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Oxidative degradation of chlorinated phenols catalyzed by a non-heme iron(III) complex

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Abstract

A new symmetric pentadentate ligand containing four pyridine groups, bis(di-2-pyridylmethyl)amine (BDPMA), has been synthesized in a good yield. The corresponding non-heme iron(III) complex, $[Fe(BDPMA)](NO_3)_3$, with potassium monopersulfate as oxidant, catalyzed the oxidative degradation of aromatic pollutants chlorinated phenols to yield the corresponding benzoquinones.

Keywords: Non-heme iron catalyst; Monopersulfate; Chlorinated phenols; Oxidation

1. Introduction

Biomimetic oxidation catalysts capable of degrading environmental pollutants are of great interest. The oxidative degradation of 2,4,6-trichlorophenol (TCP), a major pollutant produced by paper mills [1,2], by chemical ligninase models such as iron and manganese porphyrins [3–5] and iron phthalocyanines [6–9] has been investigated in recent years. The water-soluble iron or manganese sulfoporphyrins were found to be active for the oxidation of TCP to 2,6-dichloro-1,4-benzoquinone (DCQ) in the presence of potassium monopersulfate ($KHSO_5$) [5]. Recently, an efficient system involving H_2O_2, an environmentally compatible oxidant, and a water-soluble iron tetrasulfophthalocyanine has been developed [6–9]. In this case, the catalytic oxidation of the poorly biodegradable TCP led not only to the corresponding benzoquinone but also to ring cleavage products, mainly chloromaleic acid, and even to carbon dioxide [6–8].

However, little is known on the potential use of non-heme mononuclear complexes in the catalytic oxidation of pollutants. This prompted us to synthesize a new symmetric pentadentate ligand bis(di-2-pyridylmethyl)amine (BDPMA) [10] and the corresponding non-heme mononuclear iron(III) complex, $[Fe^{III}(BDPMA)](NO_3)_3$ in order to compare the catalytic activity of such a non-heme complex with macrocyclic complexes in the oxidation of pollutants. The BDPMA ligand consists of four pyridine groups linked to a dimethyl amine. The complexation of BDPMA with $Fe(NO_3)_3$ in a mixture of acetonitrile–methanol led to the corresponding mononuclear complex $[Fe^{III}(BDPMA)](NO_3)_3$ (**A**). The metal ion is probably surrounded in a plane by the four pyridine nitrogen atoms (with

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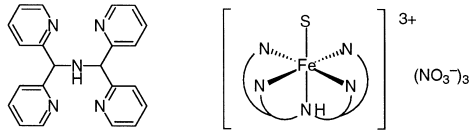
the pyridine ligands sitting perpendicular to the plane defined by these four nitrogen atoms) and by an additional nitrogen atom of the amine function at the fifth coordination site, leaving a vacant site, which is necessary for the activation of the oxidant to generate a possible peroxo or oxo complex.



Herein we report the results on the oxidation of three polychlorophenols catalyzed by the complex $[Fe^{III}(BDPMA)](NO_3)_3$ with $KHSO_5$ as oxidant at pH = 2 (this pH corresponds to a non-buffered aqueous solution of potassium monopersulfate).

2. Experimental section

2.1. Instrumentation

Elemental analyses were carried out by the 'Service de Microanalyse du Laboratoire de Chimie de Coordination'. Mass spectrometry analysis was performed on a Nermag R1010 (FAB^+/*meta*-nitrobenzyl alcohol (MNBA)) by the 'Service de Spectrométrie de Masse de Chimie UPS-CNRS de Toulouse'. EPR spectra were recorded on a Bruker ESP 300 in X Band, with an ER035 M gaussmeter (NMR Probe) and a EIP 548 hyperfrequencymeter. Mössbauer measurements were obtained on a constant-acceleration conventional spectrometer with a 25 mCi source of ^{57}Co (Rh-matrix). The magnetic susceptibility was determined by the Faraday method at room temperature, with a $HgCo(SCN)_4$ matrix ($\chi/g = 16.44 \times 10^{-6}$ emu cgs). The diamagnetism of BDPMA was corrected using Pascal's constants. EPR, magnetism and Mössbauer data were carried out by the 'Service de Mesures Magnétiques du Laboratoire de Chimie de Coordination-CNRS de Toulouse'. High performance liquid chromatography (HPLC) analyses were performed on a Waters 510 liquid chromatograph equipped with a μ-Bondapack C_{18} column (eluent: methanol/water, 60/40, v/v, flow rate: 1 ml min^{-1}, detection at 215 nm). Gas chromatography (GC) analyses were performed with a Hewlett Packard HP 4890A chromatograph equipped with a flame ionization detector and a silica capillary column HP-5 (crosslinked 5% PhMeSiloxane, 15 m $\times$ 0.53 mm $\times$ 1.5 μm) with N_2 as carrier gas. Benzonitrile was used as internal standard for the GC analyses. GC-MS data were collected on a Hewlett-Packard 5890 instrument using electron-impact ionization at 70 eV. The carrier gas was He and a 12 m $\times$ 0.2 mm HL-1 (crosslinked methyl silicone gum) capillary column was used. ^1H NMR spectra were recorded on a Bruker WM 250 spectrophotometer at 250 MHz in DMSO-d_6, with CH_2Cl_2 as internal standard.

2.2. Materials

All chemicals used were of reagent grade. $Fe(NO_3)_3 \cdot 9H_2O$ was purchased from Merck. Potassium monopersulfate, the triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, was a gift from Interox (Curox®). Hydrogen peroxide (H_2O_2) was obtained from Janssen as a 35 wt.% aqueous solution. 2,4,6-trichlorophenol was obtained from Janssen, 2,4-dichlorophenol, *p*-chlorophenol, 2,6-dichloro-1,4-benzoquinone, 2-chloro-1,4-benzoquinone, 1,4-benzoquinone and benzonitrile were purchased from Aldrich. The synthesis of the ligand bis(di-2-pyridylmethyl)amine (BDPMA) is described elsewhere [10].

2.3. Synthesis and characterization of $[Fe^{III}(BDPMA)](NO_3)_3$

To a solution of BDPMA (0.256 g, 0.724 mmol) in acetonitrile (2 ml) was added a

methanolic solution (2 ml) of $Fe(NO_3)_3 \cdot 9H_2O$ (0.293 g, 0.724 mmol). The reaction mixture turned reddish brown. After stirring for 24 h at room temperature, 100 ml of ethylacetate was added to precipitate a green glassy solid. The solvent was removed by distillation and the residue was dried under vacuum to afford a semi-crystalline green solid (400 mg, 81% yield). Analytically calculated for $[Fe(C_{22}H_{19}N_5)](NO_3)_3$, 0.8 EtOAc: C 45.63, H 2.93, N 16.86 was found: C 45.49, H 3.95, N 16.83. MS-FAB: main peak at m/z 471 corresponding to $[Fe^{II}(BDPMA)NO_3]$ (the iron complex is reduced in the mass spectrometer during the analysis). ESR measurements on a solid sample show two resonances at $g = 4.30$ and $g = 2.05$ at 293 K and one resonance centered at $g = 4.38$ at 4 K, which are typical for an iron(III) species containing a mixture of high and low spins. The Mössbauer spectra of the $[Fe^{III}(BDPMA)](NO_3)_3$ recorded at 293 and 80 K consist of two quadrupole split doublets. At 293 K, the isomer shifts are $\delta = 0.370$ and 0.442 mm s^{-1} relative to metallic iron with corresponding quadrupole splittings of $\Delta E =$ 0.771 and 1.610 mm s^{-1} with ratios of 80 and 20% respectively. A Faraday balance measurement at room temperature on a powder sample gives an effective magnetic moment per mononuclear complex of 4.1 μB which is consistent with 80% of iron(III) low spin and 20% of iron(III) high spin.

2.4. General catalytic procedures

2.4.1. Oxidation of polychlorophenols

All reactions were performed in a test tube equipped with a magnetic stirring bar at room temperature and under air. A typical reaction mixture contained 20 μmol of chlorinated phenol (500 μl of a 40 mM acetonitrile stock solution), 740 nmol of the catalyst (500 μl of a 1.48 mM aqueous stock solution; catalyst/substrate ratio = 3.7%) and 100 μmol of oxidant (30.7 mg of $KHSO_5$ or 10 μl of a 35 wt.% H_2O_2 solution in water; i.e., 5 equivalents of oxidant with respect to the substrate) and 1 ml H_2O. The final volume was 2 ml (acetonitrile/water, 1/3, v/v) and the oxidant was the last reagent added. For the quantification of the different 1,4-benzoquinones, 1.25 μmol of benzonitrile was added as internal standard for GC analyses.

2.4.2. Epoxidation of carbamazepine (CBZ)

The reaction mixture contained 500 μmol of CBZ, 5 mmol of $KHSO_5$ and 10 μmol of complex **A** and was performed in a buffered water/methanol mixture (phosphate buffer 67 mM, 8/2, v/v) at pH 5. The reaction was analyzed by HPLC (eluent: methanol/water, 6/4, v/v; flow rate = 1 ml min^{-1}; detection at 215 nm).

3. Results and discussion

3.1. Oxidation of polychlorophenols

The reactivity of the non-heme iron(III) complex **A** was tested in the oxidation of pollutants, namely TCP, 2,4-dichlorophenol (DCP) and *para*-chlorophenol (pCP) in the presence of $KHSO_5$ as primary oxidant. Catalytic oxidations were carried out with 10 mmol of substrate, 0.37 mmol of catalyst (for a catalyst/substrate ratio of 3.7%) and 50 mmol of oxidant (5 equivalents of oxidant with respect to the substrate) in a mixture of acetonitrile–water (1/3) at pH 2.

High conversions were obtained in the oxidation of the three polychlorophenols after 30 min, the conversion being nearly quantitative in the case of TCP (Table 1, entry 1). The corresponding turnover rates were 27, 22 and 23 cycles within 30 min, respectively for TCP, DCP and pCP. These results are consistent with the anodic half-wave potentials E_{pa} (Table 1), which reflect the potential for the first one-elec-

Table 1
Oxidation of chlorinated phenols catalyzed by $[Fe^{III}(BDPMA)](NO_3)_3$

Entry	Substrate	Conversion[a] (%)	Yield of **2**[b] (%)	$t^{c}_{(1/2)}$ (min)	Dechlorination[d]	E^{e}_{pa} (V/ECS)	HOMO[f]
1	**1a**	> 95	63[g](47)	2.5	0.82	0.64	0.76
2	**1b**	80	25[h](12)	2.5	0.86	0.65	0.77
3	**1c**	86	15[h](7)	< 1.0	0.95	0.65	0.79

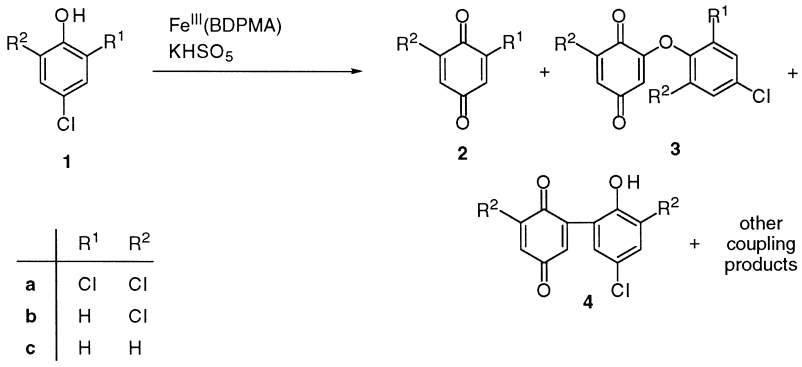
[a]After 30 min.
[b]After 30 min, in parentheses after $t_{(1/2)}$.
[c]Time for half-conversion.
[d]Chloride per converted substrate molecule.
[e]Redox potential of **1**, from Ref. [11].
[f]From Hückel calculations, values expressed as coefficients.
[g]A 30% yield of **3a** were obtained.
[h]Several other products were detected by GC-MS.

tron oxidation [11]. The reported values also show only small variations, but in the correct direction, i.e., they increase from 0.64 V/ECS (at pH 5.5) for TCP to 0.65 V/ECS for pCP. Moreover, the observed conversions are in agreement with the calculated HOMO coefficients for the three polychlorinated phenols (Table 1), which are also very similar for the three phenols. Surprisingly, the time for half-conversion was shorter in the case of pCP (Table 1, entry 3), compared to the values obtained for TCP and DCP (Table 1, entries 1 and 2). In terms of oxidation rates, the catalytic activity of the Fe(BDPMA)/$KHSO_5$ system in the degradation of TCP with 1 mol% of catalyst was lower (only 26% after 30 min) than the one obtained with 3.7% of catalyst **A**, indicating a dependence of the catalyst concentration on the reaction rate.

FeTPPS/$KHSO_5$ based on a sulfonated porphyrin ligand (TPPS: *meso*-tetrakis(4-sulfonatophenyl)porphyrinato) is able to catalyze the oxidation of TCP to DCQ with a catalyst/substrate ratio of 0.3% within 1 min at pH 3 [5]. The yield of DCQ is quantitative, 89% after 15 s, which corresponds to a catalytic activity of 20 cps [5]. This oxidative dechlorination of TCP is performed by the non-heme complex **A** at almost 5 cycles per min, based on the time for half-conversion, corresponding to a moderate catalytic activity, lower to that observed with metalloporphyrin catalysts. However, the turnover rate after 30 min gave less than one cycle per min, indicating that the catalyst was degraded during the oxidation.

The control reactions (substrate + $KHSO_5$, substrate + catalyst, and substrate + iron(III) salt + $KHSO_5$) have been carried out under the same conditions as those described in Section 2. In all these cases, no reaction was detected, confirming that the observed conversions of polychlorophenols (Table 1) are resulting from catalytic oxidations.

The benzoquinones were identified by comparison of GC data with those obtained from authentic samples and directly quantified by GC analyses, using benzonitrile as internal standard. High yield of quinone **2a** was reached when using TCP as substrate and only one other product, a dimer was detected by GC-MS and ^{1}H NMR. In the case of DCP and pCP as substrates, a variety of aromatic and quinoid compounds were obtained, excluding the possible quantification of all different oxidation products. The benzoquinones **2** were also identified qualitatively by GC-MS after extraction of the reaction mixture with diethyl ether. Some of the products, in particular dimers (**3** and **4** in Scheme 1), were not detectable without derivatization, so they were characterized as reduced and acetylated derivatives. Therefore, after complete evaporation of solvent, the crude mixture was



	R^1	R^2
a	Cl	Cl
b	H	Cl
c	H	H

Scheme 1. Oxidation of chlorinated phenols catalyzed by Fe^{III}(BDPMA).

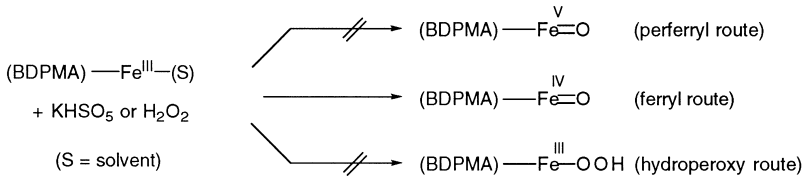
treated with acetic anhydride in the presence of a small amount of zinc and sodium acetate. In order to determine the possible existence of compounds containing phenolic and/or carboxylic acids functions, methylation was performed. Consequently, the reaction mixture was evaporated to dryness and extracted with methanol after which trimethylsulfonium hydroxide was added to generate in situ the corresponding volatile methylesters during the GC-MS analyses [12]. But no ring cleavage products could be identified by this method or by ^{1}H NMR analysis. The concentrations of Cl^- was determined by the mercuric thiocyanate method [13,14]. Approximately one Cl^- ion was released per converted substrate molecule in all three cases (Table 1), such a dechlorination being expected with regard to the observed products.

The activity of the Fe(BDPMA)/H_2O_2 system in the oxidation of TCP was tested at two different pH values (7 and 2). The experimental conditions were similar to those employed with $KHSO_5$, except that a phosphate buffer (acidified with H_3PO_4 for pH 2) was required. No conversion was observed after 30 min at both pH 7 and 2. In the case of the oxidative degradation of TCP in the presence of iron(III) sulfophthalocyanine (FePcS), full substrate conversion was reached within 5 min at pH 7 as well as pH 2. The initial oxidation product was DCQ, which rapidly underwent further catalytic transformations leading to coupling products and ring cleavage products of the produced quinone.

3.2. Possible active species in the Fe(BDPMA) / $KHSO_5$ system

In the case of the FePcS/H_2O_2 system, the proposed active species was a nucleophilic iron(III) hydroperoxo complex, responsible for the C–C bond cleavage [7]. Consequently, the results obtained with the non-heme complex **A** suggest that no Fe^{III}–OOH active species was involved in the catalytic oxidation of TCP. In order to verify the inability of activated Fe(BDPMA) to catalyze the ring cleavage of TCP, we used DCQ as substrate [7]. Two experiments were performed at pH 2 either with $KHSO_5$ or H_2O_2. Once again, no significant conversion was examined in both cases, supporting the exclusion of a Fe^{III}–OOH as active species.

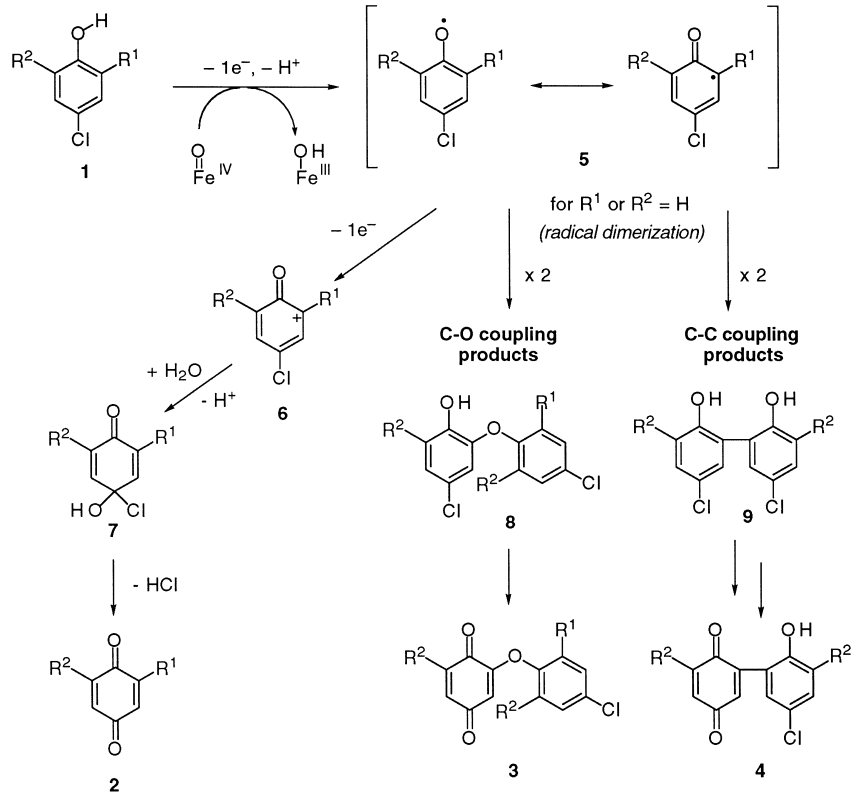
Since $KHSO_5$ is able to behave as a single oxygen atom donor, the system Fe(BDPMA)/$KHSO_5$ has been tested in the epoxidation of carbamazepine (CBZ, an analgesic and anticonvulsant drug) to CBZ-10,11-oxide, which is the main metabolite observed in vivo [15,16]. However, after 1 h at room temperature, no conversion of the substrate was detected. In the case of cationic metalloporphyrins, i.e., Mn^{III}(TMPyP) (TMPyP = *meso*-tetrakis-(4-*N*-methylpyridiniumyl porphyrin), a high-valent



Scheme 2. Proposed active species.

metal-oxo like intermediate $Mn^{V}=O$ was involved in the mechanism of the CBZ epoxidation, with a direct transfer of an oxygen atom from the active species to the olefin [17]. Owing to the fact that no CBZ-10,11-oxide was observed when the polypyridinic complex **A** was activated with $KHSO_5$, the formation of a high-valent $Fe^{V}=O$ species can be excluded. In other words, the formal $Fe^{V}=O$ oxidation state is not reached in the $Fe(BDPMA)/KHSO_5$ system since two redox equivalents above the iron(III) state are required for an efficient oxygen atom transfer.

So we propose that the oxidation of the mononuclear non-heme iron(III) complex **A** by $KHSO_5$ leads to the formation of a $Fe^{IV}=O$ species (by one-electron oxidation of an aqua or a hydroxy ligand of $Fe^{III}(BDPMA)$) that is able to abstract electrons from chlorinated phenols TCP, DCP or pCP but unable to transfer an



Scheme 3. Proposed mechanism for product formation in the $KHSO_5$ oxidation of chlorinated phenols catalyzed by $Fe^{III}(BDPMA)$(R^1 and R^2 = Cl or H).

oxygen atom to an olefin (Scheme 2). This is in agreement with liberation of one Cl^- ion during the substrates conversions. The dechlorination would be higher (2 Cl^- released per TCP molecule consumed in the $FePcS/H_2O_2$ system) in a mechanism involving an Fe^{III}–OOH species and ring cleavage of produced quinones.

3.3. Mechanistic considerations

The Fe^{IV}–oxo active species should abstract one electron and one proton from the phenolic substrate **1** to be reduced to an Fe^{III}–OH species (Scheme 3). So the first oxidation product is the radical **5** (Scheme 3), which can either be further oxidized or undergo several coupling reactions, involving two competitive pathways. In the case of TCP as substrate, the main pathway leads to the formation of the corresponding benzoquinone **2** (Scheme 3). The radical **5** is oxidized to give the carbocation **6**, which reacts with a water molecule to give rise to the corresponding quinone **2a**, with the release of one Cl^- ion. A second dimeric product, having the general formula $C_{12}H_6Cl_4O_3$ and containing a diphenyl ether structure was identified by GC-MS in its reduced and acetylated form. We observed only a single C–H resonance in ^{1}H NMR, but we have no additional structural information on this product.

In the case of DCP (and pCP), in contrast to TCP, both major pathways are involved. The first leads to the CQ (**2b**). The second pathway give rise to several dimers (Scheme 3), involving C–O or C–C coupling reactions. The dimers **8** and **9** are then potential novel substrates for oxidation and the monoquinones **3** and **4**, respectively, can be obtained. Also further condensations are possible to achieve tri- and tetramers but such oligomers were not detected. So, as a complex product mixture was obtained for phenols **1b** and **1c**, it can be concluded that the oxidation of the radical **5** to the cation **6** was rather slow for these two compounds compared to the coupling reactions. The time for half-conversion being shorter with pCP as substrate (less than 1 min) suggests that the second pathway is more pronounced than with the two other phenol substrates.

When the number of chlorine atoms on the chlorophenols decreased, the yield of the corresponding quinone also decreased and the number of detected products increased. This suggests that additional C–Cl bonds in substrates may help to prevent polymerization reactions which inhibit further degradation. Moreover, for TCP (**1a**), the coupling reactions are not possible because at least one hydrogen atom is necessary in the *ortho* position to allow the re-aromatization by deprotonation to the dimers **8** and **9**. Thus, it is straightforward to explain why a more 'selective' reaction is observed. In this case, the radical **5** can only be further oxidized to the cation **6** (Scheme 3) and the quinone **2a** is obtained after elimination of HCl.

4. Conclusion

The new polypyridine mononuclear complex $[Fe(BDPMA)](NO_3)_3$ was the first non-heme catalyst tested in the oxidative degradation of poorly degradable pollutants. The experiments, with $KHSO_5$ as primary oxidant at pH 2, suggested that a Fe^{IV}–oxo species was the active species, able to abstract H-atoms from polychlorophenols, leading to the corresponding benzoquinones. However, the catalytic activity of this complex is rather slow and polymerisation of intermediates became important with di- and mono-chlorophenols.

In order to study the ability of the BDPMA ligand to give mononuclear compounds with a rich nitrogen environment, we are currently synthesizing several complexes of first-row transition metals. These compounds will be tested in various catalytic oxidation reactions.

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