Inorg. Chem. **2005**, *44*, 6470–6475

Inorganic Chemistry Article

Kinetics and Mechanism of the Iron Phthalocyanine Catalyzed Reduction of Nitrite by Dithionite and Sulfoxylate in Aqueous Solution

Evgeny V. Kudrik,*,†,‡ Sergei V. Makarov,‡ Achim Zahl,† and Rudi van Eldik*,†

Institute for Inorganic Chemistry, University of Erlangen-Nürnberg, Egerlandstrasse 1, 91058 Erlangen, Germany, and Ivanovo State University of Chemistry and Technology, av. F. Engels 7, 153460 Ivanovo, Russia

Received April 17, 2005

The reactions of sodium nitrite with sodium dithionite and sulfoxylate ion were studied in the presence of iron(III) tetrasulfophthalocyanine, $Fe^{III}(TSPc)^{3-}$, in aqueous alkaline solution. Kinetic parameters for the different reaction steps in the catalytic reduction by dithionite were determined. The final product of the reaction was found to be nitrous oxide. Contrary to this, the product of the catalytic reduction of nitrite by sulfoxylate was found to be ammonia. The striking difference in the reaction products is accounted for in terms of different structures of the intermediate complexes formed during the reduction by dithionite and sulfoxylate, in which nitrite is suggested to coordinate to the iron complex via nitrogen and oxygen, respectively. Sulfoxylate is shown to be a convenient reductant for the synthesis of the highly reduced iron phthalocyanine species $Fe^{I}(TSPc^{\bullet})^{6-}$ in aqueous solution. The kinetics of the reduction of $Fe^{I}(TSPc)^{5-}$ to $Fe^{I}(TSPc^{\bullet})^{6-}$, as well as the oxidation of the latter species by nitrite, was studied in detail.

Introduction

Phthalocyanine complexes are effective catalysts for a variety of reactions.[1−9] The chemical, electrochemical, photochemical, and radiolytic reductions of metallophthalocyanines strongly depend on the nature of the central metal atom.[10,11] For the Cu, Ni, and metal-free compounds, the data show that the reduction involves only the ligand.[10] For the Co and Fe complexes, the first step of the reduction yields Co^{I} and Fe^{I}, respectively.[10−12] The reduction of Co^{II} tetrasulfophthalocyanine, $Co^{II}(TSPc)^{4-}$, to the Co^{I} complex was recently shown to be the first step in the catalytic reaction between sodium dithionite and sodium nitrite.[13] The final product of the reaction was found to be ammonia. Contrary to the reduction of nitrite, the products of the catalytic reduction of nitrate were found to be dinitrogen and nitrous oxide. The striking differences in the reduction products of nitrite and nitrate are explained in terms of different structures of the intermediate complex formed between Co^{I} phthalocyanine and the substrate, in which nitrite and nitrate are suggested to coordinate via nitrogen and oxygen, respectively.

The possibility of different coordination modes of nitrite in cytochrome cd_1 reductase has recently been supported by DFT calculations.[14] Although the N-isomer is energetically favored over the O-isomer, a single strong hydrogen bond may provide the energy required to place the two isomers on the same energy level. Important results have also recently been obtained for Cu-containing reductase.[15] The crystal structure of a type two copper−nitrosyl complex of nitrite reductase reveals an unprecedented side-on binding mode in which the nitrogen and oxygen atoms are nearly equidis-

---

* To whom correspondence should be addressed. E-mail: vaneldik@chemie.uni-erlangen.de (R.E.), ttoc@isuct.ru (E.V.K.).
† University of Erlangen-Nürnberg.
‡ Ivanovo State University of Chemistry and Technology.

(1) Jain, S. L.; Sain, B. *J. Mol. Catal. A: Chem.* **2003**, *195*, 283.
(2) Sharma, V. B.; Jain, S. L.; Sain, B. *Catal. Lett.* **2004**, *94*, 57.
(3) Perollier, C.; Sorokin, A. B. *Chem. Commun.* **2002**, 1548.
(4) Schutten, J. H.; Zwart, J. *J. Mol. Catal.* **1979**, *5*, 109.
(5) Brower, W. M.; Piet, P.; German, A. L. *J. Mol. Catal.* **1985**, *31*, 169.
(6) Raja, R.; Jacob, C. R.; Ratnasamy, P. *Catal. Today* **1999**, *49*, 171.
(7) Stuchinskaya, T.; Kundo, N.; Gogina, L.; Schubert, U.; Lorenz, A.; Maizlish, V. *J. Mol. Catal. A: Chem.* **1999**, *140*, 235.
(8) Hoffmann, M. R.; Lim, B. C. *Environ. Sci. Technol.* **1979**, *13*, 1406.
(9) Milos, M. *Appl. Catal., A* **2001**, *216*, 157.
(10) Rollmann, L. D.; Iwamoto, R. T. *J. Am. Chem. Soc.* **1968**, *90*, 1455.
(11) Grodkowski, J.; Dhanasekaran, T.; Neta, P.; Hambright, P.; Brunschwig, B. S.; Shinozaki, K.; Fujita, E. *J. Phys. Chem. A* **2000**, *104*, 11332.
(12) Liao, M.-S.; Scheiner, S. *J. Chem. Phys.* **2001**, *114*, 9780.
(13) Kudrik, E. V.; Makarov, S. V.; Zahl, A.; van Eldik, R. *Inorg. Chem.* **2003**, *42*, 618.
(14) Silaghi-Dumitrescu, R. *Inorg. Chem.* **2004**, *43*, 3715.
(15) Tocheva, E. I.; Rosell, F. I.; Mauk, A. G.; Murphy, M. E. P. *Science* **2004**, *304*, 867.

10.1021/ic0505955 CCC: $30.25

tant from the copper cofactor. Comparison of this structure with a refined nitrite-bound crystal structure indicates how coordination can change between copper−oxygen and copper−nitrogen during catalysis.

Despite the significant progress in the understanding of the mechanisms of catalytic nitrite reductions, several problems remain unresolved. One of them is how the type of reductant influences the rate of the overall reduction of nitrite and the composition of the products. In continuation of our studies on the reactions catalyzed by metallophthalocyanines, here we report kinetic data and their mechanistic interpretation for the reaction between sodium nitrite and sodium dithionite or sulfoxylate in the presence of iron(III) phthalocyanine. Thiourea dioxide (TDO) served as a precursor of sulfoxylate.[16] The reported data demonstrate the distinctive differences in the reactivity of sulfoxylate and dithionite and enable a comparison of the role of iron and cobalt phthalocyanines in the catalytic reduction of nitrite.

Experimental Section

Materials. Sodium nitrite, sodium dithionite (85% grade), and thiourea dioxide (TDO) were obtained from Aldrich and used as received. Iron(III) phthalocyanine was prepared and purified using a literature method.[17] BIS-TRIS, TRISINE, and CHES buffers were used to control the pH. $Na^{15}NO_2$ (95% ^{15}N grade) was used for ^{15}N NMR analysis. Oxygen-free nitrogen was used to deoxygenate solutions. Ultrapure water was used in all measurements.

Kinetic Measurements and Instrumentation. Conventional kinetic experiments were performed on a Cary 1 or Cary 5 UV−vis spectrophotometer under anaerobic conditions. No salt was added to control the ionic strength. The data were analyzed using Origin 6.1 and SPECFIT software. A thermostated (±0.1 °C) Applied Photophysics SX 18MV stopped-flow spectrophotometer with an optical path length of 1.0 cm was used to follow the faster reactions. High-pressure stopped-flow experiments were performed at pressures up to 130 MPa on a custom-built instrument described previously[18] and analyzed with the OLIS KINFIT (Bogart, GA, 1989) set of programs. ^{15}N NMR measurements were performed using a Bruker Avance DRX 400 WB spectrometer equipped with a superconducting BS-94789 magnet system at 40.56 MHz. ^{15}N chemical shifts were referenced externally to neat nitromethane. D_2O (99%) was used as a solvent for all NMR measurements.

Results and Discussion

Reaction of Sodium Dithionite with Iron Tetrasulfophthalocyanine. The reaction of an excess of sodium dithionite with iron tetrasulfophthalocyanine, $Fe^{III}(TSPc)^{3-}$, is accompanied by two consecutive color changes. The first is a very fast change from green to blue. An intense absorption maximum appears at 671 nm (Figure 1). This spectrum is essentially identical to that reported[11] for $Fe^{II}(TSPc)^{4-}$. The rate of reduction of the Fe^{III} complex was found to show a linear dependence on the dithionite concentration (Supporting Information Figure S1; the data recorded were limited by the dead time of the stopped-flow instrument at higher dithionite concentrations and temperatures), i.e.,

$$k_{obsd1} = k_1[S_2O_4^{2-}] \tag{1}$$

The value of k_1 at pH 8.06 and 25 °C is (2.63 ± 0.09) × 10^{-3} M^{-1} s^{-1}. The first-order dependence on dithionite concentration indicates that direct reduction of $^-$ by $S_2O_4^{2-}$ occurs and does not involve the monomeric species SO_2^- formed in reaction 2. Further mechanistic information can

$$S_2O_4^{2-} \rightleftarrows 2SO_2^- \tag{2}$$

be obtained from the thermal activation parameters which were determined from the Eyring plot over the temperature range 5−30 °C. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were found to be 46 ± 3 kJ mol^{-1} and +23 ± 11 J K^{-1} mol^{-1}, respectively. It is known that both $S_2O_4^{2-}$ and SO_2^-, in general, act as outer-sphere reductants.[19,20] Our data do not contradict this conclusion. Although such a reduction by $S_2O_4^{2-}$ is not common[21] (more frequently, the actual reductant is the sulfur dioxide anion radical SO_2^-), it occurs, for example, in ferricytochrome *c*,[22] $Fe(CN)_6^{3-}$,[23] and some Co^{III} complexes.[19]

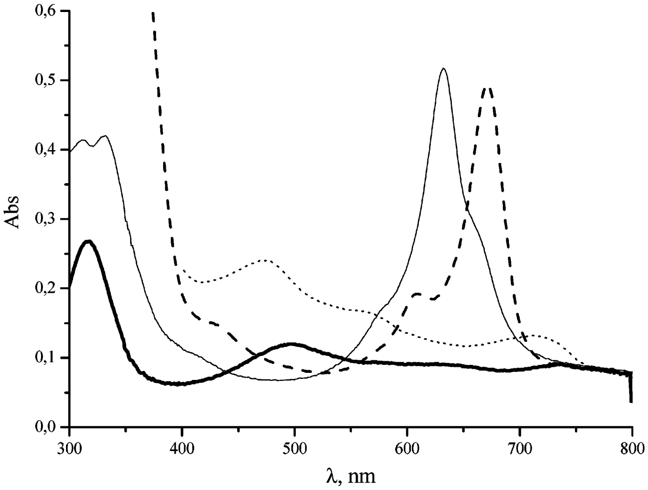


Figure 1. UV−vis spectra of $Fe^{III}(TSPc)^{3-}$ (8.6 × 10^{-6} M, solid line), $Fe^{II}(TSPc)^{4-}$ (8.6 × 10^{-6} M, dashed line), $Fe^{I}(TSPc)^{5-}$ (6.2 × 10^{-6} M, dotted line), and $Fe^{I}(TSPc^{\bullet})^{6-}$ (4.3 × 10^{-6} M, thick solid line) at pH 13 (0.1 M KOH).

The second reduction step is accompanied by a color change of the solution from blue to brown and is much slower than the first. Absorbance maxima at 480 and 712 nm appear with simultaneous disappearance of the maximum at 671 nm (Figure 1). This spectrum is very close to that reported for Fe^{I} tetrasulfophthalocyanine.[11] The rate of reduction of the Fe^{II} complex determined from the increase in the absorbance at 480 nm depends linearly on $[S_2O_4^{2-}]^{0.5}$ (Supporting Information Figure S2). This observation shows

---

(16) Makarov, S. V.; Kudrik, E. V.; van Eldik, R.; Naidenko, E. V. *J. Chem. Soc., Dalton Trans.* **2002**, 4074.
(17) Weber, J. N.; Busch, D. H. *Inorg. Chem.* **1965**, *4*, 469.
(18) (a) van Eldik, R.; Palmer, D. A.; Schmidt, R.; Kelm, H. *Inorg. Chim. Acta* **1981**, *50*, 131. (b) van Eldik, R.; Gaede, W.; Wieland, S.; Kraft, J.; Spitzer, M.; Palmer, D. A. *Rev. Sci. Instrum.* **1993**, *64*, 1355.
(19) Mehrotra, R. N.; Wilkins, R. G. *Inorg. Chem.* **1980**, *19*, 2177.
(20) Tobe, M. L.; Burgess, J. *Inorganic Reaction Mechanisms*; Longman Inc.: New York, **1999**; p 475.
(21) Tsukahara, K.; Wilkins, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2632.
(22) Lambeth, D. O.; Palmer, G. *J. Biol. Chem.* **1973**, *248*, 6095.
(23) Scaife, C. W. J.; Wilkins, R. G. *Inorg. Chem.* **1980**, *19*, 3244.

that the reduction process is consistent with eq 3, where k_2 is the second-order rate constant for the reaction of SO_2^-

$$k_{obs2} = k_2K^{0.5}[S_2O_4^{\ 2-}]^{0.5} \qquad (3)$$

with the Fe^{II} complex and K is the equilibrium constant for dissociation of $S_2O_4^{2-}$ (reaction 2, viz., 1.4 × 10^{-9} M at 25 °C).[21] Using the values of k_{obs2} and K, a rate constant, k_2, can be estimated from the dependence of k_{obs2} on $[S_2O_4^{2-}]^{0.5}$ (Supporting Information Figure S2): $k_2 = 225 \pm 18\ M^{-1}\ s^{-1}$ at 25 °C. To the best of our knowledge, this is the first time the rate constant for the reduction of the Fe^{II} complex by the SO_2^- anion radical to the corresponding Fe^I complex has been determined.

Reaction of Sulfoxylate with Iron Tetrasulfophthalocyanine. The use of sulfoxylate as a reductant leads to substantial changes in the reaction. It should be noted that “aged” alkaline solutions of TDO were used to produce sulfoxylate (herein, the term aged means solutions stored for 4−24 h in 0.1 M NaOH under anaerobic conditions).[16] This provides a possibility to prevent the influence of the decomposition of TDO to sulfoxylate (HSO_2^- or SO_2^{2-}) and urea and to study the reaction of sulfoxylate with $Fe^{III}(TSPc)^{3-}$. The N-containing product of TDO decomposition, viz., urea,[24] does not affect the redox process. Importantly, in the case of sulfoxylate, the reaction does not stop with the Fe^I complex as the final product. After the appearance of the absorption maxima at 480 and 712 nm (Fe^I complex), the red shift of the first and the gradual disappearance of the second maxima are observed (the final spectrum is shown in Figure 1). The color of the solution turns red. Because the rates of formation and reduction of the Fe^I complex differ substantially (Supporting Information Figure S3), it is possible to study them independently using the absorption maximum at 712 nm.

The kinetics of reduction of iron tetrasulfophthalocyanine by sulfoxylate was studied in 0.1 M NaOH under pseudo-first-order conditions with an excess of sulfoxylate. The reduction of the Fe^{III} complex proceeds very quickly and could not be studied using stopped-flow techniques. The rates of both subsequent reactions ($Fe^{II}(TSPc)^{4-}$ to $Fe^I(TSPc)^{5-}$ and $Fe^I(TSPc)^{5-}$ to $Fe^I(TSPc^{\bullet})^{6-}$) depend linearly on the concentration of sulfoxylate (Supporting Information Figures S4 and S5) because sulfoxylate is the only sulfur-containing product of the decomposition of TDO in deoxygenated, strongly alkaline solutions.[16] Because it is stable in these solutions, its concentration is assumed to be equal to the initial concentration of thiourea dioxide. For reduction of the Fe^{II} complex, the following thermal activation parameters were found: $\Delta H^{\neq} = 62 \pm 3$ kJ mol^{-1} and $\Delta S^{\neq} = -21 \pm 8$ J K^{-1} mol^{-1} (Supporting Information Figure S6). The volume of activation was determined from the pressure dependence of the rate constant ($\Delta V^{\neq} = -12 \pm 2$ cm^3 mol^{-1}, Figure 2). The small negative value of $\Delta S^{\neq}$ and the large negative value of $\Delta V^{\neq}$ suggest an associative process (A or I_a mechanism) presumably due to inner sphere reduction of the Fe^{II} complex, in which the associative attack of the strong SO_2^{2-} nucleophile on the electron-deficient Fe^{II} center is the rate-determining step. For reactions between Fe^{II} complexes with porphyrin-like ligands and weak nucleophiles, for example, water, pyridine, and pyrazine, a dissociative mechanism was observed.[25,26] Our data show that, in the case of a strong nucleophile such as sulfoxylate, an associatively induced redox mechanism operates.

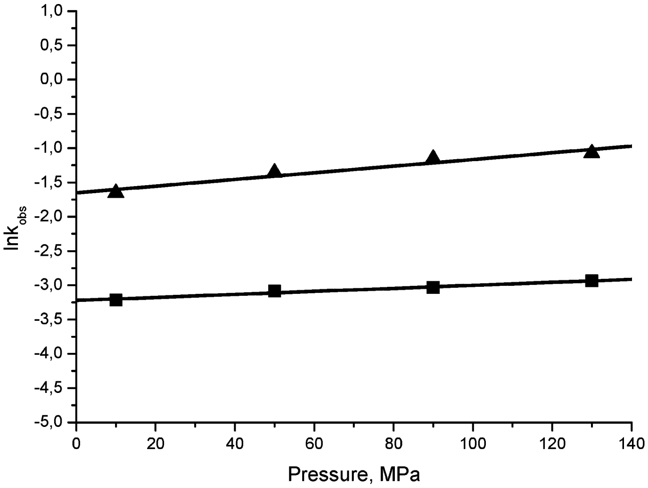


Figure 2. Plots of ln k_{obs1} and ln k_{obs2} vs pressure for the reaction between $Fe^{II}(TSPc)^{4-}$ and sulfoxylate: triangles represent the first stage, and squares represent the second stage at pH = 13 (0.1 M KOH). Best fits of the data (lines) give $\Delta V^{\neq}_1 = -12 \pm 2$ and $\Delta V^{\neq}_2 = -5.5 \pm 0.6$ cm^3 mol^{-1}.

For reduction of the Fe^I complex, both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ have substantially higher values (104 ± 2 kJ mol^{-1} and −139 ± 5 J K^{-1} mol^{-1}, respectively; see Supporting Information Figure S7) than those for the reduction of Fe^{II}. The value of $\Delta V^{\neq}$ is -5.5 ± 0.6 cm^3 mol^{-1} (Figure 2). The small negative value of $\Delta V^{\neq}$ can seemingly be explained by solvation effects because the transition state has a larger negative charge and, as a consequence, is more effectively solvated. These data show that the change in the iron redox state leads to drastic changes in the mechanism of reduction. Indeed, the increase in the overall negative charge on the iron complex leads to stronger electrostatic repulsion with negatively charged sulfoxylate. Fe^I, itself, has a large negative charge; therefore, the attack by nucleophilic sulfoxylate will be difficult. In addition, $Fe^I(TSPc)^{5-}$, being a low-spin complex,[11] has a low reactivity in ligand substitution reactions. Thus, the data mentioned above show that the most plausible mechanism for the reaction between the Fe^I complex and sulfoxylate is an outer-sphere electron transfer from sulfoxylate to the tetrasulfophthalocyanine ligand.

Reaction of Sodium Dithionite with Sodium Nitrite in the Presence of Iron Tetrasulfophthalocyanine. The catalytic reaction was studied at 315 nm for $[NaNO_2] \gg [Na_2S_2O_4]$ (direct reaction between dithionite and nitrite does not proceed with measurable rates in alkaline solutions at 15−50 °C).[16] Although nitrite also absorbs at 315 nm, its

---

(24) Svarovsky, S. A.; Simoyi, R. H.; Makarov, S. V. *J. Chem. Soc., Dalton Trans.* **2000**, 511.

(25) Kudrik, E. V.; van Eldik, R.; Makarov, S. V. *Dalton Trans.* **2004**, 429.

(26) (a) Pennesi, G.; Ercolani, C.; Ascenzi, P.; Brunori, M.; Monacelli, F. *J. Chem. Soc., Dalton Trans.* **1985**, 1107. (b) Brunori, M.; Pennesi, G.; Ercolani, C.; Monacelli, F. *J. Chem. Soc., Dalton Trans.* **1990**, 105.

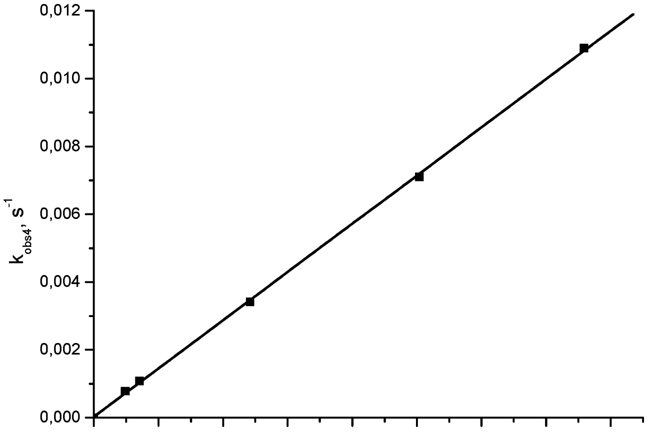


Figure 3. Plot of k_{obs4} vs $[NO_2^-]^2$ for the reaction between sodium dithionite and sodium nitrite in the presence of $Fe^{II}(TSPc)^{4-}$ (4.3×10^{-6} M). Experimental conditions: 0.1 M TRISINE buffer, pH = 8.06, 25 °C, $[S_2O_4^{2-}] = 2.8 \times 10^{-4}$ M.

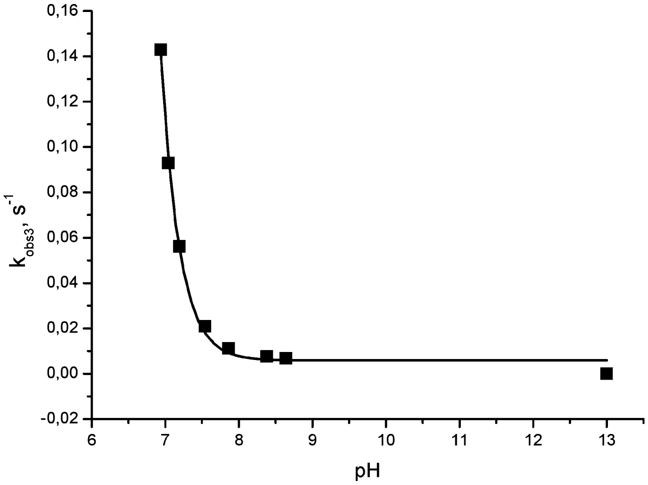


Figure 4. pH dependence of the rate of nitrite (0.056 M) reduction by dithionite (3×10^{-4} M) in the presence of $Fe^{II}(TSPc)^{4-}$ (4.3×10^{-6} M). Experimental conditions: 25 °C, 0.1 M BIS-TRIS buffer (pH 7−7.5), 0.1 M TRISINE buffer (pH 7.6−8.7), and 0.1 M KOH (pH 13).

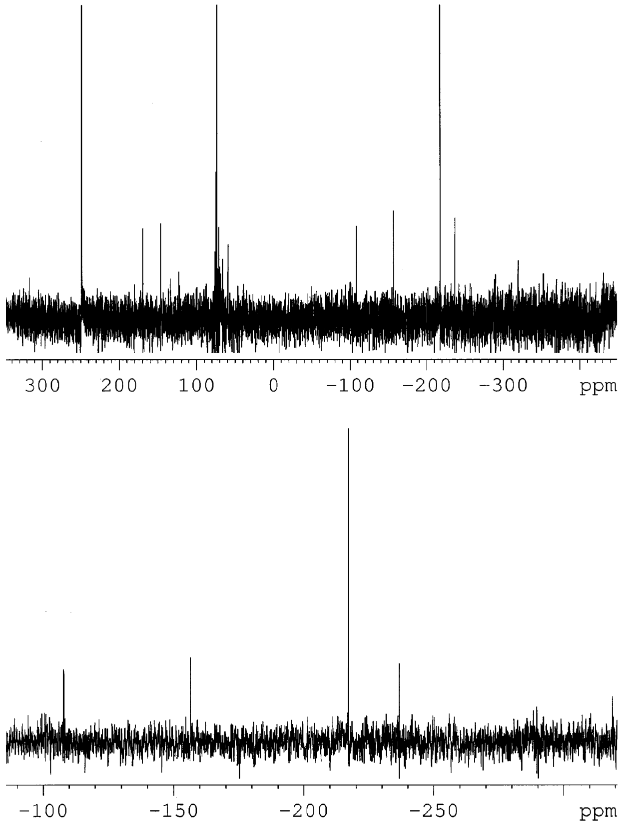


Figure 5. ^{15}N NMR spectrum of the products of the reaction between sodium dithionite and an excess of $Na^{15}NO_2$ in 0.5 M NaOD in D_2O in the presence of $Fe^{III}(TSPc)^{3-}$ (1×10^{-3} M).

molar absorbance coefficient (11 M^{-1} cm^{-1}) is much lower than that for dithionite[27] (8043 M^{-1} cm^{-1}). Because $NaNO_2$ was used in excess, changes in its absorbance at 315 nm during the reaction are negligible. Therefore, the observed decrease in absorbance at 315 nm is associated with a decrease in the dithionite concentration (Supporting Information Figure S8). The rate of the reaction depends linearly on $[NaNO_2]^2$ (Figure 3). Therefore, the overall reaction for nitrite reduction by dithionite may be written as

$$S_2O_4^{2-} + 2NO_2^- \rightarrow 2SO_3^{2-} + 2NO \qquad k_4 \qquad (4)$$

Importantly, under the same conditions, the catalytic reduction of nitrite proceeds much faster than the reduction of the Fe^{II} complex by dithionite (Supporting Information Figure S8). Thus, reduction of Fe^{II} to Fe^{I} tetrasulfophthalocyanine does not play an important role in the catalytic reduction of nitrite.

The pH dependence of the observed rate constant is shown in Figure 4. The data indicate that the reaction is substantially accelerated in more acidic media. Unfortunately, we could not determine the pK_a value of coordinated nitrite nor the rate constant for reduction of protonated nitrite because, in acidic media, dithionite is unstable and decomposes autocatalytically.[28] However, the data in Figure 4 show that, as in the case of $Co^{II}(TSPc)^{4-}$,[13] the most plausible role of the catalyst is to shift the reaction into a more alkaline pH range, i.e., to increase the pK_a of the conjugated acid of the nitrite coordinated to the metal center.

The analysis of the reaction products has been performed using ^{15}N NMR spectroscopy. In the ^{15}N NMR spectra (see Figure 5), four new signals were observed at 164, −156.3, −217.1, and −236.5 ppm. The first signal corresponds to coordinated nitrite, the second and fourth correspond to N_2O (nitrous oxide has signals at −147.3 and −237.0 ppm in the gas phase),[29] and the most intense, third signal seemingly corresponds to the nitrosyl complex of $Fe^{II}(TSPc)^{4-}$. The presence of N_2O signals and the absence of signals corresponding to free or coordinated ammonia (they are located in the −280 to −400 ppm region)[13,30] show that the reaction of nitrite with dithionite catalyzed by iron tetrasulfophthalocyanine proceeds with formation of nitrous oxide, which differs drastically from the reaction catalyzed by Co^{II}TSPc.[13]

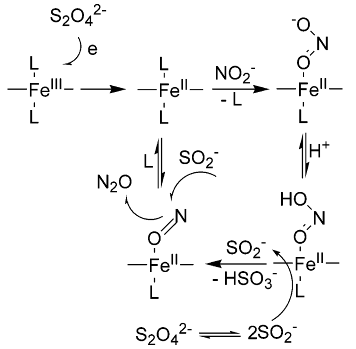
---

[27] McKenna, C. E.; Gutheil, W. G.; Song, W. *Biochim. Biophys. Acta* **1991**, *1075*, 109.

[28] Cermak, V.; Smutek, M. *Collect. Czech. Chem. Commun.* **1975**, *40*, 3241.

[29] Mastickhin, V. M.; Mudrakovsky, I. L.; Filimonova, S. V. *Chem. Phys. Lett.* **1988**, *149*, 175.

Scheme 1



The most plausible explanation for this is the difference in the structure of the intermediate complex formed between $Fe^{II}(TSPc)^{4-}$ or $Co^{I}(TSPc)^{5-}$ and the substrate, in which nitrite is suggested to coordinate via oxygen and nitrogen, respectively. Although, in iron porphyrin complexes, nitrite always binds through the nitrogen atom to form nitro complexes,[31] O-coordination of nitrite is known for iron complexes with a ligand such as tris(3,5-dimethylpyrazolyl)borate,[32] as well as for ruthenium and manganese porphyrin systems.[31] Unfortunately, so far no structural information on metallophthalocyanine complexes with nitrite has been reported. However, because phthalocyanines are known to be stronger electron acceptors than porphyrins, it is reasonable to assume that, in the complex of $Fe^{II}(TSPc)^{4-}$ with NO_2^-, coordination via oxygen occurs. The overall scheme for catalytic reduction of nitrite by dithionite may be formulated as shown in Scheme 1. It should be noted that dithionite dissociates into $2SO_2^-$ and therefore requires two catalytic cycles with nitrite for each dithionite molecule, which results in the square dependence observed for the nitrite concentration.

Reaction of Sulfoxylate with Nitrite in the Presence of Iron Tetrasulfophthalocyanine. It is known that sulfoxylate slowly reduces nitrite to nitrous oxide and dinitrogen in strongly alkaline solutions.[16] The presence of iron tetrasulfophthalocyanine leads to substantial changes in the reaction mechanism, as manifested by significant changes in the observed reaction products. The results of ^{15}N NMR studies show that the final product of the catalytic reduction of nitrite is ammonia (signal at −362 ppm; Figure 6). The ^{15}N NMR spectra in Figure 6 also indicate the formation of an intermediate at −130 ppm, which could be due to coordinated hydroxylamine, the most stable intermediate in this reaction. Contrary to reduction by dithionite, the color of the reaction mixture during the course of the catalytic reaction of nitrite and sulfoxylate is brown (Fe^{I} complex) and not blue (Fe^{II} complex). This observation indicates that, because sulfoxylate reduces Fe^{II} to Fe^{I} rapidly (see above), the latter species participates in the catalytic cycle (i.e., further reduction of the Fe^{I} complex proceeds slowly; see below). It should be noted that, in the absence of the catalyst, sulfoxylate very slowly reduces nitrite to N_2, whereas in the presence of the catalyst, nitrite is reduced to NH_3. Furthermore, no spectral changes are observed during the catalytic cycle. If all of the sulfoxylate reacts with the excess of nitrite, then the Fe(II) complex is formed. However, the UV−vis spectra are not that characteristic because of the interference of other potential nucleophiles present in the solution. It can therefore be concluded that the mechanism of catalytic reduction by sulfoxylate in the presence of the iron complex is very similar to the reduction by dithionite in the presence of $Co^{II}(TSPc)^{4-}$. In both cases, the final product is ammonia. Consequently, it is reasonable to assume that, in the intermediate complexes, nitrite coordinates via nitrogen.

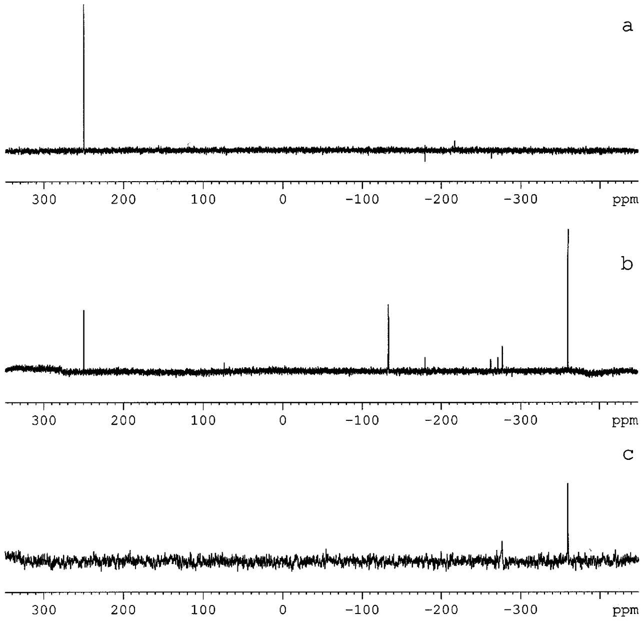


Figure 6. ^{15}N NMR monitoring of the reduction of $Na^{15}NO_2$ with an excess of sulfoxylate in 0.5 M NaOD in D_2O in the presence of $Fe^{III}(TSPc)^{3-}$ (1×10^{-3} M) at pH 13.6. (a) After addition of thiourea dioxide to the solution (1196 scans). (b) After 26 h (2500 scans). (c) After 65 h (986 scans).

From a comparison of the results for reduction by dithionite and sulfoxylate, it should be noted that, because protonated sulfoxylate (HSO_2^-) can disproportionate in weakly alkaline solutions,[33] we could not study its reactions at pH 10 as in the case of dithionite. Therefore, the influence of the pH of the solutions used for reduction by dithionite and sulfoxylate cannot be excluded completely. Because iron(II) phthalocyanine forms a relatively stable complex with NO,[34] we assume that nitric oxide undergoes an inner-sphere reduction reaction. The overall scheme for the catalytic reduction of nitrite by sulfoxylate may be written as shown in Scheme 2.

Unfortunately, we could not study the detailed kinetics of the catalytic reaction between sulfoxylate and nitrite because of its complexity. Not only sulfoxylate but also the product of its one-electron oxidation, the anion radical SO_2^-, can

---

(30) (a) Martin, G. J.; Martin, M. L.; Gouesnard, J.-P. *^{15}N NMR Spectroscopy*; Springer-Verlag: Berlin, Heidelberg, Germany, 1981; 382 pp. (b) Anderson, L.-O.; (Banus) Mason, J.; van Bronswijk, W. *J. Chem. Soc. A* **1970**, 296. (c) Chen, Y.; Lin, F.-T.; Shepherd, R. E. *Inorg. Chem.* **1999**, *38*, 973.

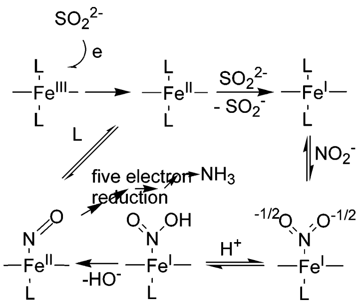
(31) Wyllie, G. R. A.; Scheidt, W. R. *Chem. Rev.* **2002**, *102*, 1067.

(32) Arulsamy, N.; Bohle, D. S.; Hansert, B.; Powell, A. K.; Thomson, A. J.; Wocaldo, S. *Inorg. Chem.* **1998**, *37*, 746.

(33) Makarov, S. V. *Russ. Chem. Rev.* **2001**, *70*, 885.

(34) Ascenzi, P.; Fruttero, R.; Ercolani, C.; Monacelli, F. *Analysis* **1996**, *24*, 316.

Scheme 2



participate in the reaction (see above). Besides this, at least three possibly catalytically active species are simultaneously present in solution.

Reaction of $Fe^I(TSPc^•)^{6-}$ with Nitrite. A very interesting aspect of the use of sulfoxylate is the possibility to study the reaction between nitrite and $Fe^I(TSPc^•)^{6-}$. The latter species is of special interest for the activation of small molecules such as CO_2.[11] It should be noted, however, that $Fe^I(TSPc^•)^{6-}$ has been much less studied than $Fe^I(TSPc)^{5-}$, possibly because of difficulties encountered with its synthesis via chemical methods in aqueous solution. In a known chemical procedure, sodium in tetrahydrofuran is used as the reductant.[11] The only known method used for reduction of $Fe^I(TSPc)^{5-}$ to $Fe^I(TSPc^•)^{6-}$ in aqueous solution is radiolysis.[11] Therefore, the use of sulfoxylate (thiourea dioxide) is a promising method for chemical synthesis of highly reduced forms of metallophthalocyanines. To prepare $Fe^I(TSPc^•)^{6-}$, a 3−4-fold excess of sulfoxylate was added to iron tetrasulfophthalocyanine and stored for 3 h under anaerobic conditions until the color changed from brown to red. After that, the deoxygenated solution of nitrite was mixed with the solution of $Fe^I(TSPc^•)^{6-}$. All experiments were performed in 0.1 M NaOH. Rate constants were determined from the decrease in absorbance at 500 nm. Because the reaction of sulfoxylate with $Fe^I(TSPc)^{5-}$ proceeds approximately 6 times slower than the reaction of $Fe^I(TSPc^•)^{6-}$ with nitrite (rate constants at 25 °C are 255 ± 18 and 1500 ± 23 $M^{-1}\ s^{-1}$, respectively; see Supporting Information Figures S4 and S5) and the ratio of $[NaNO_2]/[SO_2^{2-}]$ is ~100:1, the influence of the first reaction on the oxidation of $Fe^I(TSPc^•)^{6-}$ is negligible. Control experiments show that the direct reaction between sulfoxylate and nitrite proceeds very slowly and does not influence the oxidation of $Fe^I(TSPc^•)^{6-}$. It was found that rate constants depend linearly on the nitrite concentration (Figure 7). The reaction has relatively high positive activation enthalpy (87 ± 3 kJ mol^{-1}) and entropy (108 ± 11 J $K^{-1}\ mol^{-1}$) values (Supporting Information Figure S9). Unexpectedly, the reaction rate does not depend on the applied pressure ($\Delta V^{\neq} = 0.4 \pm 0.6$ $cm^3\ mol^{-1}$) (Supporting Information Figure S10). The absence of a kinetic saturation in the dependence of the observed rate constant on the nitrite concentration indicates that, if an intermediate complex between $Fe^I(TSPc^•)^{6-}$ and NO_2^- is formed, it is rather unstable. This is expected because both reactants, especially $Fe^I(TSPc^•)^{6-}$, are strong nucleophiles. Further difficulties are related to electrostatic problems (an overall large negative charge of −6 for the reduced iron complex and −1 for nitrite). Obviously, the observed kinetics may be explained in terms of an outer-sphere electron-transfer mechanism.

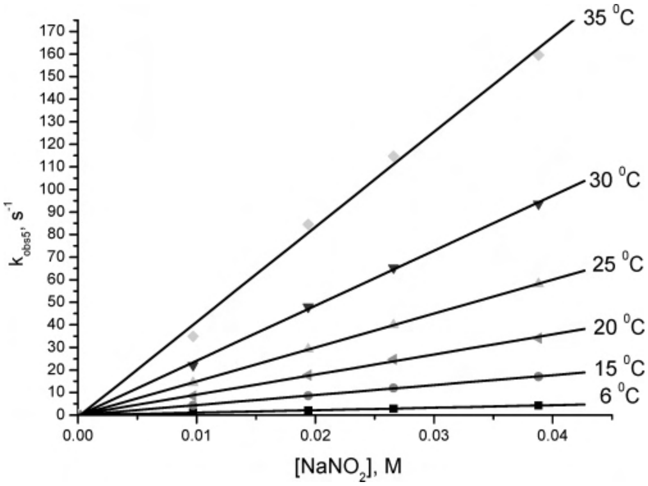


Figure 7. Plot of k_{obs5} vs $[NaNO_2]$ for the reaction between $Fe^I(TSPc^•)^{6-}$ and nitrite as a function of temperature. Experimental conditions: pH = 13 (0.1 M KOH), $[Fe^I(TSPc^•)^{6-}] = 4.3 \times 10^{-6}$ M.

Conclusions

Our results have shown that iron tetrasulfophthalocyanine is an effective catalyst for the reduction of nitrite by dithionite or sulfoxylate in aqueous solutions. In the case of dithionite, the catalytic cycle includes a reversible reaction, $Fe^{III} \rightleftarrows Fe^{II}$, and reduction of the coordinated substrate. Surprisingly, reduction of nitrite by dithionite in the presence of iron and cobalt tetrasulfophthalocyanines leads to the formation of different products, viz., nitrous oxide and ammonia, respectively. This finding suggests that differences in the structure of the intermediate complex determine the composition of the reaction products. In our opinion, in the case of $Fe^{II}(TSPc)^{4-}$, the unusual O-coordination of nitrite takes place contrary to N-coordination in the $Co^I(TSPc)^{5-} \rightarrow NO_2^-$ intermediate complex. Because sulfoxylate reduces the complex of Fe^{II} to Fe^I much faster than dithionite, the Fe^I complex participates in the catalytic cycle. The reaction of nitrite with sulfoxylate catalyzed by iron tetrasulfophthalocyanine proceeds very similarly to the reduction by dithionite in the presence of cobalt tetrasulfophthalocyanine. In both cases, the final product is ammonia, and in the intermediate complex, nitrite coordinates presumably via nitrogen. Thus, the valence state of the metal in the intermediate complex with nitrite determines the composition of the reaction products. Contrary to dithionite, sulfoxylate was shown to be able to reduce $Fe^I(TSPc)^{5-}$ to $Fe^I(TSPc^•)^{6-}$. The reaction is proposed to follow an outer-sphere electron-transfer process.

Acknowledgment. The authors gratefully acknowledge financial support from a NATO Collaborative Linkage grant (PST.CLG.979442) and a grant from the Russian Ministry of Education (E 02-5.0-345).

Supporting Information Available: Plots of reactions of sodium dithionite, sulfoxylate, and nitrite with $Fe^{III}(TSPc)^{3-}$, $Fe^{II}(TSPc)^{4-}$, $Fe^I(TSPc)^{5-}$, and $Fe^I(TSPc^•)^{6-}$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0505955