690 (s), 1680 (s), 1571 (m), 1383 (s), 1359 (s), 1168 (m), 1113(s), 1024 (s) cm^{-1}. An X-ray structure of similar tricyclic compound produced in the oxidation of 4,5,6-trichloroguaiacol has been published [34]. Coupling products of PCP resembling the structures of TCP coupling products **5**, **7**, and **8** have been preliminarily identified by MS (negative DCI). MS (negative DCI) of other coupling products then permitted the exclusion of the possibility of formation of chlorodibenzodioxins and chlorodibenzofurans in the PCP oxidation [35]. However, MS data are not enough to identify these minor coupling products unambiguously.

Acknowledgments: A. S. is indebted to ELF (1994–96) and EERO (1993) (European Environmental Research Organisation, Wageningen, Netherlands) for postdoctoral fellowships. The authors are grateful to Christian Forquy, Laurent Fraisse, Alain Rabion, and Jean-Louis Séris (ELF-Atochem, Lacq) for fruitful discussions, and to a referee for useful comments.

Received: December 12, 1995 [F265]

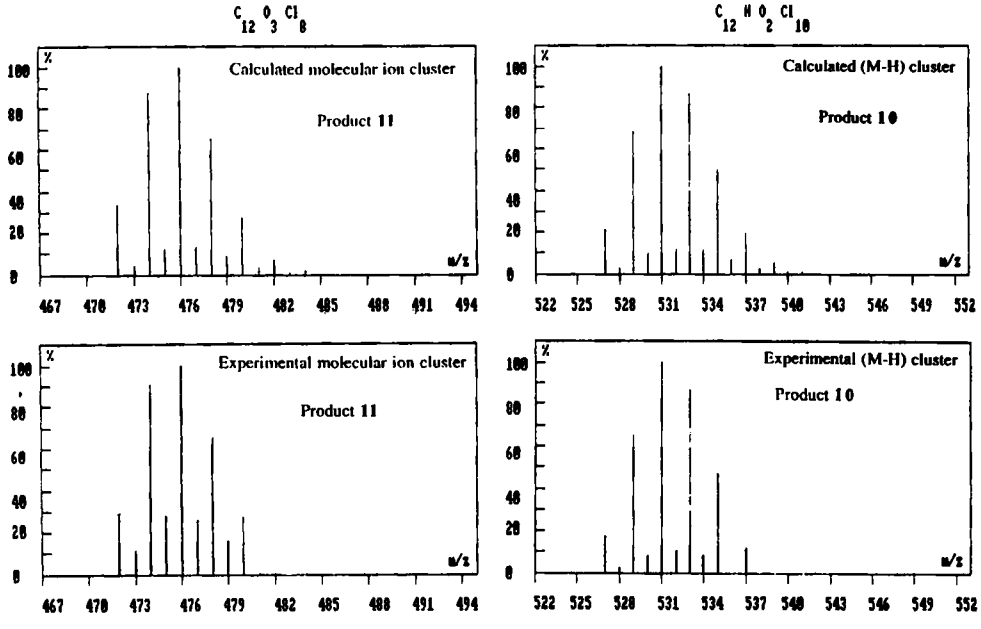

Fig. 3. Calculated and experimental mass spectra of molecular ion clusters for PCP coupling products **10** and **11**.

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[23] Note added to the revised manuscript (March 1996): The recent communication by Valentine et al., *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 206–208, strongly supports the proposed mechanism for the epoxidation the electron-deficient double bond of 2,6-dichloro-1,4-benzoquinone by a nucleophilic PcSFe–OOH species.
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