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CHEMICAL KINETICS AND CATALYSIS

Kinetic Parameters of the Electroreduction of Oxygen on a Graphitized Carbon Electrode Activated by Tetrakis(4-Methoxyphenyl)Porphyrin and Its Cobalt Complexes

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Abstract—Electrochemical and electrocatalytic properties of tetrakis(4-methoxyphenyl)porphyrin, tetrakis(4-methoxyphenyl)porphyrinatocobalt(II), and (tetrakis(4-methoxyphenyl)porphyrinato)chlorocobalt(III) are studied using the method of cyclic voltammetry. The redox-potentials of the electrode processes, the potentials of the half-wave and stationary rate constants for electroreduction of molecular oxygen are determined from an analysis of the voltammetric curves. The cobalt complex is found to be characterized by higher electrocatalytic activity than other analyzed compounds.

Keywords: macroheterocyclic compounds, electrocatalysis, electroreduction of oxygen, cyclic voltammetry, half-wave potential.

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INTRODUCTION

The reaction of electrochemical reduction of oxygen, which takes place in chemical power sources with oxygen (air) depolarization, is accompanied by strong polarization of the cathode, and quite active catalysts are thus required for it to occur [1]. Platinum group metals deposited on carbon supports are used as catalysts of electrode processes [2], but their high cost and scarcity limit the possibilities for their wide application. The search for new effective catalysts for the reduction of molecular oxygen as an alternative of noble metals is therefore of great importance [3].

One challenging line in the development of nonplatinum catalysts is the creation of carbon-based cathode materials modified by macroheterocyclic compounds (porphyrins, phthalocyanines) and their metallic complexes. According to [1], the catalytic activity of metallic porphyrins in the electroreduction of oxygen is related to their capacity for the reversible coordination of oxygen. The extracoordination of oxygen in metallic porphyrins leads to the partial transfer of electron density from the central atom of the metal to the π -antibinding orbitals of the oxygen molecule. Extracoordination is the initial stage of O₂ reduction. The stability of oxygen extracomplexes of metallic porphyrins depends strongly on the nature of the second transpositioned extraligand.

The electrochemical and electrocatalytic properties of porphyrins were studied in [1-7] in particular. The authors of [3] investigated the effect of substituents in the paraposition of the phenyl rings of cobalt porphyrins during the oxygen reduction. The main electrochemical measurements were performed using a rotating disc electrode in 0.5 M solutions of H₂SO₄. Two pairs of maxima were found for tetrakis(4-methoxyphenyl)porphyrinatocobalt(II); the first, at $E_{\rm c} =$ 0.75 V, $E_a = 0.9$ V, was attributed to the Co^{2+/3+} transition, while the weakly pronounced pair of maxima at $E_{\rm c} = 0.3$ V, $E_{\rm a} = 0.5$ V was related to the same redoxtransition of $Co^{2+/3+}$ ions. The potential of the halfwave of the O_2 reduction process is 0.22 V. The authors of [2] investigated the electrocatalytic activity of tetrakis(4-methoxyphenyl)porphyrinatocobalt(II) using a floating gas-diffusion electrode and a rotating disc electrode with ring in acidic and alkaline solutions. The potentials of electron transitions were determined in [5] for tetrakis(4-methoxyphenyl)porphyrin and its complexes with Co(II) and Co(III) in dichloromethane and DMSO.

The aim of this work was to investigate the effect of the degree of cobalt oxidation on the electrochemical and electrocatalytic properties of cobalt complexes of tetrakis(4-methoxyphenyl)porphyrin, finding the kinetic parameters of oxygen reduction on electrodes modified with H₂tetrakis(4-methoxyphenyl)porphyrin (H₂T(p-MeOPh)P), tetrakis(4-methoxyphenyl)porphyrinatocobalt(II) (Co^{II}T(p-MeOPh)P), and (tetrakis(4-methoxyphenyl)porphyrinato)chlorocobalt(III) (Co^{III}Cl(T(p-MeOPh)P)). Investigating the kinetic parameters of the oxygen reduction reaction is of particular interest both from the scientific standpoint and for the substantiated selection of a catalyst.

EXPERIMENTAL

The studied porphyrins were synthesized at the Faculty of Organic Chemistry, Ivanovo State University of Chemistry and Technology.

The synthesis of tetrakis(4-methoxyphenyl)porphyrin was accomplished by mixing 1.2 ml of a solution (10.0 mmol) of anisic aldehyde in 15 ml of nitrobenzene and 35 ml of propionic acid. Then 0.7 ml (10.0 mol) of pyrrole was added to the boiling mixture and the obtained solution was boiled for 2 h. The formed precipitate was cooled, filtered, washed with methanol to complete the decolorizing of the wash solution, and dried in the air at 70°C. The yield was 0.82 g (44.6%). Purification was accomplished using column chromatography on a silica gel (chloroform being the eluent) with subsequent recrystallization from the chloroform-hexane mixture. The obtained product was in the form of large violet crystals. The electron spectrum of the chromotographically purified tetrakis(4-methoxyphenyl)porphyrin corresponded to the literature data (λ_{max} , nm/log ϵ , chloroform): 652/3.87; 595/3.78; 557/4.07; 520/4.25; 423/5.69).

Tetrakis(4-methoxyphenyl)porphyrinatocobalt(II) was synthesized by adding 5.0 g (6.8 mmol) of tetrakis(4-methoxyphenyl)porphyrin to a boiling solution containing 5.0 g (20.1 mmol) of cobalt acetate tetrahydrate in 150 ml of acetic acid. The mixture was boiled for 0.5 h and kept at room temperature for 12 h. The precipitate was filtered, washed with hot water, and then dried in air at 70°C. The yield was 1.88 g (35%). Purification was accomplished using column chromatography on a silica gel (chloroform being the eluent) with subsequent recrystallization from the chloroform-hexane mixture. The electron spectrum of the chromotographically purified tetrakis(4-methoxyphenyl)porphyrinatocobalt(II) corresponded to the literature data (λ_{max} , nm/log ϵ , chloroform): 529/4.18; 411/5.40.

To synthesize (tetrakis(4-methoxyphenyl)porphyrinato)chlorocobalt(III), an air flow was passed through a suspension (1.0 g, 1.26 mmol) of tetrakis(4methoxyphenyl)porphyrinatocobalt(II) in 250 ml of methanol and 5 ml of concentrated hydrochloric acid for 10 h. The precipitate was filtered, the solution was neutralized by a concentrated solution of ammonia, and evaporated in the vacuum of a water-jet air pump to 50 ml. After cooling, the precipitate of the complex was filtered, washed with water, and dried in air at room temperature. The yield was 0.5 g (47%). Purification was accomplished using column chromatography on a silica gel (chloroform being the eluent) with subsequent recrystallization from the chloroformhexane mixture. The obtained product was in the form of large violet crystals. The electron spectrum of the chromotographically purified (tetrakis(4-methoxyphenyl)porphyrinato)chlorocobalt(III) corresponded to the literature data (λ_{max} , nm/log ϵ , chloroform): 583/4.02; 548/4.25; 433/5.61.

The electrochemical and electrocatalytic properties of porphyrins were investigated by means of cyclic voltammetry in a 0.1 M solution of potassium hydroxide in an argon and oxygen atmosphere. Measurements were performed in a three-electrode electrochemical cell. The main electrode was a graphitized carbon rod whose side surface was insulated with a fluorocarbon polymer shell. An extremely thin layer of the active catalyst mass was deposited on the end surface of the electrode, which was 8 mm in diameter. The active mass of the catalyst consisted of industrial elemental carbon (IEC) (TU-14-7-24-80), a suspension of fluorocarbon polymer, and the analyzed substance. A platinum electrode served as the polarizing electrode. The obtained potentials are given with respect to the reference silver chloride electrode.

Cyclic voltamperegrams (CVAs) were obtained using a PI-50-1 potentiostate. The data were recorded using a PC with preprocessing of the signal on an interface device. The I-E curves were obtained in the potential range of 0.5–1.5 V at potential scanning rates of 5, 10, 20, 50, and 100 mV/s. To analyze and assess the oxidation–reduction processes taking place on the surface of the electrode with the investigated substances, the I-E curves were recorded in electrolyte saturated with argon and then with gaseous oxygen. The oxidation–reduction potentials of the processes were calculated as the half-sum of the potentials of the cathode and anode maxima. The accuracy of determining the potentials was 5 mV.

RESULTS AND DISCUSSION

The electrochemical behavior of porphyrin compounds was studied using a metal-free compound, tetrakis(4-methoxyphenyl)porphyrin. There are two maxima for this compound on the cathodic and anodic sections of the potentiodynamic curve. Potentiodynamic scanning was performed in an argon atmosphere. The maximum corresponding to the electroreduction of a porphyrin ligand with transfer of one electron and the formation of a monoanion is observed on the cathodic branch in the potential range of -0.6 to -0.8 V. On the anodic branch of the I-Ecurve, the maximum of the reverse electrochemical process is observed in the potential range of -0.5 to -0.7 V. A second pair of maxima, corresponding to the electroreduction of the porphyrin ligand with transfer of second electron and the formation of a dianion form, can be seen in the potential range of -0.8 to -1.2 V. An increase in the scanning rate yields a shift of the cathodic maxima toward more negative potentials, while the anodic maxima are shifted toward more positive potentials.

Compound	$Co^{3+} \leftrightarrow Co^{2+}$			$L \leftrightarrow L^-$			$L^- \leftrightarrow L^{2-}$			$-E_{\rm eff}(\Omega_{\rm e})$
	$E_{\rm c}$	Ea	$E_{\rm red/ox}$	$-E_{\rm c}$	$-E_{a}$	$-E_{\rm red/ox}$	$-E_{\rm c}$	$-E_{a}$	$-E_{\rm red/ox}$	$-L_{m/2}(O_2)$
H ₂ T(<i>p</i> -MeOPh)P	_	_	-	0.680	0.540	0.585	1.100	0.960	1.030	0.290
Co ^{II} T(p-MeOPh)P	0.160	0.230	0.195	0.630	0.600	0.615	1.130	1.010	1.070	0.190
Co ^{III} Cl(T(<i>p</i> -MeOPh)P)	0.140	0.300	0.220	0.630	0.610	0.620	1.180	1.010	1.095	0,160
IEC	—	—	—	—	—	—	—	—	—	0.300

Table 1. Potentials of the cathodeic and anodic maxima E_c , E_a of the oxidation–reduction potentials $E_{red/ox}$ and the halfpeak potentials $E_{m/2}(O_2)$ of the process of electroreduction on electrodes activated by the investigated compounds (V)

When using the electrode activated with tetrakis(4methoxyphenyl)porphyrinatocobalt(II) (Table 1), the first maximum on the cathodic and anodic curves lies in the potential range of 0.1-0.3 V, which corresponds to the Co³⁺ \leftrightarrow Co²⁺ transition. The second maximum on the cathodic part of the curve in the potential range of -0.6 to -0.7 V, along with that on the anodic part of the curve in the potential range of -0.55 to -0.65 V, correspond to the L \leftrightarrow L⁻ transition. The third maximum on the cathodic part of the curve in the potential range of -1.1 to -1.2 V and that on the anodic part of the curve in the potential range of -0.95 to -1.05 V is associated with the formation of the L⁻ \leftrightarrow L²⁻ dianion form.

The same number of cathodic and anodic maxima as in the case of tetrakis(4-methoxyphenyl)porphyrinatocobalt(II) is observed for the electrode containing (tetrakis(4-methoxyphenyl)porphyrinato)chlorocobalt(III) in the active mass (Table 1). Table 1 lists the redox potentials for all observed processes.

It was found in [8] that the oxidation/reduction of the central metal ion of cobalt porphyrin complexes $(Co^{2+} \leftrightarrow Co^{+})$ and the first stage of electroreduction of an organic ligand take place at close potential values. The cathodic and anodic maxima observed for (tetrakis(4-methoxyphenyl)porphyrinato)chlorocobalt(III) and tetrakis(4-methoxyphenyl)porphyrinatocobalt(III) in the potential range of -0.5 to -0.7 V are associated with the superposition of the waves characteristic of two processes: $Co^{2+} \leftrightarrow Co^{+}$ and $L \leftrightarrow L^{-}$.

Saturation of the electrolyte with molecular oxygen yields substantial variations in the shape of the cathodic part of the I-E curve in the potential range of -0.1 to -0.4 V (Fig. 1), which corresponds to the reduction of molecular oxygen. In this case, the signal intensity increases as the electrolyte becomes saturated with dioxygen.

A comparative analysis of the electrocatalytic activity of the studied compounds was performed using the I-E curves corresponding to the limiting saturation of the electrolyte with gaseous oxygen when no changes in the shape of curves were observed during further cycling (i.e., after electrolyte blow-through with oxygen for 30–40 min).

Analysis of the half-peak potential $E_{m/2}(O_2)$ at the potential scanning rate V = 0.02 V/s indicates that the

studied compounds are effective catalysts in the reaction of electroreduction of molecular oxygen. The $Co^{III}Cl(T(p-MeOPh)P)$ complex is characterized by a higher catalytic activity than H₂T(p-MeOPh)P and $Co^{II}T(p-MeOPh)P$ (Table 1).

Figure 2 presents the CVA obtained at different potential scanning rates for the processes taking place on the electrode activated with H₂tetrakis(4-methoxy-phenyl)porphyrin. The maximum in the potential range of -0.2 to -0.5 V corresponds to the process of oxygen electroreduction. It can be seen from Fig. 3 that the maximum potential depends on the scanning rate V. This, along with the absence of maxima during the reverse (anodic) scan, points to the irreversibility of the electrochemical reaction.

The obtained experimental data were quantitatively analyzed on the basis of the results from solving the differential equation of nonstationary diffusion with the corresponding boundary conditions in [9, 10]. The potential of the maximum in the case of an irreversible electrode process linearly depends on ln*V*:

$$E_m = B - \frac{RT}{2\alpha z_{\alpha}F} \ln(\alpha z_{\alpha}V), \qquad (1)$$

 $I, mA = 12^{3}$

Fig. 1. CVA for electrodes activated with (1) tetrakis(4-methoxyphenyl)porphyrin, (2) tetrakis(4-methoxyphenyl)porphyrinatocobalt(II), (3) (tetrakis(4-methoxyphenyl)porphyrinato)chlorocobalt(III) obtained by saturating the solution with oxygen.

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Fig. 2. CVA for the electrode activated with tetrakis(4-methoxyphenyl)porphyrin at different rates of potential scanning: (1) 0.005, (2) 0.01, (3) 0.02, (4) 0.05, and (5) 0.10 V/s.



Fig. 3. Dependence of $E_m(\ln V)$ for the electrodes with deposited active mass containing (1) H₂T(*p*-MeOPh)P, (2) Co^{IIT}(*p*-MeOPh)P, (3) Co^{III}Cl(T(*p*-MeOPh)P).

where *R* is the universal gas constant, *T* is the absolute temperature, *F* is the Faraday constant, α is the transfer coefficient, and z_{α} is the number of electrons at the stage determining the reaction rate. The term *B* depends on the stationary constant of the electrochemical reaction rate k_0 and the oxygen diffusion coefficient in the solution *D*. At 298 K, it can be calculated using the equation

$$B = \frac{1}{\alpha z_{\alpha}} \left[-0.067 + 0.026 \ln \frac{k_0}{\sqrt{D}} \right].$$
 (2)

Table 2. Kinetic parameters of oxygen reduction on electrodes containing the investigated compounds contained in the active mass

Compound	α	<i>b</i> , V	$k_0 \times 10^3, $ m/s	$-E_{1/2}, V$
H ₂ T(<i>p</i> -MeOPh)P	0.241	0.123	0.166	0.255
Co ^{II} T(p-MeOPh)P	0.261	0.113	0.315	0.182
Co ^{III} Cl(T(<i>p</i> -MeOPh)P)	0.255	0.058	0.504	0.138

It follows from Eq. (1) that the tangent of the inclination of line $E_m(\ln V)$ allows us to calculate transfer coefficient α , since $z_{\alpha} = 1$ (as a rule). Analysis of the obtained experimental data showed that the dependences of $E_m(\ln V)$ for our investigated electrocatalytic systems were linearized with the correlation coefficient $R^2 = 0.90-0.99$ (Fig. 3). The calculated values of α are listed in Table 2, which also gives the values for the Tafel's slope *b* calculated using the equation

$$b = \frac{2.3RT}{z\alpha F},\tag{3}$$

where z = 2 for H₂T(*p*-MeOPh)P and Co^{II}T(*p*-MeOPh)P, z = 4 for Co^{III}Cl(T(*p*-MeOPh)P). These values of *z* (the number of electrons in the reaction) follow from our analysis of the cathodic branch of the CVA (Fig. 1). For the electrode activated with H₂T(*p*-MeOPh)P and Co^{II}T(*p*-MeOPh)P, we may assume that the first maximum in the potential range of -0.1 to -0.4 V is associated with the first stage of oxygen reduction with the participation of two electrons and the formation of a peroxide ion:

$$O_2 + H_2O + 2\overline{e} \rightarrow HO_2^- + OH^-$$

The second maximum in the potential range of -0.4 to -0.8 V corresponds to the subsequent reduction of the peroxide ion:

$$HO_2^- + H_2O + 2\overline{e} \rightarrow 3OH^-$$
.

The existence of only one maximum on the cathodic part of curve 3 (the absence of the maximum in the potential range of -0.4 to -0.8 V) depends on the four-electron process of oxygen reduction with the formation of a hydroxyl-ion for the electrode activated by Co^{III}Cl(T(*p*-MeOPh)P):

$$O_2 + 2H_2O + 4\bar{e} \rightarrow 4OH^{-1}$$

Similar results were obtained on a rotating disc electrode with ring [11], demonstrating that the yield of hydrogen peroxide on most macroheterocyclic compounds in an alkali solution is negligible. In this case, the four-electron process with the formation of a hydroxyl ion can take place, though successive twoelectron processes with the rapid reduction of the peroxide ion are also possible [11, 12].

Parameter *B* in Eq. (1) can be determined from the value of the cross section intersected by the line $E_m(\ln V)$ on the ordinate axis. Using Eq. (2) and the oxygen diffusion coefficient $D = 2.601 \times 10^{-5} \text{ cm}^2/\text{s}$ [13], we can calculate the stationary constant of the electrochemical reaction. It follows from Table 3 that the values of k_0 decline in the series Co^{III}Cl(T(*p*-MeOPh)P) > Co^{II}T(*p*-MeOPh)P > H_2T(*p*-MeOPh)P.

Another parameter that characterizes the electrocatalytic activity of the surface compound is the halfwave potential $(E_{1/2})$ of the corresponding process. In the case of an irreversible reaction, however, the potential of the maximum (the half-peak potential $E_{m/2}$) depends on the scanning rate *V*. The values of $E_{1/2}$ were therefore determined by extrapolating the $E_{m/2}(V)$ dependences to V = 0, with allowance for the non-Faraday current of the double electric layer charging. The DEL charging current was found as a rectilinear continuation of the initial section of the voltammetric curve. It follows from Table 2 that the above mentioned series of Co^{III}Cl(T(*p*-MeOPh)P) > Co^{II}T(*p*-MeOPh)P > H₂T(*p*-MeOPh)P holds for the half-wave potential values as well.

CONCLUSIONS

The results of our investigations show that among the analyzed macroheterocyclic compounds, the $Co^{III}Cl(T(p-MeOPh)P)$ complex is characterized by the greatest electrocatalytic activity, relative to the $Co^{II}T(p-MeOPh)P$ complex and the metal-free $H_2T(p-MeOPh)P$ complex. This is likely due to the charge of the complex being able to change (the formation of ionic forms) upon variations in the electrode potential during electrochemical reactions, which leads to changes in electrocatalytic activity.

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