Journal of Catalysis **202,** 177–186 (2001)
doi:10.1006/jcat.2001.3269, available online at http://www.idealibrary.com on IDEAL®

Key Role of the Phosphate Buffer in the H_2O_2 Oxidation of Aromatic Pollutants Catalyzed by Iron Tetrasulfophthalocyanine

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Received March 16, 2001; accepted April 30, 2001

The non-innocent role of the phosphate buffer has been established in the H_2O_2 oxidative decomposition of 2,4,6-trichlorophenol (TCP), a benchmark pollutant, catalyzed by iron(III) tetrasulfophthalocyanine (FePcS). The catalytic oxidation of several other substrates (3,5-dichloroaniline, tetrachlorocatechol, di-*tert*-butylcatechol and catechol itself) has been carried out, also demonstrating a crucial influence of the phosphate buffer in the decomposition of the chlorinated substrates. Three hypotheses have been studied: modification of the ionic strength, formation of a peroxyphosphate species, or catalysis by a peroxyphosphate–FePcS complex. Supports for the latter proposal have been obtained from several experimental results and attempts have been made to characterize this putative catalytic intermediate. This intermediate derivative has also been generated from the reaction of FePcS with peroxymonophosphoric acid (PMPA) and its catalytic activity has been checked on the decomposition of TCP in different reaction mixture. A short mechanistic study has allowed different reaction pathways to be proposed, dependent on the active species implicated. © 2001 Academic Press

Key Words: **iron(III) tetrasulfophthalocyanine; phosphate buffer, peroxyphosphate; pollutant oxidation; 2,4,6-trichlorophenol; 3,5-dichloroaniline; tetrachlorocatechol; 3,5-di-*tert*-butylcatechol; catechol.**

INTRODUCTION

Phthalocyanines (abbreviated as Pc) are large macrocyclic molecules with an extended, delocalized π-electron system which confers to them a large number of unique properties (1, 2). These molecules have found applications in fields as diverse as chemical sensors, electrochromism, nonlinear optics, liquid crystals, and photodynamic cancer therapy, in addition to their traditional use as dyes (1–6).

When substituted by an appropriate metal, these phthalocyanine derivatives can exhibit interesting redox properties with different chemical applications, for example in the well-known Merox industrial process for the catalytic oxidation of mercaptans in petroleum distillates (7). In the field of catalytic oxidations, we have recently shown that water-soluble metallophthalocyanines were also suitable as catalysts for the degradation of recalcitrant contaminants dissolved in water (8–14). For example, iron(III) tetrasulfophthalocyanine (FePcS) (Fig. 1) when activated by hydrogen peroxide, was able to perform the oxidative degradation of several pollutants such as polychlorinated phenols and anilines or polycondensed aromatics (8–14). All the reactions described were carried out in a phosphate buffer medium initially employed to maintain the solution in an optimized pH value for the catalytic conversion. Here, we report the non-innocent behavior of the phosphate buffer in the oxidation of some of these aromatic pollutants, in particular the chlorinated derivatives, for which an active species derived from the phosphate ions could be involved in the catalytic oxidative process.

EXPERIMENTALS AND METHODS

Methods

The conversions of TCP, 3,5-DCA, DTBC, and DCBQ were monitored by HPLC (Waters) equipped with a μ-Bondapak C18 column. The eluents were mixtures of methanol/ammonium acetate buffer 50 mM pH 4 (7/3, v/v) for TCP and DCBQ, acetonitrile/phosphate buffer 50 mM pH 7 (55/45, v/v) for 3,5-DCA and methanol/water (8/2, v/v) for DTBC. The flow rates were 1 ml/min and the detection was performed at 220 nm. The conversion of catechol and TCC were monitored by UV–visible spectroscopy with a Hewlett Packard 8452A spectrophotometer. ^1H and ^{31}P NMR spectra were recorded on Bruker AC 200 and AM 250 spectrometers. The substrates were purchased from Aldrich. Hydrogen peroxide was supplied from Acros as a 35 wt% aqueous solution. Curox ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) was a gift from Peroxid-Chemie, Germany. All solvents used were of analytical grade and milliQ-water was always used to prepare aqueous

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0021-9517/01 $35.00

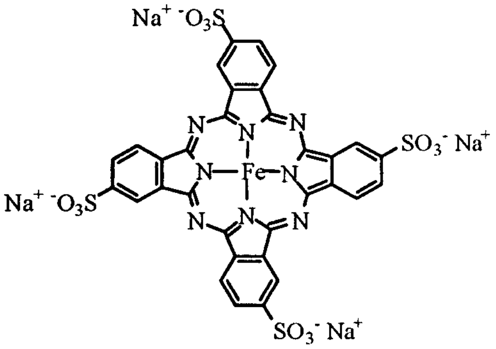


FIG. 1. Structure of the iron(III) tetrasulfophthalocyanine (FePcS); only one of the four possible regioisomers is depicted here.

solutions. Iron(III) tetrasulfophthalocyanine FePcS was prepared according to previously published modifications of the method of Weber and Busch (9, 15) and peroxymonophosphoric acid PMPA was synthesized following the procedure described by Springer *et al.* (16).

General Catalytic Procedure for TCP Degradation

The reaction mixture contained 10.0 μmol of 2,4,6-trichlorophenol (2.5 ml of a 4 mM stock solution in acetonitrile), 500.0 μmol of buffer pH 7 (1 ml of a 500 mM stock solution), 0.4 μmol of FePcS (50 μl of a 8 mM aqueous stock solution), and water until 10 ml. The catalytic oxidation was initiated by the addition of an aqueous solution of the oxidant (50 μl of a 1.2 M aqueous solution of H_2O_2, 15.4 mg of $KHSO_5$ in 100 μl of water or 180 μl of a 3.8 wt% solution of PMPA in HNO_3 65 wt%). When using PMPA as oxidant, the buffer concentration was increased until 365 mM by adding 7.3 ml of a 500 mM Tris/CH_3COOH buffer solution and without diluting with water. The reaction mixture was stirred at room temperature and aliquots were taken at defined times, diluted with eluent to stop the oxidation reaction, and analyzed by HPLC.

^{1}H NMR Analysis of the Oxidation Products of TCP Catalyzed by the FePcS/PMPA System

A catalytic oxidative degradation of TCP was performed with 32.9 mg of TCP (167.0 μmol) dissolved in 42 ml of CH_3CN, 122 ml of a 500 mM Tris/CH_3COOH buffer solution pH 7 (61.0 mmol), 835 μl of a 8 mM FePcS aqueous solution (6.7 μmol), and 3.0 g of a 3.8 wt% solution of PMPA in HNO_3 65 wt% (1.0 mmol). The reaction mixture was stirred 30 min at room temperature and the excess peroxide was neutralized by reduction with 174.0 mg of $Na_2S_2O_4$ (1 mmol). The solution was adjusted to pH 1 with 7.5 ml of conc. HCl saturated with NaCl. The organic products were then extracted with diethyl ether (3 × 150 ml) and the combined organic layers were dried under sodium sulfate. After evaporation of diethylether, the residue was dried under vacuum and dissolved in deuterated dimethyl sulfoxide for NMR analysis. Then, 3 μl of $CHCl_3$ (32.5 μmol) was added as internal standard to quantify the oxidation products. ^{1}H NMR ([D_6] DMSO): δ (ppm) 7.44 (s, 2H, DCBQ, 21%), 7.62–8.10 (br, 2H, coupling products, 13%).

General Catalytic Procedure for 3,5-DCA Degradation

The reaction mixture containing 4.0 μmol of 3,5-dichloroaniline (80 μl of a 50 mM stock solution in acetonitrile), buffer pH 7 (400 μl of a 500 mM stock solution), 0.12 μmol of FePcS (1.5 ml of a 80 μM aqueous solution) was adjusted to 4 ml with 240 μl of CH_3CN and 1.7 ml of water. The catalytic oxidation was initiated by the addition of 24.0 μmol of H_2O_2 (20 μl of a 1.2 M aqueous solution), stirred at room temperature and monitored by HPLC.

General Catalytic Procedure for TCC Degradation

The reaction mixture of 2 ml contained 20.0 μmol of tetrachlorocatechol (5.14 mg in 1 ml of CH_3CN), buffer pH 7 (500 μl of a 500 mM stock solution), 0.8 μmol of FePcS (500 μl of a 1.6 mM aqueous solution). The catalytic oxidation was initiated by the addition of 120 μmol of H_2O_2 (10 μl of a 35 wt% aqueous solution), stirred at room temperature and monitored by UV–vis (464 nm).

General Catalytic Procedure for DTBC Degradation

The reaction mixture of 2 ml contained 20.0 μmol of 3,5-di-*tert*-butylcatechol (4.45 mg in 500 μl of CH_3CN), buffer pH 7 (500 μl of a 500 mM stock solution), 0.8 μmol of FePcS (500 μl of a 1.6 mM aqueous solution). The catalytic oxidation was initiated by the addition of 120 μmol of H_2O_2 (10 μl of a 35 wt% aqueous solution), stirred at room temperature and monitored by HPLC.

General Catalytic Procedure for Catechol Degradation

The reaction mixture of 2 ml contained 20.0 μmol of catechol (500 μl of a 40 mM aqueous solution), buffer pH 10 (500 μl of a 500 mM stock solution), 0.8 μmol of FePcS (500 μl of a 1.6 mM aqueous solution). The catalytic oxidation was initiated by the addition of 120 μmol of H_2O_2 (10 μl of a 35 wt% aqueous solution), stirred at room temperature and monitored by UV–vis (500 nm).

General Catalytic Procedure for DCBQ Degradation

The reaction mixture containing 10.0 μmol of 2,6-dichloro-1,4-benzoquinone (250 μl of a 40 mM stock solution in CH_3CN), buffer pH 7 (1 ml of a 500 mM stock solution), 0.4 μmol of FePcS (50 μl of a 8 mM aqueous solution) was adjusted to 10 ml with 2.25 ml of CH_3CN and 6.45 ml of water. The catalytic oxidation was initiated by the addition of 60 μmol of H_2O_2 (50 μl of a 1.2 M aqueous solution), stirred at room temperature and monitored by HPLC.

RESULTS AND DISCUSSION

Influence of the Phosphate Buffer on the Oxidative Degradation of 2,4,6-Trichlorophenol Catalyzed by $FePcS/H_2O_2$

2,4,6-Trichlorophenol (TCP) is one of the major chlorinated phenols produced by paper mills in the delignification of wood pulp by chlorine bleaching (17). Because of its slow biodegradation by microorganisms, TCP is a well-known recalcitrant pollutant (18). On the other hand, we have shown in previous papers that TCP could be degraded in a few minutes by using 4 mol% of FePcS as catalyst, activated by the "green" oxidant H_2O_2 (9, 11–14). This efficient catalytic oxidation generates aromatic ring cleavage products (mainly C4 diacids) and oxidative coupling products (Fig. 2).

The pH of the medium was stabilized to pH 7 with a phosphate buffer in order to get mainly the more oxidizable phenolate form of TCP in solution ($pK_a = 6.2$) (19). To facilitate a possible large scale application, we tried to eliminate the phosphate buffer. The results are summarized in Table 1. Without buffering the solution, the conversion of TCP falls to 4% after 60 min (Table 1, run 2) compared to full conversion using phosphate buffer (Table 1, run 1). The replacement of phosphate buffer by the addition of sodium hydroxide to the reaction mixture until the optimal pH value of 7 was reached did not restore the decomposition reaction of TCP (Table 1, run 3). The influence of pH is unlikely to be the unique reason behind the lack of reactivity of TCP in an unbuffered medium (pH 5). However, since the addition of sodium hydroxide did not stabilize the pH during the reaction in which diacids must be formed, supplementary experiments were carried out with other buffers. We used tris(hydroxymethyl)aminomethane (Tris) buffer acidified with diverse acids: HCl, H_2SO_4, and CH_3COOH. Surprisingly, no decomposition of TCP occurred with any of these buffers (Table 1, runs 4–6). On the other hand, when this buffer was acidified with *o*-phosphoric acid, the reactivity of TCP was entirely restored with levels of conversion similar to those obtained with a phosphate-buffered medium (Table 1, run 7). So, the presence of phosphate ions seems to be absolutely necessary to perform the oxidative decomposition of TCP catalyzed by $FePcS/H_2O_2$.

TABLE 1

Influence of the Buffer on the Oxidation of TCP Catalyzed by $FePcS/H_2O_2$

Run	Buffer	pH	Conversion at 60 min (%)
1	Phosphate	7	99
2	—	5–6	4
3	—	7	5
4	Tris/HCl	7	6
5	Tris/H_2SO_4	7	7
6	Tris/CH_3COOH	7	6
7	Tris/H_3PO_4	7	91

Note. 1 mM TCP, 50 mM buffer (buffer/CH_3CN = 1/3 v/v), 0.04 mM FePcS (FePcS/TCP = 4%), 6 mM H_2O_2.

Subsequently, quantification of this strong ion influence was undertaken through a kinetic study of the oxidation of TCP with different phosphate buffer concentrations. The experiments were carried out starting from a 1 mM solution of TCP in an acetonitrile/buffered water mixture (v/v = 1/3) containing 4 mol% of FePcS catalyst. Note that the presence of CH_3CN is not essential to (but helps) the solubilization of the poorly water-soluble TCP substrate and to the monomerization of the iron tetrasulfophthalocyanine. The buffer, with a final concentration of 100 mM,

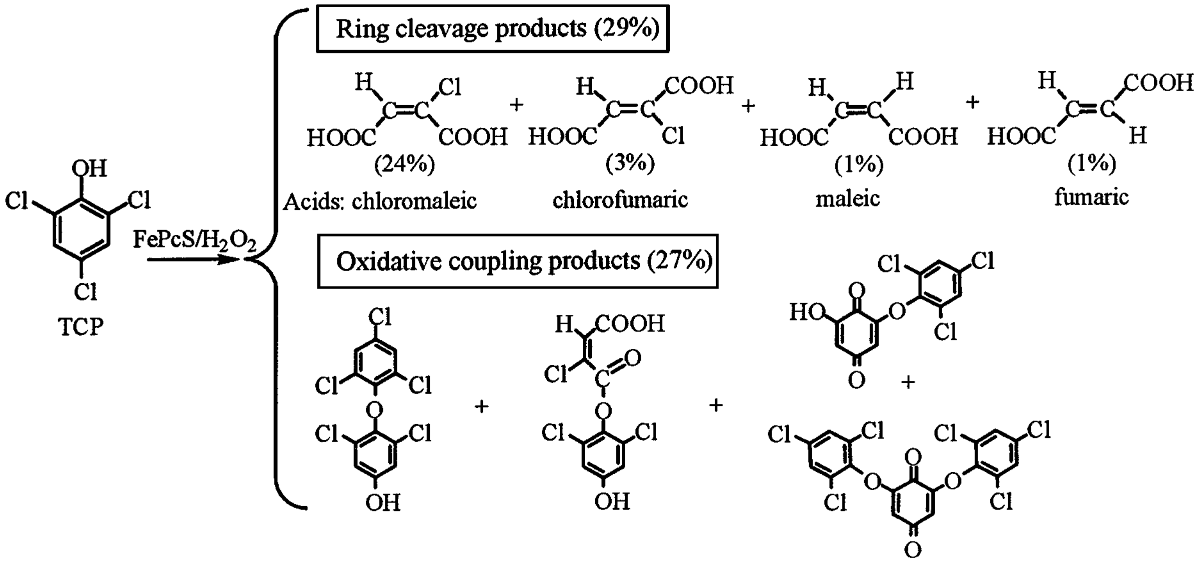


FIG. 2. Product distribution from the H_2O_2 oxidation of TCP catalyzed by FePcS.

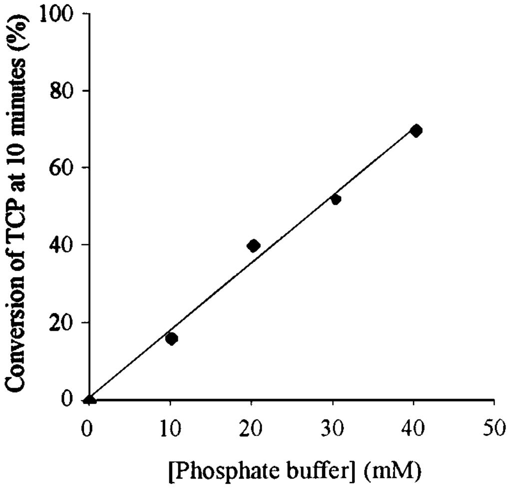


FIG. 3. Influence of the phosphate buffer concentration on the conversion of TCP catalyzed by FePcS/H_2O_2.

consisted of a mixture of phosphate buffer pH 7 and Tris/CH_3COOH buffer pH 7 with different molar ratios. The reaction was initiated by the addition of 6 equivalents of H_2O_2 and, 10 min later, the reaction mixture was analyzed by HPLC (Fig. 3). According to Fig. 3, the concentration of phosphate ions directly influences the conversion of TCP in a linear manner. Doubling the phosphate buffer concentration leads to a twofold conversion of TCP suggesting a reaction order of one with respect to the phosphate concentration.

This influence of the phosphate buffer on the TCP degradation is really surprising but it is not only confined to TCP as this effect has been also observed in degradation studies with other substrates as described in the next paragraph.

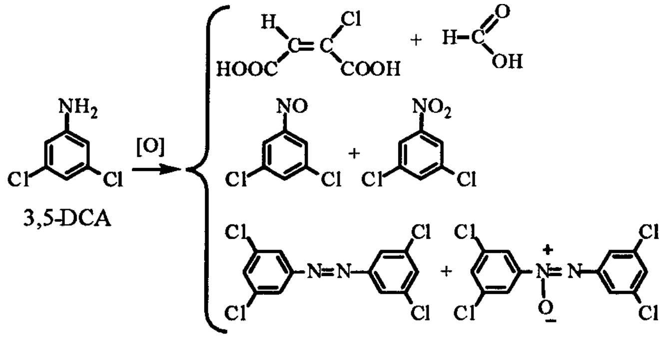
Influence of the Phosphate on the Conversion of Different Substrates

Dichloroanilines. We have seen the influence of the buffer on the decomposition of a pollutant, 2,4,6-trichlorophenol, catalyzed by FePcS/H_2O_2. Dichloroanilines (DCA) are other polychlorinated pollutants used as precursors on a large scale in the industrial synthesis of pesticides, plastics, and dyes (20, 21). 3,5-Dichloroaniline (3,5-DCA), the most toxic, is additionally a precursor in the industrial synthesis of azo dyes (22). In a recent work, we have shown that the FePcS/H_2O_2 catalytic system was able to oxidize 3,5-DCA leading to the formation of (i) ring cleavage products, (ii) compounds resulting from the oxidation of the amine function, and (iii) species resulting from oxidative coupling (Fig. 4) (8).

The experiments described were carried out at pH 7 in a phosphate buffer medium. In view of the results described above for TCP, we also tried to oxidize 3,5-DCA by the FePcS/H_2O_2 system without buffering or with a Tris buffer. In the table of Fig. 4, run 2, the nonbuffered experiment gives only 5% 3,5-DCA conversion after 60 min, whereas, in a phosphate buffer, 70% of the substrate was converted in the same time (Fig. 4, run 1), and the reaction rate slows to give only 13% conversion when using a Tris buffer acidified with sulfuric acid (Fig. 4, run 3). Again, for the degradation of 3,5-DCA catalyzed by the FePcS/H_2O_2 system, an influence of the phosphate ions was observed.

Catechols. Subsequently, we studied the degradation of catechols to evaluate whether this phenomenon is common to all the catalytic oxidation reactions initiated by the iron tetrasulfophthalocyanine. Indeed, this complex has also previously been proved to be able to catalyze the oxidation of diverse catechols, which are not pollutants but tannin models used to test the efficiency of potential additives in future washing powders (23).

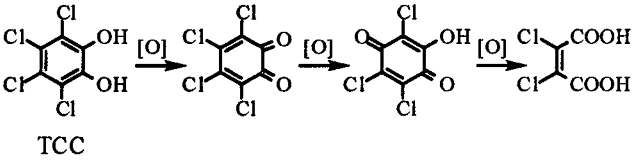
Figures 5, 6, and 7 illustrate the degradation products of catechol and its tetrachloro and di-*tert*-butyl derivatives by the FePcS/H_2O_2 system (24). These substrates were again subjected to the same catalytic system in media buffered either by the phosphate mixture KH_2PO_4/Na_2HPO_4 or by Tris acidified with sulfuric acid to the desired pH value. According to the table in Fig. 5, the decomposition reaction of tetrachlorocatechol (TCC) is very fast, reaching completion in less than 1 min with 4 mol% of catalyst in the phosphate buffer (pH 7) (Fig. 5, run 1). Using the Tris/H_2SO_4 buffer,



Run	Buffer	pH	Conversion of 3,5-DCA at 60 min (%)
1	Phosphate	7	70
2	—	5-6	5
3	Tris/H_2SO_4	7	13

Note. 1 mM 3,5-DCA, 50 mM buffer (buffer/CH_3CN = 1/3 v/v), 0.03 mM FePcS (FePcS/3,5-DCA = 3%), 6 mM H_2O_2.

FIG. 4. Influence of the buffer on the conversion of 3,5-DCA catalyzed by FePcS/H_2O_2.



Run	Buffer (pH 7)	Conversion of TCC (%)	
		1 min	5 min
1	Phosphate	>97	>97
2	Tris/H_2SO_4	<30	<30

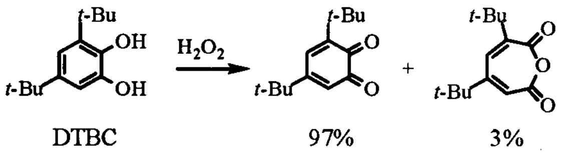
Note. 10 mM TCC, 125 mM buffer/CH_3CN (1/1, v/v), 0.4 mM FePcS (FePcS/TCC = 4%), 60 mM H_2O_2.

FIG. 5. Influence of the buffer on the conversion of TCC catalyzed by FePcS/H_2O_2.

the catalytic oxidation is slower (<30% in 1 min) and the conversion remains low (<30% after 15 min) indicating that the decomposition of this substrate is also sensitive to the presence of phosphate ions (Fig. 5, run 2).

We were very surprised to observe that the other catechol derivatives were rapidly converted to degradation products both in phosphate buffer and Tris buffer (Figs. 6 and 7). The catalytic oxidation reactions were very fast using 4 mol% of FePcS, activated with H_2O_2, and give rise to the same degradation products whatever the buffer.

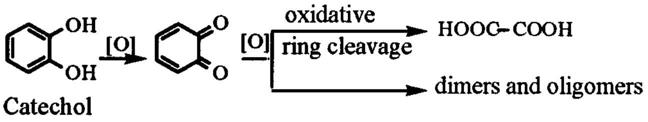
From the various substrates tested under a variety of conditions, it becomes evident that the phosphate buffer only appears to play an important role in the catalytic decomposition of chlorinated aromatic compounds, which are known to be more difficult to oxidize because of the electron-withdrawing effect of the halogen atoms. For the latter, the degradation cannot be achieved by the FePcS/H_2O_2 system under "classical" conditions but necessitates the presence of phosphate ions, which seem to play a key role. In order to verify this hypothesis, we employed an oxidant more powerful than H_2O_2 for the catalytic degradation of TCP, itself chosen as a representative chlorinated aromatic substrate.



Run	Buffer	pH	Conversion (%)	
			1 min	5 min
1	Phosphate	7	86	100
2	Tris/H_2SO_4	7	87	100

Note. 0 mM DTBC, 125 mM buffer/CH_3CN (1/1, v/v), 0.4 mM FePcS (FePcS/DTBC = 4%), 60 mM H_2O_2.

FIG. 6. Influence of the buffer on the conversion of DTBC catalyzed by FePcS/H_2O_2.



Run	Buffer pH (10)	Conversion (%)	
		1 min	5 min
1	Phosphate	81	85
2	Tris/H_2SO_4	94	95

Note. 10 mM catechol, 125 mM buffer, 0.4 mM FePcS (FePcS/catechol = 4%), 60 mM H_2O_2.

FIG. 7. Influence of the buffer on the conversion of catechol with FePcS/H_2O_2.

Utilization of $KHSO_5$ as an Alternative Oxidant for the Catalytic Decomposition of TCP with FePcS

Potassium monoperoxysulfate ($KHSO_5$), available commercially as the triple salt $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$, is used for example in Baeyer–Villiger oxidations (25) or for the synthesis of highly reactive dioxiranes (26). It is also an effective oxidant for the activation of metallophthalocyanines and metalloporphyrins (8–14, 27). As described in previous papers, in phosphate buffer, the catalytic oxidation of all the aromatic substrates cited here proceeds much faster using $KHSO_5$ instead of H_2O_2 (8–14). This raises the question of what is happening when using $KHSO_5$ as oxidant in a medium containing no phosphate ions?

2,4,6-Trichlorophenol is fully converted by the FePcS/$KHSO_5$ system after 60 min in a phosphate buffer at pH 7 (Table 2, run 1). The same result is observed in a Tris/H_2SO_4 buffer at pH 7 (Table 2, run 2) or even in the absence of a buffer (Table 2, run 3), despite the low pH of the mixture (pH 2) caused by the acidity of $KHSO_5$ ($pK_a = 1$). So, in contrast to the FePcS/H_2O_2 catalytic system, activation of the metallophthalocyanine with the powerful $KHSO_5$ oxidant does not require the presence of phosphate ions for the degradation of recalcitrant chlorinated substrates.

TABLE 2

Influence of the Buffer on the Oxidation of TCP Catalyzed by FePcS Activated with $KHSO_5$ or H_2O_2

		Conversion at 60 min (%)	
Run	Buffer	H_2O_2 (pH)	$KHSO_5$ (pH)
1	Phosphate	99 (7)	100 (7)
2	Tris/H_2SO_4	7 (7)	100 (7)
3	—	4 (5–6)	100 (2)

Note. 1.0 mM TCP, 50 mM buffer (buffer/CH_3CN = 1/3 v/v), 0.04 mM FePcS (FePcS/TCP = 4%), 6 mM H_2O_2 or 5 mM $KHSO_5$.

From all the above observations, it became apparent that elucidation of the exact role of the phosphate buffer in the catalytic oxidation of aromatic chlorinated compounds with the FePcS/H_2O_2 system was necessary.

Role of the Phosphate Ions in the Catalytic Oxidation of Aromatic Chlorinated Compounds with the FePcS/H_2O_2 System

Ionic strength. As the phosphate buffer is composed of a mixture of the potassium salt KH_2PO_4 (25 mM) and the sodium salt Na_2HPO_4 (25 mM), a first simple hypothesis was that a modification of the ionic strength could influence the course of the reaction where polar compounds are formed. In run 1, Table 3, the ionic strength of a Tris/CH_3COOH reaction mixture was increased by adding NaCl (25 mM) and KCl (25 mM). However, no improvement in the conversion of TCP was observed, effectively eliminating this hypothesis.

Peroxyphosphate hypothesis. According to the results obtained, the phosphate ions play a direct role in these catalytic oxidations. This led us to investigate whether the phosphate ions themselves could form an active species responsible for the degradation of the substrates. It is known that some salts like carbonate or borate react with hydrogen peroxide to afford hydroperoxy species showing strong oxidative abilities (28). Peroxycarbonate and peroxyborate have thus proved to be more efficient than H_2O_2 for the activation of metallotetrasulfophthalocyanines in the catalytic decomposition of catechol and its derivatives (24). Thus, we carried out chemical and analytical investigations in order to examine a putative intermediate involving the phosphate moiety, such as a peroxyphosphate (Fig. 8).

First, the oxidative reaction of TCP was tried in the presence of only phosphate and H_2O_2 (no FePcS was added). The reaction conditions were as follows: TCP (1 mM) in an acetonitrile/phosphate buffer mixture 1/3 v/v (final concentration of phosphate buffer: 50 mM, pH 7) and H_2O_2 (6 mM). No conversion of TCP was observed (Table 3, run 2). This reaction was also followed by ^{31}P NMR spectroscopy; the chemical shift corresponding to the phosphate buffer ($\delta = 6.7$ ppm) remained unchanged suggesting that peroxyphosphate was not formed under these conditions. According to ^{31}P NMR spectroscopy, no reaction occurred between 1 equivalent of phosphate buffer and 1 equivalent of H_2O_2 even after 1 h at room temperature. In contrast, this reaction has been observed to be catalyzed by the iron tetrasulfophthalocyanine complex. Hence, FePcS was added to the NMR tube but no new signal appeared in the spectrum (note: the commercial peroxydiphosphate $K_4P_2O_8$ resonates at $\delta = 9.5$ ppm). To the best of our knowledge, there are no reports in the literature concerning the formation of a peroxyphosphate salt from the reaction of hydrogen peroxide with inorganic phosphate compounds. On the other hand, several peroxyphosphorus intermediates have been postulated when reacting H_2O_2 with activated phosphorus compounds. This reaction was first used in 1956 by Rosenblatt for the fast hydrolysis of a common insecticide: paraoxon (O,O-diethyl O-*p*-nitrophenylphosphate) (29). More recently, Bunton *et al.* described the cleavage of bis(4-nitrophenyl)phosphate and 4-nitrophenylphosphorochloridate by alkaline hydrogen peroxide (30) while Yang *et al.* proposed the perhydrolysis of *O*-ethyl *S*-(2-diisopropylamino)ethyl methyl phosphonothioate (VX agent) as an efficient decontamination method for this exceedingly toxic nerve agent (31). In a last example, Kende *et al.* have activated hydrogen peroxide using organophosphorus compounds by forming more active peroxy species able to perform alkene epoxidation (32). In our case, the phosphate ion is not electrophilic enough to react with H_2O_2, but could act as an axial ligand for the cationic iron(III) FePcS complex (by replacing the initial hydroxyl group). This coordination of the phosphate to the metal center may enhance its electrophilicity and thus allow its subsequent reaction with H_2O_2. The resulting peroxyphosphate–FePcS complex which can be drawn as the two possible isomeric forms (a) and (b) would be then involved in the oxidative degradation of the chlorinated substrates (Fig. 9). It

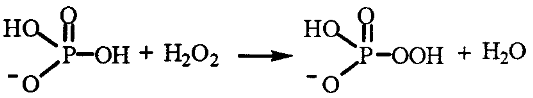


FIG. 8. Hypothetical formation of a peroxyphosphate from the reaction of phosphate ions with H_2O_2.

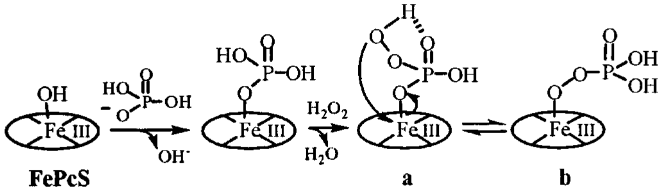


FIG. 9. Formation of the peroxyphosphate–FePcS complex.

TABLE 3

Control Reactions

Run	Conditions	Conversion at 60 min (%)
1	Tris/CH_3COOH + NaCl + KCl	9
2	Phosphate + H_2O_2	9
3	FePcS + H_2O_2	6
4	FePcS + phosphate	6

Note. 1 mM TCP, 50 mM buffer (buffer/CH_3CN = 1/3 v/v), 0.04 mM FePcS (FePcS/TCP = 4%), 25 mM NaCl, 25 mM KCl, 6 mM H_2O_2.

should be noted that the *trans*-coordination of a phosphate moiety and hydrogen peroxide could also be postulated as an active species but, in contrast to metalloporphyrin-catalyzed oxidations, no enhancement of the catalytic activity has been observed with metallophthalocyanines via a *trans*-coordination effect with nitrogen-containing ligands.

Peroxyphosphate–FePcS complex hypothesis. Several observations support the "peroxyphosphate–FePcS complex" hypothesis. First, the control reactions showed that the three partners (FePcS + phosphate + H_2O_2) are indispensable in ensuring good catalytic activities: the experiments (phosphate + H_2O_2), (FePcS + H_2O_2), and (FePcS + phosphate) did not lead to an oxidation of TCP (Table 3, runs 2–4). Finally, the peroxyphosphate–FePcS complex hypothesis might explain the ^{31}P NMR results obtained from the reaction: FePcS + phosphate + H_2O_2. The absence of new signals in the spectrum could be rationalized: (i) by the fact that even if only a small amount of this complex (but sufficient to catalyze the reaction) was formed, it will not be observable by NMR because of its paramagnetic character and (ii) its lifetime would be too short versus that of the NMR experiment. The peroxyphosphate–FePcS complex intermediate was not directly observable under reaction conditions tested so far, hence attempts were made to support its involvement.

In the literature, it has been shown that peroxymonophosphoric acid (PMPA) could be prepared by acid hydrolysis of peroxydiphosphate (PDP) (33) (Fig. 10). Since its discovery in 1910 by Schmidlin and Massini (34), PMPA has appeared in several reports concerning the oxidation of diverse organic and inorganic substrates such as arylketones and aromatic amines (35–37), amino acids (38, 39), substituted indoles (40), and thiocyanate and hydrazinium salts (41, 42). This strong oxidant has also found applications in industrial processes for the treatment of organics in waste waters (43, 44) and for the bleaching of fabrics (45).

Recently, Springer reported a new method for the delignification of wood and kraft pulp using PMPA, which afforded strong bright pulps with minimal damage to cellulose and hemicellulose (16, 46). As a result, we tried to generate the peroxyphosphate–FePcS complex, *in situ*, by adding PMPA to the phthalocyanine and subsequently react it with TCP in a Tris-buffered medium. First, a 3.8% solution of PMPA was prepared according to the procedure described by Springer (16) by hydrolyzing tetrapotassium peroxydiphosphate in a solution of nitric acid in such a manner that the final acid concentration was 2.2 mol/L. Hydrolysis was conducted at 50°C for 30 min. This freshly prepared solution was then added to a reaction mixture containing TCP (1 mM) in an acetonitrile/Tris buffer (1/3, v/v) and FePcS (0.04 mM, i.e., FePcS/TCP = 4%). The final concentrations of Tris buffer and PMPA were 365 and 6 mM, respectively. The conversion of TCP was followed by HPLC (Table 4, run 1), which indicated that after only 5 min, 89% of TCP had been decomposed, corresponding to a catalytic activity of 4.5 cycles per minute. Moreover, control reactions have shown that PMPA alone was not able to oxidize TCP (Table 4, run 2) even in the presence of a simple iron salt (Table 4, run 3). We also checked that the precursor of PMPA, PDP, was inactive (Table 4, run 4). This means that the metallophthalocyanine is really essential and does not just catalyze the production of PMPA from phosphate and H_2O_2. These observations strongly support the formation of a

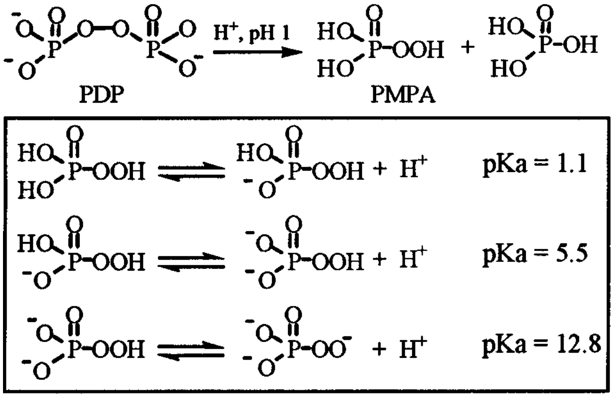


FIG. 10. Synthesis and acid dissociation constants of peroxymonophosphoric acid (PMPA).

TABLE 4

Oxidation of TCP with PMPA or PDP

Run	Conditions	Conversion of TCP (%)	
		5 min	10 min
1	PMPA + FePcS	89	100
2	PMPA	0	5
3	PMPA + Fe(NO_3)$_3$	4	11
4	PDP + FePcS	—	0

Note. 1 mM TCP, 365 mM Tris/CH_3COOH buffer (buffer/CH_3CN = 1/3 v/v), 0.04 mM FePcS or Fe(NO_3)$_3$ (FePcS/TCP = 4%), 6 mM PMPA or PDP.

TABLE 5

Product Distribution from the Oxidation of TCP Catalyzed by FePcS/Phosphate/H_2O_2 and FePcS/PMPA

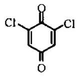
	 DCBQ	Oxidative coupling products	Ring cleavage products
FePcS/phosphate/H_2O_2	0%	29%	27%
FePcS/PMPA	13%	21%	0%

TABLE 6

Influence of the Buffer on the Oxidation of DCBQ Catalyzed by FePcS/H_2O_2

Run	Buffer	pH	Conversion at 60 min (%)
1	Phosphate	7	76
2	Tris/H_2SO_4	7	61
3	—	5–6	39

Note. 1 mM DCBQ, 50 mM buffer (buffer/CH_3CN = 1/3 v/v), 0.04 mM FePcS (FePcS/DCBQ = 4%), 6 mM H_2O_2.

peroxyphosphate–FePcS complex as active intermediate during the catalytic cycle.

Reaction products and mechanism. The organic products of the reaction of TCP with FePcS + PMPA were extracted following a method previously described (14). They were analyzed by ^1H NMR spectroscopy and compared to the products obtained from the FePcS/phosphate/H_2O_2 system. We have already mentioned that with this latter oxidant combination, the degradation products of TCP were mainly ring cleavage products (maleic acid being the major product) and oxidative coupling products (Fig. 2). The ^1H NMR analysis of the reaction catalyzed by FePcS + PMPA shows that under these conditions the major products were the compounds resulting from oxidative coupling (21%) and 2,6-dichloro-1,4-benzoquinone (DCBQ) (13%) even if some minors unidentified compounds appeared also in the ^1H NMR spectrum (Table 5). The total yield of identified products was only 34% but as already mentioned for the H_2O_2 oxidation of TCP catalyzed by FePcS in phosphate buffer, it was underestimated because of the extraction method before NMR analysis (13, 14).

DCBQ has also been detected in the reaction catalyzed by the FePcS/phosphate/H_2O_2 system, but it rapidly undergoes further degradration through Grob-type fragmentations, leading to ring cleavage products. It has been proven that this step could be accomplished either by H_2O_2 alone or *via* FePcS+H_2O_2 catalysis (47), but apparently the FePcS/PMPA complex is not able to perform the C–C bond cleavage. The same observation was made for the reaction catalyzed by FePcS/$KHSO_5$, where DCBQ was formed in 60% yield at pH 2 (13). Thus, the further oxidation of DCBQ by the FePcS/H_2O_2 system should not be expected to be sensitive to the presence of phosphate ions. This was probed by performing an oxidation of DCBQ using the FePcS/H_2O_2 system in different media. In a phosphate buffer, the conversion of DCBQ was 76% after 60 min (Table 6, run 1) and 61% using a Tris/H_2SO_4 buffer (Table 6, run 2). The lack of a significant difference between these two experiments confirms the assumption that the phosphate ions are not essential after the formation of DCBQ. Without buffering the solution, the conversion of DCBQ decreases to 39%, but in this case the solution has a lower pH value (Table 6, run 3).

Thus, the proposed peroxyphosphate–FePcS complex would be active in a step preceding the formation of DCBQ. It is interesting to note that DCBQ and the oxidative coupling products have the same precursor: a phenoxy radical that results from the one electron oxidation of the phenolate form of TCP (Fig. 11). This phenoxy radical can be further oxidized to cationic species and then to DCBQ (13). The different behavior of the three catalytic systems FePcS/phosphate/H_2O_2, FePcS/$KHSO_5$,

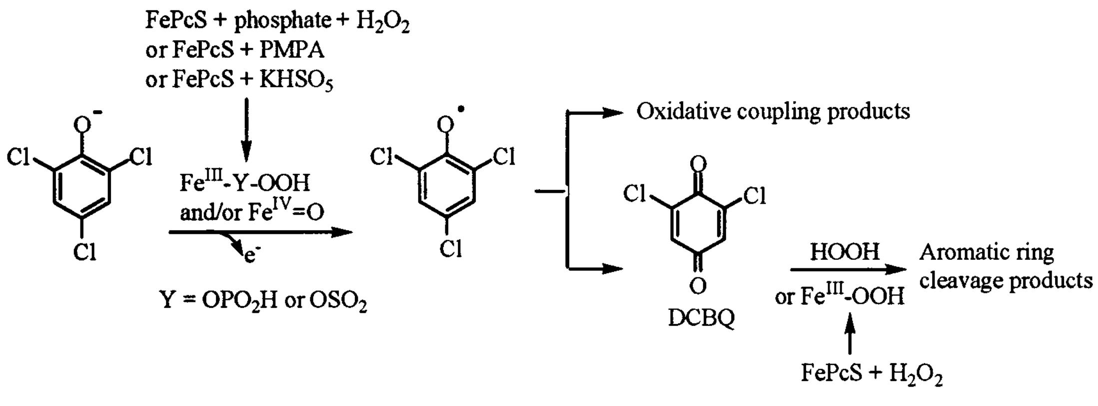


FIG. 11. Proposed mechanism for the degradation of TCP using the different catalytic systems: FePcS/H_2O_2, FePcS/phosphate/H_2O_2, FePcS/$KHSO_5$, FePcS/PMPA.

and FePcS/PMPA could result from the first degradation step of TCP, which consists of a one-electron abstraction of the phenolate derivative. We propose that the iron(III)hydroperoxo species (Fe^{III}–OOH), postulated as the predominant intermediate in the activation of FePcS by H_2O_2, is not able to perform this oxidation. On the other hand, this could be achieved by the more active Fe(IV)=O and Fe(III)-peroxyphosphate species postulated in the course of the reactions of FePcS with $KHSO_5$, FePcS with phosphate+H_2O_2, and FePcS with PMPA. Note that the behavior of the two catalytic systems activated either by $KHSO_5$ or by PMPA is very similar; we can suppose that a peroxysulfate–FePcS complex may be transiently formed in the former case as well as the corresponding Fe(IV)=O species that can also be obtained from the isomeric (**b**) form of the peroxyphosphate–FePcS complex by homolytic cleavage of the O–O bond. However, these highly oxidizing species are not able to cleave the C–C bond of the aromatic ring by a Grob-type fragmentation which can only be achieved by H_2O_2 or an iron(III)–OOH species, and the degradation reaction stops at DCBQ and oxidative coupling products. This proposed mechanism is depicted in Fig. 11.

CONCLUSION

We have highlighted the key role played by the phosphate buffer in the H_2O_2 oxidative degradation of several chlorinated aromatic substrates catalyzed by an iron(III) tetrasulfophthalocyanine. The results of the experiments and control reactions have led us to propose the transient formation of a peroxyphosphate–FePcS complex as an active species involved in the oxidation pathway. A similar intermediate could be obtained by the reaction of the peroxymonophosphoric acid (PMPA) with FePcS. Using 2,4,6-trichlorophenol as a model compound, we were able to establish that the influence of phosphate is effective only in the first reaction step, which corresponds to the one-electron oxidation of the substrate. Correlating all the experimental results obtained has allowed us to propose a mechanism involving Fe(III)–OOH, Fe(III)–peroxyphosphate, Fe(III)–peroxysulfate, and Fe(IV)=O active species, depending on the activation mode used.

ACKNOWLEDGMENTS

The financial support of CNRS is gratefully acknowledged. R.T.F thanks the Alexander von Humboldt Foundation (Feodor-Lynen grant) and the European Community (TMR Grant ERB4001GT973571) for postdoctoral fellowships.

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