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Oxidative Dehydrogenation of 2,3,5-Trimethyl-1,4-hydroquinone in the Presence of Titanium Dioxide Hydrogel

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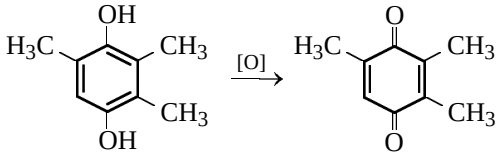
Abstract—Liquid-p[hase oxidative dehydrogenation of 2,3,5-trimethyl-1,4-hydroquinone in the presence of titanium dioxide hydrogel was studied by a kinetic method. Associative interactions between the substrate, oxidant, and gel were detected by voltammetry and ESR and IR spectroscopy.

We showed in our previous papers how active polydisperse highly ordered oxide systems can affect liquid-phase oxidation processes as catalytically active structuring ingredients [1, 2]. Here we consider oxidative dehydrogenation of 2,3,5-trimethyl-1,4-hydroquinone **I** (a model hydroxyarene) in the presence of titanium dioxide gel **II**.

Electrophilic liquid-phase oxidation of **I** with atmospheric oxygen in a neutral medium occurs selectively by the concerted molecular mechanism and yields 2,3,5-trimethyl-1,4-benzoquinone **III** [3]:



I **III**

The reaction was performed in aqueous methanol at 50°C in air. Its progress was monitored by GLC [4].

Hydrogel **II**, when present in the sphere of reaction of **I** with atmospheric oxygen, decreases the initial reaction rate v_0 to 0.10 mol l^{-1} h^{-1} (v_0 without gel **II** is 0.26 mol l^{-1} h^{-1}). This result suggests the occurrence of competing interparticle interactions involving gel **II** and reactants. Indeed, an IR study of substrate **I** sorbed on gel **II** reveals significant changes in the absorption bands at 1344 and 1412 cm^{-1}, which are superpositions of the C–O stretching bands and vibration bands of the aromatic ring [5]. In going from free to sorbed **I**, the band maximum at 1344 cm^{-1} shifts to 1324 cm^{-1}, and the ratio of the intensity of this band to that of the reference $\delta(CH_3)$ band at 1464 cm^{-1} (*A*) decreases from 0.932 to 0.772; the band at 1412 cm^{-1} changes in the shape and intensity, with its *A* decreasing from 0.969 to 0.597. Furthermore, the bending vibration band of the OH group of **I** (δ 1216 cm^{-1}) transforms into a doublet at 1232 and 1220 cm^{-1}. The hydroxonium absorption band at 1730–1680 cm^{-1}, characteristic of gel **II** [6], disappears upon sorption of **I**. The maxima of the stretching (ν 3400 cm^{-1}) and bending (δ 1620 cm^{-1}) bands of hydration water in **II** shift to 3280 and 1640 cm^{-1}, respectively. Weak Ti–OH bending bands of **II** (δ 1192, 1168, 1090 cm^{-1}) are not observed in the spectrum of the sample with sorbed **I**.

These changes in the IR spectra are apparently due to binding of the hydroxonium proton and hydrogen atoms of water molecules localized on the surface of gel **II** with the π-electron system and hydroxyl oxygen atoms of **I**. Formation of hydrogen-bonded complexes decreases the electron density on the oxygen atoms of the hydroxy groups in **I** [7, 8], which is responsible for the decreased reactivity of **I** in electrophilic oxidation.

Addition of gel **II** to the reaction system in oxidation of **I** with Cu^{2+} ions in the presence of oxygen accelerates the reaction: v_0 becomes as high as 1.05 mol l^{-1} h^{-1}, against 0.54 mol l^{-1} h^{-1} in the absence of gel **II**. In this system, substrate **I** is involved in two parallel reactions, one of which is inhibited by gel **II** (see above). Intensification of the reaction involving Cu^{2+} ions is apparently due to their associative interaction with fragments of the added hydrogel **II**.

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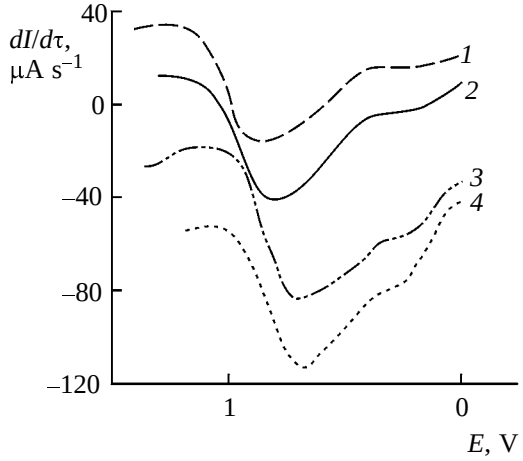

Fig. 1. Oxidation of substrate **I** on carbon paste electrode: (*1*) no additions, (*2*) in the presence of 5×10^{-3} M Cu^{2+} solution, (*3*) with introduction of TiO_2–Cu^{2+}_{ads} into the electrode, and (*4*) with introduction of TiO_2 into the electrode in the presence of 5×10^{-3} M Cu^{2+} solution.

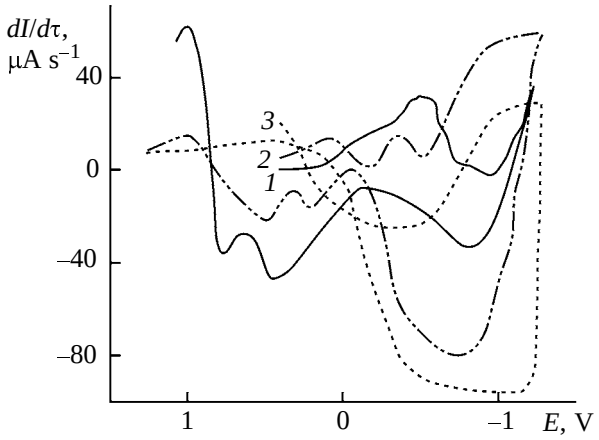

Fig. 2. Influence of adsorption on the surface of TiO_2 gel on the electrochemical behavior of Cu^{2+} ions: (*1*) solution of Cu^{2+} ions and carbon paste electrode, (*2*) Cu^{2+} ions adsorbed on the surface of TiO_2 gel introduced into carbon p[aste electrode, and (*3*) carbon paste electrode with introduced TiO_2 (background).

Oxidation of hydroquinone **I** in the presence of Cu^{2+} ions was also studied electrochemically with a carbon paste electrode into which air-dry gel **II** was introduced. Upon addition of Cu^{2+} ions into solution, or upon preliminary adsorption of Cu^{2+} on gel **II** followed by introduction of the gel into the carbon paste electrode, the course of oxidation of **I** changes compared to the process performed on the carbon paste electrode without introduced gel **II** (Fig. 1). The current of the oxidation peak of **I** increases, and the shift of the peak potential reaches 0.15–0.16 V, which is indicative of increased oxidation rate; also, an additional oxidation peak appears at a lower potential (0.35–0.40 V).

Study of the electrochemical behavior of Cu^{2+} ions adsorbed on gel **II** shows that reduction of Cu^{2+} to Cu^{+} and of Cu^{+} to Cu^{0} is facilitated (Fig. 2, curves *1*, *2*). Whereas the reduction of Cu^{2+} from solution on a carbon paste electrode is characterized by a common two-electron wave, reduction of Cu^{2+} ions adsorbed on gel **II** occurs in several steps. In adsorption on gel **II**, the waves of copper oxidation shift, and the process of copper oxidation/reduction becomes more reversible (the difference between the peaks of Cu^{2+}/Cu^{0} reduction/oxidation is 1.27 and 0.86 V, respectively). These data suggest that, upon adsorption of Cu^{2+}, its reduction to Cu^{+} and reverse oxidation to Cu^{2+} are appreciably facilitated, and the Cu^{2+} and Cu^{+} ions can form with gel **II** two strongly bound and one weakly bound complexes. Formation of the latter is suggested by broadening of the peak of copper anodic oxidation (at +0.5 V) and by an ill-defined oxidation peak at +0.8 V (Fig. 2, curve *2*).

An ESR study of Cu^{2+}-containing hydrogels **II** based on TiO_2 showed that Cu^{2+} ions, depending on their content in the sorbent phase ($\gamma_{Cu^{2+}}$), form mononuclear complexes **IV**, associates of mononuclear complexes **V** with increased local concentration of metal ions, and Cu^{2+} compounds **VI** giving no ESR signal at the given frequency and temperature. Such structures were also revealed on the surface of nanostructured films and powders based on TiO_2 [9]. We believe that a separate phase of insoluble $Cu(OH)_2$ can play the role of compound **VI** at relatively low content of sorbed Cu^{2+} ions, and at their high content ESR-inactive bridged polynuclear Cu^{2+} compounds (clusters with strong exchange coupling or polynuclear structures with bridging OH groups) can also form, by analogy with the related structures formed in ion exchangers [10, 11].

By varying $\gamma_{Cu^{2+}}$, we evaluated the quantitative relationships between mononuclear complexes **IV**, their associates **V**, and Cu^{2+} compounds **VI**. As $\gamma_{Cu^{2+}}$ is increased, the content of mononuclear complexes **IV** ($n_{\mathbf{IV}}$) decreases, and that of compounds **VI** ($n_{\mathbf{VI}}$) grows. The content of associates **V** ($n_{\mathbf{V}}$) passes through a maximum at $\gamma_{Cu^{2+}}$ 0.37 mmol Cu^{2+} per gram of gel **II**. In this case, the three types of Cu^{2+} species **IV**–**VI** are present in the phase of gel **II** in approximately equal amounts. At $\gamma_{Cu^{2+}}$ 0.57 mmol Cu^{2+} per gram of gel **II**, the ratio $n_{\mathbf{IV}} : n_{\mathbf{V}} : n_{\mathbf{VI}}$ was 0.06 : 0.20 : 0.74. The reactivities of species **IV**–**VI**

were judged from the initial reaction rates $v_{0(\mathbf{IV}-\mathbf{VI})}$, estimated at 0.35, 1.00, and 1.20 mol l^{-1} h^{-1}, respectively. That is, the Cu^{2+} ions bound in magnetic associates **V** and polynuclear compounds **VI** are more reactive than those in mononuclear complexes **IV**. This is apparently due to the mobility of electrons in systems **V** and **VI**, in which the Cu^{2+} ions are linked to each other and the electron density transfer is facilitated. Previous measurements of the microwave conductivity [12, 13] revealed a correlation between the electron mobility and catalytic activity of Cu^{2+} ions. Acceleration of the dehydrogenation is due to the fact that oxidation of substrate **I** and reduction of oxygen can be in this case separated in space.

Thus, we can conclude from our results that the oxidative transformation of **I** in the presence of gel **II** occurs in the sphere of homo- and heteroassociative interparticle interactions involving the gel, substrate, and oxidant.

EXPERIMENTAL

Titanium dioxide gel **II** with the specific surface area S_{sp} 260 ± 13 m^2 g^{-1} (as determined by adsorption of an inert gas) was prepared by hydrolysis of an alcoholic solution of tetrabutoxytitanium with water at room temperature with vigorous stirring.

Experiments were performed in a temperature-controlled reactor equipped with a reflux condenser and a bubbler for air supply. The mixture was stirred at a rate of 2 s^{-1}; the air flow rate was 6.2 l h^{-1}. These conditions ensure kinetic control of the reaction. The reaction was performed in aqueous methanol (water : methanol = 1 : 1 by volume) at 50 ± 0.2°C. Oxygen and copper dichloride dihydrate in the presence of atmospheric oxygen were used as oxidants. The substrate was dissolved in aqueous methanol to obtain a 6.6×10^{-2} M solution, and the gel (0.13 mol l^{-1}) and $CuCl_2 \cdot 2H_2O$ (0.59×10^{-2} M) were added. This amount of $CuCl_2 \cdot 2H_2O$ was completely sorbed on the gel within 45 s (content of sorbed Cu^{2+} ions on the gel $\gamma_{Cu^{2+}}$ 0.57×10^{-3} mol g^{-1} gel).

Kinetic measurements were performed by taking aliquot samples and determining the content of the starting compound. The functions obtained were approximated by polynomials. The initial reaction rates v_0 were determined by numerical differentiation and interpolation; their error did not exceed ±10%.

The initial reaction rates $v_{0(\mathbf{IV}-\mathbf{VI})}$ characterizing the individual reactivities of Cu^{2+} species **IV**–**IV** in the phase of gel **II** were calculated by solving a system of equations of the form

$$v_{0i} = v_{0\mathbf{IV}} n_{\mathbf{IV}i} + v_{0\mathbf{V}} n_{\mathbf{V}i} + v_{0\mathbf{VI}} n_{\mathbf{VI}i},$$

where v_{0i} is the initial reaction rate at a Cu^{2+} content in the gel phase of γ_i; $v_{0\mathbf{IV}}$, initial reaction rate in the presence of mononuclear Cu^{2+} complexes **IV**; $v_{0\mathbf{V}}$, initial reaction rate in the presence of associates **V** of mononuclear complexes; $v_{0\mathbf{VI}}$, initial reaction rate in the presence of Cu^{2+} hydroxide **VI**; $n_{(\mathbf{IV}-\mathbf{VI})i}$, relative contents of species **IV**–**VI** at a total Cu^{2+} concentration in the gel phase of γ_i. The quantities $v_{0(\mathbf{IV}-\mathbf{VI})}$ were determined with an error of ±15%, which includes the error of determining $n_{(\mathbf{IV}-\mathbf{VI})}$ by ESR.

Quantitative determination of **I** was performed by GLC on a Chrom-4 chromatograph similarly to [4].

The IR spectra were recorded on a Specord M-80 spectrometer in the range $4000 - 400$ cm^{-1} in KBr and mineral oil. The spectra were taken in the optical density scale; the error of indication of the optical density was 0.0001. Samples for measurements were prepared by sorption of hydroquinone **I** from solution on gel **II**, followed by drying in an inert gas flow. The band assignment was based on [5].

The ESR spectra of Cu^{2+} in the gel phase were recorded on a PS-100Kh ESR radiospectrometer in the 3 cm wavelength range at room temperature in thin-walled round quartz ampules (*d* 4 mm). The spectra were processed with special programs from the spectrometer software. The integral intensioties of ESR signals were analyzed using a reference sample and software for spectrum processing, following the procedures suggested in [14–16]. Samples for studies were prepared by sorption of Cu^{2+} ions on gel **II** from $CuCl_2 \cdot 2H_2O$ solutions, followed by drying at room temperature. The concentration of Cu^{2+} ions in the gel phase was determined by atomic absorption spectroscopy on a Perkin–Elmer-403 spectrometer.

The procedure of voltammetric experiments was described in [17]. The supporting electrolyte was 0.025 M HCl in aqueous methanol (1 : 1 by volume); the Cu^{2+} concentration in solution was 5×10^{-3} M, and the concentration of **I** in solution, 10^{-2} M. The potential sweeping rate was 20 mV s^{-1}.

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