

Catalytic Properties of Cobalt Complexes with Tetrapyrzino Porphyrazine and Phthalocyanine Derivatives

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Received January 10, 2014

Abstract—The catalytic activity of cobalt complexes with octaphenyltetrapyrzino porphyrazine and phthalocyanine derivatives containing branched peripheral substituents is studied in heterogeneous catalysis of the oxidation of sodium diethyldithiocarbamate (SDC) with atmospheric oxygen. Cobalt phthalocyanines are shown to display higher catalytic activity than cobalt complexes with octaphenyltetrapyrzino porphyrazine. The highest efficiency of heterogeneous catalysts is attained at temperatures of 298–303 K.

Keywords: porphyrazine, phthalocyanine, cobalt complex, heterogeneous catalysis, sodium diethyldithiocarbamate

DOI: 10.1134/S0036024414120395

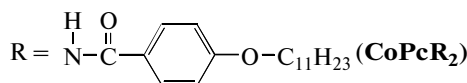
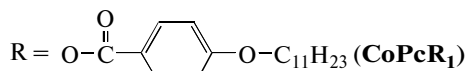
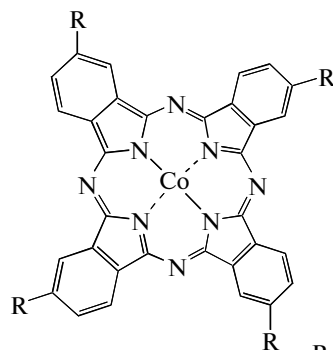
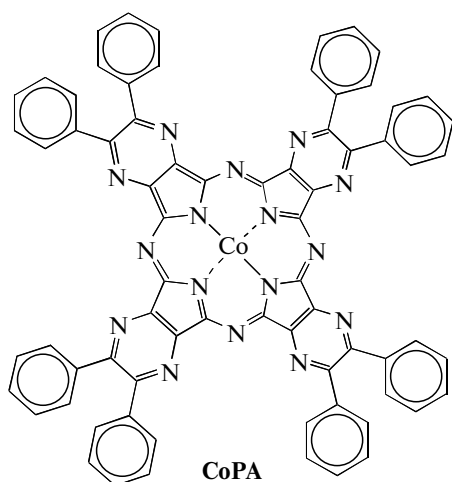
INTRODUCTION

Cobalt complexes of porphyrine compounds and their analogues are finding increasingly wide application as catalysts for the oxidation of olefins [1], cycloalkenes [2], carbamates [3–5], and mercaptanes [6–10]. According to [11, 12], not only the central metal cation in a macromolecule [13] but the nature of the peripheral substituent affects the catalytic process with the participation of tetrapyrrole macroheterocyclic compounds as well. Cobalt complexes with phthalocyanines are therefore widely used to purify oil from sulfur-containing products as active catalysts for the mild oxidation of mercaptanes and hydrogen sulfide [14, 15]. The problem of their selective oxidation is also of great interest for the organic synthesis of industrial-grade disulfides [8, 15–18]. Dithiocarbamic acid derivatives—thiuram sulfides synthesized via the oxidation of carbamates in aqueous alkaline solutions in the presence of cobalt tet-

rasulfophthalocyaninates—are products of tonnage oil processing [14–17]. The use of atmospheric oxygen in their synthesis improves the quality of the target product and is environmentally friendly [6, 9, 19, 20].

It is difficult to include phthalocyanine catalysts in homogeneous catalysis due to their self-association in aqueous and aqueous alkaline media [21–23] and the engineering complexity of their subsequent separation and activation for recycling. The use of substituted porphyrazine and phthalocyanine complexes as heterogeneous catalysts is therefore very promising.

In this work, cobalt complex with octaphenyltetrapyrzino porphyrazine (CoPA) was obtained and its catalytic properties were studied upon mild SDC oxidation with atmospheric oxygen in aqueous alkaline media, in contrast to the cobalt complexes of phthalocyanines (CoPcR₁ and CoPcR₂) synthesized earlier with branched peripheral substituents:



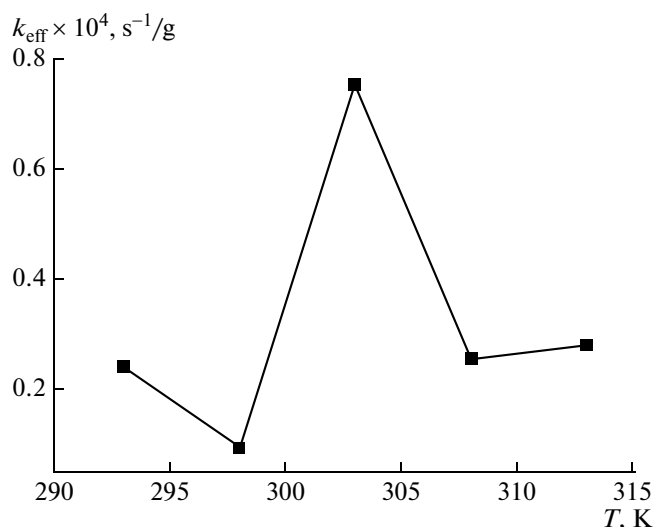


Fig. 1. k_{eff} versus temperature for the oxidation of SDC in the presence of CoPA.

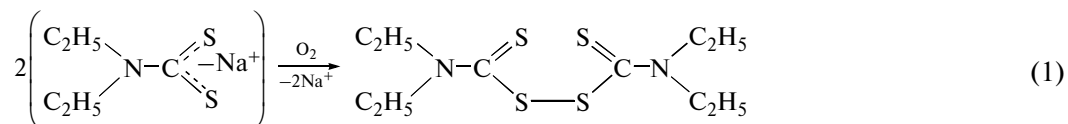
EXPERIMENTAL

Octaphenyltetrapyrzazinoporphyrazine was synthesized as described in [24]. The free ligand was dissolved in dimethylsulfoxide, and a hundredfold excess of cobalt acetate was added. The reaction mixture was heated to 313 K and allowed to stand for 60 min. The solution was then evaporated. The dry mass was washed with distilled water to remove any unreacted salt. The absorption band ($\lambda = 635 \text{ nm}$) in the visible spectral region exhibits a 30-nm hypsochromic shift

upon the formation of CoPA, thus indicating the synthesis of a chelate complex. Complexes CoPcR₁ and CoPcR₂ were synthesized by the standard method in [25]. Electronic absorption spectra were recorded on a Shimadzu UV 1800 spectrophotometer in 10-mm thick quartz cells. The solvents were purified as described in [26]. The SDC oxidation reaction was studied in a light-tight temperature-controlled cell 650 mL in volume within a 2.7×10^{-3} – 8.3×10^{-3} mol/L range of SDC concentrations at temperatures of 293–313 K. Experiments were performed in aqueous alkaline solutions at pH 8–10. A setup consisting of a thermostat, a temperature-controlled sampling cell, and an oxygen delivery device was used. A reference sample was taken before each experiment. Experiments on the oxidation of SDC without a catalyst were performed beforehand. To perform the catalytic oxidation of SDC, a catalyst was added to the solution and air was supplied to the cell through a capillary. The moment air was supplied was considered as the beginning of the reaction. To determine the current SDC concentration, samples 2 mL in volume were taken at specific time intervals throughout each experiment. The procedure for analytical spectrophotometric estimates of a current SDC concentration was described in [27, 28].

RESULTS AND DISCUSSION

The catalytic activity of our cobalt complexes was investigated oxidizing SDC with atmospheric oxygen according to the scheme



It was established in preliminary experiments that the noncatalytic oxidation of SDC is slow and is characterized by $k_{\text{eff}} = 1.7 \times 10^{-5} \text{ s}^{-1}$.

Under the condition of an unchanging oxygen concentration, catalyst, and medium pH, the rate of SDC oxidation is described by the first-order kinetic equation [3, 29]

$$dc/d\tau = -k_{\text{eff}}c, \quad (2)$$

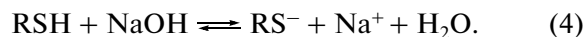
where c is the current SDC concentration, τ is the time, k_{eff} is the effective reaction rate constant. This is confirmed by the linear character of dependence $\ln c = f(\tau)$ and the unchanging nature of the rate constants calculated with the equation

$$k_{\text{eff}} = (1/\tau)\ln(c_0/c), \quad (3)$$

where c_0 is the initial SDC concentration, and c is the SDC concentration at a specific moment in time τ .

It should be noted that the catalytic oxidation of SDC proceeds efficiently only in alkaline media,

where thiol exists in the form of RS^- anions due to the equilibrium shifting to the right:



The first kinetic order obtained for SDC oxidation in all of the systems within our range of concentrations (2.7×10^{-3} to 8.3×10^{-3} mol/L) suggests that the formation of RS^\bullet particles with their subsequent conversion into alkyldisulfide RS-SR is the rate-determining stage of the oxidation process [11].

Our study of the temperature dependence of the efficiency of SDC oxidation in the presence of CoPA revealed the nonlinear character of the change in k_{eff} (Fig. 1). The highest efficiency was attained at a temperature of 303 K. The rate of SDC oxidation grew by a factor of 5, relative to noncatalytic oxidation ($k_{\text{eff}} = 7.5 \times 10^{-5} \text{ s}^{-1} \text{ g}^{-1}$). Conversion in this case is 70–80%, due most likely to both the shift of equilibrium (4) toward the formation of RS^- anions and the higher efficiency of RS^\bullet radical formation.

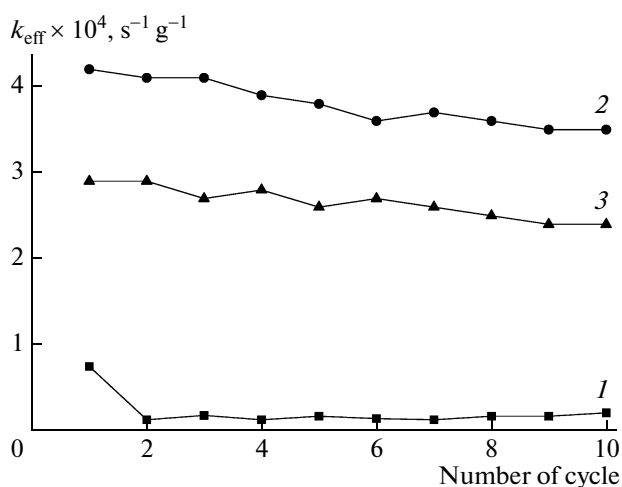


Fig. 2. k_{eff} versus the number of oxidation cycles at 303 K for (1) CoPA, (2) CoPcR₁, and (3) CoPcR₂.

Phthalocyanine catalysts displayed better SDC oxidation efficiency even at 298 K. Effective SDC oxidation rate constants $k_{\text{eff}} = 3.5 \times 10^{-4}$ and $2.3 \times 10^{-4} \text{ s}^{-1} \text{ g}^{-1}$ for CoPcR₁ and CoPcR₂, respectively—an order of magnitude higher than for CoPA.

The difference between the values of k_{eff} for phthalocyanines CoPcR₁ and CoPcR₂ is quite likely due to the effect of the spacer group of the peripheral substituent of a phthalocyanine molecule with the resulting redistribution of electron density in the macrocyclic ring. The nitrogen atom in the peripheral substituent shifts the electron density to the macrocycle, thereby hindering the coordination of dithiocarbamate and oxygen to the central cobalt cation. In contrast, the oxygen atom shifts the electron density from the macrocoring, thereby raising the probability of SDC–phthalocyanine–substrate coordination interactions.

When studying the catalytic activity of CoPA in a series of consecutive experiments (Fig. 2), the catalyst was found to deactivate by 60% as early as the second catalytic cycle, limiting the possibilities for its industrial application. The behavior of this catalyst in subsequent cycles is identical, and its activity remains unchangeable up to the tenth cycle. However, even though k_{eff} is 2.3 times higher than for noncatalytic oxidation, this is insufficient to obtain high-purity thiram sulfide.

CONCLUSIONS

The drop in the catalytic activity of CoPA is likely due to the saturation of its active sites and the formation of oxygen adducts [30] that obstruct substrate–porphyrazine–oxygen coordination interaction and the transfer of electron pairs.

The reduction in catalytic activity upon moving from CoPcR₁ and CoPcR₂ to CoPA is due to the destruction of the macrocoring in strongly alkaline

media with the simultaneous distortion of its π -chromophore system and the formation of low-temperature colorless products [31]. A 5–10% reduction in catalytic activity that corresponding to technological requirements was also observed for phthalocyanine catalysts.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 13-03-00615-a).

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Translated by E. Glushachenkova