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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Oxidation of 2,3,6-Trimethylphenol on Titanium Dioxide Xerogel by Hydrogen Peroxide in the Absence of an Organic Solvent

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Abstract—Fundamental aspects of the synthesis of 2,3,5-trimethylbenzoquinone by oxidation of 2,3,6-trimethylphenol adsorbed on the surface of a titanium dioxide xerogel and on TiO_2 modified with powdered cellulose with hydrogen peroxide without any organic solvent involved in the process were studied.

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The heterogeneous catalytic oxidation of 2,3,6-trimethylphenol (TMP) by hydrogen peroxide is of great practical interest as one of the most ecologically safe ways to obtain 2,3,5-trimehylbenzoquinone (TMBQ), which is the main half-product for synthesis of vitamin E. As catalysts serve aerogels TiO_2 and TiO_2–SiO_2 [1], sol-gels of the TiO_2–SiO_2 system [2], titanosilicates SBA-15 [3], and commercial silica grafted with Ti(IV) [4]. The reaction of TMP oxidation into TMBQ is conventionally performed with an aqueous solution of hydrogen peroxide in an organic solvent, whose role is played by alcohols, aldehydes, and carboxylic acids.

The oxidation of TMP is a heterogeneous process mostly occurring at the catalyst surface [5], which suggests that this process can be performed without an organic solvent. This satisfies the increasingly stringent requirements to the ecological safety and efficiency of chemical processes and markedly simplifies the technology for synthesis of the target product.

We chose a titanium dioxide xerogel and TiO_2 modified with powdered cellulose (PCe) as catalysts for peroxide oxidation. The choice of the TiO_2–PCe composite was due to previously obtained experimental data on formation and stabilization of highly dispersed TiO_2 particles by hydrolysis of tetrabutoxititanium (TBT) in the matrix of powdered cellulose [6, 7].

The goal of our study was to assess the possibility of synthesizing TMBQ by oxidation of TMP adsorbed on the surface of a TiO_2 xerogel and on TiO_2–PCe with hydrogen peroxide in the absence of an organic solvent.

EXPERIMENTAL

The titanium dioxide xerogel was produced by hydrolysis of a methanolic solution of TBT with water (TBT : methanol = 1 : 1 v/v). The solution was hydrolyzed with a triple volume of water at 20°C under vigorous agitation. The resulting precipitate was washed on a vacuum-filter until no butanol was found in washing water. The washed precipitate was dried at 100°C to constant weight. The specific surface area S_{sp} of the xerogel was 60 $m^2 g^{-1}$.

Powdered cellulose was produced by hydrolysis of sulfate cellulose from Baikal pulp-and-paper combine [TU OP (Technical Specification for Nature Preservation) 13-027 94 88-08–91] in 2.5 N hydrochloric acid at 100°C. The hydrolysis was performed for 2 h. The resulting product was washed with distilled water on a vacuum-filter to neutral pH and dried at 100°C.

To obtain a composite material of composition TiO_2 : PCe = 0.4 : 0.6 (w/w), we dissolved 60 ml of TBT in 60 ml of methanol and added 20 g of PCe to

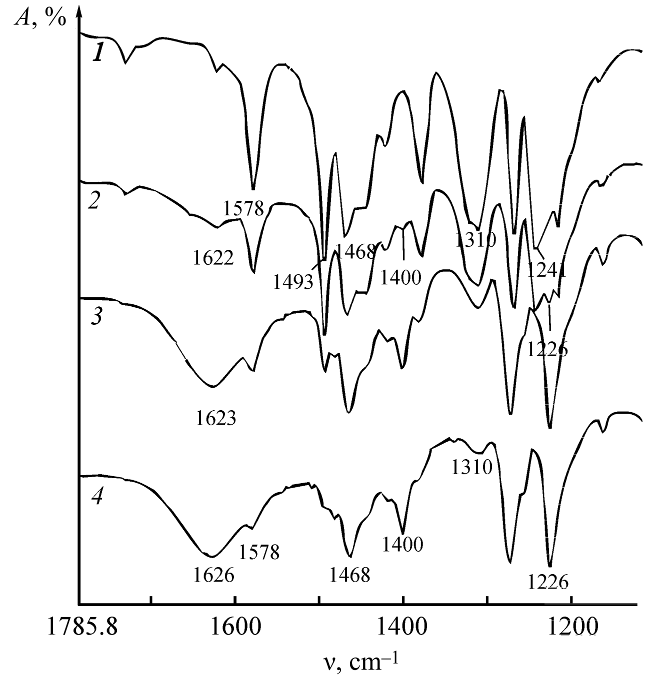

Fig. 1. IR spectra of TMP sorbed on the TiO_2 xerogel. (*A*) Absorption and (ν) wave number. (*1*) TMP; TiO_2 : TMP mass ratio: (*2*) 1 : 2, (*3*) 1 : 1, and (*4*) 1 : 0.5.

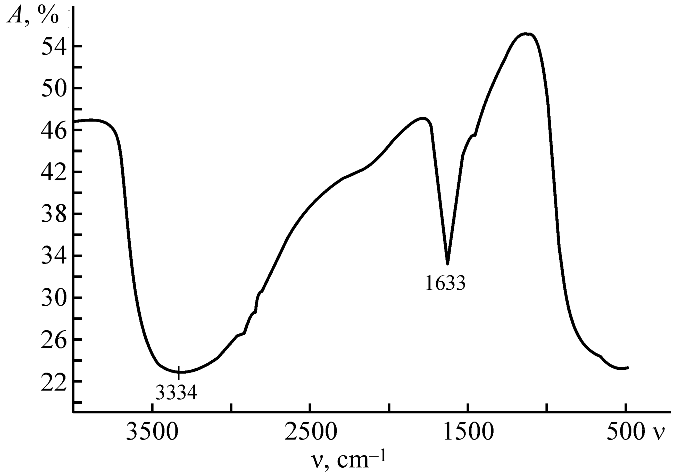

Fig. 2. IR spectrum of the TiO_2 xerogel. (*A*) Absorption and (ν) wave number.

the resulting solution. The mixture was hydrolyzed with 400 ml of water at 20°C under agitation. The precipitate formed was washed on a vacuum-filter until no butanol was fond in washing water. The washed precipitate was dried at 100°C to constant weight. The S_{sp} of the composite was 270.5 $m^2 g^{-1}$.

The specific surface area of the samples was determined by the method of thermal desorption of nitrogen on a SoftSorbi-II ver. 1.0 instrument with an accuracy of 5%.

IR spectra were recorded with a Perkin–Elmer Spectrum One IR Fourier spectrometer in the frequency range 4000–370 cm^{-1} for solid powders with a diffuse-reflection attachment. The band assignment was made using the data of [8].

The spectral intensities were processed and calculated using special programs from the software package of the spectrometer.

The reaction of TMP oxidation was performed in a thermostated 150-ml reactor (thermostating temperature 24 ± 0.1°C) equipped with a thermometer and mechanical stirrer. A 0.25-g portion of TMP (1.84 mmol) was heated in the reactor to the melting point (62°C), a weighed portion of the titanium dioxide xerogel (0.3–0.5 g, 3.8–62.5 mol) or the TiO_2–PCe composite (0.6–3.5 g, 3.0–17.5 mmol TiO_2) was added, and the mixture was agitated. Visually, the sorption interaction of TMP and TiO_2 was accompanied by a change in the xerogel coloration from white to bright orange. The mixture was agitated to a homogeneous mass and then 24 ml of a 3.9 M aqueous solution of hydrogen peroxide was introduced into the reactor at 24°C. The choice of the H_2O_2 concentration was governed by the need to provide a sufficient rate of the oxidation process of TMP at its minimum desorption from the xerogel surface under conditions of self-heating of the reaction mass. The reaction was performed under agitation with a stirrer rotation speed of 2 rps for 2 h, with the temperature of the reaction mass measured.

TMP and TMBQ were quantitatively determined by GLC on a Kristall-2000 M chromatograph with an MDN-5s capillary column (L = 30 m, d = 0.25 mm) in the programmed-temperature mode. The flow rate of the carrier-gas through the capillary column was 1 ml min^{-1}. Decane was used as the internal standard.

To reveal interactions occurring in adsorption of the substrate onto the TiO_2 surface, we carried out an IR spectroscopic study of the TiO_2–TMP system.

An analysis of the IR diffuse-reflection spectra of TMP (Fig. 1) demonstrated that the absorption at 1578, 1493, and 1468 cm^{-1} is due to bond vibrations in the aromatic ring. Stretching vibrations of the C–O bond and deformation vibrations of the hydroxy group, δ(OH), appear as absorption bands peaked at 1310 and 1241 cm^{-1}, respectively.

The IR spectrum of the titanium dioxide xerogel

(Fig. 2) contains a high-intensity band in the range 400–900 cm^{-1}, which can be regarded as a superposition of vibrations of Ti–O bonds and symbate vibrations of water. The absorption band peaked at 1633 cm^{-1} corresponds to deformation vibrations of water. The broad high-intensity band peaked at 3334 cm^{-1} is associated with stretching vibrations of hydroxy groups and water.

The sorption interaction of TMP with the surface of the titanium dioxide xerogel results in that the absorption bands associated with vibrations of not only the hydroxy group of the sorbate, but also the aromatic ring (Fig. 1). For example, already at a TiO_2 : TMP ratio of 1 : 2, there appear a new absorption band peaked at 1400 cm^{-1} and an absorption band peaked at 1226 cm^{-1} on the low-frequency wing of the band at 1241 cm^{-1}. The intensity of both new bands increases with the TiO_2 : TMP ratio, and there is no absorption band peaked at 1241 cm^{-1} in the spectra beginning at TiO_2 : TMP = 1 : 1. In the spectrum of the sample with TiO_2 : TMP = 1 : 1, the intensity ratio of the absorption bands 1493/1468 changes, with the band at 1493 cm^{-1} disappearing at TiO_2 : TMP = 1 : 0.5. Beginning at TiO_2 : TMP = 1 : 0.5, the intensity of the absorption band 1310 cm^{-1} decreases.

As a result of the interaction between the sorbent and TMP, the absorption band associated with deformation vibrations of water, $\delta(H_2O)$, is shifted to lower frequencies, from 1633 cm^{-1} (Fig. 2) to 1623 cm^{-1} (TiO_2 : TMP = 1 : 1) (Fig. 1).

Thus, our analysis of the IR spectra suggests that an OH group and the π-electron system of the aromatic ring of the sorbate are involved in the sorption interaction. In the case of the xerogel, the sorption activity is exhibited by its hydroxy-hydrate cover. Similar results have been obtained previously in a sorption of 2,3,5-trimethylhydroquinone on a titanium dioxide xerogel and TiO_2–PCe composite [6, 9].

To determine the dynamics of TMP oxidation by hydrogen peroxide on a TiO_2 xerogel matrix, we analyzed how the reaction mass temperature depends on the amount of TiO_2 (Fig. 3).

The observed exothermic effect (Fig. 3, curves *1–4*) is a sum of two components: (i) exothermic effect appearing in interaction of hydrogen peroxide with the xerogel surface (Fig. 3, curves *6–9*) and (ii) increase in temperature due to the reaction of substrate oxidation. At molar ratios in the range TiO_2/TMP = 2.1–4.1 (H_2O_2/TiO_2 = 12.5–25.0) (Fig. 3, straight line *5*), the initial temperature remains unchanged. Apparently, the active centers of the catalyst are largely blocked by the adsorbed substrate. The reaction is slow and the exothermic effect is neutralized by the cooling of the reactor. An increase in the TiO_2/TMP ratio leads not only to a better accessibility of the xerogel surface to the oxidizing agent, but also to a stronger dispersion of the substrate in the titanium dioxide matrix, and just this circumstance intensifies the reaction (Fig. 3, curves *1–4*).

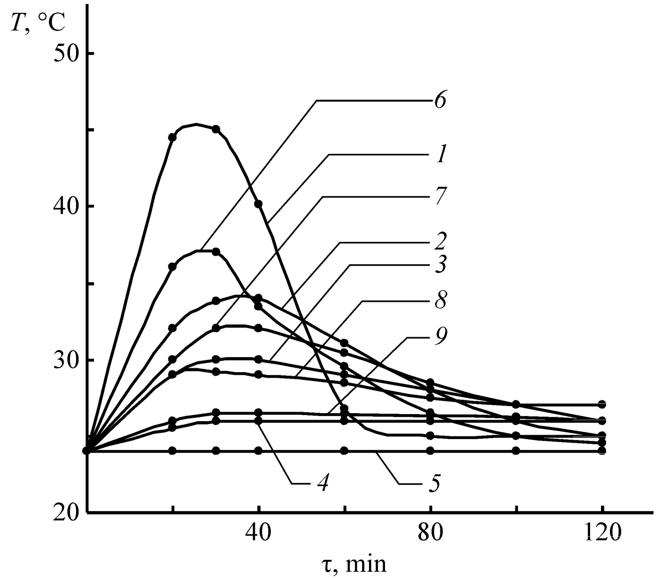

Fig. 3. Reaction mass temperature *T* vs. the reaction duration τ. H_2O_2/TiO_2 molar ratio: (*1, 6*) 1.5, (*2, 7*) 2.1, (*3, 8*) 3.1, (*4, 9*) 6.2, and (*5*) 12.5–25.0. (*1–5*) In the presence of the substrate, (*6–9*) in the absence of a substrate.

The TMBQ formed in the course of the reaction is partly desorbed from TiO_2 and comes to the surface of the reaction mass, which prevents the reaction product from further oxidation. The melting point of TMBQ is 32°C; the elevated temperature in the reactor promotes its desorption from the catalyst surface. This opens up new active centers for sorption of subsequent portions of hydrogen peroxide.

Similar conclusions are applicable in analysis of the data in Fig. 4, when the TiO_2–PCe composite is used as the matrix.

Using the results presented in Figs. 3 and 4, we plotted the dependence of the maximum temperature T_{max} to which the reaction mass warms up on the content of titanium dioxide (Fig. 5).

In the given case, T_{max} is regarded as an indication

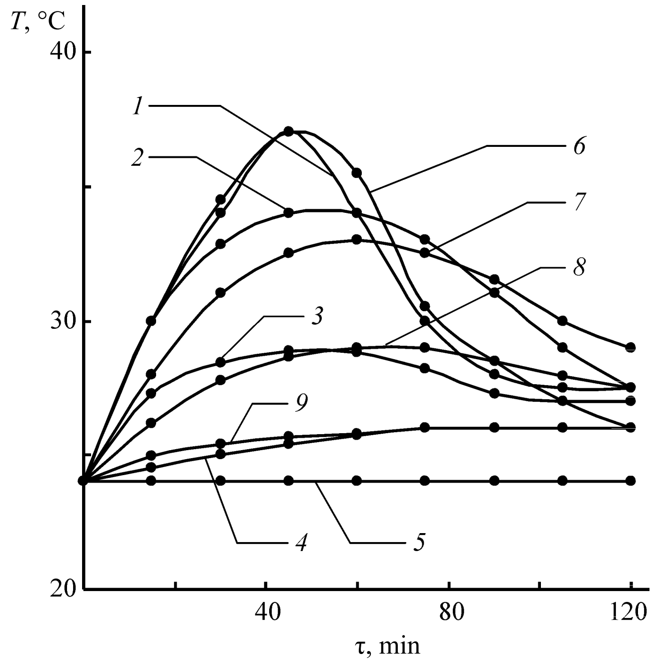

Fig. 4. Reaction mass temperature T vs. the reaction duration τ on TiO_2–PCe. H_2O_2/TiO_2 molar ratio: (*1*) 5.4, (*2*) 6.2, (*3*) 9.4, (*4*) 18.7, and (*5*) 31.2 (in the presence of the substrate); (*6*) 4.7, (*7*) 5.9, (*8*) 9.4, and (*9*) 18.7 (in the absence of a substrate).

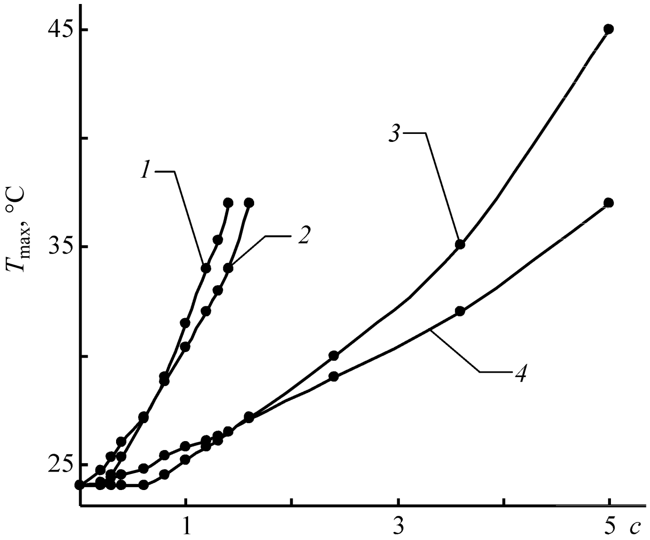

Fig. 5. Maximum temperature T_{max} of the reaction mass vs. the TiO_2 content c. (*1, 2*) TiO_2–PCe and (*3, 4*) TiO_2. (*1, 3*) Reaction in the presence of TMP and (*2, 4*) without a substrate.

TMP oxidation by hydrogen peroxide on TiO_2 (TiO_2–PCe)

Molar ratio		TMP conversion	Selectivity with respect to TMBQ
TiO_2/TMP	H_2O_2/TiO_2	%	
TiO_2 sample			
34.0	1.5	99.1	70.7
24.5	2.1	98.3	69.0
16.3	3.1	98.4	69.0
8.2	6.2	98.3	66.9
4.1	12.5	54.3	56.5
2.1	25.0	19.1	58.7
TiO_2–PCe sample			
9.5	5.4	98.9	44.9
8.2	6.2	98.9	43.9
5.4	9.4	98.8	42.3
2.7	18.7	98.9	43.1
1.6	31.2	95.8	40.1

of the intensity of the processes occurring in the reactor. The exothermic effect starts to be noticeable in the TMP–TiO_2–H_2O_2 system on the composite at a titanium dioxide content 3 times lower than that on the TiO_2 xerogel. Apparently, this distinction can be attributed to the higher dispersity of titanium dioxide particles in a modified sample.

It should be noted that the bulk density of TiO_2–PCe is 2.6 cm^3 g^{-1}, and that of the xerogel, 2.13 cm^3 g^{-1}. Consequently, the substrate on the composite is distributed in a larger volume of the substance, which makes the catalyst more accessible to an interaction with H_2O_2.

The table lists results of a chromatographic analysis of the oxidate after 2 h of the reaction of TMP oxidation, when, according to the temperature dependences, the process is nearly complete in the whole range of TiO_2/TM and H_2O_2/TiO_2 ratios. The TiO_2/TMP ratio of 16.3–34.0 in the reaction space provides a ~98% conversion of the substrate at a selectivity of 69% with respect to the main product.

Our experiment demonstrated that TMP deposited onto the PCE surface is not oxidized by hydrogen peroxide and the inorganic component is the active origin in TiO_2–PCe. In the composite at TiO_2/TMP ratios of 2.7–9.5, the substrate conversion approached 99%; however, the selectivity with respect to TMBQ was 40% lower than that in the case of the unmodified

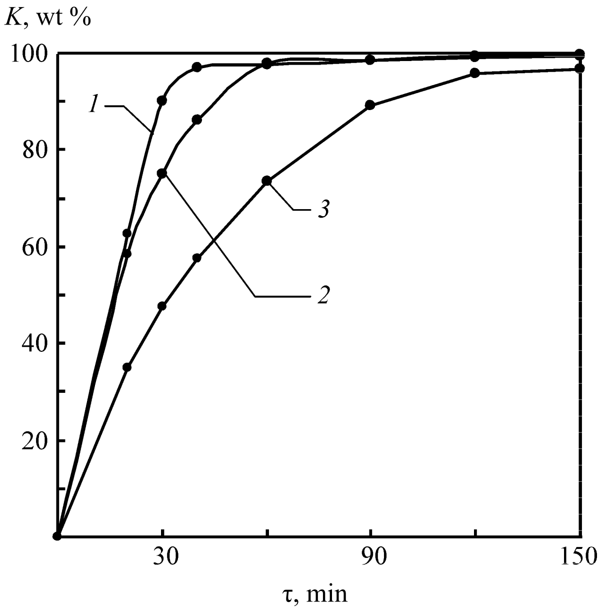

Fig. 6. TMP conversion K vs. the reaction duration τ. TiO_2/TMP ratio: (*1*) TiO_2 8.2–34.0, (*2*) TiO_2–PCe 2.7, and (*3*) TiO_2–PCe 1.6.

catalyst. Apparently, side processes are more active in the presence of TiO_2–PCe. It should be noted that, according to IR spectroscopic data, the cellulose matrix of the composite does not undergo oxidative destruction under our experimental conditions.

A comparison of chromatographic data with the temperature dependences we obtained demonstrated that there is no correlation between T_{max} and the yield of TMBQ at a titanium dioxide content at which the substrate conversion is the highest (TiO_2 1.2–5 g, TiO_2–PCe 0.4–1.4 g of TiO_2).

Figure 6 shows curves describing the substrate consumption in the course of oxidation. The time dependence of the TMP conversion indicates that the main amount of TMP (>95%) is consumed in the presence of a titanium dioxide xerogel during 35 min after the reaction onset (Fig. 6, curve *1*), whereas in the presence of TiO_2–PCe (curve *2*), this time is about 60 min, which corresponds to the time in which the maximum in the temperature dependences is reached (Figs. 3 and 4).

CONCLUSIONS

It was demonstrated that the reaction of trimethylphenol oxidation by hydrogen peroxide on a TiO_2 xerogel can be performed without using an organic solvent.

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