ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2009, Vol. 83, No. 12, pp. 2050–2053. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © A.S. Pogorelova, S.V. Makarov, E.S. Ageeva, R. Silagi-Dumitresku, 2009, published in Zhurnal Fizicheskoi Khimii, 2009, Vol. 83, No. 12, pp. 2250–2254.

Cobalt Tetrasulfophthalocyaninate as a Catalyst of the Reduction of Nitrite with Thiourea Dioxide

A. S. Pogorelova[a], **S. V. Makarov**[b], **E. S. Ageeva**[b], **and R. Silagi-Dumitresku**[c]
[a] *Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, Russia*
[b] *Ivanovo State University of Chemical Technology, Ivanovo, Russia*
[c] *Babes-Bolyai University, Cluj-Napoca, Romania*
e-mail: makarov@isuct.ru

Received December 24, 2008

Abstract—The kinetics of reduction of nitrite with thiourea dioxide in the presence of cobalt tetrasulfophthalocyaninate was studied. The process was shown to involve the $Co^{II} \longleftrightarrow Co^{I}$ catalytic cycle. The kinetic parameters of the reduction of Co^{II} and Co^{I} tetrasulfophthalocyaninates were determined

DOI: 10.1134/S0036024409120085

INTRODUCTION

In recent years, views on the importance of and role played by nitrite in biological processes have changed substantially. Earlier, nitrite was treated only as a harmful substance. Studies of the past decade showed that nitrite played the most important role in controlling blood pressure [1, 2]. It is the main reservoir of nitrogen(II) oxide in organism, which is especially important for hypoxia [1, 2]. The use of nitrite for curing such a serious illness as cystic fibrosis offers much promise [3]. The earlier unknown function of hemoglobin and myoglobin as nitrite reductases was revealed [4–6].

It was found that cobalt tetrasulfophthalocyaninate had high catalytic activity in the reduction of nitrite and nitrate with dithionite in alkaline solutions [7]. The end reaction products were ammonia and nitrogen(I) oxide depending on the nature of the oxidizer. These differences were likely caused by the formation of intermediate complexes in the reaction between the reduced form of phthalocyaninate and nitrite or nitrate. The complexes had different structures: the substrate was coordinated at the nitrogen atom with nitrite and oxygen atom with nitrate [7]. The composition of nitrite reduction products was shown to be influenced substantially by the nature of the reducing agent and metal in its complex with tetrasulfophthalocyanine. For instance, the use of iron tetrasulfophthalocyaninate as a catalyst of the reduction of nitrite with dithionite and sulfoxylate (thiourea dioxide was used as a precursor of sulfoxylate) resulted in the formation of nitrogen(I) oxide and ammonia, respectively [8].

In this work, we present the results of a kinetic study of the reduction of nitrite with thiourea dioxide (TUDO) in the presence of cobalt tetrasulfophthalocyaninate ($Co^{II}(TSPc)^{4-}$). The results are compared with the data on the kinetics of catalytic nitrite reduction with dithionite.

EXPERIMENTAL

Cobalt tetrasulfophthalocyaninate was prepared and purified following the known procedure [9, 10]. Sodium nitrite and thiourea dioxide (Aldrich) were used without additional purification. The products of the reduction of nitrite were determined by the ^{15}N NMR method using $N^{15}NO_2$ (95% ^{15}N). Solution pH was maintained at the required level with the use of the universal Britton–Robinson buffer mixture. Kinetic experiments were performed under temperature controlled conditions on a Specord M-40 spectrophotometer in the absence of oxygen (argon was preliminarily bubbled through solutions). The results were analyzed using the Origin 7.5 program. The NMR spectra were recorded on a Bruker Avance DRX400 WB spectrometer. The metal complex was reduced with both freshly prepared and aged solutions of TUDO. “Aged” means held in 0.1 N NaOH under anaerobic conditions for 4 h [8], which caused the formation of SO_2^{2-} (SO_2H^-)—sulfoxylate reducing particles (the only nitrogen-containing product of the decomposition of thiourea dioxide in strongly alkaline media; urea did not influence the rate of redox processes). The use of sulfoxylate allows the influence of the decomposition of TUDO to be excluded and the reaction between SO_2^{2-} (SO_2H^-) and $Co^{I}(TSPc)^{5-}$ to be studied.

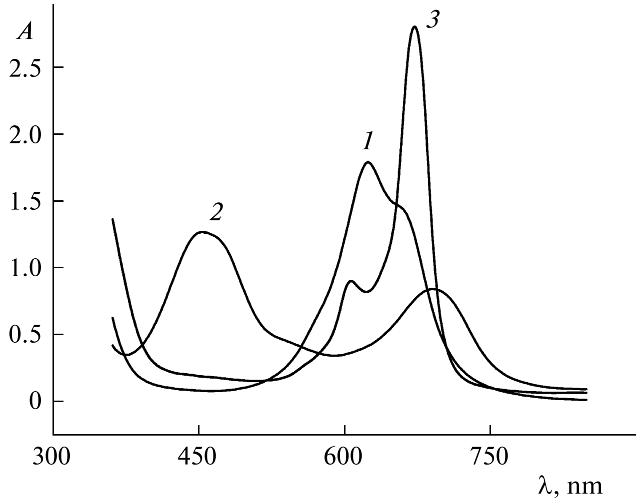

Fig. 1. Absorption spectra of (*1*) $Co^{II}(TSPc)^{4-}$, (*2*) the product of its reduction, $Co^{I}(TSPc)^{5-}$, and (*3*) the product of the oxidation of the reduced form with oxygen, $Co^{III}(TSPc)^{3-}$; $[Co^{II}(TSPc)^{4-}] = 4.96 \times 10^{-5}$ mol/l, $T = 298$ K.

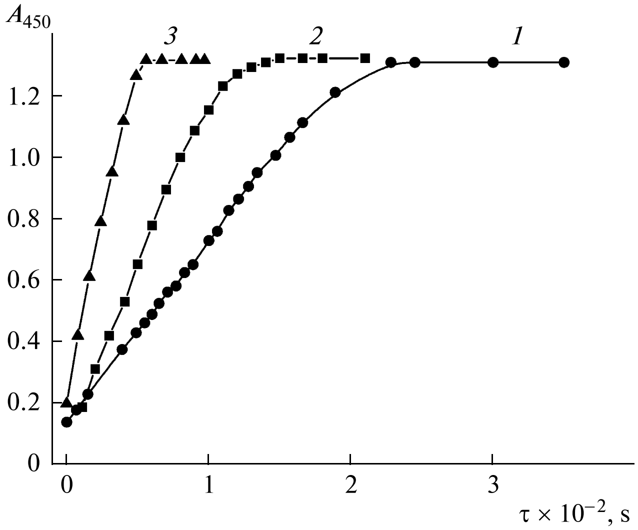

Fig. 2. Kinetic curves of the reduction of $Co^{II}(TSPc)^{4-}$ with thiourea dioxide at pH (*1*) 9.4, (*2*) 10.9, and (*3*) 13 (0.1 mol/l NaOH); [TUDO] = 1×10^{-3} mol/l, $[Co^{II}(TSPc)^{4-}] = 4.96 \times 10^{-5}$ mol/l, $T = 298$ K.

RESULTS AND DISCUSSION

The reduction of $Co^{II}(TSPc)^{4-}$ with thiourea dioxide is accompanied by a change in solution color from blue to olive. An intense band at 450 nm appears in the absorption spectrum (Fig. 1); simultaneously, a bathochromic shift of the *Q* band is observed. According to the literature data [7, 11, 12], the resulting spectrum corresponds to $Co^{I}(TSPc)^{5-}$.

The kinetics of reduction of $Co^{II}(TSPc)^{4-}$ was studied under pseudofirst-order reaction conditions in the presence of excess TUDO (in this series of experiments, we used freshly prepared solutions of thiourea dioxide, because reduction with sulfoxylate occurred almost instantaneously). The kinetic curves obtained by measuring optical density at 450 nm (this wavelength corresponds to the reduced form) and various pH are shown in Fig. 2. We found that the rate of reduction was independent of the concentration of the metal complex; that is, the reaction was described by the kinetic equation $r = k$[TUDO]. The rate constants calculated from the experimental data were commensurate with the rate constants for the decomposition of TUDO in alkaline solutions. For instance, at pH 11 and $T = 298$ K, the rate constant for the decomposition of TUDO in solution was 6×10^{-4} s^{-1} [13], and the rate constant for the reduction of cobalt phthalocyaninate determined by dividing the observed zero-order rate constant by the concentration of TUDO was 4.4×10^{-4} s^{-1} under equal conditions. It can therefore be assumed that the decomposition of TUDO in solution according to the reaction

$$NH_2NHCSO_2^- + H_2O \longrightarrow SO_2H^- + (NH_2)_2CO \quad (1)$$

is the limiting stage of the process.

The absorption spectrum of the reduced complex did not change for 2–3 min. Optical density then slowly decreased over the whole wavelength range. The solution gradually underwent discoloration. It follows that $Co^{I}(TSPc)^{5-}$ is not the final product of the reaction under consideration. Similar effects were observed during the radiolytic reduction of $Co^{I}(TSPc)^{5-}$ [11]. According to [11], the reduction of the macroring occurred in that reaction.

The kinetic curves of the reduction of $Co^{I}(TSPc)^{5-}$ with thiourea dioxide at various temperatures are shown in Fig. 3. The kinetics of reduction was studied under pseudofirst-order reaction conditions in the presence of excess TUDO. The reaction was found to be described by the equation $r = k[Co^{I}(TSPc)^{5-}]$[TUDO]. The activation parameters found from the Eyring dependence were $\Delta H^{\neq} = 50 \pm 2$ kJ/mol and $\Delta S^{\neq} = -160 \pm 10$ J/(mol K). Importantly, the kinetic characteristics were almost independent of whether freshly prepared or aged solutions of thiourea dioxide were used in experiments. We can therefore assume that the rate-determining stage is the formation of the $[Co^{I}(TSPc)SO_2H]^{6-}$ complex,

$$\begin{gathered} Co^{I}(TSPc)^{5-} + SO_2H^- \\ \longleftrightarrow [Co^{I}(TSPc)^{5-} \cdot SO_2H^-] \longrightarrow \text{products}. \end{gathered} \quad (2)$$

Note that the introduction of oxygen into the system immediately after the highest optical density at 450 nm was reached, that is, into a solution of $Co^{I}(TSPc)^{5-}$, caused the formation of the initial complex $Co^{II}(TSPc)^{4-}$. At the same time, the oxidation of the product of $Co^{I}(TSPc)^{5-}$ reduction with oxygen resulted in the formation of $Co^{III}(TSPc)^{3-}$ ($\lambda_{max} = 605$,

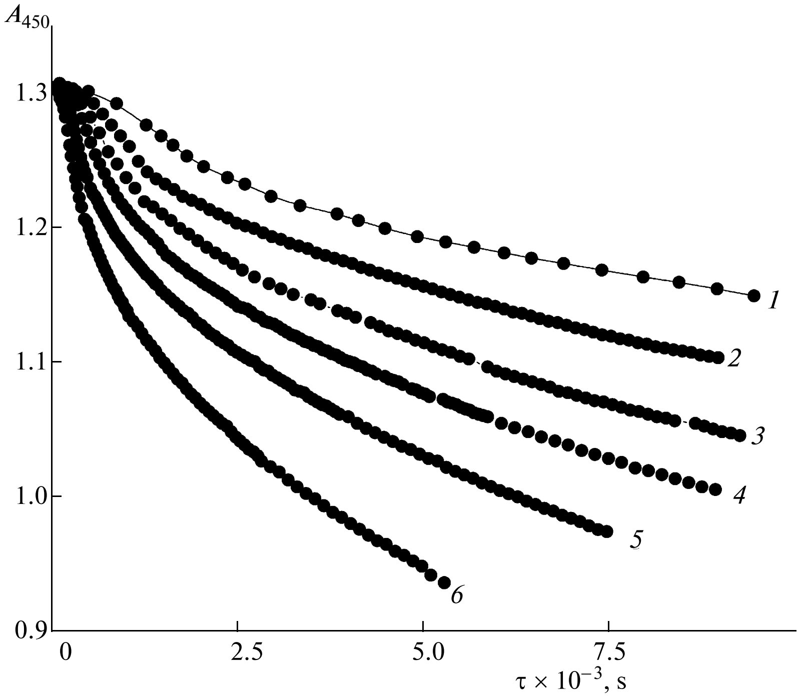

Fig. 3. Kinetic curves of the reduction of $Co^{I}(TSPc)^{5-}$ with thiourea dioxide at temperatures of (*1*) 298, (*2*) 303, (*3*) 308, (*4*) 313, (*5*) 318, and (*6*) 323 K; pH 10.7, [TUDO] = 1×10^{-3} mol/l, $[Co^{I}(TSPc)^{5-}] = 4.96 \times 10^{-5}$ mol/l.

670 nm) (Fig. 1) [7, 12], which was accompanied by a solution color change from olive to blue-green. Let us consider the reasons for this difference. It is known that $Co^{III}(TSPc)^{3-}$ is formed in the reaction between $Co^{II}(TSPc)^{4-}$ and sulfite in the presence of oxygen [7]. Under these conditions, the SO_5^- particle, which is a strong oxidizer, is formed. In our system, sulfite is formed in the decomposition of TUDO. The reduction of $Co^{II}(TSPc)^{4-}$ to $Co^{I}(TSPc)^{5-}$ occurs at a high rate, the concentration of sulfite is therefore low, and it does not influence the oxidation of the complex. Conversely, the reduction of $Co^{I}(TSPc)^{5-}$ occurs at a low rate, and a substantial amount of sulfite is accumulated during the reaction. Sulfite reacts with oxygen to produce SO_5^-, which results in deeper oxidation of the metal complex to $Co^{III}(TSPc)^{3-}$.

The kinetics of interaction between $Co^{I}(TSPc)^{5-}$ and nitrite was studied under anaerobic conditions at pH 10 and 298 K. Changes in absorption at 450 nm were used to monitor kinetics. Reduction was studied under pseudofirst-order reaction conditions in the presence of excess nitrite, which was introduced into a solution of the reduced phthalocyaninate form immediately after the highest optical density at 450 nm was reached, that is, before the beginning of the second stage of metal complex reduction. Freshly prepared solutions of TUDO were used. A typical kinetic curve is shown in Fig. 4. We see from this figure that the oxidation of $Co^{I}(TSPc)^{5-}$ with nitrite develops with an induction period, the duration of which depends on the concentrations of both nitrite and TUDO. Note that the kinetic curves are similar in shape to those obtained in the reduction of nitrite with sodium dithionite in the presence of cobalt phthalocyaninate [7].

The presence of an induction period is explained by the redox cycle of the metal complex. During this cycle, $Co^{I}(TSPc)^{5-}$ is oxidized to $Co^{II}(TSPc)^{4-}$ with nitrite and again reduced with excess dithionite in solution. This cycle works until all reducing agent is consumed. After this, only the oxidation of $Co^{I}(TSPc)^{5-}$ to $Co^{II}(TSPc)^{4-}$ occurs, and a decrease in the concentration of the reduced form with time is well described by the exponential law. We found in this work that, as with dithionite [7], the rate constant observed at nitrite concentrations up to 0.025–0.03 mol/l increased linearly as the concentration of nitrite grew and reached a constant value (Fig. 5).

It is noteworthy that the observed rate constants obtained in this work from a decrease in optical density at 450 nm were much lower than when dithionite was used as a reducing agent [7]. For instance, the rate constant corresponding to a plateau in Fig. 5 was 4.4×10^{-4} s^{-1} against 1.21×10^{-2} s^{-1} for dithionite [7]. Clearly, this is related to different natures of the rate-determining stage when two different reducing agents are used. With dithionite, the rate constant for the reduction of the Co^{II} complex is 2.2 s^{-1} [7], and, with TUDO, this rate constant is only 4.4×10^{-4} s^{-1}. It fol-

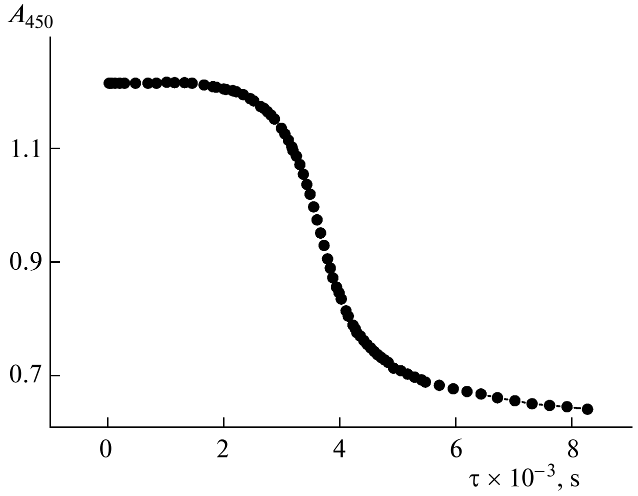

Fig. 4. Kinetic curve of the reduction of nitrite with thiourea dioxide in the presence of $Co^I(TSPc)^{5-}$; [TUDO] = 1×10^{-3} mol/l, $[NaNO_2]$ = 0.03 mol/l, $[Co^I(TSPc)^{5-}]$ = 4.96×10^{-5} mol/l, T = 298 K, pH 10.0.

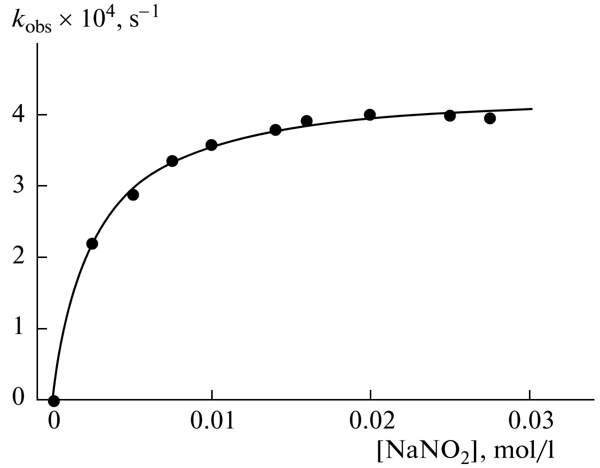

Fig. 5. Dependence of the rate constant for the reduction of nitrite with thiourea dioxide in the presence of $Co^I(TSPc)^{5-}$ on the concentration of nitrite; [TUDO] = 1×10^{-3} mol/l, $[Co^I(TSPc)^{5-}]$ = 4.96×10^{-5} mol/l, T = 298 K, pH 10.0.

lows that, with dithionite, the rate-determining stage of the reduction of nitrite is its interaction with $Co^I(TSPc)^{5-}$, whereas, with TUDO, this is the reduction of $Co^{II}(TSPc)^{4-}$. For this reason, we were unable to determine the kinetic characteristics of the interaction of nitrite with $Co^I(TSPc)^{5-}$.

A comparison of the observed rate constant for the interaction of $Co^I(TSPc)^{5-}$ with NO_2^- (this rate constant was calculated from the data reported in [7], 9.2×10^{-3} s^{-1} at $[NO_2^-]$ = 0.03 M, pH 10.0, and 298 K) and the k_{obs} value obtained under equal conditions in this work for the reduction of $Co^I(TSPc)^{5-}$ (5.8×10^{-6} s^{-1}) leads us to conclude that the catalytic reaction involves the $Co^{II} \longleftrightarrow Co^I$ cycle. The composition of nitrite reduction products favors this conclusion. It is known that, in alkaline solutions, sulfoxylate slowly reduces nitrite to nitrogen(I) oxide and N_2 [14]. In the presence of $Co^{II}(TSPc)^{4-}$, the mechanism of the reaction changes, which results in the formation of other products. The ^{15}N NMR spectra contain signals at –283 and –381 ppm. The first signal corresponds to coordinated $^{15}NH_3$, and the second one, to free $^{15}NH_3$ [7]. Ammonia is also the product of nitrite reduction with dithionite in the presence of $Co^{II}(TSPc)^{4-}$, when the reaction involves the $Co^{II} \longleftrightarrow Co^I$ catalytic cycle. It follows that the data of this work are evidence of the determining influence of the nature of the catalytic cycle on the composition of nitrite reduction products.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research and Romanian Academy, project no. 07-03-91687-RA-a.

REFERENCES

1. S. N. Bryan, Free Rad. Biol. Med. **41**, 691 (2006).
2. M. T. Gladwin, A. N. Schechter, D. B. Kim-Shapiro, et al., Nature Chem. Biol. **1** (6), 308 (2005).
3. S. S. Yoon, R. Coakley, G. W. Lau, et al., J. Clin. Invest. **116**, 436 (2006).
4. A. Cossins and M. Berenbrink, Nature **454** (416) (2008).
5. U. B. Cotta, M. W. Merx, S. Shiva, et al., Proc. Natl. Acad. Sci. USA **105**, 10256 (2008).
6. J. Yi, M. K. Safo, and G. B. Richter-Addo, Biochemistry **47**, 8247 (2008).
7. E. V. Kudrik, S. V. Makarov, A. Zahl, and R. van Eldik, Inorg. Chem. **42**, 618 (2003).
8. E. V. Kudrik, S. V. Makarov, A. Zahl, and R. van Eldik, Inorg. Chem. **44**, 6470 (2005).
9. J. N. Weber and D. H. Busch, Inorg. Chem. **4**, 469 (1965).
10. Y.-C. Yang, R. J. Ward, and R. P. Seiders, Inorg. Chem. **24**, 1765 (1985).
11. J. Grodkowski, T. Dhanasekaran, P. Neta, et al., J. Phys. Chem. A **104**, 11332 (2000).
12. W. A. Nevin, W. Liu, M. Melnik, and A. B. P. Lever, J. Electroanal. Chem. **213**, 217 (1986).
13. S. A. Svarovsky, R. H. Simoyu, and S. V. Makarov, Dalton Trans. **4**, 511 (2000).
14. S. V. Makarov, E. V. Kudrik, R. van Eldik, and E. V. Naidenko, J. Chem. Soc., Dalton Trans. **22**, 4074 (2002).