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Oxidation of 3,4-dimethoxybenzyl alcohol in water catalyzed by iron tetrasulfophthalocyanine

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Abstract

Iron tetrasulfophthalocyanine (FePcTs) catalyzes oxidation of 3,4-dimethoxybenzyl alcohol (DMBA) to $\leq 11\%$ 3,4-dimethoxybenzaldehyde (DMBAL), $\leq 7\%$ 2-hydroxymethyl-5-methoxy-1,4-benzoquinone (HMBQ) and other unidentified products in aqueous hydrogen peroxide at 30–40°C. The FePcTs is unstable under the reaction conditions, as UV–visible spectra show its complete decomposition in 2 min. Immobilization of the FePcTs on an anion exchange resin gave oxidation and catalyst decomposition results similar to those in homogeneous solutions. In contrast, potassium monopersulfate gave $> 75\%$ conversion of DMBA to 11–13% DMBAL and at least 8 other products at 30°C using either free or immobilized FePcTs, and 71% conversion in absence of FePcTs. Potassium monopersulfate also oxidized 2,4,6-trichlorophenol to 100% conversion in 6 min at 30°C in the presence of FePcTs and 75% conversion in the absence of FePcTs. Potassium monopersulfate bleaches FePcTs within seconds at 30°C. Thus FePcTs is not a useful catalyst for DMBA oxidation because of its oxidative instability, and potassium monopersulfate is a powerful oxidant even without a catalyst.

Keywords: Oxidation; Hydrogen peroxide; Potassium monopersulfate; 3,4-dimethoxybenzyl alcohol; 2,4,6-trichlorophenol; Iron tetrasulfophthalocyanine

1. Introduction

Lignin is the second most abundant solid component of wood, consisting mainly of phenylpropanoid units substituted with ether oxygens at the 3, 4 and 5 positions [1]. It must be removed from wood pulp to produce white papers. The most common processes for delignification currently employ chlorine or chlorine dioxide, and produce chlorinated phenol residues, which create waste disposal problems [2]. Cleaner, more efficient methods of delignification are needed.

In nature, white rot fungi degrade lignin to CO_2 and H_2O through cleavage of the β-aryl ether bonds. Two active enzymes, lignin peroxidase (LiP) [3,4] and manganese peroxidase (MnP) [5] have been isolated from the wood rotting fungus *Phanerochaete chrysosporium*. Both contain one heme group per molecule. The products of LiP-catalyzed oxidation of lignin model compounds can be rationalized by one-electron oxidations via α-hydroxylation, demethoxylation, aromatic ring cleavage and quinone formation [6]. The crystal structure of LiP [7–9] shows the active site of the heme buried in the protein, so that direct interaction with a lignin polymer is unlikely. Therefore, oxidation is likely accomplished by long range electron transfer and/or by a mediator, which

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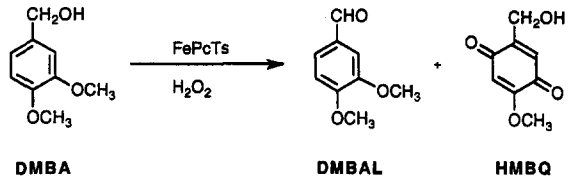
has been proposed to be a radical cation of 3,4-dimethoxybenzyl alcohol (DMBA; common name veratryl alcohol) [6,10–12]. DMBA is a secondary metabolite of lignin degradation by *P. chrysosporium*, and hence is always present in the natural degradation process [6].

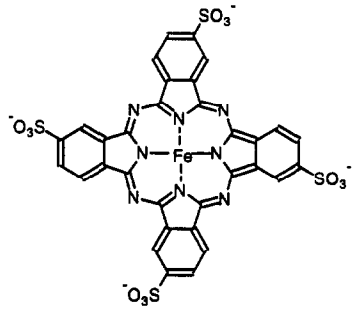
A simple iron porphyrin is less bulky than the enzymes, and should be able to interact directly with the lignin polymer. Several research groups have studied iron porphyrins as LiP mimics to understand the natural oxidations of lignin [13–22]. However, catalysis by these mimics usually falls short of the goal of complete lignin degradation. For industrial application, a catalyst should be low in cost, active at temperatures below 100°C in ambient atmosphere, and effective in aqueous media.

Labat and Meunier have described the oxidation of DMBA to 3,4-dimethoxybenzaldehyde (DMBAL) and 2-hydroxymethyl-5-methoxy-1,4-benzoquinone (HMBQ) catalyzed by water-soluble iron *meso*-tetrakis (*p*-sulfonatophenyl)porphyrin (FeTPPS) and by FeTPPS bound to an anion-exchange resin, Amberlite IRA-900 [19,20], and bound to poly(4-vinylpyridine) [21]. The oxidations were performed with hydrogen peroxide and potassium monopersulfate ($KHSO_5$) in buffered acetonitrile/water solutions under aerobic conditions. The free FeTPPS (0.2 mol% of DMBA) gave DMBA conversions of 5% with H_2O_2 as oxidant, and 67% with $KHSO_5$, while the FeTPPS on IRA-900 (10 mol% DMBA) gave DMBA conversions of 6% with H_2O_2 and 50% with $KHSO_5$ in 1 min at room temperature.

From an industrial standpoint, phthalocyanines are already produced as pigments, and if they have suitable catalytic activity, should be preferred to porphyrins because of lower cost and generally greater stability. Both free FePcTs and immobilized FePcTs catalyze oxidation of 2,4,6-trichlorophenol [23,24]. Various water-soluble phthalocyanines are photocatalysts for the air oxidation of 2-mercaptoethanol in alkaline solutions containing cetyltrimethylammonium chloride (CTAC) micelles [25], and



DMBA DMBAL HMBQ



FePcTS

Scheme 1.

CoPcTs bound to cationic polyelectrolytes is highly active for the air oxidation of 2-mercaptoethanol [26].

The FePcTs-catalyzed oxidations of DMBA with hydrogen peroxide (Scheme 1), and concentrations of 1–3 mol% FePcTs based on DMBA, all resulted in the same 31% conversion of DMBA during 15 minutes at 85°C [27]. The oxidations proceeded to higher conversion at pH 3 than at higher pH. Our initial goal in the present investigation was to find lower and optimum FePcTs concentration and temperature for the oxidation of DMBA with hydrogen peroxide. The long term goal is to find convenient conditions for the complete degradation of lignin. This paper reports the short term results.

2. Experimental

2.1. Materials and analysis

UV–visible spectra were obtained in aqueous solution on a Hewlett Packard HP 8452A UV–

visible diode array spectrophotometer. GC-MS analyses were performed on a Hewlett Packard G1800A GCD spectrometer. HPLC was performed on a Partisil® 5 ODS-3 reversed phase column (Whatman) with water/methanol 6.5/3.5 v/v eluant at a flow rate of 1 mL min^{-1} with UV detection at 280 nm. All organic chemicals were used as received from Aldrich Chemical. DMBA was 98% pure by HPLC analyses, and contained < 1% vanillin and 2% DMBAL. Amberlite IRA-900 was rinsed with methanol and water, and dried overnight under vacuum. FePcTs (an isomeric mixture) was provided by Srinivasan [28] and was prepared by a literature method [29]. Aqueous hydrogen peroxide (Fisher, 30%) contained 28.2% H_2O_2 by iodometric titration [30]. Potassium monopersulfate (DuPont Oxone) contained 3.15 mmol $KHSO_5$ per gram by iodometric titration. Water was deionized twice and distilled.

2.2. Oxidation of DMBA. Method 1

A mixture of an aqueous stock solution of FePcTs (173 μL, 0.865 μmol, 0.25 mol% based on DMBA) and water (3.24 mL, giving a total of 3.5 mL of aqueous phase) was dispensed into a UV cuvette. The cuvette was placed in the spectrophotometer and thermostated by circulating water from a bath maintained at 40°C for 10–15 min. The reaction was started by the addition of DMBA (51 μL, 0.35 mmol) and H_2O_2 (36 μL, 0.35 mmol). After 60 min, the reaction mixture was added to dichloromethane, 0.8 g of NaCl was added to decrease the solubility of organic compounds in the aqueous phase, and the mixture was extracted 5 times with a total of 10 mL of dichloromethane. The organic phase was dried over anhydrous sodium sulfate, rotorary evaporated until approximately 1 mL of liquid remained, diluted with 5 mL of methanol/water (35/65, v/v), and rotorary evaporated until 0.5 mL remained. The solution was transferred to a 1 mL volumetric flask, the reaction flask was washed with methanol/water (35/65, v/v), the washings were added to the extract to make 1.00 mL, 1,2-dimethoxybenzene (DMB) (51 μL, 5.1 μmol) was added as an internal standard, and the solution was analyzed by HPLC in comparison with standard mixtures of DMBA, DMBAL, and DMB.

2.3. Method 2

A mixture of an aqueous stock solution of FePcTs (1 mL, 5.0 μmol, 1 mol% based on DMBA) and water (1.74 mL, giving a total of 5.0 mL of aqueous phase) was placed in a flask containing a magnetic stirring bar. The flask was attached to a reflux condenser and placed in a 40°C bath for 10–15 min. DMBA (2 mL, 0.5 mmol) and 30 wt% of H_2O_2 (0.26 mL, 2.5 mmol) were added. The mixture was stirred for 60 min, extracted, and analyzed as in method 1.

2.4. Method 3

A mixture of an aqueous stock solution of FePcTs (500 μL, 200 nmol, 1 mol % based on DMBA) (or 30 mg FePcTs–Amb and 500 μL of water) and water (500 μL) was dispensed into a test tube containing a magnetic stirring bar. The tube was capped with a rubber stopper and placed in a 30°C bath for 10–15 min. DMBA (500 μL, 20 μmol) and 500 μL of a solution containing 100 μmol of oxidant (32.1 mg of $KHSO_5$ in phosphate (pH 7) buffer or 10 μL of 30% H_2O_2 in water) were added with stirring. After 60 min, the mixture was extracted 3 times with a total of 4 mL of dichloromethane. The organic phase was dried and analyzed as in method 1.

2.5. Oxidation of TCP

Method 3 was followed using 2 mL of aqueous mixture both in the presence and in the absence of FePcTs. Analyses of the 20°C mixtures were performed by rapid dilution of the solution into 65/35 water/methanol and immediate HPLC analysis. Analyses of the 30°C mixtures were performed after extraction of organic components into CH_2Cl_2 as before.

2.6. Product identification

To obtain enough material for identification of HMBQ, the oxidation was carried out using 1 mmol DMBA, 1 wt% (based on DMBA) of FePcTs, and 5 mmol of H_2O_2. After extraction, the products were purified by preparative TLC using silica gel 60 F_{254} (Analtech) plates developed in hexane/ethyl acetate. The plate was developed once, dried in air, and developed a second time in the same solvent. The bands were scraped off, and the products were extracted into methanol. HMBQ was analyzed by ^{1}H-NMR and GC-MS. HMBQ: MS, m/e (%): 168 (M^+, 100), 139 (49), 122 (10), 109 (21), 77 (19), 69 (36). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 3.85 (s, 3H), 4.64 (d, 2H), 5.82 (s, 1H), 6.48 (t, 1H).

2.7. Binding of FePcTs to Amberlite IRA-900

Amberlite IRA-900, 1.0 g, was added to a solution of 10.0 mg of FePcTs in 40 mL of (1/1) water/acetonitrile. After 48 h of gentle shaking, the solid was isolated by filtration and washed with 40 mL of (3/1) water/acetonitrile. The filtrate was analyzed for FePcTs by visible spectrophotometry to contain 0.9 mg of unbound FePcTs. The resin was dried in air at room temperature for 24 h and at 65°C for 72 h. The amount of FePcTs bound was 7.9 μmol/g, and the mol ratio of N^+ sites in the resin to FePcTs was 500.

3. Results and discussion

3.1. Oxidations monitored by visible spectrophotometry (method 1)

All reactions were carried out in ambient air in unbuffered aqueous solutions containing no organic cosolvent at 40°C for direct comparison to the results of Zhu [27]. Oxidations of DMBA by H_2O_2 were conducted in a quartz cell so that the visible spectrum of FePcTs could be recorded simultaneously. In experiment 1 (Table 1), the deep blue color of the FePcTs solution faded to a pale green within 2 min after addition of H_2O_2, as shown in the spectra of Fig. 1. Even the first spectrum in Fig. 1, taken about 10 s after addition of H_2O_2, has absorbance at λ_{max} = 634 nm only 23% as much as calculated from spectra measured in the absence of H_2O_2, assuming linear dependence of absorbance on FePcTs concentration. Under these conditions the initial absorbance before addition of H_2O_2 is too high to measure. The initial concentration was chosen to be identical to that used in oxidation method 1. The *Q* band at 634 nm can be assigned to either a face-to-face van der Waals dimer or a μ-oxo dimer of FePcTs [27,28]. During the first two minutes, a weaker absorption band appeared at about 720 nm, and it faded, too. No further spectral changes occurred over 60 min. Blank spectra of a solution containing the same initial concentrations of FePcTs and H_2O_2, but no DMBA, are shown in Fig. 2. The first spectrum, taken 10 s after mixing, shows only 19% of the absorbance of FePcTs at 634 nm, less of the 720 nm band than in the presence of DMBA, and almost the same final spectrum after 2 min as that in Fig. 1. The spectra indicate complete degradation of FePcTs by H_2O_2 within 2 min of mixing, with or without DMBA present.

Isolation of the dichloromethane-soluble components of the mixture of experiment 1 (Table 1) after 60 min and analysis by HPLC showed conversion of more than half of the

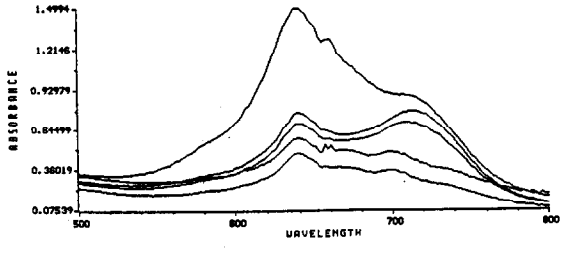


Fig. 1. Visible spectra showing decomposition of 0.25 mM FePcTs in the presence of 0.1 M each of H_2O_2 and DMBA. The top spectrum, taken 10 s after mixing, shows loss of 77% of the initial FePcTs. The bottom spectrum was obtained 120 s after mixing.

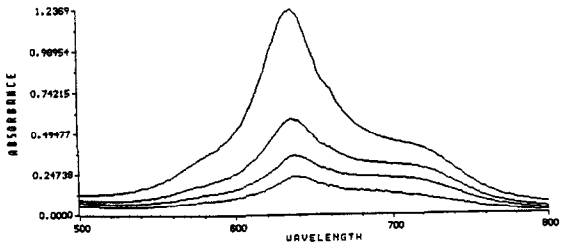


Fig. 2. Visible spectra showing decomposition of 0.25 mM FePcTs in presence of 0.1 M H_2O_2. The top spectrum shows 81% decomposition of FePcTs 10 s after mixing. The bottom spectrum was obtained 120 s after mixing.

DMBA to a mixture of DMBAL, HMBQ, and other products that were not identified but gave 6 additional peaks by HPLC. During experiment 1, the pH of the solution decreased from 6.9 to 5.1, which suggests that one or more carboxylic acids or phenols were in the mixture. Experiments 3 and 4 in Table 1 show that no oxidation occurred in the absence of H_2O_2 or FePcTs. The isolation procedure gave recovery of only 91–93% of the DMBA. We presume that less of more-water-soluble products, and more of less-water-soluble products would be recovered. In experiment 2, use of a much higher initial concentration of DMBA, equimolar to that of H_2O_2, gave products similar to that of experiment 1 and left much more unreacted DMBA.

3.2. Oxidation of DMBA with varied FePcTs concentration (method 2)

Oxidations of DMBA by 5 molar equivalents of H_2O_2 were conducted in unbuffered aqueous solutions at 40°C in ambient air (Table 2) for comparison with the results of Zhu [27]. In each experiment, the blue color of FePcTs faded to light green or colorless, and DMBAL was accompanied by several unidentified products. Products were isolated in experiment 1 without added NaCl to salt organic compounds out of water during extractions with dichloromethane. The otherwise identical experiment 2, in which NaCl was used during extractions, gave higher recovery of unreacted DMBA and almost the same product mixture. Experiment 3, conducted under nitrogen instead of air, gave slightly higher conversion of DMBA to both DMBAL and unidentified products. New peaks appeared in the HPLC that were not observed with product mixtures obtained under air. The control experiment 4, conducted with no DMBA and a higher concentration of FePcTs, shows that none of the unidentified products detected by HPLC come from the FePcTs. The visible spectra of Fig. 1 suggest that all of the oxidation occurs during the first two minutes if FePcTs is the catalyst. However, a decomposition product of the FePcTs could also catalyze further oxidation over a longer time. Experiment 5, conducted at a shorter reaction time of 2 min, shows lower conversion and less oxidation products when compared to experiment 6 at a reaction time of 20 h.

3.3. Oxidations of DMBA by H_2O_2 and $KHSO_5$ with free and immobilized FePcTs (method 3)

A series of experiments carried out with a 5/1 mol ratio of oxidant to DMBA under air at

Table 1
Oxidation of DMBA at 40°C for 1 h

Expt.	Initial concn. (mM)			Product mixture (mol%)			
	DMBA	H_2O_2	FePcTs	DMBA	DMBAL [a]	HMBQ	other [b]
1	1.5	100	0.25	44	4	5	6
2	100	100	0.25	82	2	2	4
3	1.5	100	0	91	0	0	0
4	1.5	0	0.25	93	0	0	0

[a] In excess of DMBAL in the starting DMBA.
[b] Number of unidentified peaks in HPLC.

Table 2
Effect of FePcTs concentration on oxidation of DMBA with 0.50 M H_2O_2 at 40°C for 1 h

Expt.	Initial concn. (mM)		Product mixture (mol%)			
	DMBA	FePcTs	DMBA	DMBAL [a]	HMBQ	other [b]
1	100	1.0	64	9	6	4
2	100	0.5	89	8	5	4
3 [c]	100	0.5	77	11	4	5
4	0	1.0	0	0	0	0
5 [d]	100	1.0	75	3	2	3
6 [e]	100	1.0	58	11	7	8

[a] In excess of DMBAL in the starting DMBA.
[b] Number of unidentified peaks in HPLC.
[c] Conducted under nitrogen, not air.
[d] Reaction time 2 min.
[e] Reaction time 20 h.

30°C is reported in Table 3. The conditions were selected to be as much as possible like those reported by Labat and Meunier for iron tetrasulfoporphyrin (FeTPPS)-catalyzed oxidations of DMBA [19,20]. They reported 5–7% conversion of DMBA to DMBAL by H_2O_2 in one minute at room temperature using 0.02 mM FeTPPS, and 65–67% conversion using $KHSO_5$, in pH 3 citrate–phosphate buffered 25/75 acetonitrile/water. The major difference between their results and ours in Table 3 is that our longer reaction times and slightly higher temperature give more of the unidentified products, presumably from further oxidation of DMBAL. In experiments 3 and 4 with $KHSO_5$ as the oxidant, the FePcTs bleached completely, both in solution and bound to the ion exchange resin, and the deep amber color of Amberlite IRA-900 turned to white. Experiment 5, in the absence of FePcTs, shows that $KHSO_5$ is such a powerful oxidant that the FePcTs catalyst is not needed to oxidize the DMBA.

Experiment 6, using H_2O_2 and a 0.1 M solution of a cationic surfactant, cetyl trimethylammonium chloride (CTACl), which should also bind the anionic FePcTs, gave the same results as with no surfactant or with the anion exchange resin. In the presence of CTACl, there was a new shoulder at about 680 nm in the visible spectrum (Fig. 3) that is attributed to a monomeric form of FePcTs [31,32]. This new spectral band disappeared within 2 min after addition of H_2O_2 just as the 634 nm band did. CTACl does not stabilize the FePcTs signifi-

Table 3
Oxidations of DMBA using H_2O_2 and $KHSO_5$ with soluble and immobilized FePcTs catalyst [a]

Expt.	Oxidant	Catalyst	Product mixture (mol%)			
			DMBA	DMBAL [b]	HMBQ	other [c]
1	H_2O_2	FePcTs	81	3	> 1	1
2	H_2O_2	FePcTs–Amb [d]	80	2	> 1	1
3	$KHSO_5$	FePcTs	24	13	12	7
4	$KHSO_5$	FePcTs–Amb [d]	23	11	9	8
5	$KHSO_5$	none	29	10	11	6
6	H_2O_2	FePcTs–CTACl [e]	84	3	> 1	3

[a] All experiments used initial concentrations of 10 mM DMBA, 50 mM oxidant, and 0.10 mM FePcTs at 30°C under air for 60 min.
[b] In excess of DMBAL in the starting DMBA.
[c] Number of unidentified HPLC peaks.
[d] FePcTs bound to Amberlite IRA-900.
[e] Solution contained 0.10 M cetyltrimethylammonium chloride.

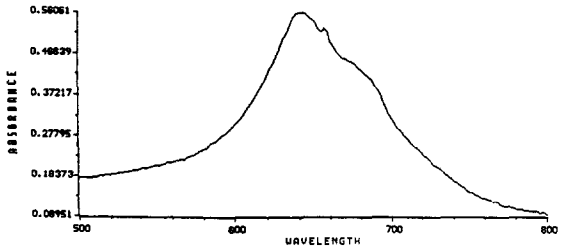


Fig. 3. Visible spectrum of 1.0×10^{-5} M FePcTs in aqueous 0.1 M CTACl solution at 25°C.

cantly against oxidation by H_2O_2. The monomeric band at about 680 nm in the visible spectrum becomes more intense when a FePcTS solution containing no buffer or surfactant is heated to 70°C, as expected from previous observations of other metal tetrasulfophthalocyanines [33].

3.4. Oxidation by oxygen catalyzed by CoPcTS, ZnPcTS and AlPcTS

Previous oxidations of 2-mercaptoethanol, 1-decylmercaptan, and inorganic sulfide with dioxygen catalyzed by CoPcTS, and with singlet oxygen photocatalyzed by ZnPcTS and AlPcTS, gave higher conversion in the presence of CTACl micelles, and in the presence of cationic polyelectrolytes and latexes, because the decomposition of the metallophthalocyanine was retarded when bound to cationic micelles [25,26]. We found low activity for CoPcTS-catalyzed reaction of dioxygen with DMBA with or without cationic latexes [27]. During the present investigation, we tried to oxidize DMBA with singlet oxygen generated by photosensitization with ZnPcTS and with AlPcTS in pH 7 and pH 11 aqueous solutions under one atmosphere pressure of dioxygen [26]. The amount of oxygen consumed during one hour at room temperature in every experiment was less than five percent of the theoretical amount required for oxidation of DMBA to DMBAL. Since exactly the same experimental procedure leads to rapid consumption of dioxygen by reaction with inorganic sulfide or 2-mercaptoethanol, we conclude that DMBA does not react readily with singlet oxygen.

3.5. Oxidation of 2,4,6-trichlorophenol with $KHSO_5$

Sorokin and Meunier reported that the ubiquitous pollutant 2,4,6-trichlorophenol (TCP) is completely oxidized in one minute at room temperature by $KHSO_5$ with FePcTs catalysis in an acetonitrile/water solution buffered at pH 3 or 7, and is oxidized at a slower rate by H_2O_2 [23,24]. Because of our earlier observations that $KHSO_5$ rapidly oxidizes alkenes of low water solubility in aqueous dispersions with no added organic solvent or catalyst [34], we tested the oxidation of the poorly water-soluble TCP with $KHSO_5$ in the presence and in the absence of FePcTs under the conditions of method 3. The color of the FePcTs was completely bleached within 10 s after addition of $KHSO_5$. Experiment 1 in Table 4 shows that oxidation of TCP with $KHSO_5$ and no organic solvent was 75% complete in 6 min at 30°C even in the absence of FePcTs, and experiment 2 shows 100% oxidation in the presence of 1 mol% of FePcTs. We did not identify the products that give 4 peaks by HPLC. Chloromaleic, chlorofumaric, maleic, and fumaric acids and four coupling products were identified before [24]. Control experiment 3 shows that the extraction method of product isolation recovered 90% of the TCP. Experiment 4 shows that $KHSO_5$ oxidized TCP

Table 4
Oxidation of 2,4,6-trichlorophenol with $KHSO_5$ [a]

Expt.	pH	Time (min)	Temp. (°C)	$KHSO_5$ (mM)	Mol% FePcTs	%TCP left
1	3	6	30	50	0	25
2	3	6	30	50	1	0
3	3	6	30	0	0	90
4	7	6	30	50	0	66
5	2	1	20	50	0	81 [b]
6	2	5	20	50	0	72 [b]

[a] 10 mM TCP; pH 2 unbuffered; pH 3 citrate buffer; ph 7 phosphate buffer.
[b] Average of 2 experiments ±3%.

more slowly at pH 7 than at pH 3. Experiments 5 and 6 show that the oxidation of TCP is substantially slower at 20°C than at 30°C. Thus $KHSO_5$ alone oxidizes TCP without any catalyst and completely oxidizes TCP in the presence of 1 mol% FePcTs under conditions where the FePcTs is also oxidized rapidly.

4. Conclusions

FePcTs catalyzes the oxidation of DMBA by hydrogen peroxide, but the catalyst degrades too fast to be useful for delignification. FePcTs bound to Amberlite IRA-900 has about the same activity and the same stability as it does in solution. FePcTs catalyzes the oxidations of DMBA and 2,4,6-trichlorophenol with potassium monopersulfate, and these oxidations proceed even in the absence of a catalyst. Useful catalysts for lignin degradation must be more oxidatively stable than FePcTs.

Acknowledgements

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References

[1] N.G. Lewis and E. Yamamoto, Ann. Rev. Plant Physiol. Plant Mol. Biol. 41 (1990) 455.
[2] A.M. Thayer, Chem. Eng. News (Nov. 1, 1993) 28.
[3] M. Tien and T.K. Kirk, Science 221 (1983) 661.
[4] J.K. Glenn, M.A. Morgan, M.B. Mayfield, M. Kuwahara and M.H. Gold, Biochem. Biophys. Res. Commun. 114 (1983) 1077.
[5] M. Kuwahara, J.K. Glenn, M.A. Morgan and M.H. Gold, FEBS Lett. 169 (1984) 247.
[6] H.E. Schoemaker, T.K. Lundell, A.I. Hatakka and K. Piontek, FEMS Microbiol. Rev. 13 (1994) 321, and references therein.
[7] K. Piontek, T. Glumoff and K. Winterhalter, FEBS Lett. 315 (1993) 119.
[8] S.L. Edwards, R. Raag, H. Wariishi, M.H. Gold and T.L. Poulos, Proc. Natl. Acad. Sci. USA 90 (1993) 750.
[9] T.L. Poulos, S.L. Edwards, H. Wariishi and M.H. Gold, J. Biol. Chem. 268 (1993) 4429.
[10] P.J. Kersten, M. Tien, B. Kalyanaraman and T.K. Kirk, J. Biol. Chem. 260 (1985) 2609.
[11] K.E. Hammel, M. Tien, B. Kalyanaraman and T.K. Kirk, J. Biol. Chem. 260 (1985) 8348.
[12] H.E. Schoemaker, P.J. Harvey, R.M. Bowen and J.M. Palmer, FEBS Lett. 183 (1985) 7.
[13] B. Meunier, Chem. Rev. 92 (1992) 1411.
[14] B. Meunier, in: Metalloporphyrins in Catalytic Oxidations, ed. R.A. Sheldon (Dekker, New York, 1994) p. 133.
[15] M. Shimada, T. Habe, T. Umezawa, T. Higuchi and T. Okamoto, Biochem. Biophys. Res. Commun. 122 (1984) 1247.
[16] R. DiCosimo and H.-C. Szabo, J. Org. Chem. 53 (1988) 1673.
[17] F. Cui and D. Dolphin, ACS Symp. Ser. 399 (1989) 279.
[18] F. Cui and D. Dolphin, Can. J. Chem. 70 (1992) 2314.
[19] G. Labat and B. Meunier, New J. Chem. 13 (1989) 801.
[20] G. Labat and B. Meunier, J. Org. Chem. 54 (1989) 5008.
[21] G. Labat and B. Meunier, C. R. Acad. Sci. Paris II 311 (1990) 625.
[22] P.A. Watson, L.J. Wright and T.J. Fullerton, J. Wood Chem. Tech. 13 (1993) 371, 391, 411.
[23] A. Sorokin and B. Meunier, J. Chem. Soc. Chem. Commun. (1994) 1799.
[24] A. Sorokin, J.-L. Séris and B. Meunier, Science 268 (1995) 1163.
[25] G. Schneider, D. Wöhrle, W. Spiller, J. Stark and G. Schulz-Ekloff, Photochem. Photobiol. 4 (1994) 333.
[26] J. van Welzen, A.M. van Herk, H. Kremer, T.G.L. Thijssen and A.L. German, J. Mol. Catal. 59 (1990) 311, and references therein.
[27] W. Zhu and W.T. Ford, J. Mol. Catal. 78 (1993) 367.
[28] S. Srinivasan and W.T. Ford, J. Mol. Catal. 64 (1991) 291.
[29] J.H. Weber and D.H. Busch, Inorg. Chem. 4 (1965) 469.
[30] G.H. Jeffery, J. Bassett, M. Mendham and R.C. Denney, Vogel's Textbook of Quantitative Chemical Analysis, 5th Ed. (Longman, England, 1989) p. 394.
[31] H. Sigel, P. Waldmeier and B. Prijs, Inorg. Nucl. Chem. Lett. 7 (1971) 161.
[32] S. Gupta, H. Huang and E. Yeager, Electrochim. Acta 36 (1991) 2165.
[33] Y. Yang, J.R. Ward and R. Seiders, Inorg. Chem. 24 (1985) 1765.
[34] W. Zhu and W.T. Ford, J. Org. Chem. 56 (1991) 7022.