Kinetics and mechanism of the oxidation of alkyl substituted phenols and naphthols with ^{t}BuOOH in the presence of supported iron phthalocyanine

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2,3,5-Trimethylbenzoquinone (precursor of vitamin E) and 2-methylnaphthoquinone (vitamin K_3) were obtained in good yields by oxidation of 2,3,6-trimethylphenol and 2-methyl-1-naphthol, respectively, with ^{t}BuOOH catalyzed by supported iron tetrasulfophthalocyanine. The mechanism of this heterogeneous oxidation was studied using $^{18}O_2$ labeling experiments, EPR spectroscopy with spin traps, kinetic studies, and complete analysis of reaction products including minor ones. $^{18}O_2$ labeling experiments did not indicate the involvement of O_2 in the oxidative process. EPR study of reaction mixtures of 2,3,6-trimethylphenol and 2-methyl-1-naphthol oxidations in the presence of 3,5-dibromo-4-nitrosobenzenesulfonic acid spin trap showed no formation of any radical intermediates. Besides the target quinones, epoxyquinones and formyldimethyl-1,4-benzoquinones, as over-oxidation minor products have been found. C–C and C–O coupling products relevant to one-electron oxidation pathways were detected in trace amounts. Based on the experimental results, a mechanism of oxidation of alkyl-substituted phenols and naphthols mediated by the supported iron phthalocyanine catalyst has been proposed which involves two successive electron transfers without escape of radical species in solution.

Introduction

Phthalocyanine metal complexes are very attractive catalysts for industrial applications because of their low cost and accessibility on the large scale. Homogeneous and supported metal phthalocyanine complexes have widely been used as catalysts in the liquid phase oxidation of phenols,[1,2] hydrocarbons,[3] thiols[4] (Merox process) and other compounds.[5] In particular, iron tetrasulfophthalocyanine grafted on SiO_2 (FePcS–SiO_2) is very useful for the preparation of functionalized quinones which are important intermediates in fine chemistry for the preparation of vitamins and drugs.[2,6] FePcS–SiO_2 showed high activity and selectivity in the oxidation of 2,3,6-trimethylphenol (TMP) by ^{t}BuOOH providing 87% yield of 2,3,5-trimethyl-1,4-benzoquinone (TMBQ), a precursor of vitamin E,[2c] while 2-methyl-1-naphthol (MNL) was converted to 2-methyl-1,4-naphthoquinone (MNQ), vitamin K_3, with almost 60% yield.[7] It should be noted that these valuable quinone products are still prepared in industry by stoichiometric oxidation often using toxic oxidants.[8] The FePcS–SiO_2–^{t}BuOOH catalytic system exhibits a remarkable selectivity in aromatic oxidation to quinones even in the presence of easily oxidizable olefinic and alcohol groups to provide an access to functionalized quinones.[6] Such elaborated structures bearing several different functionalities at the same molecule are versatile building blocks in fine chemistry. However, the reason for this high selectivity of oxidation of functionalized phenols is not yet clear. The mechanistic study of aromatic oxidation by the FePcS–SiO_2–^{t}BuOOH system is therefore of much interest.

There are two general mechanisms of the oxidation of phenols to hydroquinones and quinones proposed in the literature. The first heterolytic mechanism involves a two-electron pathway operating *via* electrophilic hydroxylation.[9–12] An alternative homolytic mechanism involves the formation of radical aryloxyl intermediates.[13–15] The homolytic mechanism was proposed for H_2O_2-based oxidation over hydrophilic mesoporous titanium–silicates[16] and Ti-substituted polyoxometallates.[17] Based on the nature of the EPR spectra, data of kinetic studies and analysis of minor oxidation products, the formation of phenoxyl radicals was suggested. A heterolytic mechanism was suggested for the oxidation of phenols in the presence of microporous TS-1 and TS-2 titanium-silicate catalysts.[9–11]

We report here the study of the oxidation of alkyl-substituted phenols and naphthols, exemplified by TMP and MNL, by the catalytic system FePcS–SiO_2–^{t}BuOOH. To gain insight into the mechanism we have used $^{18}O_2$ labeling experiments, EPR spectroscopy with spin traps, kinetic studies, and complete analysis of the reaction products.

Results and discussion

Covalent anchoring of metal complexes onto inorganic supports allows preparation of heterogeneous catalysts with high stability against leaching of catalyst in the reaction

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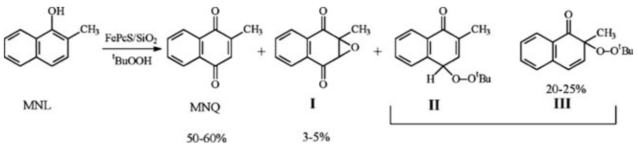
solution. This phenomenon has often been observed in heterogeneous catalysis.[12] We have found that FePcS supported in μ-oxo dimer form provided better selectivity in the oxidation of phenols.[2] A high potential of dimeric phthalocyanine complexes as catalysts for oxidation has been demonstrated in our recent studies. We have discovered that diiron μ-nitrido tetra-*tert*-butylphthalocyanine catalyzed oxidation of methane and benzene by H_2O_2 under very mild conditions.[18] This system represents the first bio-inspired example for the mild oxidation of methane in water.

The covalent grafting of FePcS onto an amino-modified SiO_2 surface was carried out using triphenylphosphine ditriflate for direct activation of sulfonate groups for reaction with surface amines as previously described.[6] This is a convenient, rapid one-pot procedure affording the μ-oxo dimer as the main grafted form according to DR UV-Vis spectroscopy. The position of the Q band was at 640 nm. The nitrogen sorption isotherm analysis showed a specific surface area of 185 $m^2\ g^{-1}$ while the Fe loading was 43 μmol g^{-1}. FePcS–SiO_2 was shown to be an efficient catalyst for the selective oxidation of alkyl-substituted phenols and naphthols, as well as phenols with other functional groups, to the corresponding quinones.[2,6,7] In particular, we have found that oxidation of TMP selectively afforded 87% TMBQ yield at 96% substrate conversion under the optimal reaction conditions: [TMP] = 0.02 M, [^{t}BuOOH] = 0.11 M, 1.6 μmol of FePcS–SiO_2 in 8 mL of 1,2-dichloroethane, 30 °C, 2 h.[2c] When MNL was used as the substrate the yield of MNQ was about 60% at 98% MNL conversion of MNL under optimal conditions: [MNL] = 0.1 M, [^{t}BuOOH] = 0.5 M, 0.5 μmol of FePcS–SiO_2 in 1 mL of 1,2-dichloroethane, 80 °C, 1 h.[7] The mechanism of these oxidations was studied under these reaction conditions.

Analysis of reaction products

The products of MNL oxidation were identified and quantified by GC-MS, GC and ^{1}H NMR methods. The target quinone MNQ was the principal product with 50–60% yield depending on the reaction conditions. Importantly, only 0.5 mol% of catalyst was sufficient to achieve these good yields. A small amount of MNQ was further oxidized to 2-methyl-2,3-epoxy-1,4-naphthoquinone with ~5% yield (Scheme 1, **I**).

Along with the two expected products we have detected the highly reactive *tert*-butylperoxo derivative of naphthalene with 25% isolated yield (molecular ion at m/z = 246, corresponding to $C_{15}H_{18}O_3$). This compound was unstable under GC-MS analysis conditions. According to ^{1}H NMR, ES-MS and CI-MS we suggested two possible structures **II** or **III** (Scheme 1). Along with the proton signals of the unsubstituted aromatic ring at 7.36, 7.42, 7.64 and 7.96 ppm, two doublet signals at 6.28 and 6.72 ppm (J = 7.5 Hz) can be attributed to signals of vinylic protons of structure **III**. The downfield shift of the signal of the CH_3 group in MNL from 2.41 ppm to 1.14 ppm in the intermediate is more compatible with structure **III**. The effect can be explained by the influence of the *tert*-butylperoxo group at the same carbon atom as was found for the 4-hydroperoxide carbon of 4-methyl-2,6-di-*tert*-butylphenol, where the signal was found to be downfield shifted from 2.27 to 1.37 ppm.[19] These results can be rationalized by assuming the formation of a radical or cation intermediate with two resonance forms leading to *para*- and *ortho*-peroxo quinol derivatives **II** and **III**, respectively. Intermediate **II** should be significantly less stable and can further be converted to MNQ. Note that only substituted *ortho*- and *para*-quinol derivatives have been described.[20]



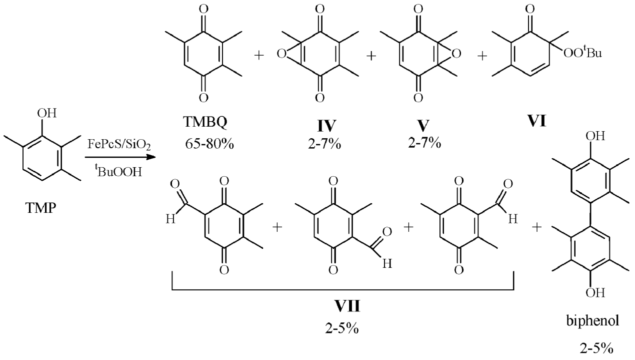
Scheme 1 Oxidation of MNL by ^{t}BuOOH in the presence of FePcS–SiO_2.

Oxidation of TMP afforded TMBQ with 65–80% yield depending on the reaction conditions. Several minor products were also detected and identified by GC-MS and ^{1}H NMR. Two isomeric epoxides 2,5,6-trimethyl-2,3-epoxy-1,4-benzoquinone **IV** and 2,3,6-trimethyl-2,3-epoxy-1,4-benzoquinone **V** were obtained in 2–7% yields (Scheme 2).

The oxidation of the aromatic phenol ring is quite selective. Only trace amounts of products of oxidation of methyl groups were found. Isomeric formyldimethyl-1,4-benzoquinones **VII** were obtained in 2–5% total yield. In contrast with the Ti–Si catalyst –H_2O_2 system where C–C and C–O coupling products were the main by-products,[21] only a small amount of biphenol, due to oxidative coupling of phenoxy radicals, was also detected. Since the yield of biphenol determined by NMR[2c] is only 2–5%, one can conclude that phenoxyl radicals are not long-lived major species. The formation of the *tert*-butylperoxo derivative of TMP by analogy with MNL oxidation can also be possible (**VI**, Scheme 2). This putative compound **VI** is less stable then the naphthalene derivative **II** or **III** and undergoes degradation during purification by TLC and during GC-MS analysis giving only hardly identifiable fragments.

$^{18}O_2$ labeling experiments

To probe the mechanism of the phenol/naphthol oxidation mediated by FePcS–SiO_2 the oxidation of MNL was performed in the presence of $^{18}O_2$ (99.6% ^{18}O isotope purity). The reaction flask was filled up with a mixture of 79.6% of Ar and 20.4% of $^{18}O_2$, modelling air composition. The isotopic



Scheme 2 Oxidation of TMP by ^{t}BuOOH in the presence of FePcS–SiO_2.

composition of the gas phase and the reaction mixture was analyzed by GC-MS before the reaction started and 2 h after ^{t}BuOOH addition. The isotopic composition of dioxygen before and after the reaction gas was practically constant, around 99% $^{18}O_2$. This finding indicates no appreciable ^{t}BuOOH decomposition *via* a homolytic mechanism which would result in $^{16}O_2$ formation. ^{t}BuO$^\bullet$ radical formed from homolytic cleavage of ^{t}BuOOH should react with ^{t}BuOOH to form ^{t}BuOH and ^{t}BuOO$^\bullet$ radical. Then, $^{16}O_2$ should be formed according to the Russell scheme from ^{t}BuOOOO^{t}Bu.[22] Recently, we have demonstrated a significant increase of $^{16}O_2$ content in the gas phase in the course of $^{18}O_2$ labeling experiments using the catalytic system Ti–Si catalyst–H_2O_2 due to unproductive decomposition of oxidant during the oxidation of substituted phenols.[23] Thus, these isotopic labeling data suggest different mechanisms of the phenol/naphthol oxidation in the presence of iron- and titanium-containing catalysts.

The isotopic compositions of the substrate and products were constant during the entire reaction course indicating no blank oxygen exchange with dioxygen. GC-MS analysis of the final reaction mixture showed that MNQ contained 91.6 ± 0.2% of unlabeled product and only 8.4 ± 0.2% of labeled quinone with ^{18}O label in one position. This low incorporation of ^{18}O in quinone is not consistent with a radical pathway involving alkoxy- or peroxy-radicals which would rapidly generate phenoxyl radicals from phenol. Phenoxyl radicals would easily react with $^{18}O_2$ leading to significant ^{18}O incorporation in the products, as has been previously observed.[5a,b]

EPR study in the presence of a spin trap

EPR spectroscopy allows the detection of short-living radicals *via* their trapping by spin traps to form EPR-detectable long-lived radicals.[24] Based on the characteristics of the EPR spectrum one can suggest the nature and structure of the radical. We have recently demonstrated the possibility of the identification of phenoxyl/naphthoxyl radicals formed in the Ti–Si catalyst–H_2O_2 system by EPR spectroscopy using 3,5-dibromo-4-nitrosobenzenesulfonic acid (DBNBS) as a spin trap.[16c]

When FePcS–SiO_2 mediated oxidation of MNL was carried out in the presence of DBNBS, the EPR spectrum did not contain the signals of any radical adduct. The signals were very weak (background level) when TMP was used as substrate. This means that phenoxyl and naphthoxyl radicals were not formed in appreciable amounts suggesting the non-radical mechanism of phenol/naphthol oxidation in the presence of the iron-containing catalyst. This suggestion was confirmed by the absence of significant amounts of coupling products that are typical for one-electron processes occurring *via* formation of radical intermediates.[25] This conclusion is also in accordance with the following observation. While studying the influence of MNL concentration on the selectivity of oxidation in the system FePcS–SiO_2–^{t}BuOOH, we have found that selectivity towards MNQ did not decrease with the growth of MNL concentration.[7] When the MNL concentration was increased from 0.025 to 0.1 M the selectivity in MNQ was raised from 44 to 50%. The same trend was observed when the catalyst amount was decreased.[7] These findings contradict the one-electron mechanism of MNL oxidation *via* ArO$^\bullet$ radicals, for which an inverse dependence is expected. For example, considerable decrease of selectivity to MNQ in the MNL oxidation was observed upon increasing of the MNL concentration or the catalyst amount in the Ti–Si catalyst–H_2O_2 system.[8,23] The formation of radical species in this system was evidenced and a homolytic mechanism was established.[16c,23]

Kinetic of TMP oxidation

The kinetic study of the oxidation of TMP in the absence and in the presence of DBNBS showed that the addition of the spin trap did not affect the rate of TMP consumption and the rate of TMBQ formation (Fig. 1). This result also indicates that the formation of TMBQ does not occur *via* formation of phenoxyl radicals. For the Ti–Si-catalyst a significant decrease of the rate of both TMP consumption and TMBQ formation was observed in the presence of DBNBS.[16c]

Typical kinetic curves of TMP consumption and TMBQ formation show no induction period (Fig. 1). In the absence of catalyst a non-selective reaction was very slow, the conversion reached only 20% after 7 h. The apparent activation energy of the catalytic reaction measured at 25–85 °C was determined as 22 kJ mol^{-1} (Fig. 2).

We detected a small but distinctive increase of the initial rate with increase of the concentration of water (Table 1). Further increase of water amount led to decrease of the reaction rate.

The reaction is first order both in ^{t}BuOOH (Fig. 3(a)) and in catalyst (Fig. 3(b)).

It is important to note that under typical reaction conditions the reaction order in TMP is close to zero (Fig. 4). This result can be explained by binding of phenol with the iron active center.

When complete formation of the complex between FePcS and phenol occurs, the reaction rate should not further depend

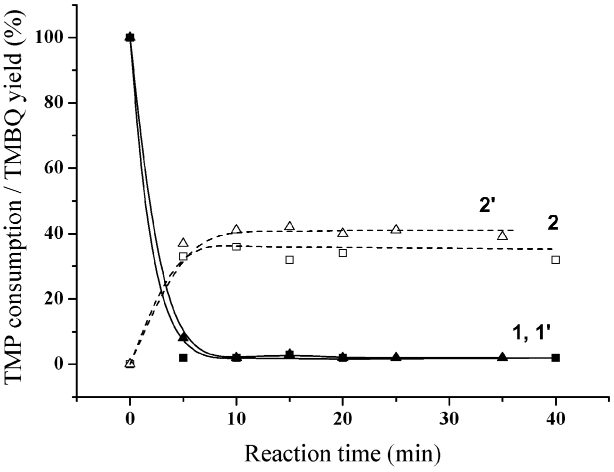


Fig. 1 TMP conversion and TMQ yield *vs.* time: curves **1**, **2** without DBNBS, curves **1**′, **2**′ in the presence of DBNBS. *Reaction conditions*: 0.1 M TMP, 0.5 M ^{t}BuOOH, 0.02 M DBNBS (**1**′ and **2**′), 12 mg FePcS–SiO_2, [H_2O] = 0.65 M, 1 mL MeCN, 50 °C.

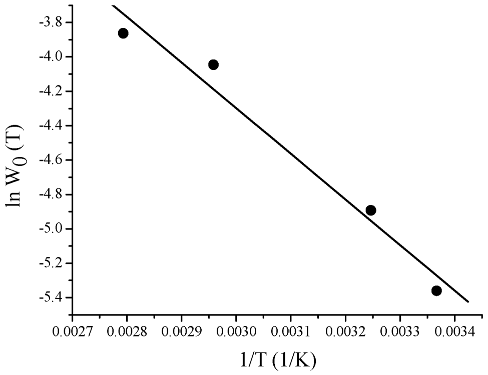


Fig. 2 Temperature dependence of TMP oxidation with ^{t}BuOOH in the presence of FePcS–SiO$_2$. *Reaction conditions*: [TMP] = 0.1 M, [^{t}BuOOH] = 0.2 M, 3.2 mg of FePcS–SiO$_2$ (0.14 mol%), 1 mL of MeCN.

on the phenol concentration. To check this hypothesis we have studied the interaction between TMP and FePcS by UV-Vis spectroscopy.

UV-Vis study

First, the titration of FePcS by TMP was performed in water because FePcS is not soluble in acetonitrile or other common organic solvents. In aqueous solution, even at spectrophotometric concentrations, FePcS exists in a dimeric form.[25] After the addition of TMP solution to the solution of FePcS the band at λ_{max} = 630 nm, corresponding to the dimer, disappears while a new band appears at λ_{max} = 655 nm (Fig. 5(a)).

Similar changes have previously been observed during titration of an aqueous solution of FePcS by 2,4,6-trichlorophenol.[26] These changes were explained by the cleavage of the μ-oxo dimer upon phenol coordination with formation of the monomeric [Fe^{III}PcS]$^+$ form with phenolate as anion. We propose that the same phenomenon occurs in the case of other phenols, in particular with TMP and MNL. Addition of ^{t}BuOOH to an aqueous solution of FePcS also resulted in a red shift, as was previously observed and explained by the coordination of ^{t}BuOOH with the iron site.[3g] However, the situation was complicated by the concomitant bleaching of the phthalocyanine core that made the analysis difficult. Anyway, the first-order dependence in ^{t}BuOOH oxidant and near-zero order dependence in TMP substrate allow to suggest that phenol should be bound to iron phthalocyanine more strongly than the oxidant.

A different situation should occur in the case of the supported FePcS–SiO$_2$ catalyst. Covalent grafting of phthalocyanine onto a support *via* sulfonate groups should stabilize the dimeric form against monomerization.[2d] Indeed, the DR UV-Vis spectrum of FePcS–SiO$_2$ treated with a TMP solution in MeCN, separated by filtration and dried at 80 °C was the same as that of initial material except for a decrease of the shoulder at 690 nm (Fig. 5(b)). After the same treatment of FePcS–SiO$_2$ with MeCN alone the DR-UV spectrum was unchanged. One can propose that the grafted dimer retains

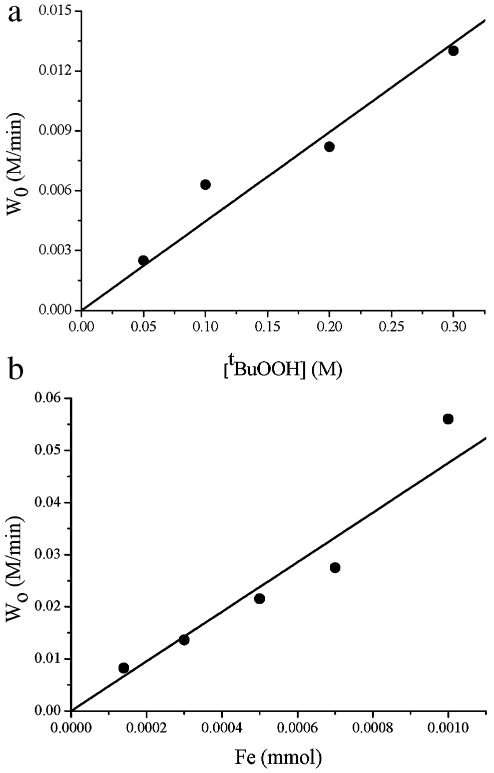


Fig. 3 Dependence of the initial rate W_o on [^{t}BuOOH] (a) and catalyst amount (b) in the TMP oxidation by ^{t}BuOOH mediated by FePcS–SiO$_2$. *Reaction conditions*: [TMP] = 0.1 M, [H$_2$O] = 0.65 M, 1 mL of MeCN, 35 °C; (a) 3.2 mg of FePcS–SiO$_2$ (0.14 mol% Fe); (b) [^{t}BuOOH] = 0.2 M.

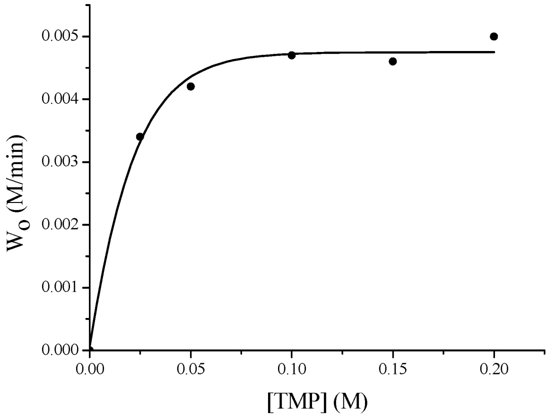


Fig. 4 Dependence of the initial oxidation rate W_o on [TMP]. *Reaction conditions*: [^{t}BuOOH] = 0.2 M, 3.2 mg of FePcS–SiO$_2$ (0.14 mol% Fe), [H$_2$O] = 0.65 M, 1 mL of MeCN, 35 °C

Table 1 The influence of [H$_2$O] on the initial rate (W_o) of TMP oxidation by H$_2$O$_2$ in the presence of FePcS–SiO$_2$[a]

[H$_2$O]/M	0.64	1.0	1.5	2.0	3.0
$10^2 W_0$/M min^{-1}	0.73	0.71	0.80	0.93	0.98

[a] *Reaction conditions*: [TMP] = 0.1 M, [^{t}BuOOH] = 0.2 M, 3.2 mg of FePcS–SiO$_2$ (0.14 Fe mol%)), 1 mL of MeCN, 35 °C.

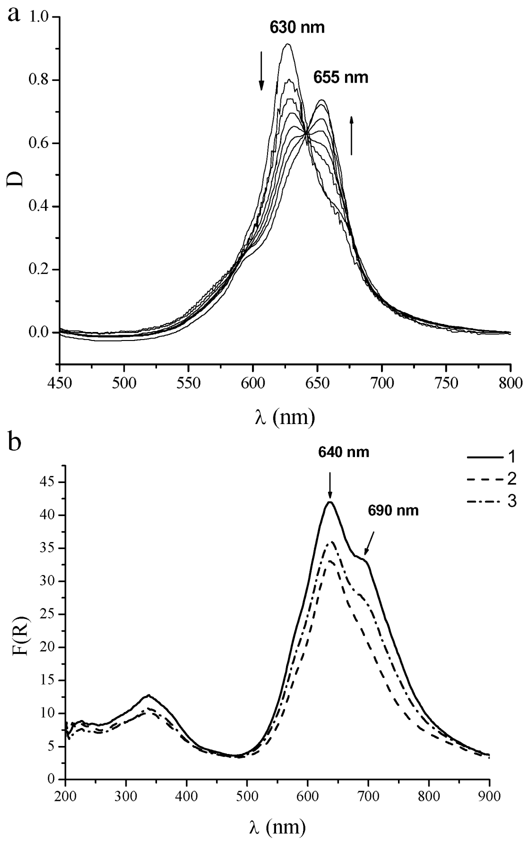
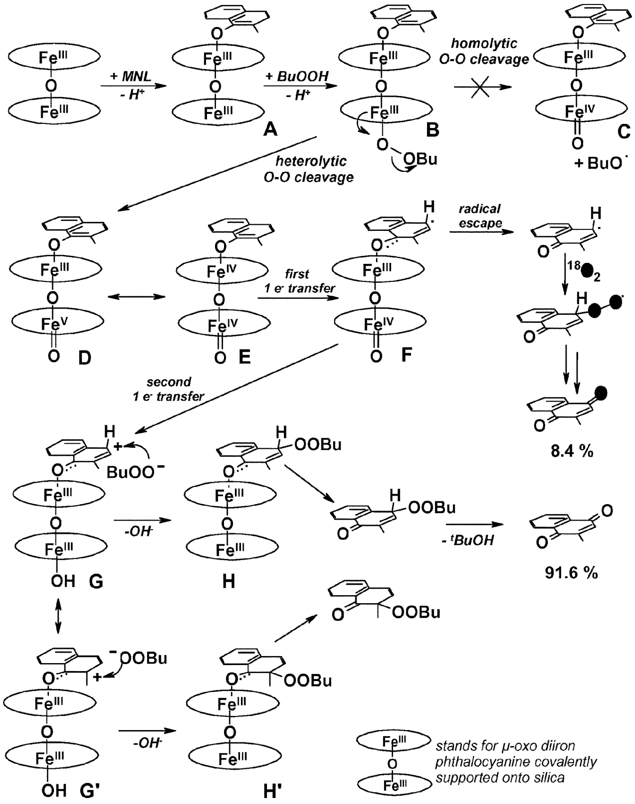


Fig. 5 (a) Modification of the visible spectrum of FePcS (water, 10^{-5} M) upon addition of TMP; (b) DR UV-Vis spectra of FePcS–SiO$_2$: (1) initial; (2) treated with a solution of TMP in MeCN and (3) treated with MeCN.



Scheme 3 Proposed mechanism of oxidation of MNL by ^{t}BuOOH mediated by FePcS–SiO$_2$.

its dimeric structure upon coordination of phenol without significant influence on its UV-Vis spectrum in the Q band region. The Q band corresponds to π–π* transfer of the phthalocyanine ligand which is sensitive to π–π interaction of phthalocyanine cores and less sensitive to ligation of metal iron.

Proposed mechanism of phenol oxidation

Based on the obtained results we propose the following mechanism of the oxidation of alkyl substituted phenols by ^{t}BuOOH mediated by supported iron phthalocyanine catalyst using MNL as an example (Scheme 3).

In the first step the coordination of phenol with supported μ-oxo diiron phthalocyanine takes place. Similar coordination of phenol was previously proposed for iron phthalocyanine[2e] and iron porphyrin mediated oxidation.[27] Our UV-Vis and kinetic data (near-zero order in TMP oxidation) support this hypothesis. The phenolate complex **A** can coordinate BuOO$^-$ to form intermediate **B** which can undergo homolytic or heterolytic O–O cleavage. Homolytic cleavage of the O–O bond would result in the concomitant formation of a BuO$^\bullet$ radical. However, the low incorporation of ^{18}O in MNQ in the experiment with ^{18}O$_2$, the increase of the selectivity to MNQ when increasing starting MNL concentration and, especially, the absence of detected radicals in the EPR experiments in the presence of the radical trap DBNBS strongly suggest that homolytic cleavage of the peroxo bond in **B** to form intermediate **C** does not occur to a significant extent. Heterolytic cleavage of the O–O bond in **B** produces Fe^{III}Fe^{V} intermediate **D** which should exist mainly in Fe^{IV}Fe^{IV} form **E** due to delocalisation of the charge on two Fe ions. It should be noted that diiron structural unit should provide the stabilization of the high-valent species. An intramolecular one-electron transfer in the intermediate **E** will lead to the radical species **F**. The naphthol radical escaping from **F** can undergo trapping by dioxygen which should be observed in the ^{18}O$_2$ trapping experiment. Labeled (in one position) quinone accounted only for 8.4% of products indicating that this is only a minor pathway. Further, naphthol radicals should produce biphenol *via* bimolecular oxidative coupling, yet only traces of biphenol (2–5%) were observed in the case of TMP oxidation. Yet, we were unable to detect MNL coupling product(s). A second one-electron transfer in **F** can lead to cationic species **G** or **G′** which can undergo a nucleophilic attack of BuOO$^-$ to form **H** or **H′**. Intermediate **II** formed from **H** should not be stable under the reaction conditions and gives rise to MNQ obtained with 55–60% yield. In turn, intermediate **H′** should lead to more stable intermediate **III** which was indeed obtained in 20–25% isolated yield in MNL oxidation. Alternatively, the coordinated or escaped MNL cation might react with water or hydrogen peroxide to produce a quinol derivative and quinone, respectively. Indeed, increasing of water concentration up to 2 M led to higher MNQ selectivity (Table 1). A higher amount of water led to a decrease of the selectivity, probably *via* coordination of water with the diiron complex thus preventing coordination with

MNL or with ^{t}BuOOH. All possible quinols can further be transformed to unlabeled MNQ. An analogous mechanism should be operating in the oxidation of TMP where similar trends have been observed.

Experimental

2,3,6-Trimethylphenol (Fluka), 2-methyl-1-naphthol (Aldrich), 2-methyl-1,4-naphthoquinone (Aldrich), ^{t}BuOOH (Aldrich), 70% aqueous solution, $^{18}O_2$ (98.5 atom%, Euriso-top) and 3,5-dibromo-4-nitrosobenzenesulfonic acid (DBNBS) were used as received without further purification.

Iron tetrasulfophthalocyanine was prepared according to the published procedure.[28] Covalently supported FePcS–SiO$_2$ material (0.2–0.3 wt% Fe, S_{BET} = 185 m^2 g^{-1}, average particle size 12 nm) was obtained by grafting of FePcS onto the surface of amino-modified SiO$_2$ (Aerosil) as described.[6]

Instrumentation

GC analyses were performed using an Agilent 4890D and Tsvet-500 gas chromatograph equipped with a flame-ionization detector and a DB-5MS capillary column (30 m × 0.25 mm) filled with Durabond phase. CG-MS analyses of organic products were carried out using HP 5973/6890 and VG-7070 instruments. Electrospray ionization mass-spectrometry (ESI-MS) and chemical ionization mass-spectrometry (CI-MS) analyses were performed using ThermoFinnigan LCQ and ThermoFinnigan MAT 95 XL instruments, respectively. EPR spectra were recorded at room temperature using a Bruker ER-200D. ^{1}H NMR spectra of the reaction products were run on MSL-400 Bruker or AM 250 Bruker instruments. UV-Vis spectra were recorded using a Specord M40 spectrophotometer. DRS-UV spectra were acquired on a Shimadzu UV-Vis 2501PC spectrophotometer.

Catalytic oxidations

The products of TMP and MNL oxidation were identified using ^{1}H NMR and mass spectrometric methods (GC-MS, ESI-MS, CI-MS). The substrate conversion and the yield of TMBQ and MNQ were quantified by GC using biphenyl as the internal standard.

TMP oxidation in the presence of spin trap DBNBS was performed in a thermostated glass vessel at 50 °C. The reactions were initiated by addition of 0.5 mmol of ^{t}BuOOH to a mixture of 0.1 mmol of TMP, 12 mg of FePcS/SiO$_2$, 0.02 mmol of DBNBS and internal standard (biphenyl) in 1 mL of MeCN. The course of reaction was followed by GC.

1,2-Dihydro-2-*tert*-butylperoxo-2-methyl-1-oxonaphthalene. ESI-MS: m/z = 246 $(M)^+$; ^{1}H NMR (CD_3COCD_3, 250 MHz): δ 1.14 (s, 3H, CH$_3$), 1.29 (s, 9H, *tert*-Bu), 6.28 (d, 1H, H^3, J = 7.8 Hz), 6.72 (d, 1H, H^4, J = 7.8 Hz), 7.36 (d, 1H, H^5, J = 7.5 Hz), 7.42 (t, 1H, H$^{6(7)}$, J = 7.5 Hz), 7.64 (t, 1H, H$^{7(6)}$, J = 7.5 Hz), 7.96 (d, 1H, H^8, J = 7.5 Hz).

2,3,6-Trimethyl-2,3-epoxy-1,4-benzoquinone. m/z (%) 166 (7) M^+, 151 (100) $(M - CH_3)^+$, 138 (17) $(M - CO)^+$, 124 (33) $(M - CCH_3, CH_3)^+$, 109 (13) $(M - CCH_3, 2CH_3)^+$, 95 (22) $(M - CCH_3, CH_3, CHO)^+$.

2,5,6-Trimethyl-2,3-epoxy-1,4-benzoquinone. m/z (%) 166 (3) M^+, 151 (73) $(M - CH_3)^+$, 138 (79) $(M - CO)^+$, 124 (100) $(M - CCH_3, CH_3)^+$, 109 (20) $(M - CCH_3, 2CH_3)^+$.

Formyldimethyl-1,4-benzoquinone. m/z (%) 164 (58) $(M)^+$, 149 (2) $(M - CH_3)^+$, 136 (71) $(M - CO)^+$, 121 (100) $(M - CO - CH_3)^+$, 108 (13) $(M - 2CO)^+$, 93 (31) $(M - 2CO - CH_3)^+$.

^{18}O labeling experiments

The oxidation of MNL in the presence of labeling $^{18}O_2$ was performed under an atmosphere containing 20.4% of $^{18}O_2$ (99.6% ^{18}O enrichment) and 79.2% of Ar. The 50 mL reaction flask containing 0.025 mmol of MNL, 5.2 mg of FePcS–SiO$_2$ (0.25 μmol of Fe) in 1 mL of MeCN was filled up with this gas mixture. Reaction was started by addition of 0.125 mmol of ^{t}BuOOH. Isotopic composition of products and the gas phase were determined by GC-MS. Each sample was analyzed three times and m/z intensities of each peak were obtained by the integration of all scans of the peak. The degree of ^{18}O incorporation into MNQ was calculated from ratio of m/z 172/174 intensities in the mass spectra of MNQ.

Spin-trap experiments

Experiments were carried out in thermostated vessels under magnetic stirring at 50 °C (TMP) and 25 °C (MNL). Reaction was initiated by addition of 0.088 mmol of ^{t}BuOOH to the mixture containing 0.025 mmol of TMP or MNL, 3–5 mg of FePcS–SiO$_2$ and 0.005 mmol of DBNBS in 250 μL of MeCN. After 30 min the reaction mixture was placed into a quartz cell which is typically used to perform EPR measurements in polar solvents. The EPR spectra were run at room temperature.

UV-Vis and DR UV-Vis measurements

UV-Vis experiments were performed at room temperature. The acetonitrile solution containing 10^{-6} mol TMP was added in 10 μL portions (50 equiv.) to a 10^{-5} M homogeneous FePcS solution in 2 mL of MeCN. The spectra were recorded on after each addition.

For DR-UV analyses of solid catalysts, 0.2 mmol of TMP was dissolved in 10 mL of MeCN. 200 mg of FePcS–SiO$_2$ was added to the solution which was stirred for 10 min at room temperature. Then the catalyst was filtered off, dried at room temperature, dried at 80 °C for 16 h and analyzed by DR UV-Vis spectroscopy. In a blank experiment 200 mg of FePcS–SiO$_2$ was added to 10 mL of MeCN. Preparation for the other procedures was made in the same manner.

Kinetic study

The kinetic studies of TMP oxidation were carried out in a thermostated glass vessel at 25–85 °C under vigorous stirring (500 rpm). Reactions were initiated by addition of 0.05–0.3 mmol of ^{t}BuOOH to a solution of 0.05–0.2 mmol of TMP, 3–25 mg of catalyst (0.14–1.00 μmol of Fe), internal standard (biphenyl) in 1 mL of MeCN. The dependence of the reaction rate on [^{t}BuOOH] was studied at a constant concentration of H_2O (0.64 M) to make a correction of the reaction conditions on changing the amount of added aqueous solution of ^{t}BuOOH. The reaction orders were determined from the dependence of the initial rate of TMP consumption on the concentration of one of the reagents when the concentrations of other reagents were kept constant.

Conclusions

Iron tetrasulfophthalocyanine covalently supported onto silica in the μ-oxo dimeric form in combination with ^{t}BuOOH shows high selectivity in the industrially important oxidation of 2,3,6-trimethylphenol and 2-methyl-1-naphthol to the corresponding quinones. The mechanism of this oxidation has been studied using $^{18}O_2$ labeling experiments, EPR spectroscopy with spin traps, kinetic studies and complete analysis of reaction products including minor ones. Several lines of evidence indicate that long-living phenoxyl radicals are not involved in the reaction as principal reaction species. Based on the obtained data we propose the initial coordination of phenol to the diiron center followed by activation of peroxide oxidant. The principal and minor products are formed *via* two successive one-electron transfers in this intermediate. The selectivity and kinetics of oxidation as well as ^{18}O labeling results are in accordance with proposed mechanism.

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