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Journal of Molecular Catalysis A: Chemical 252 (2006) 96–102
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Manganese(III) porphyrins as catalysts for the oxidation of aromatic substrates: An insight into the reaction mechanism and the role of the cocatalyst

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Received 13 December 2005; received in revised form 8 February 2006; accepted 8 February 2006
Available online 27 March 2006

Abstract

Manganese porphyrins bearing electron-withdrawing nitro substituents on the *beta*-positions catalyse the oxidation of activated aromatic compounds by hydrogen peroxide. The reaction yields based on the starting compounds, are largely lowered by complexation of the metal by the final or starting phenolic compounds and depend on the concentration of the added co-catalyst, e.g. imidazole.

Using hindered silyl or *sec*-butyl ether derivatives of cresol, the reaction gives better results. In this case, it is possible to isolate the corresponding benzyl alcohol and benzoic acid derivatives in a moderate yield for such substrates. For the *sec*-butyl ether derivative, the corresponding quinone has also been isolated. The conversion of the benzyl alcohols into the benzoic acid derivatives under the experimental conditions was also demonstrated.

Keywords: Manganese(III); Metalloporphyrins; Oxidation; Hydrogen peroxide; Aromatic compounds

1. Introduction

Manganese(III) porphyrins have been studied for a long time as catalysts able to mimic the in vivo activity of the family of the cytochrome P_{450} dependent monooxygenases [1,2].

Several papers have reported on the epoxidation reactions of alkenes and hydroxylation of alkanes in association with a wide variety of oxygen donors such as iodosylarenes [3–5], peroxo-compounds [6–8], hypochlorites [9–12], hydrogen peroxide [13–16] or monopersulfates [17]. Less information was available for the oxidation reaction of aromatic substrates catalysed by metalloporphyrins although some authors reported the formation of phenols and quinones as the final products of the metalloporphyrins oxidation of electron-rich aromatic substrates by hydrogen peroxide [18–21].

In such papers, the yield of the reactions has been reported versus the moles of the oxidant, which is always in defect comparing with the substrates. In this case, the total yield, calculated from the oxidant, is generally high but the conversion of the substrates looks quite negligible. However, some of us recently found that the oxidation of some aromatic compounds can be performed with an excess of hydrogen peroxide, depending on the substrates, the catalyst and the reaction conditions [22–24].

These facts prompted us to investigate in detail which parameters affect the reaction and look for the possibility to quantitatively oxidize the substrates in order to obtain valuable derivatives which can be useful for further transformations. In particular, we focused our attention on the complexation equilibrium of the metalloporphyrins with the phenolic compounds which could inhibit further oxidation of the metal center.

Complexation of metalloporphyrins by added ligands [25] is a feature well known in literature; however, to our knowledge, a correlation between the reactivity of an aromatic ring in oxidation reactions and the presence of phenolic compounds as axial ligands is not evident. In this paper, we will report on the results obtained for the optimization of the oxidation conditions and on evidences of the inhibition of the catalyst activity by the final phenolic products.

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doi:10.1016/j.molcata.2006.02.043

2. Experimental

2.1. General remarks

Chromatographic purifications were performed on silica gel (35–70 mesh, Merck) columns. Thin-layer chromatography was carried out using Merck Kiesegel 60-F254 plates. ^{1}H NMR spectra were recorded as $CDCl_3$ solutions on a Bruker AM 400 instrument using tetramethylsilane (TMS) as an internal standard. FAB Mass spectra were measured on a VG-Quattro spectrometer using 3-nitrobenzyl alcohol (NBA) as a matrix. GC–MS spectra were obtained with a VG-Quattro spectrometer equipped with a 30 m Supelco SPB-5 capillary column.

2.2. GC separation conditions

The products yield for all the reactions was determined by GC analyses performed on a Carlo Erba HRGC 5160 instrument equipped with a 30 m Supelco SPB-5 capillary column and a FID detector. Chemical yields were determined by adding a suitable internal standard (dodecane, tetradecane or acetophenone) to the reaction mixture at the end of each experiment and were reproducible within ±2% for multiple experiments.

2.3. Chemicals

All the reagents and solvents (Carlo Erba, Aldrich, Fluka or Acros) were of the highest analytical grade and used without further purification.

2.4. Synthesis

The free bases H_2TDCPP, **1** was synthesized by literature methods [26], while the H_2(2-NO_2)TDCPP, **2** was obtained by the standard nitration reaction of the free bases with $Zn(NO_3)_2$ and subsequent demetallation by CF_3CO_2H [27]. The manganese derivative, of H_2(2-NO_2)TDCPP **3** was obtained by literature methods [28]. Mn[(Cl_8)TDCPP]Cl, **5** was obtained from Mn(TDCPP)Cl by a method reported in the literature [29]. Sodium phenoxide standard solution was obtained by reaction of an excess of sodium with phenol in anhydrous THF and the title was obtained by titration with a standard HCl solution.

2.5. tert-Butyldimethylsilyl 4-methylphenyl ether, *6*

0.526 g (4.87 mmol) of 4-methylphenol were dissolved, under argon, in 5 mL of anhydrous DMF in a 10 mL round bottomed flask. *tert*-Butyldimethylsilyl chloride, 1.016 g (6.75 mmol) and imidazole, 0.811 g (11.9 mmol) were added at room temperature. The solution was stirred for 2 h, after that the solvent was evaporated under vacuum and the residue redissolved in dichloromethane. The organic solution was washed with water, dried on anhydrous sodium sulfate, filtered and evaporated under vacuum. The residue was purified by column chromatography on silica gel, eluting with petroleum ether. The fractions containing the desired compound were collected and evaporated under vacuum giving 0.984 g (4.43 mmol) of a colourless oil. Yield 91%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.0 (d, 2H, J = 8.0 Hz), 6.72 (d, 2 H, J = 8.0 Hz), 2.26 (s, 3 H), 0.96 (s, 9 H), 0.14 (s, 6 H); EI MS: *m/z* (%) 222 (20), 165 (100), 149 (3), 135 (3), 91 (15).

2.6. sec-Butyl 4-methylphenyl ether, *9*

1.103 g (10.2 mmol) of 4-methylphenol were dissolved, under argon, in 10 mL of anhydrous acetone in a 100 mL round bottomed flask. 2-Bromobutane, 4.5 g (31.1 mmol) and anhydrous potassium carbonate 2.0 g (14.5 mmol) were added at room temperature. The solution was then refluxed for 14 h and after a TLC checking, 4.5 g of 2-bromobutane were added and the solution was further refluxed for 8 h. The solution was then filtered and the solvent was evaporated under vacuum. The residue, redissolved in dichloromethane, was washed with water and the organic solution was dried on anhydrous sodium sulfate, filtered and evaporated under vacuum. The residue was purified by column chromatography on silica gel, eluting with petroleum ether. The fractions containing the desired compound were collected and evaporated under vacuum giving 0.888 g (5.41 mmol) of a colourless oil. Yield 53%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.2 (d, 2 H, J = 9 Hz), 6.9 (d, 2 H, J = 9 Hz), 4.35 (m, 1 H), 2.4 (s, 3 H), 1.7 (m, 2 H), 1.4 (d, 3 H, J = 6 Hz), 1.1 (t, 3 H, J = 7 Hz); EI MS: *m/z* (%) 164 (25), 108 (100), 77 (20).

2.7. Methyl 4-sec-butyloxybenzoate

3.7 mg of 4-*sec*-butyloxybenzoic acid were dissolved in 1 mL of BF_3·CH_3OH (1.3 M) and the solution was maintained at 50 °C for 3 h.

The solution was then evaporated and the residue redissolved in ethyl acetate. This solution was washed with water, dried on anhydrous sodium sulfate and the solvent was evaporated under vacuum giving the desired compound quantitatively.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (d, 2 H, J = 9.1 Hz), 6.96 (d, 2 H, J = 9.1 Hz), 4.47 (m, 1 H), 3.83 (s, 3 H), 1.79 (m, 1 H), 1.69 (m, 1 H), 1.39 (d, 3 H, J = 6.1 Hz), 1.02 (t, 3 H, J = 8 Hz); EI MS: *m/z* (%) 152 (42), 121 (100), 79 (45).

2.8. Methyl 4-tert-butyldimethylsilyloxybenzoate

3.9 mg of 4-*tert*-butyldimethylsilyloxy-benzoic acid were dissolved in 1 mL of BF_3·CH_3OH (1.3 M) and the solution was maintained at 50 °C for 3 h. The solution was then evaporated and the residue redissolved in ethyl acetate. This solution was washed with water, dried on anhydrous sodium sulfate and the solvent was evaporated under vacuum giving the desired compound quantitatively.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, 2 H, J = 9.1 Hz), 6.92 (d, 2 H, J = 9.1 Hz), 3.85 (s, 3 H), 1.04 (s, 9 H), 0.25 (s, 6 H); EI MS: *m/z* (%) 238 (72), 223 (100).

2.9. General procedure for the oxidation reactions

In a 10 mL flask were introduced 3 mL of acetonitrile, 0.37 mmol of substrate, 0.37 μmol of the catalyst and 3.7 mmol of ammonium acetate. 0.4 mL of a 3.5% solution of hydrogen peroxide, prepared from the 35% commercial solution by dilution with acetonitrile, were slowly added. The progress of the reaction was monitored by GC and the reaction was stopped after the disappearing of the starting compound. The solution was diluted with water and extracted with dichloromethane. The organic solution was then washed with water, dried on anhydrous sodium sulfate and evaporated under vacuum. The reaction products were isolated by column chromatography on silica gel, eluting with petroleum ether/diethyl ether mixtures.

2.10. Epoxidation of styrene in the presence of 2- or 4-metoxyphenol

In a 10 mL flask were introduced 4 mL of a solution prepared by dissolving 6.8 mg (5.5 μmol) of the catalyst **3**, 10.7 mg (0.157 mmol) of imidazole, and 447.6 mg (4.3 mmol) of styrene in 10 mL of 1:1 acetonitrile/dichloromethane. Hydrogen peroxide, 80 mL (0.91 mmol) was added in four portions every 2 min. After 4 min from the last addition, tetradecane was added as internal standard and the mixture was analyzed by GC.

2.11. Kinetic measurements

In a 10 mL flask were introduced 3 mL of acetonitrile, 0.44 mmol of substrate, 0.49 μmol of the catalyst **5**, 4.4 mmol of ammonium acetate and 0.79 mmol of acetophenone as internal standard. The standard is stable under the oxidation conditions even after hours. Four millilitres of a solution of hydrogen peroxide, prepared from the commercial 35% solution by dilution with acetonitrile 1/10, were slowly added in 8 portions waiting 15 min between two consecutive additions. The progress of the reaction was monitored every 15 min by GC.

2.12. Characterization of the reaction products

2.12.1. 4-tert-Butyldimethylsilyloxy benzyl alcohol, *7*

^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.24$ (d, 2 H, $J = 7.8$ Hz), 6.85 (d, 2 H, $J = 7.8$ Hz), 4.62 (m, 1 H), 2.62 (s, 2 H), 1.0 (s, 9 H), 0.21 (s, 6 H); EI MS: *m/z* (%) 238 (25), 181 (100), 163 (20), 151 (100).

2.12.2. 4-tert-Butyldimethylsilyloxy benzoic acid, *8*

^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 8.02$ (d, 2 H, $J = 8.1$ Hz), 6.90 (d, 2 H, $J = 8.1$ Hz), 1.02 (s, 9 H), 0.26 (s, 6 H).

2.12.3. 2-sec-Butyloxy-5-methylbenzoquinone, *12*

^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 6.56$ (s, 1 H), 5.88 (s, 1 H), 4.22 (m, 1 H), 2.07 (s, 3 H), 1.8 (m, 1 H), 1.68 (m, 1 H), 1.36 (d, 3 H, $J = 6.1$ Hz), 0.97 (t, 3 H, $J = 6.2$ Hz); EI MS: *m/z* (%) 194 (5), 140 (50), 110 (20), 69 (90), 56 (100).

2.12.4. 4-sec-Butyloxy-benzyl alcohol, *10*

^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.30$ (d, 2 H, $J = 11$ Hz), 6.89 (d, 2 H, $J = 11$ Hz), 4.63 (s, 2 H), 4.31 (m, 1 H), 1.75 (m, 1 H), 1.63 (m, 1 H), 1.31 (d, 3 H, $J = 6$ Hz), 0.99 (t, 2 H, $J = 5$ Hz); EI MS: *m/z* (%) 180 (15), 124 (93), 106 (87), 95 (100), 78 (48).

2.12.5. 4-sec-Butyloxy-benzoic acid, *11*

^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 8.05$ (d, 2 H, $J = 9.2$ Hz), 6.93 (d, 2 H, $J = 9.2$ Hz), 4.42 (m, 1 H), 1.78 (m, 2 H), 1.67 (m, 12 H), 1.35 (d, 3 H, $J = 6$ Hz), 1.0 (t, 3 H, $J = 8$ Hz).

3. Results and discussion

The biomimetic oxidation of organic substrates by metalloporphyrin catalysis has been deeply studied in the last twenty years by several groups and the use of hydrogen peroxide as environment friendly oxygen donor has been well established [30]. For such a reason, we decided to use, for our studies, that oxidant which is actually considered, together with the molecular oxygen, the clean reagent for a green biomimetic approach [31].

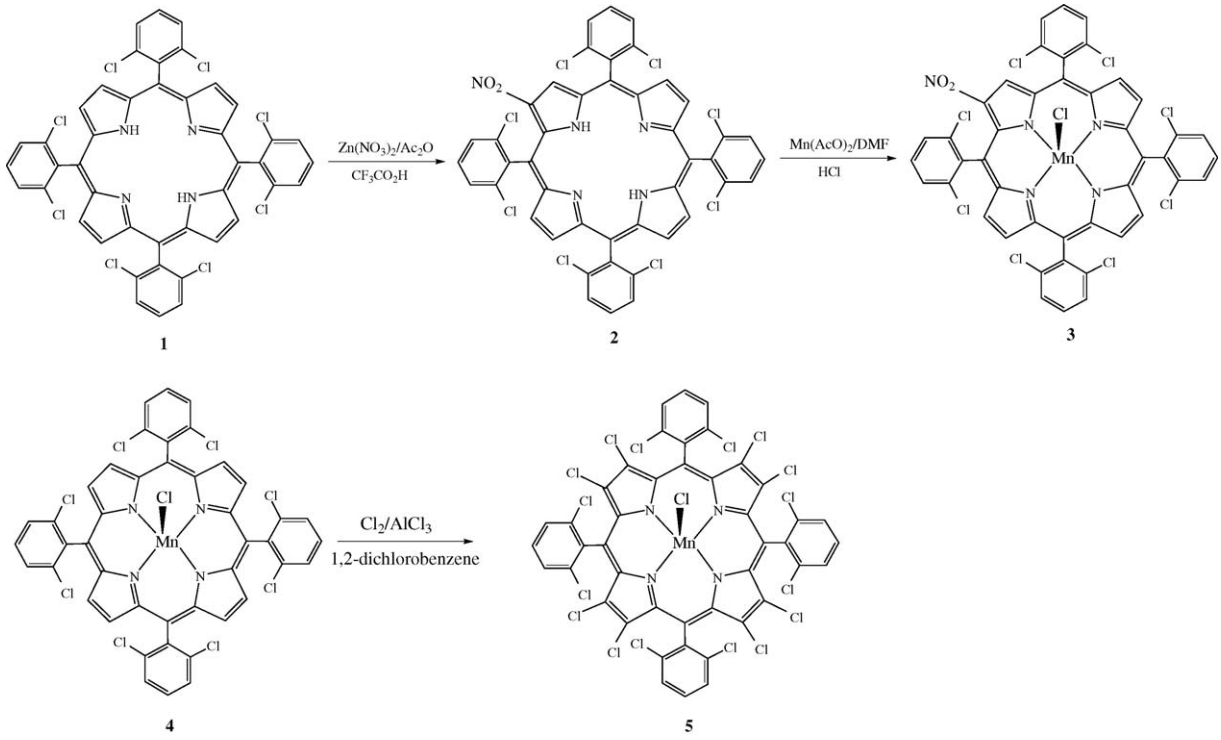
Considering certain literature content, at the beginning of this work we decided that the electron-poor manganese porphyrins were our primary targets for studying the catalytic oxygenation of aromatics [18–24]. The catalysts used for this work have been Mn[(2-NO_2)TDCPP]Cl, **3**, where (2-NO_2)TDCPP is the dianion of 2-nitro-5, 10, 15, 20-tetrakis(2′,6′-dichlorophenyl)porphyrin and Mn[(Cl_8)TDCPP]Cl, **5**, where (Cl_8)TDCPP is the dianion of 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(2′,6′-dichlorophenyl)porphyrin. The synthetic approaches for obtaining the manganese porphyrins follow the literature procedures [25–28] and are reported in Scheme 1.

The first observations we made on the oxidation of anisole by hydrogen peroxide and the manganese catalysts, followed what was previously reported by Mansuy and co-workers, and such observations were in perfect agreement with their data [18]. In fact, when we tried to oxidize the substrates using both porphyrin catalysts and imidazole as axial ligand, under Mansuy conditions, the total yield of the products, the 2- and 4-methoxyphenol, based on the substrate amounts used never exceeded 1%. Further experiments performed with excess of the oxidant, never gave more than 1% yield in phenolic compounds.

This fact was quite surprising and the further step was then to investigate the coordination capability of the two methoxyphenol derivatives towards the manganese porphyrins. In Fig. 1, the UV–visible spectra of the manganese porphyrin **5**, before and after the addition of 2-methoxyphenol and after the addition of imidazole, are reported.

From such figure, looking at the shift of the Soret band after the addition of the phenol, it is possible to argue that the metalloporphyrin undergoes complexation with a coordinating species. Other information can be obtained from the spectra reported in Fig. 2. In this figure, the spectra of the manganese catalyst **5** after the simultaneous addition of 5 equivalents of imidazole and 5 equivalents of 2-methoxyphenol in multiple steps are reported.

It is evident that the band at 458 nm is generated by the complexation of an extra ligand on the metal and not from the



Scheme 1. Synthesis of the catalysts used in this work.

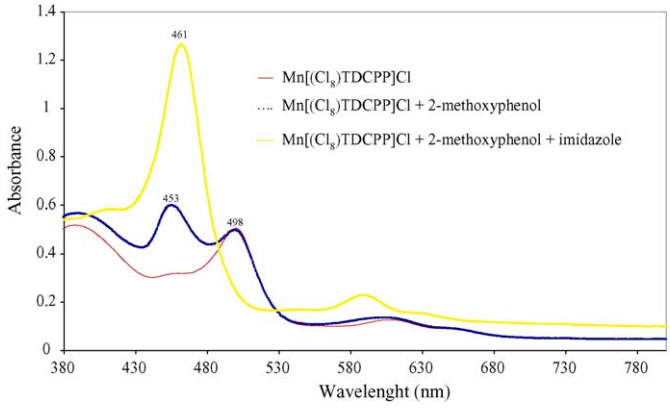


Fig. 1. UV–vis spectra of **5**, before and after the addition of 2-methoxyphenol and after the addition of imidazole.

imidazole which gives a complex with a band at 492 nm. The next question to be considered was centred on which species is so powerful to bind the metal ion making it not available for the hydrogen peroxide coordination. The phenolate anion was a good candidate and to prove its coordination capability, the manganese porphyrin **5** was titrated with a stock solution of sodium 4-methoxyphenolate (see Section 2). The results are reported in Fig. 3.

In this case, we have the Soret band shifting to 453 nm which is near the position of the band when 2-methoxyphenol is added to the metalloporphyrin; this is the proof that the phenolate anion binds the metal centre during the oxidation reaction, thus inhibiting the coordination of hydrogen peroxide. From Figs. 1 and 2, we can also extrapolate that imidazole plays a role during the complexation through an acid-base equilibrium with phenols.

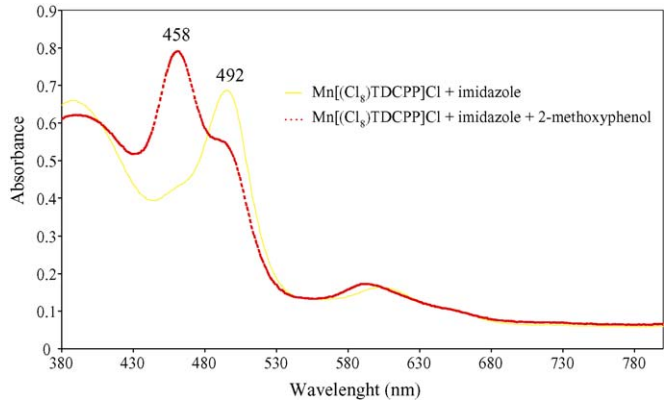


Fig. 2. UV–vis spectra of **5** after the contemporary addition of 5 equivalents of imidazole and 5 equivalents of 2-methoxyphenol in multiple steps.

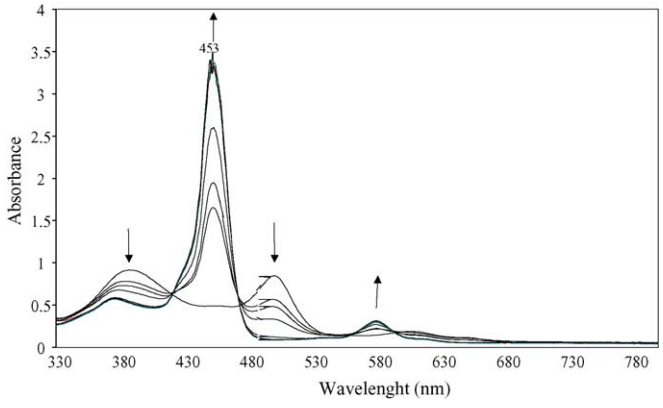


Fig. 3. UV–vis spectra of **5** during the titration with a stock solution of sodium 4-methoxyphenate.

In fact after the addition of imidazole to the metalloporphyrin and 2-methoxyphenol mixture, the Soret band shift to 461 nm, a value very close to 453 nm. Furthermore, the oxidation of anisole by catalyst **5**, using ammonium acetate as axial ligand under the conditions reported by other authors [32] for the epoxidation of olefins was unsuccessful. But an experiment to prove the inhibition of the catalyst has been set up by using the catalyst **5** for the epoxidation of styrene by hydrogen peroxide.

Two reactions were performed, one of them in the presence of 0.1 equivalent of 4-methoxyphenol. The epoxidation, in the presence of 4-methoxyphenol, gave only 30% yield while without it the yield was 92%.

After having found which was the problem in our experiments for the oxidation of the aromatics, the next question was how to oxidize biomimetically and in high yield such aromatics and prevent the complexation of the metal by the phenolic products. A possibility could consider the introduction of bulky groups to protect the *ortho* and *para* positions, but maintaining the electron-donating substitution.

We decided to use a new substrate, 4-methylphenol, protecting the hydroxy group with the *tert*-butyldimethylsilyl or *sec*-butyl groups. In this way, three effects could be obtained, the lack of the formation of phenolic complexes with manganese, the impossibility to oxidize the position 4 and the protection from the oxidation of the 2 and 6 positions due to the steric hindrance. The cited compounds were easily synthesized by standard procedures [33] and purified by column chromatography. The oxidation reactions were performed using catalyst **3** because, from preliminary experiments, it was found to be more active than **5**.

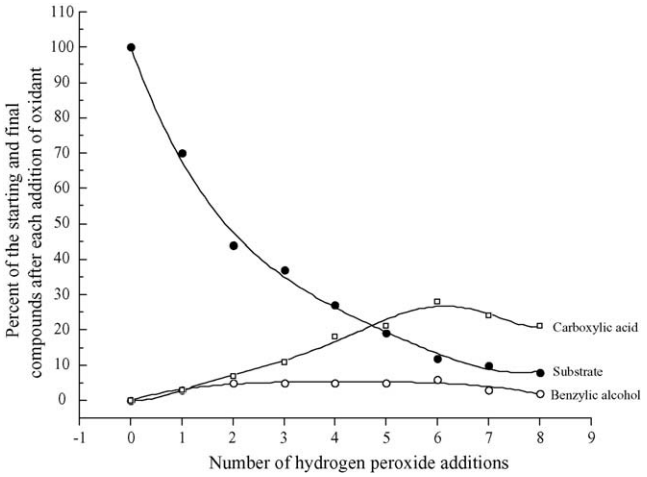
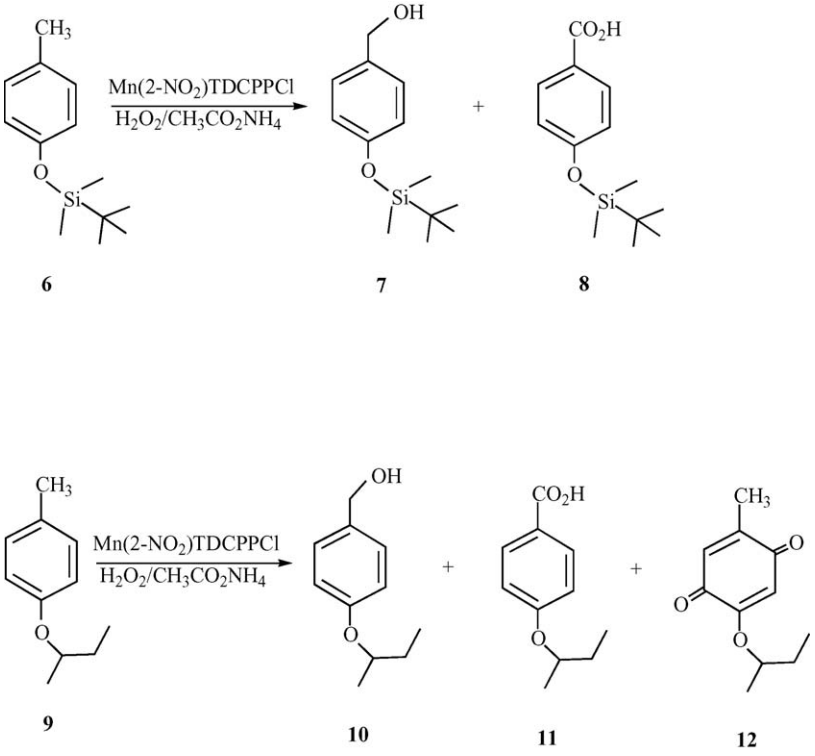


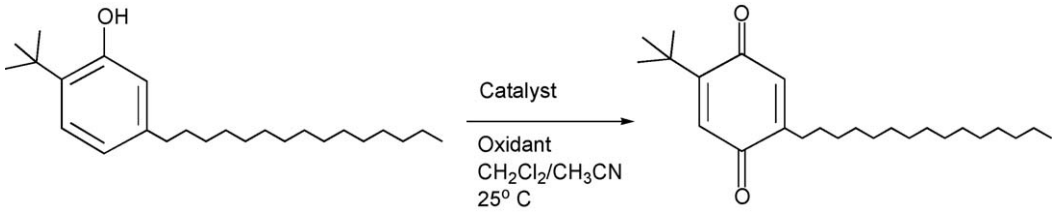
Fig. 4. Percentage of the starting **6** and the final **7** and **8** compounds as a function of the quantity of added oxidant.

Hydrogen peroxide was used in a slight excess (30% versus the substrate) and the additions were always stopped when the quantity of remaining substrates, at the GC analysis, appeared to be constant after two consecutive additions of the oxidant. For both substrates, the reaction products were isolated by column chromatography and in Scheme 2 the molecular structures of the starting compounds (**6** and **9**) and final products (**7**, **8**, **10**, **11**, **12**) are reported.

In this scheme it can be seen that both the substrates undergo to the oxidation of the methyl group giving the corresponding benzyl alcohol and benzoic acid derivatives, while only the



Scheme 2. Oxidation reactions of the substrates **6** and **9**.



Scheme 3. Oxidation reaction of 2-*tert*-butyl-5-pentadecylphenol.

Table 1
Yields of the oxidation reactions on **6** and **9** catalyzed by **5**[a]

Starting compounds	Yield (%)		
	Benzyl alcohols[b]	Benzoic acids[c]	1,4-Quinones[b]
6	4.1	26.8	–
9	31.0[d]	5.0	14.0

[a] Reactions carried out at 20 °C with a molar ratio substrate/oxidant/porphyrin 100/300/1.
[b] Determined by GC analysis.
[c] Determined by GC analysis on the methyl ester derivatives.
[d] The corresponding aldehyde was detected in trace.

isobutyl derivative is able to give also the corresponding 1,4-benzoquinone derivative. In Table 1, the yields of all the reaction products, determined by GC analysis, are reported. The benzoic acid derivatives were converted into the methyl ester by standard procedure [34] for both the GC analysis and characterization.

The reaction on *tert*-butyldimethylsilyl-4-methylphenyl ether, **6** was also checked as a function of the quantity of the added oxidant and the results are reported in Fig. 4. In this figure, the molar quantities of the starting product, the benzyl alcohol, **7** and benzoic acid, **8** derivatives are reported as a percent.

From the reported data it is possible to see the decrease of **6** and the simultaneous increase of **8**. The molar quantity of alcohol derivative **7** seems to remain constant after each addition. This fact could be due to the transformation of the benzyl alcohol into the corresponding acid; this hypothesis has been proved by running the oxidation reaction on the benzyl alcohol which in fact is quantitatively converted into the carboxylic acid, under the reaction conditions. These results are in agreement with those reported in the papers published by our laboratories in the past on the oxidation of aromatic compounds. In fact the oxidation of the 2-*tert*-butyl-5-pentadecylphenol by hydrogen peroxide with manganese porphyrins as catalysts, gave the corresponding quinone derivatives as the main products with high conversion of the substrate (see Scheme 3) [35].

This fact in our opinion is due to the steric hindrance that the two alkyl groups exert on the 1,4-positions of the benzene ring, avoiding the complexation of the metal by the phenolic products. In fact the UV–vis titration of the catalyst **3** by 2-methylphenol does not give any spectral modification even after the addition of 50 equivalents of the phenol.

Furthermore, the previously reported oxidation of toluene gives the quinone derivative as the main product using manganese 2-nitro-tetrakis(pentafluorophenyl)porphyrin and the benzoic acid when manganese 2-nitro-tetrakis(2,6-dichlorophenyl)porphyrin was used. For ethylbenzene and cumene, the main products were the benzoic acid and the benzylic alcohol derivatives [24]. Finally, the oxidation of the substrate **6** with hydrogen peroxide has also been considered with catalyst **3** in the presence of an excess of 4-methoxyphenol giving no reaction products even after several hours of reaction and thus proving the inhibition by the phenolic products.

4. Conclusions

In this paper, the inhibition of the manganese porphyrins catalytic efficiency by the final products of the oxidation of aromatic compounds by hydrogen peroxide, has been demonstrated by UV–vis spectroscopy and reactivity studies. The investigation also demonstrated that the steric hindrance obtained by the derivatization of phenols with hindered groups plays a key role for obtaining the oxidation of the substrates and giving in some cases moderate yield of quinone or benzoic acid derivatives. It has been also demonstrated that the benzylic alcohols obtained in low yields are intermediates in the oxidation reaction of a methyl group into a carboxylic function.

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