

EPR study on the mechanism of H₂O₂-based oxidation of alkylphenols over titanium single-site catalysts

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Abstract

The selective oxidation of 2,3,6-trimethylphenol (TMP) and 2-methyl-1-naphthol (MNL) with H₂O₂ catalyzed by titanium single-site catalysts, TiO₂-SiO₂ aerogel and mesostructured hydrothermally stable titanium-silicate, Ti-MMM-2, have been studied by means of EPR spectroscopic technique with spin traps. The formation of phenoxyl (naphthoxyl) and hydroxyl radical intermediates during the oxidation process have been detected using 3,5-dibromo-4-nitrosobenzene-sulfonic acid (DBNBS) and 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) spin traps, respectively. The character of the EPR spectra of the DBNBS adducts strongly depends on the nature of the organic substrate and the reaction temperature. A compilation of the EPR and by-product studies strongly supports a homolytic oxidation mechanism. Study by DR-UV-vis spectroscopy has confirmed the previously suggested chemical adsorption of phenol on the titanium center.

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Keywords: Titanium single-site catalysts; 2,3,6-Trimethylphenol; 2-Methyl-1-naphthol; H₂O₂; EPR spectroscopy; Spin traps; Oxidation mechanism

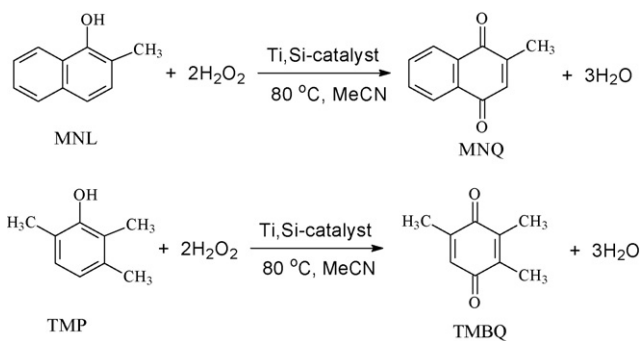
1. Introduction

Heterogeneous titanium single-site catalysts have received an increasing attention in the area of liquid phase selective oxidation [1–3]. Developed in the early 1980s, microporous titanium-silicate, TS-1, shows remarkable catalytic properties in H₂O₂-based oxidations of small organic substrates (<6 Å) and is currently employed in three industrial processes [4–8]. Titanium framework-substituted aluminophosphate TAPO-5 was found to be efficient in cyclohexene conversion to adipic acid by H₂O₂ [9]. Because of the tremendous importance of this class of catalysts a large scientific effort has been made on the synthesis and characterization of various mesoporous titanium-containing materials to open new opportunities in selective oxidations

of large organic substrates [10–18]. Earlier, several research groups have demonstrated a synthetic potential of mesoporous titanium-containing molecular sieves in H₂O₂-based selective oxidation of bulky phenols/naphthols [10,16,19–28]. A particular attention was drawn to the practically important oxidation of 2,3,6-trimethylphenol (TMP) [17,21–24,28,29] and 2-methyl-1-naphthol (MNL) [26,27] to the corresponding quinones. The oxidation of MNL is currently considered as a perspective route to 2-methyl-1,4-naphthoquinone (MNQ, menadione, vitamin K₃) [30], while the selective oxidation of TMP is of significant interest as a method for the preparation of 2,3,5-trimethyl-1,4-benzoquinone (TMBQ, a key intermediate in the synthesis of vitamin E) (Scheme 1) [31].

TiO₂-SiO₂ aerogels [22,24] and titanium grafted onto mesoporous commercial silica [16,28] appeared to be among the most efficient catalysts for TMP oxidation with H₂O₂ and demonstrated 96–98% selectivity to TMBQ at 99–100% TMP

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Scheme 1. Production of MNQ and TMBQ over Ti, Si-catalysts.

conversion. It has been shown that catalysis is of truly heterogeneous nature, and no titanium leaching occurs from the solid matrices [17,18,23,24,28].

Considerable efforts, both theoretical and experimental, have been directed to rationalize the activity and selectivity of TS-1 and related materials in alkene epoxidation [1–3,5,9,32–44]. At the same time, much remains to be understood in the oxidation of phenols regarding the nature of the active intermediates and specific chemical interactions at the molecular level.

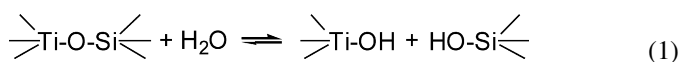
Two general mechanisms are reported in the literature for the selective catalytic oxidation of phenols. The first one is a homolytic mechanism (one electron pathway) that involves either hydrogen atom abstraction or an electron transfer process followed by elimination of H^+ leading to the formation of phenoxyl radicals at the first step [45,46]. These processes are fast and efficient because of the rather low O–H bond dissociation energy in phenols [47]. The second general mechanism implies a heterolytic oxygen atom transfer (two electron pathway) from an activated oxidant to a phenolic substrate [5].

It is generally accepted that the two-electron route is typical of H_2O_2 -based oxidations over hydrophobic microporous titanium-silicates TS-1 and TS-2 [1,5–7,48], while the one-electron mechanism occurs for hydrophilic mesoporous titanium-silicates [1,3]. Based on the character of the isomer distribution of dihydroxybenzenes in phenol oxidation with H_2O_2 over TS-1 and TS-2, a mechanism via electrophilic substitution in aromatic nuclear has been suggested [5,49,50].

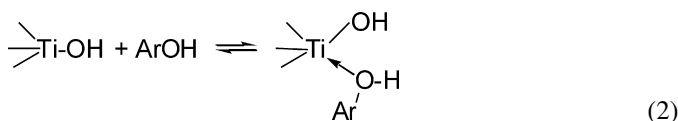
In the oxidation of toluene, the lack of CH_3 -group oxidation products also supported an oxygen transfer mechanism for the TS-1/ H_2O_2 system [5]. To the contrary, side-chain oxidation products were found predominantly in toluene oxidation with H_2O_2 over amorphous TiO_2 – SiO_2 mixed oxides, which indicated a homolytic mechanism involving participation of hydroxyl radicals [51].

Recently, based on the results of the product [23], kinetic [29] and model [3,52–54] studies, we suggested a homolytic mechanism for TMP oxidation with H_2O_2 in the presence of Ti single-site catalysts that comprises the following reaction steps:

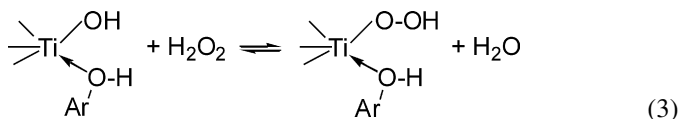
hydrolysis of Ti–O–Si bonds



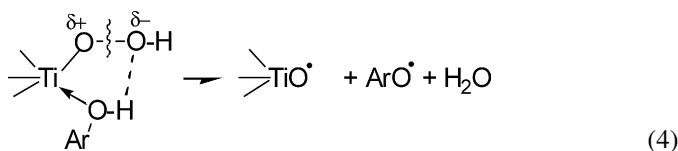
chemisorption of phenol



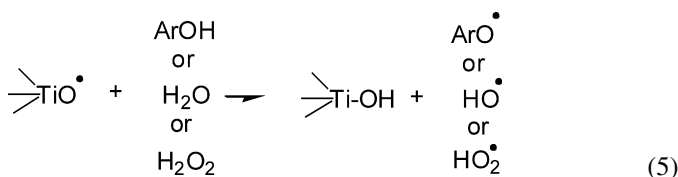
formation of a titanium hydroperoxo complex



electron transfer leading to the formation of a phenoxyl radical



regeneration of the catalytic site



The following transformations of ArO^\bullet include their recombination leading to C–C- and C–O-coupling products



and/or further oxidation resulting finally in the formation of the four-electron oxidation product, *p*-benzoquinone (BQ):



The main argument in favour of the homolytic oxidation mechanism was the identification of the C–C and C–O coupling products [23]. The increase of the benzoquinone yield and the decrease of the coupling products yield when reducing phenol concentration also supported that reaction scheme [23,29]. Meanwhile, a direct evidence of the formation of ArO^\bullet and $\bullet OH$ radicals during the reaction is crucial to verify the hypothesis about the homolytic oxidation mechanism and to clarify the role of these radicals in the formation of the target quinone.

EPR spectroscopy employing the spin-trapping technique when short-lived radicals are transformed into more stabilized and thus much longer-lived ones, making them accessible to detection, has been successfully used to monitor radical intermediates in biological systems [55–57] and in the presence of both porous [58] and non-porous catalysts [59,60]. In this work, we applied the spin-trap method to probe TMP and MNL oxidation over two representative titanium single-site catalysts, such as TiO_2 – SiO_2 aerogel and hydrothermally stable mesostructured titanium-silicate Ti-MMM-2. The results obtained agree with the results of the by-product and $^{18}O_2$

labelling studies and strongly support the homolytic oxidation mechanism.

2. Experimental

2.1. Catalysts and materials

TiO₂–SiO₂ aerogel (1.68 wt.% Ti, surface area $S=770\text{ m}^2\text{ g}^{-1}$, average pore diameter $d=15.6\text{ nm}$, mesopore volume $V=3.03\text{ cm}^3\text{ g}^{-1}$) was synthesized by the sol–gel method [24,61]. Mesostructured titanium-silicate Ti-MMM-2 (1.68 wt.% Ti, $S=1147\text{ m}^2\text{ g}^{-1}$, $d=3.2\text{ nm}$, $V=0.74\text{ cm}^3\text{ g}^{-1}$) was prepared by hydrothermal synthesis using C₁₆H₃₃N(CH₃)₃Br as template under weak acidic conditions as described earlier [17]. 2,2',3,3',5,5'-Hexamethyl-4,4'-bisphenol (BP) was prepared according to the literature procedure [62]. 3,5-Dibromo-4-nitrosobenzene-sulfonic acid (DBNBS), 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO), 2-methyl-1-naphthol (MNL), 2,3,6-trimethylphenol (TMP) and the corresponding quinones were purchased from Aldrich and used as received. All other reactants were obtained commercially and used without further purification. The concentration of hydrogen peroxide (28–33 wt.% in water) was determined iodometrically prior to use.

2.2. Catalytic experiments and product analysis

Catalytic oxidations were performed in thermostated glass vessels at 25–80 °C under vigorous stirring (500 rpm). The rate of TMP consumption remained constant while the stirring rate varied in the range of 200–1000 rpm indicating no diffusion limitation. Typically, the reactions were initiated by adding 0.35 mmol of H₂O₂ to a mixture containing 0.1 mmol of substrate and 12 mg of catalyst in 1 mL of MeCN. The oxidation products were identified by GC–MS and ¹H NMR. The substrate conversions and product yields were quantified by GC using biphenyl as the internal standard. The ratio between TMBQ, BP and C–O coupling dimer, 2,3,6-trimethyl-4-(2,3,6-trimethylphenoxy)phenol (PP), was also estimated using ¹H NMR by integrating signals of the aromatic proton at δ 6.55 (q, 1H), 6.72 (s, 2H) and 6.68 (s, 1H) ppm, respectively. The 2-methyl-1-naphthol oxidation products were isolated using preparative thin-layer chromatography (SiO₂; eluents—toluene and toluene/ether (30:1). The structure of the isolated compounds was determined by ¹H NMR, chemical ionization mass-spectrometry, electrospray mass-spectrometry and by comparison of the physical properties with the literature data.

2.2.1. 2,2',3,3',5,5'-Hexamethyl-4,4'-bisphenol

GC–MS (EI) m/z (relative int.): 270 (100, [M]⁺), 255 (57, [M–CH₃]⁺), 240 (61, [M–2CH₃]⁺), 225 (15, [M–3CH₃]⁺), 210 (3, [M–4CH₃]⁺), 195 (7, [M–5CH₃]⁺).

2.2.2. 2,3,6-Trimethyl-4-(2,3,6-trimethylphenoxy)phenol

GC–MS (EI) m/z (relative int.): 270 (100, [M]⁺), 255 (5, [M–CH₃]⁺), 225 (4, [M–3CH₃]⁺), 208 (5, [M–3CH₃–OH]⁺), 136 (63, [M–C₆H(CH₃)₃O]⁺), 135 (59, [M–C₆H(CH₃)₃OH]⁺),

121 (21, [M–C₆H(CH₃)₃OH–CH₂]⁺), 105 (10, [M–C₆H(CH₃)₃OH–CH₂–O]⁺), 91 (32, [M–C₆H(CH₃)₃OH–3CH₃]⁺).

2.2.3. 4,4'-Di(2-methyl-1-naphthol)

MS (ESI) m/z (relative int.): 315 (27, [MH]⁺), 314 (100, [MH–H]⁺), 313 (62, [MH–2H]⁺), 298 (5, [MH–OH]⁺), 285 (7, [MH–2CH₃]⁺), 257 (3, [MH–2COH]⁺), 242 (15, [MH–CH₃–2COH]⁺).

2.2.4. 4,4'-Di(2-methyl-1-naphthoquinone)

MS (ESI) m/z (relative int.): 313 (100, [MH]⁺), 285 (8, [MH–2CO]⁺), 242 (52, [MH–CH₃–2CO]⁺).

2.3. Spin trap experiments

Spin trap experiments were carried out by adding 0.088 mmol of H₂O₂ to a mixture, containing 0.025 mmol of TMP, 3 mg of TiO₂–SiO₂ aerogel (or Ti-MMM-2) and the spin trap (0.005 mmol of DBNBS or 0.013 mmol of DMPO) in 250 μ L CH₃CN. The reactions were performed either directly in thermostated (50 °C) quartz EPR tubes using Ar bubbling for stirring the reaction mixture or in thermostated (25–80 °C) glass vessels using a magnetic stirrer. In the latter case, after 30–45 min, a part of the reaction mixture was placed into a flat quartz cell which is typically used to perform EPR measurements in polar solvents. The EPR spectra were run at room temperature.

2.4. DRS-UV-vis measurements

2.2 mmol of TMP were dissolved in 15 mL of MeCN. 200 mg of Ti-MMM-2 were added to the solution under stirring. The catalyst was immediately filtered off and analyzed by means of DR-UV-vis spectroscopy. In a blank experiment, 210 mg of Ti-MMM-2 were added to 17 mL of MeCN, the slurry was stirred for 5 min, then the catalyst was filtered off and analyzed by DRS-UV-vis.

2.5. Instrumentation

EPR spectra were recorded at room temperature using a Bruker EMX X-band spectrometer (Stuttgart University) and a Bruker ER-200D (Boreskov Institute of Catalysis). DRS-UV-vis measurements were performed on a Shimadzu UV-vis 2501PC spectrophotometer. GC analyses were performed using a Crystall 2000 gas chromatograph equipped with a flame ionization detector and quartz capillary column (30 m \times 0.25 mm) filled with Supelco MDN-5S. GC–MS analyses of organic products were carried out using a HP 5973/6890 system (carrier gas He, 30 m \times 0.25 mm cross-linked 5% PHME siloxane (0.25 μ m coating) capillary column; HP-5MS) or a Saturn 2000 gas chromatograph equipped with a CP-3800 mass spectrometer (30 m \times 0.32 mm WCOT fused silica CP-SIL 8 CB capillary column). Electrospray mass-spectrometry analysis was performed on ThermoFinnigan LCQ Advanage. ¹H NMR spectra of the reaction products were run on AM 250 Bruker.

3. Results and discussion

3.1. Oxidation in the presence of DMPO

The diamagnetic spin trap molecule, 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO), has been widely used for identification of $\cdot\text{OH}$ radicals [58,63–66]. The rate constant of the reaction of DMPO with $\cdot\text{OH}$ radical is $3.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [63]. The product is a metastable nitroxyl radical ($\cdot\text{OH}$ -adduct), which has a lifetime that is long enough to be detected by EPR measurements [64]. Fig. 1 presents an EPR spectrum obtained upon the addition of DMPO to the reaction solution containing TiO_2 - SiO_2 aerogel, TMP, H_2O_2 and CH_3CN . The spectrum consists of a 1:2:2:1 quartet with hyperfine splittings $a(\text{N}) = a(\beta\text{H}) = 12.4 \text{ G}$ and $g = 2.006$. The same spectrum is observed also in the absence of TMP, indicating non-productive decomposition of hydrogen peroxide. Such a signal is very characteristic for the $\text{DMPO}\cdot\text{OH}$ radical adduct. Earlier, a similar EPR spectrum was revealed in CH_3CN solution during the H_2O_2 catalytic decomposition or photolysis in the presence of DMPO [58,65,66].

The identification of the $\text{DMPO}\cdot\text{OH}$ adduct in TMP oxidation with H_2O_2 over Ti, Si-catalysts was not surprising because non-productive decomposition of H_2O_2 had been previously established by $^{18}\text{O}_2$ labelling experiments [26] and agreed with a rather low selectivity based on H_2O_2 (40–60%) observed in both TMP and MNL oxidation over Ti, Si-catalysts [23,24,26,27].

Highly reactive $\cdot\text{OH}$ radicals can react with phenol and H_2O_2 molecules to form $\text{ArO}\cdot$ and $\text{HO}_2\cdot$, respectively, via reactions (9) and (10):

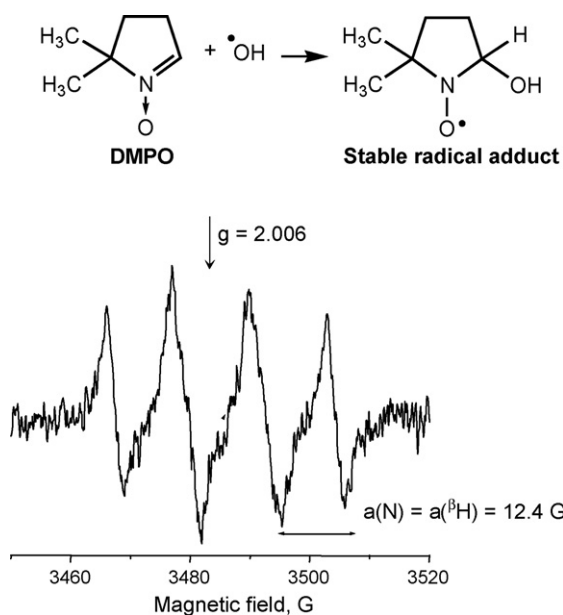
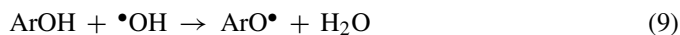
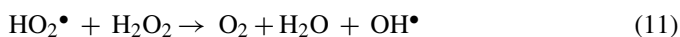
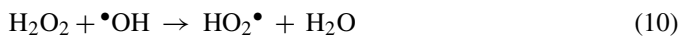


Fig. 1. EPR spectrum (CH_3CN , 20°C) of the $\text{DMPO}\cdot\text{OH}$ radical adduct formed during TMP oxidation with H_2O_2 in the presence of TiO_2 - SiO_2 aerogel. Reaction conditions: 0.1 M TMP, 0.35 M H_2O_2 , 0.05 M DMPO, 3 mg catalyst, 250 μL CH_3CN , 15 min, 50°C . Without TMP the spectrum was the same.



In principle, reaction (9) may proceed concurrently with reaction (4), which takes place at the catalyst surface. Tuel and Hubert-Pfalzgraf suggested reaction (9) as the main route leading to $\text{ArO}\cdot$ radicals in TMP oxidation over Ti, Si-catalysts [16]. However, a fractional reaction order (between 0 and 1) in TMP, revealed by the kinetic study of TMP oxidation over TiO_2 - SiO_2 aerogel [29] points out the reaction mechanism involving steps (2)–(4). Furthermore, the reaction scheme suggested by the authors [16] cannot explain the effect of the substrate/Ti molar ratio on the selectivity to quinone that we observed for different Ti single-site catalysts [23,24,26,27,52].

3.2. DRS-UV study

The phenol binding to Ti-center via reaction (2) has been confirmed by the DRS-UV-vis measurements that we performed in this work. The addition of a concentrated solution of TMP in MeCN to Ti, Si-catalysts resulted in the appearance of a pale yellow surface intermediate, which was not formed upon treatment of the catalyst with MeCN alone. The colouring was manifested in a long-wave shift of the band in the DR-UV spectrum shown in Fig. 2. Earlier, we have synthesized a yellow aryloxy derivative of Ti-substituted heteropolytungstate where the ArOH molecule was bound to titanium [53].

3.3. Oxidation in the presence of DBNBS

While phenoxyl radicals formed in the oxidation of hindered phenols, such as 2,4,6-*tert*-butylphenol, 2,4,6-triphenylphenol, 2,6-di-*tert*-butyl-4-methylphenol, etc., are stable enough to be monitored in solution by means of EPR spectroscopy [45,46,67], less hindered phenols, such as TMP and MNL, produce radicals which are significantly less stable. Their stationary concentration in solution is very low. Consequently, the radicals, if present, cannot be directly detected by EPR.

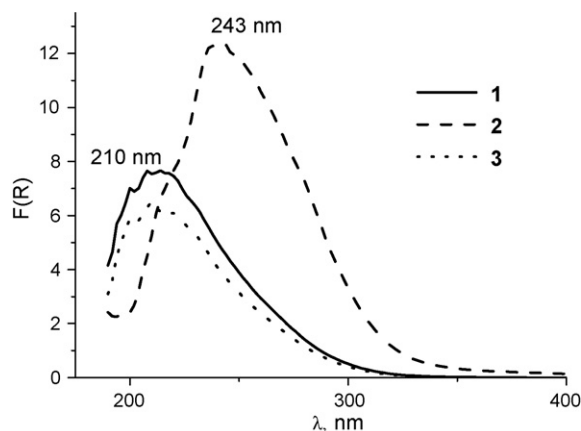


Fig. 2. DR-UV spectra of Ti-MMM-2: (1) initial, (2) after treatment with the solution of TMP in MeCN and (3) after treatment with MeCN.

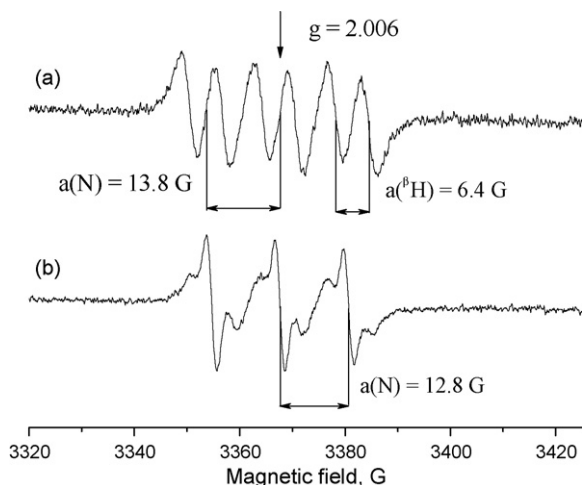
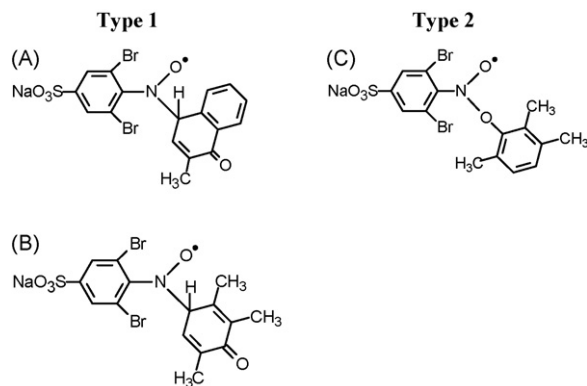


Fig. 3. EPR spectra (CH_3CN , 20°C) of the DBNBS radical adducts formed during oxidation of (a) MNL and (b) TMP. Reaction conditions: 0.1 M substrate, 0.35 M H_2O_2 , 0.02 M DBNBS, 3 mg Ti-MMM-2, 250 μL CH_3CN , 45 min at 50°C (TMP) or 35 min at 25°C (MNL).

To catch aryloxy radicals in TMP and MNL oxidation over Ti, Si-catalysts 3,5-dibromo-4-nitrosobenzene-sulfonic acid was used. In the presence of DBNBS we managed to identify stable radical adducts which gave the isotropic EPR spectra shown in Fig. 3. Importantly, no EPR signals were observed in the presence of DBNBS, H_2O_2 and Ti, Si-catalyst but without a phenol substrate indicating, in agreement with the literature data [68], that DBNBS does not form stable adducts with hydroxyl radicals.

MNL is significantly more reactive substrate than TMP. It can be readily oxidized even at room temperature by various oxidants but the key point is the selectivity of oxidation [30]. When MNL was oxidized by H_2O_2 over Ti, Si-catalysts in the temperature range of $50\text{--}80^\circ\text{C}$, both MNQ and C–C-coupling products were formed along with some amount of tars [26]. Under optimal reaction conditions the MNQ yield reached 75%. The by-product study performed in this work has revealed that under these conditions the isolated yield of the corresponding dinaphthol and dinaphthoquinone attains 13 and 8%, respectively, no C–O-coupling products being identified. The ratio of MNQ/C–C-coupling products decreases with increasing MNL concentration and decreasing reaction temperature. At 25°C , only the C–C-dimers are formed.

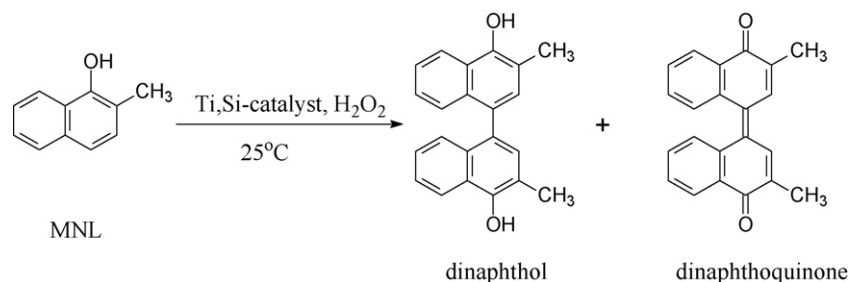
When MNL oxidation was carried out at elevated temperature ($50\text{--}80^\circ\text{C}$), very weak EPR signals were detected in



Scheme 2. Probable structures of radical adducts of DBNBS formed during TMP and MNL oxidation with H_2O_2 over Ti, Si-catalysts.

the presence of DBNBS. Meanwhile, MNL oxidation at 25°C produced a rather stable adduct with DBNBS, which gave an isotropic EPR spectrum consisting of six lines (triplet of doublets) with hyperfine splittings $a(\text{N}) = 13.8\text{ G}$, $a(\text{H}) = 6.4\text{ G}$ and $g = 2.006$ (Fig. 3a). The observed hyperfine splitting from nitrogen and hydrogen nuclei allows attributing the spectrum to adduct A (Scheme 2). Such an adduct would form if the ArO^\bullet radical is bound to spin trap via p-carbon but not oxygen atom [68]. We designate such adducts as type 1. The assignment is supported also by the composition of the by-products formed. Indeed, as we mentioned above, only C–C-coupling dimers, dinaphthol and dinaphthoquinone, have been identified in MNL oxidation over Ti, Si-catalyst (Scheme 3).

When TMP was oxidized with H_2O_2 over Ti, Si-catalysts in the presence of DBNBS, a more complicated isotropic EPR spectrum was detected (Fig. 3b). Typically, this spectrum consisted of a triplet with hyperfine splitting $a(\text{N}) = 12.8\text{ G}$ and $g = 2.006$ and six lower intensity signals (triplet of doublets) with hyperfine splittings $a(\text{N}) = 13.1\text{ G}$, $a(\text{H}) = 7.6\text{ G}$ and $g = 2.006$. The presence of two types of signals points out the formation of two different radical adducts of DBNBS. The triplet belongs to an adduct C, that we designate as type 2, while the triplet of doublets is most likely due to adduct B of type 1 (Scheme 2). Importantly, the ratio between the two adducts is influenced only slightly by the catalyst nature but is strongly affected by the reaction temperature. A temperature rise causes a significant increase of the intensity of the triplet of doublets related to the triplet (Fig. 4). This observation of temperature dependent relative intensities also rules out an alternative interpretation of



Scheme 3. Oxidation of MNL over Ti, Si-catalysts at 25°C .

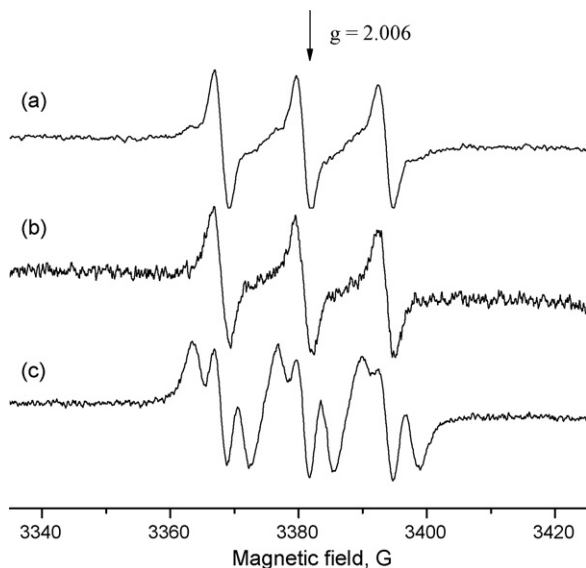
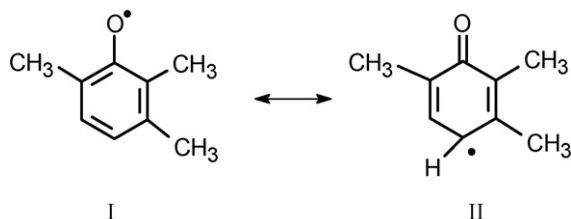


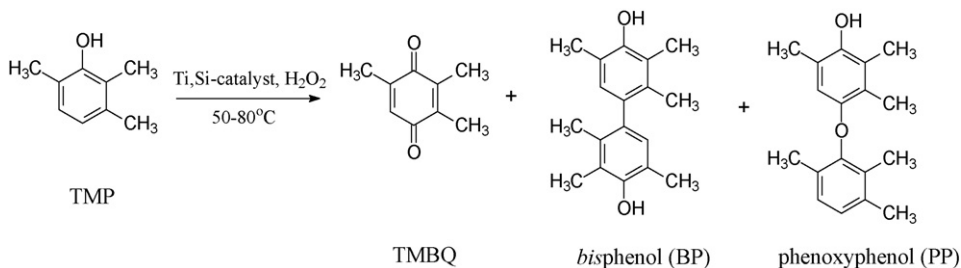
Fig. 4. EPR spectra (CH_3CN , 20°C) of the DBNBS radical adducts formed during TMP oxidation in the presence of (a) $\text{TiO}_2\text{-SiO}_2$ aerogel (50°C), (b) Ti-MMM-2 (50°C) and (c) Ti-MMM-2 (80°C). Reaction conditions: 0.1 M TMP, 0.35 M H_2O_2 , 0.02 M DBNBS, 3 mg Ti-MMM-2, 250 μL CH_3CN , 45 min.



Scheme 4. Resonance structures of the TMP phenoxyl radical.

Fig. 3b as a 1:2:1 ($2a_{\text{H}}$) triplet of a 1:1:1 (a_{N}) triplet, for which a straightforward assignment of a structure would have been difficult.

Keeping in mind possible resonance structures of the TMP phenoxyl radical (Scheme 4) it seems reasonable to assume that



Scheme 5. Oxidation of TMP over Ti, Si-catalysts at 50°C .

Table 1
TMP oxidation with H_2O_2 over Ti-MMM-2^a

T ($^\circ\text{C}$)	Time (h)	TMP conversion (%)	TMBQ yield (%)	C–C dimer yield (%)	C–O dimer yield (%)
50	2.0	88	48	18	22
80	0.5	98	75	8	15

^a Reaction conditions: TMP 0.1 M, H_2O_2 0.35 M, catalyst 14 mg (0.006 mmol Ti), MeCN 1 mL.

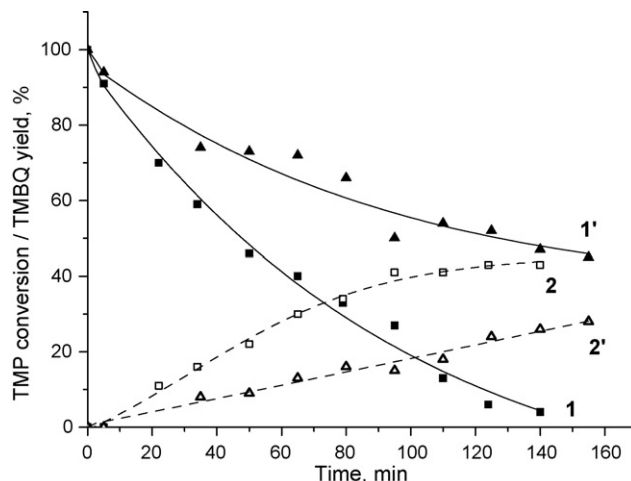


Fig. 5. TMP conversion and TMBQ yield versus time: (1), (2) without DBNBS and (1'), (2') in the presence of DBNBS. Reaction conditions: 0.1 M TMP, 0.35 M H_2O_2 , 0.02 M DBNBS (1' and 2'), 12 mg Ti-MMM-2, 1 mL MeCN, 50°C .

adducts **C** and **B** are formed upon capturing by DBNBS of O- and C-centered radicals I and II, respectively.

The difference in the EPR spectra observed for the oxidation of MNL and TMP in the presence of DBNBS can be rationalized if we consider by-products of these two reactions. As we pointed out already, no C–O-coupling products were detected in MNL oxidation over Ti, Si-catalysts. On the contrary, oxidation of TMP produced TMBQ along with the tail-to-tail dimer BP and the head-to-tail dimer PP which were both identified by GC–MS and ^1H NMR (Scheme 5).

The mass balance and the ratio of TMBQ/BP/PP were first determined in this work. The results obtained with Ti-MMM-2 catalyst are shown in Table 1. One can see that the TMBQ yield increases with rising reaction temperature, while the yield of the coupling products reduces. That is understandable if we take into account that recombination of two radicals usually proceeds without activation energy. The presence of BP and PP in comparable amounts is in agreement with the presence of the two types of signals that we observe in the EPR spectra for TMP

oxidation in the presence of DBNBS. The interaction of DBNBS with the TMP phenoxyl radical via the oxygen atom seems to be less hindered sterically than the interaction via carbon atom and, probably, requires lower activation energy. This may be the reason why the formation of adduct **B** enhances with increasing reaction temperature.

Comparison of the kinetic curves of the TMP consumption and TMBQ accumulation in the presence and in the absence of DBNBS is shown in Fig. 5. It is clearly seen that the spin trap causes a pronounced inhibitory effect on both the rate of substrate consumption and the rate of TMBQ formation. Importantly, the selectivity to TMBQ is not affected by the addition of the spin trap. This means that both the target product (TMBQ) and by-products (BP and PP) derive from the same radical intermediate, which is ArO^\bullet formed in the first step of the homolytic oxidation process.

4. Conclusion

Using EPR spectroscopy with spin traps DMPO and DBNBS, the formation of the radical adducts $\text{DMPO}\text{-}\bullet\text{OH}$ and $\text{DBNBS}\text{-}\text{ArO}^\bullet$ has been detected in the H_2O_2 -based oxidation of TMP and MNL over Ti, Si-catalysts. The EPR study thus confirmed the previously postulated homolytic mechanism of alkylphenol oxidation in $\text{H}_2\text{O}_2/\text{Ti(IV)}$ systems involving the formation of phenoxyl radicals in the first stage. The character of the EPR spectra in the presence of DBNBS depended on the nature of the phenol substrate and the reaction temperature. Two types of $\text{DBNBS}\text{-}\text{ArO}^\bullet$ adducts were identified during TMP oxidation. The first one most likely forms upon interaction of the spin trap with the carbon atom of the phenoxyl (naphthoxyl) radical. The second adduct derives from the interaction of the spin trap with the oxygen atom of the phenoxyl radical. During MNL oxidation, only the first type of the $\text{DBNBS}\text{-}\text{ArO}^\bullet$ adducts was found. The results of the EPR study are in good agreement with the results of the by-product study that revealed both C–C and C–O coupling dimers in TMP oxidation and only C–C dimers in MNL oxidation.

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