ISSN 0023-1584, Kinetics and Catalysis, 2007, Vol. 48, No. 5, pp. 660–663. © MAIK "Nauka/Interperiodica" (Russia), 2007.
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Cobalt 4-Octasulfophenyltetrapyrazinoporphyrazine As a Catalyst for the Oxidation of Organic Substrates with Atmospheric Oxygen

V. N. Shishkin, E. V. Kudrik, S. V. Makarov, and G. P. Shaposhnikov

Ivanovo State Univesity of Chemical Technology, Ivanovo, Russia

e-mail: ttoc@isuct.ru

Received April 26, 2006

Abstract—Cobalt 4-octasulfophenyltetrapyrazinoporphyrazine is an efficient catalyst for the oxidation of diethylamine and cysteine with atmospheric oxygen. This complex activates the substrate through its one-electron oxidation, not an oxygen molecule. The role of oxygen is the oxidation of the intermediate anionic complex (catalyst regeneration step).

DOI: 10.1134/S0023158407050102

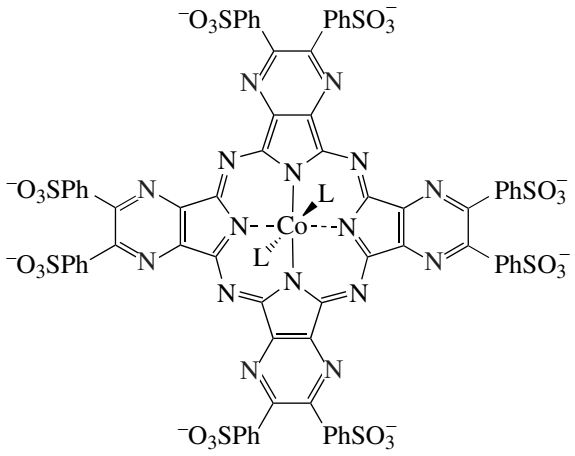
INTRODUCTION

Oxygen activation in oxidation reactions is a challenging problem of modern chemistry and biochemistry. Numerous studies showed that complexes of divalent cobalt and iron are promising catalysts for these reactions [1–3]. In particular, the latter play the most important role in biochemical processes. A series of enzymes containing a Fe^{2+} cation in their active-site cavity react with O_2 to form high-valence iron–oxygen adducts [4]. The Fe(III) complexes also can react with oxygen. For instance, it has recently been shown [5] that the Fe(III) complex with tetraamido macrocyclic ligands reacts with oxygen to form the Fe(IV)–O–Fe(IV) μ-oxo dimer, which is a strong oxidizer. Co(II) complexes are involved in the one-electron reduction of oxygen to form the superoxo (Co(III)–O_2^-) or peroxo derivatives (Co(III)–O_2^{2-}–Co(III)) [6–8]. We found earlier [9] that the cobalt complex with 4-octasulfophenyltetrapyrazinoporphyrazine (a ligand with pronounced electron-withdrawing properties) catalyzes the reactions of thiourea and *N*,*N*′-dimethylthiourea with oxygen. The reaction occurs under mild conditions to form the corresponding urea and sulfur in high yield. In the present work, we studied the catalytic oxidation reactions of other organic substrates (diethylamine and cysteine) with oxygen.

EXPERIMENTAL

General

Cobalt 4-octasulfophenyltetrapyrazinoporphyrazine (**I**) was synthesized and purified according to earlier described procedures [9].



I

The reactions were carried out by quickly mixing deoxygenated solutions of complex **I** (2.25×10^{-5} mol/l) and excess reactant (diethylamine ot cysteine). Kinetic curves were obtained by the stop-flow method using an SX-17 MV (Applied Photophysics) temperature-controlled (±0.1°C) instrument. The measurements were taken at a wavelength of 500 nm, which corresponds to the absorption of the reduced form of the complex. Solutions were prepared using ultrapure water. A 0.1 M solution of the TRIS (tris(hydroxymethyl)aminomethane) buffer was used to maintain pH in the reaction with cysteine. The ionic strength was maintained constant (in all experiments it was 0.2) by the addition of appropriate amounts of sodium perchlorate. NMR, ESR, and mass spectra were recorded on Bruker

Avance DPX 300 NB, Bruker ESR 300 E, and JEOL M 700 spectrometers, respectively.

Oxidation of Diethylamine

Complex **I** (~10^{-5} mol) was added to freshly distilled diethylamine (30 ml), and air was bubbled through the resulting red solution for 12 h. The reaction mixture obtained was fractionated, and the fraction with a boiling point of 117–120°C was collected. The single oxidation product was tetraethylhydrazine (4.4 g). Mass spectrum (field desorption, solution in CH_3OH): 162 ($M^+ + H_2O$), 144 (M^+). ^1H NMR (300 mHz, CD_3OD), δ, ppm: 2.89–2.94 (quadruplet, 4H, CH_2), 1.28–1.25 (triplet, 6H, CH_3). ^{13}C NMR (75 mHz, CD_3OD), δ, ppm: 41.9 (CH_2), 12.4 (CH_3).

To determine the diethylamine conversion, a known amount of the substrate (m_{subs}) was oxidized with atmospheric oxygen. Then the reaction mixture was distilled (first diethylamine and then tetraethylhydrazine were distilled off), and the resulting amount of tetraethylhydrazine was determined. Then the amount of diethylamine consumed in the reaction (m_{1subs}) was found using these data. The (m_{1subs}/m_{subs}) × 100% value was taken to be the diethylamine conversion. The total material balance of the reaction was not calculated, because part of the diethylamine was lost during distillation.

Oxidation of Cysteine

Complex **I** (~10^{-5} mol/l) was added to a saturated solution of *L*-cysteine in a 0.1 M TRIS buffer (pH 7) or a 0.1 M acetate buffer (pH 5), and air was passed through the resulting reaction mixture until the end of precipitation. The precipitate was filtered, washed with water, and recrystallized from water. The cysteine yield at pH 7 and 5 was 96 and 91%, respectively. The melting point was 256–258°C (with decomposition), which is in agreement with reference data [10] (256–257°C). ^{13}C NMR (75 mHz, 2% DCl in D_2O), δ, ppm: 170.48 (COOH), 51.76 (CH), 36.25 (CH_2).

RESULTS AND DISCUSSION

The electronic absorption spectra of an aqueous solution of compound **I** are shown in Fig. 1. As follows from these data, the shape of the spectrum is virtually independent of the presence of oxygen in the solution. Based on this, we can conclude that, on the one hand, complex **I** cannot give stable adducts with oxygen. On the other hand, the addition of excess diethylamine substantially changes the spectrum. The long-wave *Q* band disappears almost completely, a new absorption band peaking at 505 nm appears, and the color of the solution changes from green to red. We assume that the coordinated diethylamine molecule undergoes one-electron oxidation to form a pentacoordinate anionic complex.

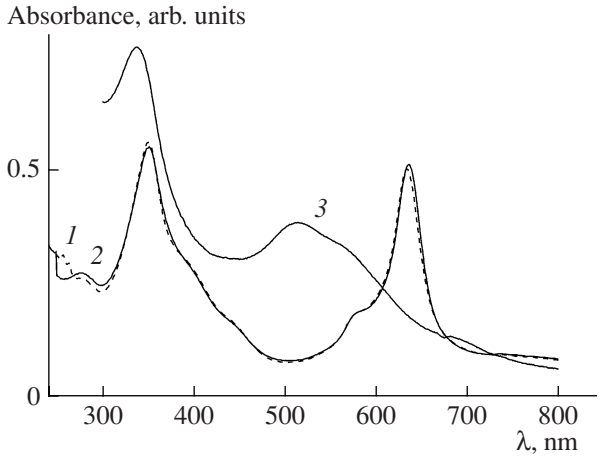


Fig. 1. Electronic absorption spectra of complex **I** in a 0.1 M TRIS buffer (pH 7): (*1*) in the presence of oxygen, (*2*) after oxygen was removed by purging with argon, and (*3*) in the presence of diethylamine.

The formation of the pentacoordinate anionic complex in the reaction of compound **I** with *N*,*N*'-dimethylthiourea is characterized by fast equilibration followed by the slow elimination of the coordinated water molecule [9]. The kinetics of the process is well described by the Michaelis–Menten equation.

In the present work, we studied the oxidation of diethylamine, whose concentration was varied in a rather wide range (from 0.005 to 0.1 mol/l). The reaction was of the pseudo-first order and proceeded at a constant pH ($[HN(C_2H_5)]/[H_2N^+(C_2H_5)_2Cl^-] = 1 : 1$). A linear dependence of the apparent reaction rate constant $k_{app\,1}$ on $[HN(C_2H_5)_2]^2$ with a slope ratio of 10480 ± 50 was experimentally found. The observed dependence corresponds to the following scheme:

$$\begin{aligned} &Co(H_2O)_2L + HN(C_2H_5)_2 \\ &\xrightleftharpoons{K_1} Co(H_2O)L(HN(C_2H_5)_2) \\ &\xrightarrow{k_1} Co(N^+(C_2H_5)_2)L^- + HN(C_2H_5)_2 \\ &\xrightarrow{k_2} Co((C_2H_5)_2N{-}N^+H(C_2H_5)_2)L^-. \end{aligned} \qquad \text{(I)}$$

The apparent pseudo-first-order rate constant can be expressed as

$$k_{app1} = \frac{K_1 k_1 k_2}{1 + K_1}[HN(C_2H_5)_2]^2. \qquad (1)$$

The key step of the catalytic oxidation of diethylamine is, most likely, the nucleophilic attack of a free base molecule on the nitrogen atom of the coordinated diethylamine molecule. The role of oxygen in the catalytic cycle is to participate in the one-electron oxidation of the anionic complex with the regeneration of compound **I**. From this, one can draw the important conclu-

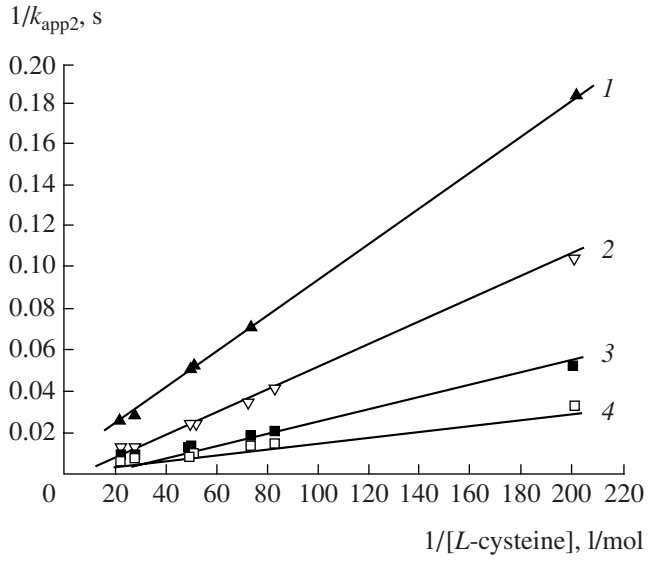


Fig. 2. Plots of $1/k_{app2}$ versus 1/[L-cysteine] at (*1*) 15, (*2*) 25, (*3*) 35, and (*4*) 45°C. Reaction conditions: 0.1 M TRIS buffer, pH 7, [**I**] = 2.2×10^{-5} mol/l.

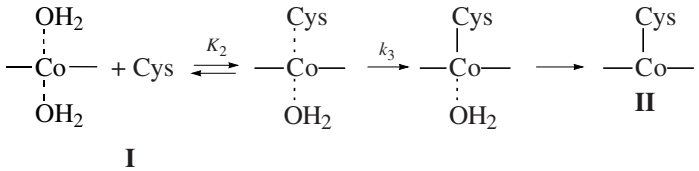
sion that the coordination of diethylamine with complex **I** induces the inversion of its reactivity: its nitrogen atom becomes an electrophilic center. A similar inversion of reactivity was observed previously for the aniline complexes with the high-valence cation of osmium [11]. The coordination of aniline with osmium makes it possible to perform the nucleophilic substitution of a pyrrolidine residue for the hydrogen atom in the *para*-position to the amino group.

One of the best known reactions catalyzed by the cobalt complexes of porphyrazines and phthalocyanines is the oxidation of cysteine with atmospheric oxygen. In the presence of the catalysts, this reaction results in the formation of cysteine. However, this takes place only in strongly alkaline media because cysteine is involved in the catalytic cycle in the form of a dianion. The process was shown [12] to proceed through the formation of the complex O_2^- ⟶ Co(III)SR followed by the homolytic cleavage of the Co–S bond and the recombination of the resulting two radicals into an S–S bond. By contrast, complex **I** is inactive in strongly alkaline media, but it efficiently catalyzes the reaction in neutral and weakly acidic media. The use of the 5,5-dimethylpyrroline-1-oxide (DMPO) radical trap indicated that no radicals form in the catalytic cycle. This implies that complex **I** catalyzes cysteine oxidation via a fundamentally different mechanism.

In order to elucidate this mechanism, we studied the kinetics of the reaction of complex **I** with *L*-cysteine at pH 7 in the absence of oxygen. Under these conditions, the plots of the reaction rate versus the amino acid concentration at different temperatures are nonlinear, but they can be linearized in the coordinates $1/k_{app2} - 1/$[L-cysteine] in the entire concentration range examined (Fig. 2). The kinetic parameters of this reaction at different temperatures are given below (for designations, see Scheme (II)).

T, °C	K_2	k_3, s^{-1}
45	56080 ± 3450	8.3 ± 1
35	15910 ± 760	3.93 ± 0.31
25	3360 ± 430	1.74 ± 0.37
15	850 ± 65	0.76 ± 0.13

The following activation parameters of the rate-determining step of the process were determined from the Eyring dependence: $\Delta H^{\neq} = 58.4 \pm 0.4$ kJ/mol, $\Delta S^{\neq} = -45 \pm 2$ J mol^{-1} K^{-1}. Thus, the rate-determining step is characterized by a relatively low activation enthalpy, and the activation entropy is also low and negative. In view of this, we can assume that the overall rate of the process is determined by the rate of intramolecular electron transfer with the formation of the Co–S covalent bond and the subsequent fast elimination of the coordinated water molecule:



(II)

Next, intermediate anionic complex **II** reacts rapidly with atmospheric oxygen, as in the reaction involving thiourea, and is oxidized, returning to its initial state.

Thus, it is shown in the present work that the cobalt 4-octasulfophenyltetrapyrazinoporphyrazine complex is an efficient catalyst for the oxidation of cysteine and diethylamine with atmospheric oxygen. Unlike the derivatives of cobalt phthalocyanine, this complex is first reduced by the substrate and then the reduced form is oxidized by oxygen. It is important that diethylamine can be selectively oxidized to tetraethylhydrazine in the absence of the corresponding hydroxylamine in the reaction mixture. The kinetic study showed that the key

step of both reactions (oxidation of diethylamine and cysteine) is the formation of an anionic complex.

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