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Kinetics and Mechanism of 2,3,6-Trimethylphenol Oxidation by Hydrogen Peroxide in the Presence of $\text{TiO}_2\text{--SiO}_2$ Aerogel

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Abstract—The product and kinetics studies of 2,3,6-trimethylphenol (TMP) oxidation by 30% aqueous H_2O_2 in the presence of a heterogeneous catalyst, $\text{TiO}_2\text{--SiO}_2$ aerogel, are performed in an MeCN medium. The main reaction products are 2,3,5-trimethyl-1,4-benzoquinone and 2,2',3,3',6,6'-hexamethyl-4,4'-biphenol. The reaction is first-order in H_2O_2 and fractional order (1–0) in TMP. The reaction rate is proportional to the catalyst amount and depends on the water concentration in the reaction mixture in a complex manner. The results suggest the formation of an active intermediate on the titanium center. In this intermediate containing both a TMP molecule and the hydroperoxide group, inner-sphere one-electron oxidation of TMP occurs to give the phenoxyl radical.

INTRODUCTION

The selective oxidation of organic compounds by environmentally friendly and cheap oxidants, such as molecular oxygen and hydrogen peroxide, is one of the main tasks of fine organic synthesis [1–6]. Despite the higher cost of hydrogen peroxide compared to molecular oxygen, the technological equipment employing H_2O_2 might be cheaper [3]. Titanium silicates TS-1 and TS-2 developed by Enichem proved to be highly efficient heterogeneous catalysts for the liquid-phase oxygenation of various organic compounds by hydrogen peroxide [1–4]. However, their application for the oxidation of larger molecules is restricted because of the small pore size (5.4×5.6 Å). That is why the number of studies on the synthesis, investigation, and use of mesoporous titanium silicates (such as Ti-MCM-41 [7–14], Ti-MCM-48 [15], Ti-HMS [8, 16], and Ti-SBA-15 [17]) and mixed oxides $\text{TiO}_2\text{--SiO}_2$ (aerogels and xerogels) [18–21] is increasing so rapidly. Among various mesoporous titanium silicates, the $\text{TiO}_2\text{--SiO}_2$ aerogel exhibits the highest catalytic activity and selectivity (up to 98%) in the oxidation of 2,3,6-trimethylphenol (TMP) to 2,3,5-trimethyl-1,4-benzoquinone (TMBQ), which is the main intermediate in the synthesis of vitamin E, by 30% hydrogen peroxide [21]. The oxidation of TMP occurs in the heterogeneous matrix of the catalyst without leaching active titanium centers into the solution [14, 21]. Here we report the kinetics and mechanism of this reaction.

EXPERIMENTAL

Acetonitrile (high-purity grade, Ekros) was dried and kept over activated molecular sieves (4 Å). 2,3,6-Trimethylphenol (Fluka) and 2,6-dimethylphenol were recrystallized from hexane. Aqueous hydrogen peroxide (30%) was concentrated to 80% at a reduced pres-

sure, and its concentration was determined iodometrically immediately before use in experiments on the effect of water on the reaction rate. Deuterated TMP (ArOD) was synthesized from D_2O with an atomic deuterium concentration of 99%. 2,2',3,3',6,6'-Hexamethyl-4,4'-biphenol (BP) was synthesized and purified as described in [22]. Other reactants (reagent and analytical grades) were used without additional purification. $\text{TiO}_2\text{--SiO}_2$ aerogels (the Ti loading was 3.70 and 6.52 wt %, $S_{\text{sp}} = 651$ and 695 m²/g, the average pore diameter (d) was 12.35 and 15.18 nm, and the mesopore volume (V) was 2.20 and 2.41 cm³/g, respectively) and xerogel $\text{TiO}_2\text{--SiO}_2$ (3.90 wt % Ti; $S_{\text{sp}} = 657$ m²/g, $d = 2.67$ nm, and $V = 0.26$ cm³/g) were synthesized and described as in [21].

The oxidation of TMP was carried out in a thermostatically controlled vigorously stirred glass reactor at 45–75°C (1000 rpm). The reaction was initiated by adding 0.14–1.40 mmol of H_2O_2 to the reaction mixture containing 0.02–0.20 mmol of TMP, 2–11 mg of the catalyst ($1.8\text{--}8.1 \times 10^{-6}$ mol of Ti, the internal standard (biphenyl), and 1 ml of MeCN. The dependence of the reaction rate on $[\text{H}_2\text{O}_2]$ was studied at a constant concentration of H_2O (6.7 M) to standardize the reaction conditions on changing the amount of added aqueous H_2O_2 . The reaction orders were determined from the dependence of the initial rate of TMP consumption (w_0) on the concentration (amount) of one reactant when other concentrations were kept constant. The error in determining the initial rates was 5–7%. The kinetic isotope effect was studied by introducing D_2O (3.3 M) instead of H_2O (3.3 M) into the reaction mixture 10 min before the reaction. The isotope exchange $\text{ArOH} + \text{D}_2\text{O} \rightleftharpoons \text{ArOD} + \text{HDO}$ occurs rapidly and is easy to control by the ¹H NMR technique. The effect of acid and base additives on oxidation was investigated by adding HCl

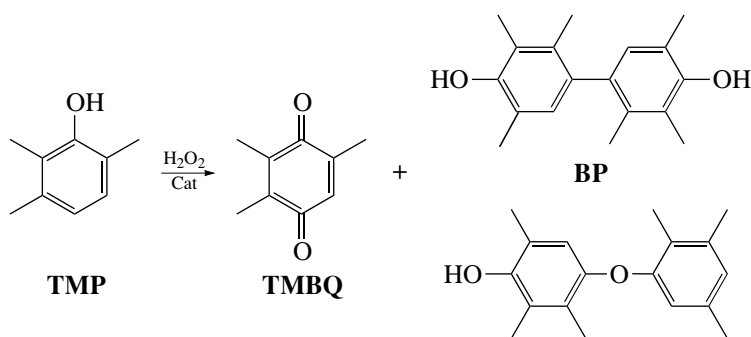
(0.2 M), NaCl (12 mg), zeolite (4 Å) (74 mg), and zeolite 4 Å (74 mg)/NaHCO₃ (16 mg). The products of TMP oxidation were identified by their ¹H NMR and mass spectra. The yield of TMBQ and BP, as well as the phenol conversion, were determined by gas chromatography (GC).

The GC analyses were performed on a Tsvet-500 chromatograph equipped with a flame-ionization detector and a quartz capillary column (35 m × 0.3 mm) filled with Carbowax 20M. The chromatographic/mass spectrometric analysis was conducted using a Saturn 2000 chromatograph equipped with an SP-3800 mass

spectrometer. The ¹H NMR spectra were registered on an MSL-400 Bruker spectrometer.

RESULTS AND DISCUSSION

The results of GC, GC–MS metric analyses, and ¹H NMR spectroscopic study showed that the products of TMP oxidation included TMBQ (the main product), 2,2',3,3',6,6'-hexamethyl-4,4'-biphenol (BP) (the product of the C–C coupling), and trace amounts of the dimer product of C–O coupling.



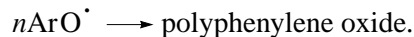
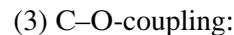
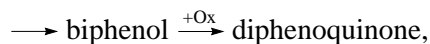
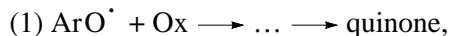
For example, the TMP conversion reached 84%, the TMBQ and BQ yields were 53% and 20%, respectively, based on the initial substrate at 60°C, [TMP] = 0.10 M, and [H₂O₂] = 0.35 M in the presence of a TiO₂–SiO₂ aerogel (3 mg, 6.52 wt % Ti) in 1 ml of MeCN. BP oxidation by hydrogen peroxide carried out separately in the presence of a TiO₂–SiO₂ aerogel results in the formation of polymeric products of C–O coupling. Under optimal conditions, the selectivity to TMBP is 96–98% with a TMP conversion of 99–100%. The TMBQ yield decreases, while the BQ yield increases with an increase in the phenol concentration and a decrease in the catalyst amount [14, 21]. The products of oxidation of 2,6-dimethylphenol (DMP) included 2,6-dimethyl-1,4-benzoquinone and 2,2',6,6'-tetramethyl-4,4'-diphenyl-1,4-benzoquinone, which is the product of C–C coupling.

The oxidation of phenols by H₂O₂ (Ox) can occur via the heterolytic mechanism of electrophilic hydroxylation via the formation of the corresponding hydroquinone followed by its rapid oxidation to benzoquinone [4, 23]. In this case, the main by-product of TMP oxidation is hydroxytrimethyl-*p*-benzoquinone [23]. The oxidation products of TMP and DMP (dimethylphenol) in the H₂O₂/Ti,Si-catalyst system and the dependences of the TMBQ/BP ratio on the TMP concentration and the catalyst amount suggest that the

reaction has a homolytic mechanism, including the formation of the ArO[•] phenoxyl radical:



Further transformations of ArO[•] result in the formation of different oxidation products:



TMP is not oxidized in the absence of the catalyst or H₂O₂. Typical kinetic curves of TMP consumption and TMBQ accumulation during oxidation by hydrogen peroxide in the presence of a TiO₂–SiO₂ aerogel have no induction period. The rate of TMP oxidation is independent of the intensity of mixing the reaction mixture in the range from 200 to 1000 rpm. The activation energy measured at 45–75°C is 81 kJ/mol (Fig. 1). Therefore, the oxidation of TMP by H₂O₂ in the presence of a TiO₂–SiO₂ aerogel is not limited by diffusion as it takes place in the presence of a TiO₂–SiO₂ xerogel that has much smaller pores (*E*_a = 29 kJ/mol is the typ-

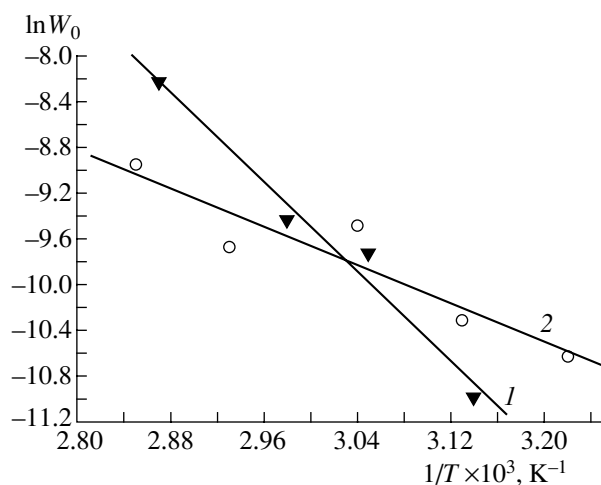


Fig. 1. A plot of $\ln w_0$ vs. $1/T$ for TMP oxidation by 30% H_2O_2 in the presence of the (1) TiO_2 - SiO_2 aerogel and (2) TiO_2 - SiO_2 xerogel. $[\text{TMP}] = 0.1 \text{ M}$; $[\text{H}_2\text{O}_2] = 0.35 \text{ M}$; the TiO_2 - SiO_2 aerogel (Ti, 3.7 wt %), 6 mg; TiO_2 - SiO_2 xerogel (Ti, 3.9 wt %), 5 mg; and MeCN, 1 ml.

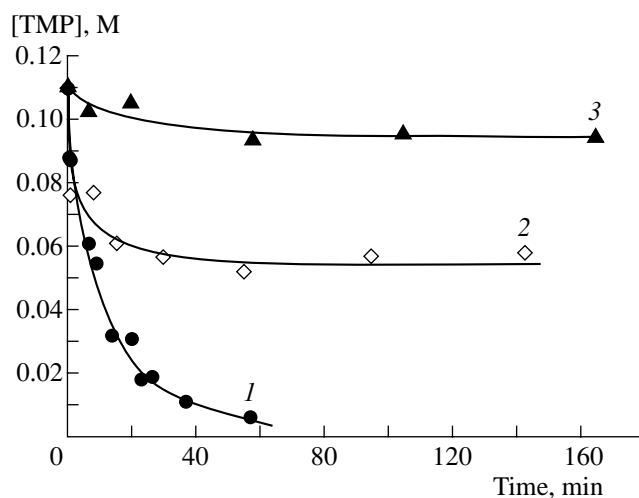
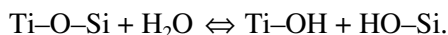


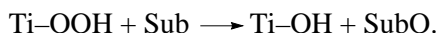
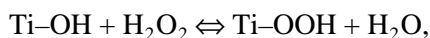
Fig. 2. The oxidation of TMP by 30% H_2O_2 in the presence of the TiO_2 - SiO_2 aerogel (1) without additives, (2) in the presence of zeolite 4Å, and (3) in the presence of zeolite 4Å and NaHCO_3 .

ical value for the processes controlled by diffusion [24]).

The rate of TMP oxidation heavily depends on the amount of H_2O (Table 1). First, the reaction rate increases with an increase in $[\text{H}_2\text{O}]$ and attains its maximum at $[\text{H}_2\text{O}] = 1 \text{ M}$. This may be due to the acceleration of Ti-O-Si bond hydrolysis to give Ti-OH [25–27]:



It is known that the Ti-OH bonds are highly reactive toward H_2O_2 and favor the formation of the active form of a catalyst, titanium hydroperoxo species, which further participates in the oxidation of organic substrates (Sub) [28–31]



A further increase in the $[\text{H}_2\text{O}]$ value results in a gradual decrease in the reaction rate, which may partially be due to the structure decomposition of the TiO_2 - SiO_2 aerogel caused by water [13, 14, 21] and due to the competition between water and reactants for the active Ti center (see below).

We studied the influence of acid and base additives on the kinetics of TMP oxidation. The addition of the basic salt NaHCO_3 results in a dramatic retardation of the reaction (Fig. 2), and this can be explained by the transformation of the active titanium hydroperoxo species into the inactive peroxo complex [29, 30]. The HCl and NaCl additives do not cause any change in the rate but affect the distribution of reaction products (Table 2).

The reaction studied is first-order in H_2O_2 (Fig. 3). The order in TMP ranges from 1 to 0 with an increase

in the TMP concentration (Fig. 4). The reaction rate depends on the nature of the substrate. Thus the ratio of the initial rates $w_0(\text{TMP})/w_0(\text{DMP})$ is 1.6 for the competitive oxidation of TMP and DMP. The rate of TMP oxidation is proportional to the amount of the catalyst (Fig. 5). Data obtained in this work suggest that TMP is bound to the active center of the catalyst, as was assumed earlier for the oxidation of alcohols by H_2O_2 in the presence of TS-1, for which similar kinetic regularities were found [32], and for alcohol oxidation in the presence of a TiO_2 - SiO_2 xerogel [33]. The addition of methanol to the reaction mixture results in reaction

Table 1. Effect of $[\text{H}_2\text{O}]$ on the initial rate of TMP oxidation by H_2O_2 (w_0) in the presence of the TiO_2 - SiO_2 aerogel

$[\text{H}_2\text{O}]$, M	$w_0 \times 10^2$, $\text{mol l}^{-1} \text{ min}^{-1}$
0.2	0.96
0.6	0.95
1.0	2.36
1.9	1.89
3.5	1.59

Note: Reaction conditions: $[\text{TMP}] = 0.11 \text{ M}$; $[\text{H}_2\text{O}_2] = 0.40 \text{ M}$; the TiO_2 - SiO_2 aerogel (Ti, 3.7 wt %), 10.5 mg; MeCN, 1 ml; 50°C .

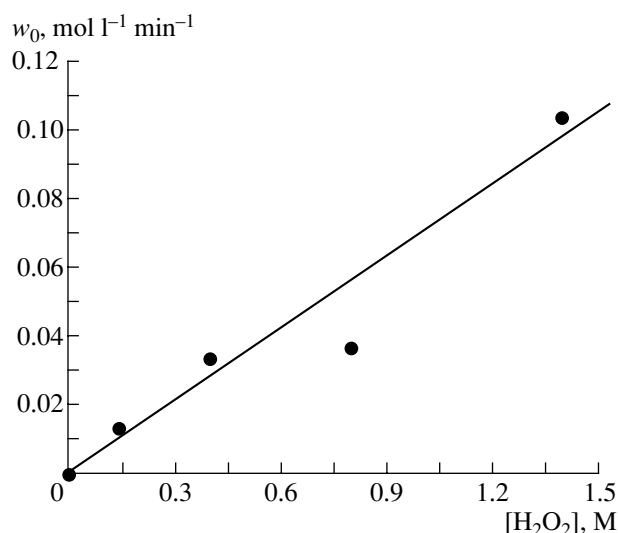


Fig. 3. A plot of w_0 vs. $[H_2O_2]$ for the oxidation of TMP by 30% H_2O_2 in the presence of the TiO_2-SiO_2 aerogel: $[TMP] = 0.11$ M; the TiO_2-SiO_2 aerogel (Ti, 3.7 wt %), 10.5 mg; and MeCN, 1 ml.

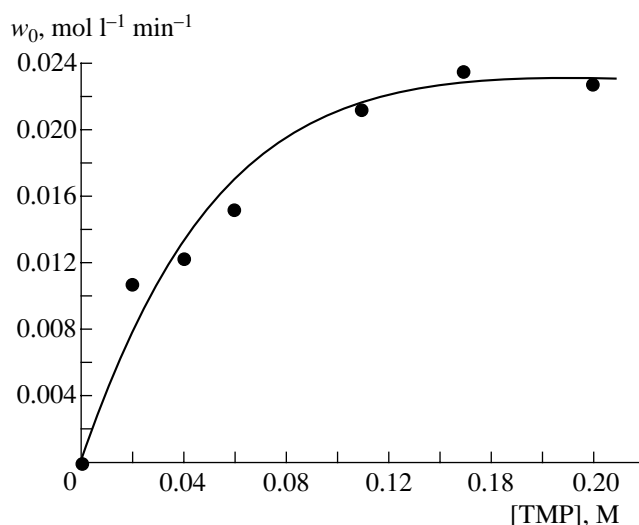
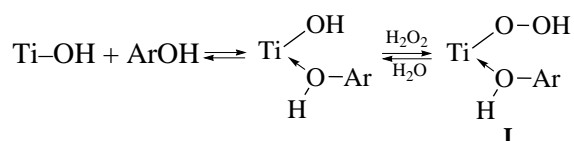


Fig. 4. w_0 vs. $[TMP]$ for TMP oxidation by 30% H_2O_2 in the presence of the TiO_2-SiO_2 aerogel. $[H_2O_2] = 0.4$ M; the TiO_2-SiO_2 aerogel (Ti, 3.7 wt %), 10.5 mg; and MeCN, 1 ml.

retardation because alcohol competes with phenol for the coordination site in intermediate **I**.



The absence of the kinetic isotope effect ($k_{ArOH}/k_{ArOD} = 1$) indicates that hydrogen atom abstraction from the phenol molecule is not a rate-limiting step of the reaction, as was observed during phenol oxida-

tion by chromium(III) superoxo complex [35]. We believe that inner-sphere electron transfer occurs from the coordinated phenol molecule to the hydroperoxy group in intermediate **I** followed by the formation of the phenoxyl radical.

Our data suggest the following mechanism of TMP oxidation by aqueous hydrogen peroxide in the presence of the titanium-silicate catalyst:

(1) The hydrolysis of Ti-O-Si bonds:

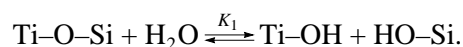


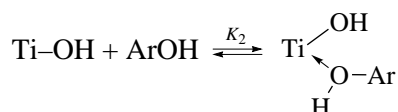
Table 2. TMP oxidation by 30% H_2O_2 in the presence of the TiO_2-SiO_2 aerogel and different additives

Additive	Time, min	TMP conversion, %	TMBQ yield*, %
—	60	94	89
HCl (0.2 mmol)	100	96	55
NaCl (12 mg)	100	100	48
Zeolite 4Å (74 mg)	100	50	40
Zeolite 4Å (74 mg)/NaHCO ₃ (16 mg)	100	15	5

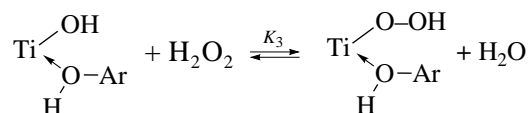
Note: The reaction conditions: $[TMP] = 0.11$ M; $[H_2O_2] = 0.4$ M; the TiO_2-SiO_2 aerogel (Ti, 3.7 wt %), 10.5 mg; MeCN, 1 ml; 50°C.

* Based on TMP (according to GLC).

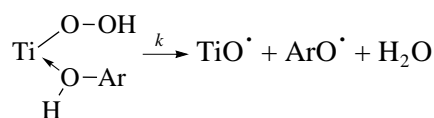
(2) The binding of TMP to Ti;



(3) The formation of an active intermediate;



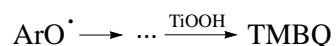
(4) Electron transfer inside the coordination sphere;



(5) The recombination of phenoxyl radicals;



(6) The further oxidation of phenoxyl radicals;



Assuming rapid equilibria (1)–(3), we arrive at the following equation for the rate of TMP oxidation, which agrees well with experimental data:

$$w = \frac{kC_0K_1K_2K_3[\text{H}_2\text{O}][\text{H}_2\text{O}_2][\text{ArOH}]}{1 + K_1[\text{H}_2\text{O}] + K_1K_2[\text{H}_2\text{O}][\text{ArOH}] + K_1K_2K_3[\text{H}_2\text{O}][\text{H}_2\text{O}_2][\text{ArOH}]},$$

where C_0 is the total concentration of the active catalyst sites.

Taking into account the high selectivity of the reaction to TMBQ and the fact that the reaction rate is independent of the presence of oxygen and light and remains unchanged upon the addition of small amounts (0.001 M) of inhibitors of radical chain processes (ionol or hydroquinone), we can exclude a chain radical mechanism and assume a mechanism with a short chain length.

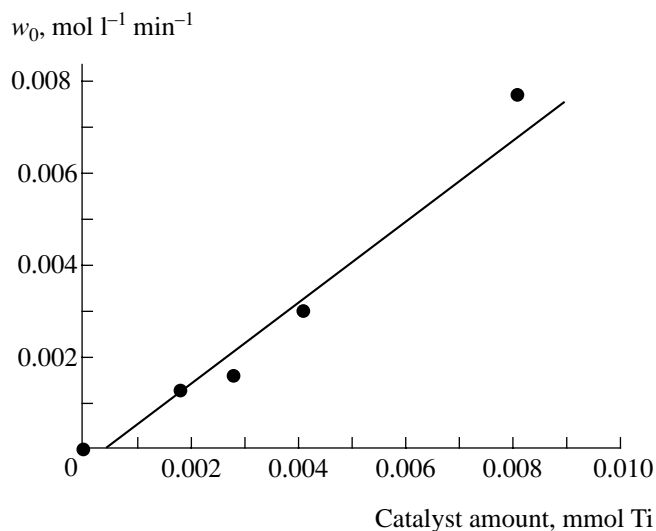


Fig. 5. (1) w_0 vs. the catalyst amount ($\text{TiO}_2\text{-SiO}_2$ aerogel) for oxidation by 30% H_2O_2 . $[\text{TMP}] = 0.11$ M; $[\text{H}_2\text{O}_2] = 0.40$ M; and $[\text{MeCN}] = 1$ ml.

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