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Metallophthalocyanine-catalyzed oxidation of catechols by H_2O_2 and its surrogates

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Abstract

Iron sulfophthalocyanines are powerful catalysts for the oxidation of catechols when using hydrogen peroxide or percarbonate as oxidants. Dichloromaleic acid is an oxidation product of tetrachlorocatechol, indicating that the aromatic ring was cleaved.

Keywords: Iron/manganese/cobalt tetrasulfophthalocyanines; Catechol oxidation; Aromatic cycle cleavage; Hydrogen peroxide; Percarbonate

1. Introduction

Water-soluble iron and manganese sulfoporphyrins and sulfophthalocyanines have been developed during the last decade as catalysts in the modeling of ligninase and manganese peroxidase, two extracellular peroxidases of *Phanerochaete chrysosporium* [1–9]. In the case of metallo-sulfophthalocyanines, it should be noted that these complexes are more active as catalysts than the corresponding hydrophobic complexes [10–12]. We have recently evidenced that a poorly biodegradable pollutant like 2,4,6-trichlorophenol was easily oxidized by hydrogen peroxide in the presence of catalytic amounts of soluble or supported iron sulfophthalocyanine (FePcS, see Fig. 1 for structure), not only to the corresponding 2,6-dichloro-1,4-benzoquinone as observed with iron sulfoporphyrins, but ring cleavage products (mainly chloromaleic acid) [13–15] and also carbon dioxide [16]. We decided to investigate the efficiency of the $FePcS/H_2O_2$ system in the bleaching of simple organic substrates like catechols, which are considered as good models of tannins since condensed tannins are among the main stains [17]. In addition catechols are relevant to the biological oxidation of aromatic rings [18–22]. There is an obvious need of an environmentally friendly bleaching process to replace the chlorine-based bleaching of wood pulp in the paper industry [23] and of efficient catalysts in the new generation of washing powders [17].

Here we report a detailed study of the oxida-

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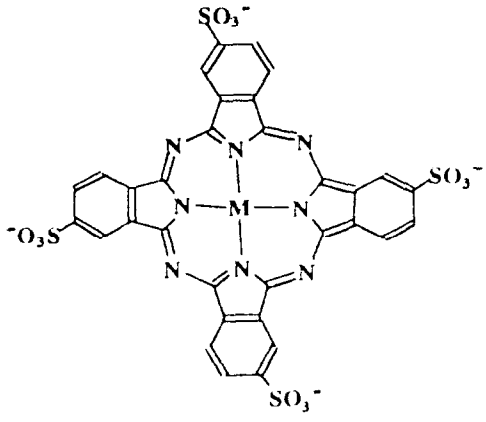

Fig. 1. Structure of metal complexes of 2,9,16,23-tetrasulfophthalocyanine (M = Fe, Mn, Co, Ni).

tion of catechols catalyzed by metal complexes of tetrasulfophthalocyanine in the presence of hydrogen peroxide or its surrogates.

2. Experimental

2.1. Instrumentation

GC-MS data were collected with a Hewlett-Packard 5890 instrument using electron-impact ionization at 70 eV. The carrier gas was He and a 12 m × 0.2 mm HL-1 (crosslinked methyl silicone gum) capillary column was used. UV–visible spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. High performance liquid chromatography (HPLC) analyses were performed on a Waters-486 liquid chromatograph equipped with a μ-Bondapak C18 column, the eluent being a mixture of methanol and water (1/1, v/v) at a flow rate of 1 mL min^{-1}, detection at 280 nm. ^{1}H NMR spectra were recorded on Bruker WM 250 spectrometer (working at 62.9 MHz for ^{13}C nucleus).

2.2. Materials

All chemical used were of reagent grade. Sodium percarbonate, $Na_2CO_3 \cdot 1.5H_2O_2$ and sodium perborate, $NaBO_3 \cdot 4H_2O$ were purchased from Aldrich. Tetraacetylethylenediamine (TAED) was a gift from ELF-Lacq. Hydrogen peroxide was obtained from Janssen Chimica as a 35 wt% aqueous solution. Nickel and copper tetrasulfophthalocyanines (NiPcS, CuPcS) were purchased from Aldrich. Iron, manganese and cobalt complexes of tetrasulfophthalocyanine (FePcS, MnPcS and CoPcS) were prepared by the method of Weber and Busch [24]. A manganese complex of 1,4,7-trimethyl-1,4,7-triazacyclononane, $Mn_2(1,4,7\text{-}Me_3TACN)_2(\mu\text{-}O)_3(PF_6)_2$, (MnTACN) was prepared by published method [25]. Catechol, 3-methylcatechol, 3-methoxycatechol, 3,5-di-*tert*-butylcatechol and tetrachlorocatechol monohydrate were obtained from Aldrich.

2.3. General analytical procedures

The catalytic oxidations of catechol, 3-methylcatechol and 3-methoxycatechol were monitored spectrophotometrically by the nitrite method [26]. The corresponding derivatives were quantified at 512 nm ($\varepsilon = 10{,}200$) for catechol, at 510 nm ($\varepsilon = 12{,}800$) for 3-methylcatechol and at 504 nm ($\varepsilon = 13{,}100$) for 3-methoxycatechol. The concentrations of free Cl^- ions were determined by the mercuric thiocyanate method [27]. Trimethylsulfonium hydroxide solution was used to generate, in situ during the GC-MS analyses, volatile methyl esters of compounds containing phenolic and carboxylic acid functions [28]. The other methylating agent, diazomethane, was prepared from *N*-methyl-*N'*-nitro-*N*-nitrosoguanidine [29].

2.4. General catalytic procedures for catechol oxidations

All reactions were performed in a thermostated reaction tube equipped with a magnetic stirring bar at 20 or 40°C under air. In a typical experiment 20 μmol of a catechol (500 μL of a 40 mM solution, water for catechol, 3-methylcatechol and 3-methoxycatechol, or acetonitrile for 3,5-di-*tert*-butylcatechol and te-

trachlorocatechol) were added to 100 μmol of the oxidant (1000 μL of a 0.1 M aqueous solution). The reaction mixture was adjusted to the desired pH value with 0.5 M HCl or 1 M NaOH and, if necessary, with water in order to reach a final volume of 2 mL after addition of the catalyst solution. The reaction was initiated by addition of the catalyst solution (200, 20 or 2 nmol of catalyst 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 stirred at 20 or 40°C. Phosphate buffer (pH 7.0, 500 μL of 0.5 M stock solution) was used for experiments performed at pH 7. Aliquots were withdrawn during the reaction course and analyzed by the nitrite method (catechol, 3-methylcatechol, 3-methoxycatechol) or by HPLC (3,5-di-*tert*-butylcatechol and tetrachlorocatechol).

2.5. Oxidation of catechol in the presence of ethanol and mannitol

These experiments were performed as describe above at pH 10.5 and 40°C using 0.1% catalyst/catechol ratio. The reaction mixture contained 20 or 200 mM D-mannitol or 1 M EtOH to provide 2, 20 or 100-fold excess of the trapping agent to catechol, respectively.

2.6. Experiments on bleaching of catechols

The evolution of color of reaction mixture was followed at 482 nm by using 2 mm cuvette. The bleaching experiments were performed under ambient temperature, pH 10.5, 0.1% catalyst/substrate ratio, the other conditions being identical to that ones described above.

2.7. Identification and characterization of oxidation products of the different catechols

Oxalic acid was identified in catechol oxidation under the conditions of run 10 of Table 1 as follows. After 1 h of reaction several drops of 20% HCl were added to acidify the reaction mixture to pH 1 followed by extraction with diethylether (3 × 2 mL). The organic layer was treated with CH_2N_2 solution in diethylether. Oxalic acid dimethyl ester was identified by GC-MS. MS (70 eV, EI): m/z (%) 118 (M^+, 5), 59 ($(M-COOCH_3)^+$, 100).

Dichloromaleic anhydride was identified as an aromatic ring cleavage product in the tetrachlorocatechol (TCC) oxidation. This product, also found in the metallophthalocyanine-catalyzed oxidation of pentachlorophenol, was isolated as previously described [15]. Isolation and characterization of 3,5,6-trichloro-2-hydroxy-1,4-benzoquinone, an intermediate product in tetrachlorocatechol oxidation, was carried out as follows. To a TCC solution (160 mg, 0.6 mmol, in 30 mL of acetonitrile) were added 15 mL of a 1.48 mM FePcS aqueous stock solution (22.2 μmol of FePcS), 7.5 mL of water and 7.5 mL of a 0.5 M phosphate buffer solution, pH 7.0. Then 300 μL of 35% H_2O_2 (3.4 mmol) were added dropwise and the reaction mixture was stirred for 5 min. The dechlorination was 1.0 Cl^- per molecule of TCC. The violet reaction mixture was acidified to pH 2 with 1 M HCl saturated with NaCl and extracted with diethylether (3 × 60 mL). The dark yellow ether solution was dried over Na_2SO_4 and evaporated to dryness. 147 mg of crude product were recovered. 3,5,6-trichloro-2-hydroxy-1,4-benzoquinone was purified by preparative TLC (Merck Kieselgel 60 F_{254}, 2 mm, ethylacetate/methanol = 8/2, v/v). 48 mg of this violet product were recovered. UV–vis (phosphate buffer pH 7.0), λ = 296 nm, 524 nm (broad). Since ^{13}C NMR and MS data could not be obtained owing to the instability of this violet product during NMR experiment and under MS analysis conditions (EI, 70 eV), we further characterized this product as reduced and acetylated derivative, 3,5,6-trichloro-1,2,4-triacetoxybenzene prepared according to [30]. 67 mg of the 3,5,6-trichloro-2-hydroxy-1,4-benzoquinone were treated for 5 min with 2 mL of acetic anhydride in the presence of a small amount of zinc and sodium acetate at 100°C. 5 mL of water were added to the cooled reaction mixture and the product was extracted with

diethylether (3 × 5 mL). The combined diethylether phases were washed with an aqueous $NaHCO_3$ solution, dried over Na_2SO_4 and evaporated to dryness. 71 mg of product were recovered after drying for 1 h under vacuum. MS (DCI/NH_3): 376 ((M + 4)NH_4^+, 34.4), 374 ((M + 2)NH_4^+, 100), 372 (MNH_4^+, 100). ^{1}H NMR (250 MHz, $CDCl_3$, 298 K): δ = 2.33 (s, 3H), 2.34 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (62.9 MHz, $CDCl_3$, 298 K): δ = 20.10 (3 × CH_3), 122.43 (C_3–Cl), 126.22 (C_5–Cl), 126.88 (C_6–Cl), 139.68 (C_1–O), 140.12 (C_2–O), 143.28 (C_4–O), 166.45 (C=O), 166.57 (2 × C=O). UV–vis, ^{1}H NMR, ^{13}C NMR and MS data were close to those published for the same product [30].

Table 1
Oxidation of catechols catalyzed by FePcS at 40°C

Run	Substrate	% cat./sub.	pH	Oxidant	Conversion (%)			
					1 min	10 min	30 min	60 min
1	catechol	1	9	percarbonate	74	78	88	100
2	catechol	0.1	9	percarbonate	5	12	21	27
3	catechol	0	9	percarbonate	0	0	2	6
4	catechol	1	10	percarbonate	100	—	—	—
5	catechol	0.1	10	percarbonate	49	57	76	91
6	catechol	0.01	10	percarbonate	9	25	51	82
7	catechol	1	10.5	percarbonate	100	—	—	—
8	3-MeO-catechol	1	10.5	percarbonate	100	—	—	—
9	3-Me-catechol	1	10.5	percarbonate	100	—	—	—
10	catechol	0.1	10.5	percarbonate	49	58	80	98
11	3-MeO-catechol	0.1	10.5	percarbonate	59	66	84	87
12	3-Me-catechol	0.1	10.5	percarbonate	51	66	95	100
13	catechol	0.1	11	percarbonate	84	90	100	—
14	catechol	0.01	11	percarbonate	24	47	73	98
15	catechol	0	11	percarbonate	0	13	22	37
16	catechol	0.1	9	H_2O_2	0	3	5	15
17	catechol	0.1	10	H_2O_2	1	2	17	36
18	catechol	1	10	H_2O_2	18	30	38	48
19	catechol	0.1	10.5	H_2O_2	0	6	29	38
20	catechol	1	10.5	H_2O_2	15	20	36	40
21	catechol	0.1	10	$Na_2CO_3 + H_2O_2$	33	39	77	100
22	catechol	1	9	perborate + TAED	92	94	97	99
23	catechol	1	9	perborate	62	67	73	77
24	catechol	0.1	9	perborate + TAED	67	70	70	73
25	catechol	0.1	9	perborate	3	8	13	17
26	catechol	1	10	perborate + TAED	100	—	—	—
27	catechol	1	10	perborate	100	—	—	—
28	catechol	0.1	10	perborate + TAED	78	81	82	84
29	catechol	0.1	10	perborate	9	16	24	30
30	catechol	1	10.5	perborate + TAED	100	—	—	—
31	3-MeO-catechol	1	10.5	perborate + TAED	100	—	—	—
32	3-Me-catechol	1	10.5	perborate + TAED	100	—	—	—
33	catechol	1	10.5	perborate	94	97	97	98
34	3-MeO-catechol	1	10.5	perborate	100	—	—	—
35	3-Me-catechol	1	10.5	perborate	100	—	—	—
36	catechol	0.1	10.5	perborate + TAED	62	68	68	76
37	3-MeO-catechol	0.1	10.5	perborate + TAED	84	96	97	98
38	3-Me-catechol	0.1	10.5	perborate + TAED	80	97	99	100
39	catechol	0.1	10.5	perborate	29	33	43	50
40	3-MeO-catechol	0.1	10.5	perborate	29	26	42	51
41	3-Me-catechol	0.1	10.5	perborate	25	31	42	52

The products of DTBC oxidation were analyzed by ^1H NMR as described [31,32].

3. Results and discussion

Five different catechol derivatives were used as substrates: catechol itself, 3-methylcatechol, 3-methoxycatechol, 3,5-di-*tert*-butylcatechol and tetrachlorocatechol in the metallophthalocyanine-catalyzed oxidations with sodium percarbonate, $Na_2CO_3 \cdot 1.5H_2O_2$, sodium perborate, $NaBO_3 \cdot 4H_2O$ alone or with tetraacetylethylenediamine (TAED) to generate peracetic acid in situ, or H_2O_2. Three tetrasulfophthalocyanine complexes were used as catalysts: iron (FePcS), manganese (MnPcS) and cobalt (CoPcS). As expected CuPcS and NiPcS were catalytically inactive. All catalytic reactions were carried out in aqueous solutions at 20 or 40°C and at different pH values: 7, 9, 10, 10.5 and 11. Four different aspects of these catalytic oxidations were studied: (i) the rate of catechols oxidation; (ii) the influence of two scavengers of hydroxyl radicals, ethanol or mannitol, on the oxidation of catechols; (iii) the bleaching of catechols (during the catalytic oxidation of the different catechols the reaction mixture became intensively colored from the beginning of the reaction and the evolution of the color (monitored at 482 nm) was found to be dependent both on catalyst and oxidant); and finally (iv) the identification of the oxidation products of catechols.

3.1. Influence of pH, catalyst and oxidant on the oxidation rate of catechols

Conversions of catechol, 3-methylcatechol and 3-methoxycatechol in the presence of catalytic amounts FePcS are listed in Table 1. Activities of FePcS-percarbonate, FePcS-perborate and FePcS-perborate-TAED systems increase with increasing of pH indicating that catecholates are easy to be oxidized. It should be noted that with perborate-TAED the initial rate of oxidation is very high but then there is practically no further conversion of catechol. Under these reaction conditions these metallophthalocyanines are active not only at 40°C but also at 20°C. For example, under conditions of run 4, Table 1, but at 20°C, the catechol is completely oxidized within 1 min. With 0.1% FePcS/catechol ratio (run 5, Table 1) at 20°C the conversions are equal to 10% (1 min), 33% (10 min), 44% (30 min) and 65% (60 min).

Table 2
Oxidation of catechol catalyzed by metallophthalocyanines (0.1% catalyst/substrate, pH 10.5 and 40°C)

	Conversion (%)			
	1 min	10 min	30 min	60 min
Percarbonate				
FePcS	49	58	80	98
MnPcS	88	100		
MnTACN	100 (26) [a]	(86) [a]	(100) [a]	
CoPcS	100 (63) [a]	(100) [a]		
Perborate				
FePcS	29	33	43	50
MnPcS	38	89	100	
MnTACN	70	100		
CoPcS	93	100		
Perborate-TAED				
FePcS	62	68	68	76
CoPcS	24	71	94	95
MnPcS	50	87	93	97
MnTACN	76	100		
H_2O_2				
FePcS	0	6	29	38
MnTACN	81	86	86	86

[a] Data obtained with a 0.01% catalyst/substrate ratio.

The comparison of catechols oxidations, catalyzed by FePcS, MnPcS or CoPcS (0.1% catalyst/substrate ratio) at 40°C indicates that percarbonate is more efficient as an oxidant than perborate or perborate/TAED (Table 2). The catalytic activity of metallophthalocyanines in catechol oxidation increases in the following order: FePcS < MnPcS < CoPcS.

3.2. Oxidation of catechol in the presence of ethanol and mannitol, inhibitors of HO·

The formation of hydroxyl radicals has a disastrous consequences in bleaching processes,

because of the high reactivity of HO˙ towards organic structures. For example, if cellulose is damaged during a wood pulp bleaching process, this will result in the drop of mechanical and strength properties of paper. An occurrence of hydroxyl radicals in washing results in fast tissue degradation. In order to examine whether HO˙ radicals are involved in catechol oxidations we carried out the experiments in the presence of ethanol and mannitol, effective trapping agents, to inhibit oxidation reactions mediated by hydroxyl radicals [34]. If HO˙ radicals are generated, a large excess of EtOH or mannitol should prevent or significantly diminish the catechol oxidation by FePcS/peroxide. An addition of 2–100 equivalents of EtOH or mannitol with respect to the substrate was unable to significantly influence the rates of catechol oxidation by metallophthalocyanine/peroxide systems (Table 3). This strongly suggests that hydroxyl radicals are not involved in these catechol oxidations. Consequently, these metallophthalocyanine/peroxide systems can be considered as reasonable candidates in bleaching processes.

3.3. Bleaching of the different catechols

During the catalytic oxidation of the different catechols the reaction mixture became intensively colored and then the color disappeared. The initial products of catechol oxidation were

Table 3
Oxidation of catechol in the presence of hydroxyl radical traps with 0.1% cat./sub. at pH 10.5 and at 40°C

Run	Oxidant	Additive	Ratio (additive/substrate)	Conversion (%)			
				1 min	10 min	30 min	60 min
FePcS							
1	percarbonate	—	—	49	58	80	98
2	percarbonate	D-mannitol, 20 mM	2	43	57	82	100
3	percarbonate	D-mannitol, 200 mM	20	41	50	71	90
4	percarbonate	EtOH, 1 M	100	35	53	82	100
5	perborate/TAED	—	—	62	68	68	76
6	perborate/TAED	D-mannitol, 20 mM	2	49	62	64	67
7	perborate/TAED	D-mannitol, 200 mM	20	33	37	39	39
8	perborate/TAED	EtOH, 1 M	100	39	54	60	62
9	perborate	—	—	29	33	43	50
10	perborate	D-mannitol, 200 mM	20	6	32	33	40
11	perborate	EtOH, 1 M	100	17	22	27	33
MnPcS							
12	percarbonate	—	—	88	100		
12	percarbonate	D-mannitol, 20 mM	2	75	100		
CoPcS							
13	percarbonate	—	—	100			
14	percarbonate	D-mannitol, 20 mM	2	65	100		
15	percarbonate	EtOH, 1 M	100	78	100		
MnTACN							
16	percarbonate	—	—	100			
17	percarbonate	D-mannitol, 200 mM	20	100			
18	percarbonate	EtOH, 1 M	100	100			
19	perborate	—	—	70	100		
20	perborate	D-mannitol, 200 mM	20	99	100		
21	perborate/TAED	—	—	76	100		
22	perborate/TAED	D-mannitol, 200 mM	20	97	99	100	
23	perborate/TAED	EtOH, 1 M	100	41	92	99	

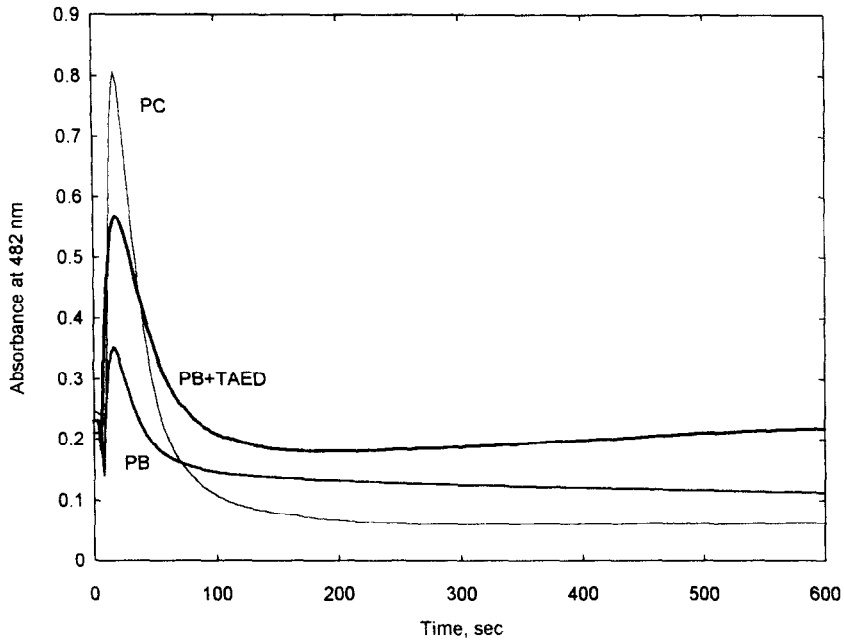

Fig. 2. Comparison of the efficiency of different oxidants in the catechol bleaching catalyzed by iron tetrasulfophthalocyanine (FePcS). PC: percarbonate, PB: perborate, PB/TAED: perborate in the presence of tetraacetylethylenediamine.

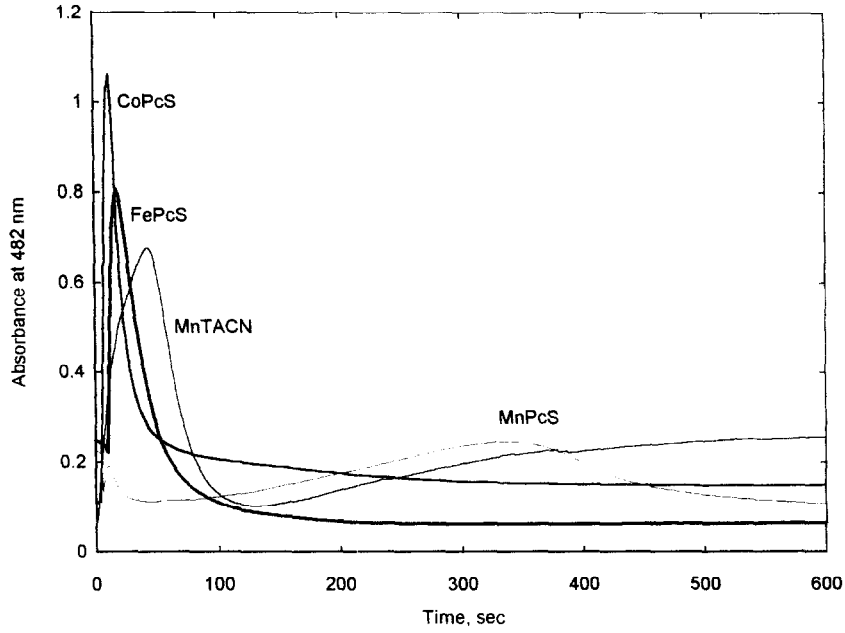

Fig. 3. Comparison of the catalytic bleaching of catechol in the presence of different metallophthalocyanines or MnTACN with percarbonate as an oxidant.

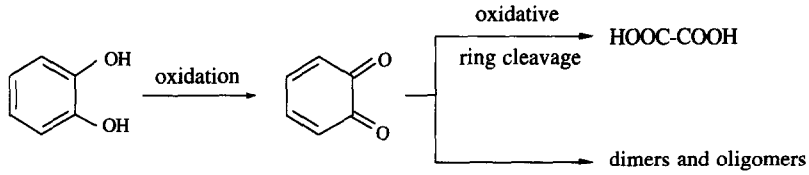

Fig. 4. Different possible routes in the catechol oxidation.

expected to be quinone derivatives. The evolution of color (detection at 482 nm) depends on the nature of the oxidant (Fig. 2) and also on the catalyst (Fig. 3). A fast fading and a low final optical density are typical characteristics of a highly efficient bleaching system. The comparison of the different oxidants indicates that percarbonate is the most powerful oxidizing agent when FePcS was used as catalyst (Fig. 2). In the absence of catalyst no staining–fading phenomenon was observed. FePcS and CoPcS have better bleaching activities compared to MnPcS. FePcS provides a lower final optical density of the reaction mixture. The presence of mannitol does not provoke significant changes in the kinetics of staining–fading phenomenon, suggesting again that hydroxyl radicals were not involved in the oxidation of intermediate quinones, initial products of catechol oxidation.

3.4. Products of catechol oxidations

o-Quinones are the initial oxidation products of the different catechols. The further oxidative degradation of the corresponding quinones to aromatic cycle cleavage products is a necessary condition for an efficient bleaching. We detected oxalic acid by GC-MS (as dimethyl ester) as final product of the aromatic cycle cleavage of catechol (Fig. 4). The detailed product analysis in the case of catechol is complicated because of the polymerization of intermediately formed *o*-quinone [33]. Then we decided to use 3,5-di-*tert*-butylcatechol (DTBC) as catechol substrate, since *tert*-butyl substituents prevent a polymerization reaction. DTBC is a widely used substrate in studies of dioxygenases and models and the products of DTBC oxidation have been characterized by NMR methods [31,32].

The results on the catalytic oxidation of DTBC at 20°C are listed in Table 4. This substrate is easily oxidized by percarbonate in the absence of catalysts (runs 1–3). 3,5-di-*tert*-butyl-5-(carboxyhydroxymethyl)-2-furanone **1** was identified by ^{1}H NMR as principal product of DTBC oxidation, and in the presence of catalysts the yields were higher. Several possible mechanisms were considered for the formation of **1**. From labeling studies, White et al. concluded that furanone **1** was formed after the

Table 4
Oxidation of 3,5-di-*tert*-butylcatechol (1% catalyst/substrate at pH 10.5 and at 20°C)

Run	Catalytic system	Conversion in % (time, in min)	Product (yield in %)
1	FePcS-percarbonate	100 (1)	furanone **1** (80%)
2	CoPcS-percarbonate	98 (60)	furanone **1** (69%)
3	percarbonate	85 (1) 100 (3)	furanone **1** (30%)
4	FePcS-perborate	90 (60)	DTBQ (70%)
5	perborate	40 (60)	DTBQ (30%)
6	FePcS–H_2O [a]	77 (1) 100 (5)	DTBQ (97%)anhydride **2** (3%)
7	H_2O_2	< 10 (60)	

[a] Data obtained with a 3.7% catalyst/substrate ratio.

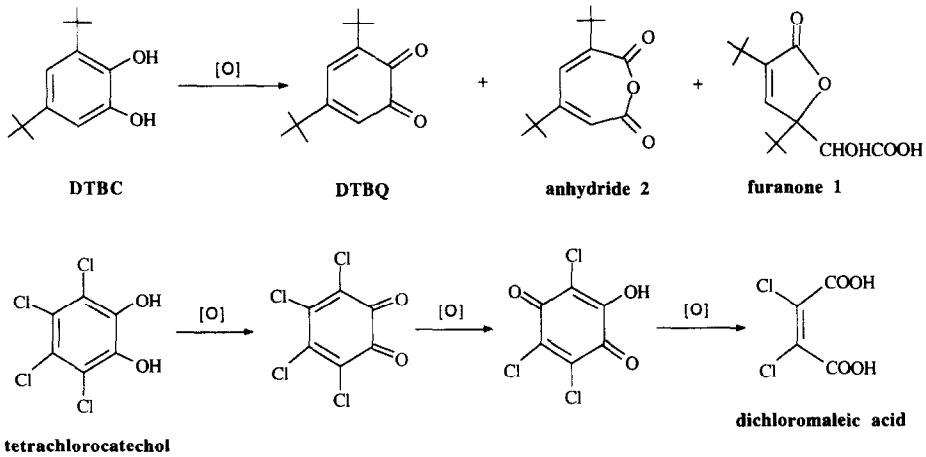

Fig. 5. Products of metallophthalocyanine catalyzed oxidation of 3,5-di-*tert*-butylcatechol (DTBC) and tetrachlorocatechol (TTC). DTBQ: 3,5-di-*tert*-butyl-1,2-benzoquinone; anhydride **2**: 3,5-di-*t*-butylmuconic anhydride; furanone **1**: 3,5-di-*tert*-butyl-5-(carboxyhydroxymethyl)-2-furanone. [O] stands for oxidation.

intradiol cleavage of 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBQ) by basic hydrogen peroxide [31]. DTBQ was found to be a principal product in DTBC oxidation by perborate (runs 4 and 5, Table 4). Again percarbonate was the preferential oxidant over perborate, because it provided a deeper oxidation of catechols. When H_2O_2 (at pH 7.0) was used as oxidant the non-catalytic reaction was negligible (run 7, Table 4). The main product of DTBC oxidation by FePcS–H_2O_2 system was found to be DTBQ and the traces of 3,5-di-*tert*-butylmuconic acid anhydride **2** were detected by ^1H NMR as a product of intradiol cleavage of the corresponding catechol (Fig. 5).

We also studied the oxidation of tetrachlorocatechol (TCC). The amount of Cl^- released during TCC oxidation by FePcS–H_2O_2 or percarbonate was monitored in order to appreciate the efficiency of TCC oxidation. With percarbonate as oxidant we detected again, a very important non-catalytic reaction (run 2, Table 5), although the results on dechlorination indicate catalytic reaction resulting in dechlorination of 2.7 Cl^- per molecule of TCC versus 1.8 Cl^- in the absence of catalyst. In hydrogen peroxide oxidation of TCC catalyzed by FePcS we observed the release of 1.6 Cl^- per molecule of TCC. Dichloromaleic acid was identified by GC-MS as product of the oxidative aromatic ring cleavage. This diacid has also been detected in the oxidation of pentachlorophenol by FePcS–H_2O_2 [15]. During the TCC oxidation the reaction mixture turned violet immediately after the addition of the oxidant. The same phenomenon has been observed in the course of

Table 5
Oxidation of tetrachlorocatechol (1% catalyst/substrate at pH 10.5 and at 20°C)

Run	Catalytic system	Conversion in % (time, in min)	Dechlorination, Cl^-/1 TCC
1	FePcS-percarbonate	81 (1) 90 (10) 96 (60)	2.7
2	percarbonate	60 (1) 69 (10) 75 (60)	1.8
3	FePcS–H_2O_2 [a]	81 (10)	1.6
4	H_2O_2	34 (10) 39 (60)	0

[a] Data obtained with a 3.7% catalyst/substrate ratio.

2,4,6-trichlorophenol oxidation by FePcS–H_2O_2 [15]. This intermediate violet product was identified as 3,5-dichloro-2-hydroxy-1,4-benzoquinone. We isolated and characterized the intermediate violet product in the TCC oxidation as being 3,5,6-trichloro-2-hydroxy-1,4-benzoquinone **3** (Section 2). The similar intermediate products (hydroxyquinones) and final products of aromatic cycle cleavage (C_4 unsaturated diacids) in the course of tetrachlorocatechol and polychlorophenols catalytic oxidations strongly suggest that the mechanisms of oxidation of TCC and polychlorophenols are very similar. This mechanism involves two main reactions: (i) a nucleophilic addition of an Fe(III)–peroxo complex ($PcSFeOO^-$) to the electron-deficient double bonds of intermediate quinones leading to epoxides, which, after rearrangement provide derivatives with a hydroxy group adjacent to a carbonyl group; (ii) then the same nucleophilic peroxo complex can attack the carbonyl groups leading to the ring cleavage via a Grob fragmentation [15].

3.5. Comparison of metallophthalocyanine catalysts with the manganese complex of 1,4,7-trimethyl-1,4,7-triazacyclononane (MnTACN)

MnTACN complex was published as potential catalyst for the bleaching of stains by H_2O_2 at low temperatures [17]. We have compared this MnTACN complex and metallophthalocyanine complexes in terms of their catalytic activity, bleaching efficiency and an influence of scavengers of hydroxyl radicals on these parameters. We used optimal reaction conditions (pH 10.5, 0.1% catalyst/substrate ratio, 40°C for kinetic experiments and 20°C for bleaching experiments) for both kind of catalysts (Table 2). In terms of catechol conversion MnTACN is very active, even slightly more active than metallophthalocyanines (with H_2O_2 and perborate/TAED system). The presence of mannitol or ethanol has no significant influence on catechol conversion, except, probably, perborate/TAED system. However, we observed the influence of mannitol on staining–

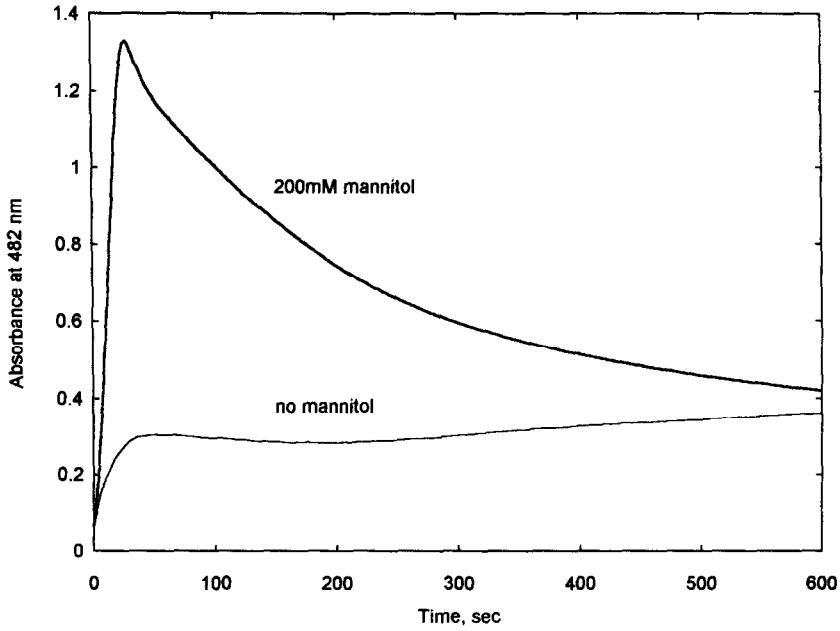

Fig. 6. Influence of mannitol (200 mM) on the bleaching of catechol by the MnTACN-perborate/TAED system.

fading phenomena in bleaching experiments with a MnTACN–perborate/TAED system. It should be noted that in MnTACN based systems a staining–fading phenomenon occurs only with percarbonate. With perborate and perborate/TAED no staining–fading phenomenon was observed, but in presence of mannitol the reaction mixture became intensively colored and the color disappeared quite slowly (Fig. 6). This fact suggests that in MnTACN–perborate/TAED system hydroxyl radicals could be responsible for oxidation of intermediate colored catechol oxidation products. This radical route adds to metal–oxo activity initially observed [17]. As consequence of this possible hydroxyl radical involvement MnTACN could provoke damages of tissues when this complex wad used as bleaching catalyst in washing powders.

4. Conclusion

Tetrasulfophthalocyanine complexes of iron, manganese and cobalt are efficient catalysts of the oxidation of catechols by hydrogen peroxide and its surrogates. The catalytic experiments in the presence of ethanol and mannitol strongly suggest that hydroxy radicals are not involved in these catechol oxidations. FePcS and CoPcS exhibit better bleaching activities compared to MnPcS, sodium percarbonate being the preferential oxidant. The first products of oxidation of catechols were the corresponding *o*-quinones. 3,5-di-*tert*-butyl-5-(carboxyhydroxymethyl)-2-furanone was the principal product of DTBC oxidation, supporting the intradiol cleavage of the aromatic ring. The final product of TCC oxidation was dichloromaleic acid, 3,5,6-trichloro-2-hydroxy-1,4-benzoquinone being the intermediate product. The high bleaching capacity of this catalytic system at ambient temperature due to its ability to cleave the aromatic cycle of catechols without formation of hydroxyl radicals strongly suggests that it might be possible to use these efficient and inexpensive catalysts in environmentally friendly bleaching processes.

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