

MECHANISM OF THE COBALT PHTHALOCYANINE-CATALYZED AUTOXIDATION OF ALIPHATIC THIOLS

E. I. Kozliak, A. Navid, Chemistry Dept., University of North Dakota, Grand Forks, ND 58202.

Keywords: cobalt phthalocyanines, autoxidation of thiols, Mercox process

INTRODUCTION

Cobalt phthalocyanine (CoPc)-catalyzed autoxidation of thiols to disulfides has been used for the deodorization of oil distillates and exhaust gases in the fuel industry (1):



The mechanism of this reaction is known to include the formation of a ternary complex of CoPc with both substrates: the thiolate-ion (RS^-) and molecular oxygen (1-5). Based on the results of our kinetic studies of cobalt tetrasulfophthalocyanine (CoTSPc)-catalyzed autoxidation of cysteine, we suggested that two thiolates and one oxygen may be bound by one molecule of CoPc to comprise the intermediate ternary complex (5). This hypothesis may be summarized by the kinetic scheme presented on Fig. 1.

In this paper we address the elucidation of the nature of the second thiolate binding to CoTSPc as well as the oxidation state of cobalt in the proposed intermediates. Association of CoTSPc occurring in the aqueous media (6) is not considered here since we have presented evidence that this phenomenon does not appear to affect the mechanism of reaction (1) (5).

EXPERIMENTAL

CoTSPc was synthesized as described by Weber and Busch (7), with minor modifications in purification. Initial reaction rates were measured by the oxygen consumption, which was monitored by one of two methods: amperometrically at a fixed potential of -0.6 V using a self-made Clark oxygen electrode, and also using an Intech oxygen monitoring system connected to a Gateway computer. The catalytic reaction rate was calculated as a difference between the rates of oxygen consumption with and without CoTSPc. All experiments were carried out at 25°C in 0.1 M sodium borate (for pH 9.0-12.2) or phosphate buffer (for pH 7.8-9.5); the reaction rates in different buffers for overlapping values of pH were similar within the margin of the experimental error. 0.5 M sodium perchlorate was added to all solutions to assure the constancy of the ionic strength. Spectral studies were conducted using a self-made evacuated cuvet on two spectrophotometers: Beckman-3600 and Shimatsu-260; the two devices gave comparable results. Before mixing, solutions of reagents (CoTSPc and a thiol) were frozen a few times by liquid nitrogen followed by the removal of the air and thawing the samples. Reactive grade reagents were used without purification.

RESULTS AND DISCUSSION

Binding of thiolate-ions by CoTSPc. Reaction of CoTSPc with low concentrations of cysteine (10^{-4} - 10^{-2} M) in anaerobic conditions results in the appearance of new bands at 450 and 643 nm. Previously this spectrum was believed to be that of the plain reduced Co(I)TSPc (8). Now we report that this is not quite true. Whereas the band at 450 nm is, indeed, characteristic for any reduced complex of Co(I)TSPc, regardless of the reducing agent used, the band at 640-650 nm turned out to be specific only for thiols (cysteine, mercaptoethanol, sodium hydrosulfide, and ethyl mercaptan have been tested). The spectra of CoTSPc with different concentrations of cysteine are provided on Fig. 2, curves 1-5). CoTSPc reduced by other reducing agents [hydrazine at pH 13, NaBH_4 , or Cr(II)] adsorbs light at 680 nm (Fig. 2, curve 8). Upon increasing the cysteine concentration to $5 \cdot 10^{-1}$ M at pH 9.5, the difference in spectra for different reduced forms of CoTSPc disappears (Fig. 2, curves 6-8). This points to a successive binding of two thiolate molecules to CoTSPc. The stability constants found from the data of Fig. 2 are $1.7 \cdot 10^4 \text{ M}^{-1}$ and 52 M^{-1} ; they correspond, respectively, to K_1 and K_5 from the suggested kinetic scheme [Fig. 1, equations (1') and (3')].

Analysis of the adsorption at 450 nm shows that binding of the first thiolate is accompanied only by a partial reduction of Co(II)TSPc, whereas the second thiolate binding

results in its quantitative reduction to Co(I)TSPc (see Fig. 2). Perhaps, this is related to an increase of the electron density on the cobalt ion upon the binding of the second basic thiolate ligand. It is logical to suggest that even more basic hydroxyl anion would cause the same effect. Indeed, at pH 12.2 the absorbance at 450 nm, reflecting the reduction of Co(II) to Co(I), is much higher than at pH 9-11.5 (Fig. 3) for any non-saturating concentration of cysteine. Actually, at pH 12.2 even as low as 10^{-2} M cysteine reduces Co(II) as efficiently as 10^{-1} M cysteine at lower pH, and at $5 \cdot 10^{-2}$ M cysteine at pH 12.2 the reduction is complete (not shown). This phenomenon cannot be ascribed to the deprotonation of the amino group of cysteine since the threshold pH value 12.2 is much higher than the pK_a of the amino group [10.36 (2)]. We assumed that pH 12 appears to be the pK_a of deprotonation of the water molecule coordinated to cobalt in the monothiolate complex, $(RS^-)Co(II)TSPc(H_2O)$.

There are other indications that pH 12 is a threshold value for the reduction of Co(II)TSPc. It is known that hydrazine and hydroxylamine reduce Co(II)TSPc only at $pH > 11.7$, and their autoxidation occurs only at those high values of pH (9,10). In the absence of reducers in aerobic conditions, the binuclear adducts of CoTSPc with hydroxyl anion and oxygen are formed only at $pH > 12$ (6). It was also shown that in the water-DMF system the coordination of hydroxyl anion to CoTSPc in anaerobic conditions results in the reduction of Co(II) to Co(I); in aerobic conditions the labile oxygen adduct is formed (11). In aqueous solutions, hydroxyl anion itself does not reduce Co(II)TSPc. Perhaps, the association of CoTSPc in aqueous solutions (6) interferes with the reduction of Co(II). However, despite this association, hydroxyl anion appears to reduce the monothiolate complex of Co(II)TSPc or other CoTSPc complexes with basic reducing ligands (hydrazine, hydroxylamine).

Kinetics of reaction (1) at different pH. The kinetic constants of CoTSPc-catalyzed autoxidation of cysteine at different pH are shown in Table 1. Comparison of binding constants of cysteine to CoTSPc obtained by kinetic and spectroscopic methods appears to confirm our hypothesis suggested in (5) that binding the first substrate molecule (K_1) does not show up in the kinetics because the concentration of thiolate is too high for any free CoTSPc to exist in the solution. Therefore, only the binding of the second thiol molecule shows up kinetically as K_5 , see Table 1 and Fig. 1.

Kinetic data also appear to confirm the presence of a critical point at $pH > 12$ for reaction (1) (Table 1). The value of K_5 is virtually not changed at pH 9-10 when the deprotonation of the amino group of cysteine occurs, but it drops at pH 12.2 along with the reaction rate. Leung and Hoffmann (4) and Shirai *et al.* (13) observed the drop of the rate of reaction (1) for other aliphatic mercaptans, such as mercaptoethanol, aminoethanol, and ethane thiol. Therefore, this drop seems to be an inherent feature of reaction (1) and does not depend on the presence of other functional groups in cysteine. This occurs at the same value of pH 12 as the reduction of the monothiolate Co(II)TSPc complex discussed above (see Fig. 3). Hydroxyl anion, therefore, may be considered a competitive inhibitor of this reaction. The word "competitive", however, does not necessarily mean the literal competition of the hydroxyl ion and thiol for the same binding site; it merely reflects the fact that binding of the hydroxyl anion results in a decrease of the second thiolate binding constant, K_5 . Apparently, the observed reduction of the monocysteinate CoTSPc complex by OH^- makes binding of the second electronodonor ligand, such as a thiol or thiolate, unfavorable.

In turn, the drop of K_5 would result in the first kinetic order with respect to a thiol in alkaline solutions ($pH > 12$) even for higher concentrations of the substrate (see kinetic equation (7') on Fig. 1). This indeed has been observed by Fomin *et al.* (14). In contrast, at lower pH, the order of reaction (1) with respect to the mercaptan should be 1 and 0 at low and high concentrations of the thiol, respectively, which has been observed in (4,5,15).

As mentioned above, the rate of reaction (1) drops at higher pH (Table 1). It may be explained in two ways: either the k_{cat} or binding constants of thiols drop above that pH, see kinetic equation (7') on Fig. 1. Both effects have been observed for the CoTSPc-catalyzed autoxidation of cysteine (Table 1). However, there are indications that the drop of k_{cat} at $pH > 9.5$ is specific for cysteine, whereas the decrease of the thiolate binding to CoTSPc at $pH > 12$ is a more general feature of the CoTSPc-catalyzed autoxidation of all aliphatic thiols. The drop of k_{cat} takes place at pH about 10, which is way below 12, and thus appears to be caused by the deprotonation of the amino group of cysteine [$pK_a = 10.36$ (2)]. This deprotonation may result in a non-productive binding of some cysteine (by the amino group), thus causing the observed drop of k_{cat} . Indeed, Skorobogaty and Smith (15) did not observe any drop of the rate of reaction (1) for mercaptoethanol (no amino group) while increasing pH up to 11.5 at saturation by the thiol (zero kinetic order), when the value of k_{cat} determines the rate of the reaction.

It is interesting that the values of the constant of cysteine binding to CoTSPc, K_S , obtained from kinetic data, slightly increase while pH is decreased in the interval of pH 7.8-10.0, see Table 1. It apparently means that the complex $(RS^-)CoTSPc(RSH)$ may be a little more stable than $(RS^-)_2CoTSPc$. That makes sense, because thiolates are much stronger electron donors than thiols, and the second thiolate binding to the electron-rich partially reduced monothiolate complex of CoTSPc may be slightly hindered even if this binding, as suggested below, takes place on the ligand.

Besides changes of K_S , there is one more kinetic parameter which is greatly affected by pH: parameter α . This parameter is actually the ratio of the oxygen binding constants of bis- and monocysteinate complexes (see equations 2' and 4' on Fig. 1). The question is: why the biscysteinate complex of CoTSPc is able to efficiently bind oxygen, especially at pH>12? It should have very low affinity to oxygen if the latter competes with the second cysteine for the second axial position of cobalt.

The most plausible explanation is the second thiolate binding is at least in part not coordinative and involves some weak interactions with the phthalocyanine ligand rather than with cobalt. Since the binding of the second thiolate results in the complete reduction of Co(II), one may assume that the RS radical formed may be shifted from cobalt into the ligand. A similar migration of the alkyl and acyl radicals was observed for alkyl- or acylcobalt(III) porphyrins by Dolphin *et al.* (12). The suggested non-axial binding of the second thiolate molecule may explain why the value of parameter α is not much less than 1 at all studied values of pH (Table 1); in other words, the second thiolate does not appear to be much in the way of the oxygen.

Let us consider the pH-dependence of α . Binding of the thiol should not contribute in the oxygen binding as much as that of the thiolate; perhaps, this is why α gets slightly lower when pH decreases within the range 7.8-10. One question remains to be answered: why the value of α sharply increases at pH 12.2? It appears to be related to the above suggested deprotonation of the water molecule coordinated to cobalt. Unfortunately, in contrast to the binding of cysteine, we have no spectral data to discuss the binding of oxygen to CoTSPc; ternary thiolate-oxygen complexes of CoTSPc are unstable in aqueous media. We may only speculate that at pH>12 the monocysteinate complex appears to have hydroxyl anion as the second axial ligand, and it may result in a poorer oxygen binding by this complex than at lower pH. So, perhaps, the axially bound hydroxyl ion slightly hinders the oxygen binding by the monothiolate CoTSPc complex (although it is not a big obstacle, the value of K_O at pH 12.2 is only slightly lower, see Table 1). However, the binding of the second thiolate increases the electron density on cobalt, thus forcing the OH⁻ out and facilitating the binding of the electron-acceptor oxygen molecule. The combination of those effects may result in the observed increase of α at pH 12.2, although this effect needs to be further studied.

Evidence of the hydrophobic binding of thiols to CoPc. Thus far we have considered the binding of the thiolates or thiols to CoTSPc only through coordination by their sulfur atoms. However, it is possible that hydrophobic interactions of the phthalocyanine ligand with the R group of a thiol may play some role in the substrate binding. Fomin *et al.* (14) studied the cobalt disulfophthalocyanine (CoDSPc)-catalyzed autoxidation of aliphatic thiols in very alkaline solutions (0.1 M sodium hydroxide). They found that longer-chain mercaptans are oxidized much faster, and tried to explain it by the electronic and steric effects. However, both of these effects appear to be insufficient to account for the significant increase of reaction (1) rates observed with the elongation of the carbon chain. The switch of the methyl group in the RSH to the ethyl group would result in the biggest inductive effect, and the subsequent addition of each methylene group would result in much less prominent changes. However, the observed effect is just the opposite (Table 2). This phenomenon may alternatively be explained by the binding of the R groups of thiols (RSH) or thiolates (RS⁻) to the hydrophobic region of the phthalocyanine ligand. In contrast with electron effects, the hydrophobic binding would become more tenacious with addition of each methylene group, as it was observed in (14), see Table 2. We obtained a good correlation between the values of the observed first-order reaction rate constants for RSH from (14) and the distribution coefficients of the corresponding alcohols (ROH) in the system octanol-water [(16), Table 2]. Since at pH above 12 the first-order kinetics with respect to the thiol have been observed (14), the effective first-order kinetic constant should include K_S and be proportional to any factor affecting binding of the thiol, including its hydrophobicity. This is one more indication that the binding of one of the thiol molecules to CoTSPc appears to be non-coordinative.

PRACTICAL CONCLUSION

The Merox process of the removal of mercaptans from oil fractions consists of the extraction of mercaptans by alkaline solutions followed by the CoPc-catalyzed autoxidation of the mercaptides in the aqueous phase (1). For both processes the high concentrations of NaOH were considered optimal (1,17). However, we assumed that the increase of the rate of reaction (1) upon the addition of the extra sodium hydroxide observed in (17) may be irrelevant to the change of pH and may be accounted for by an unusually high salt effect in reaction (1) (5). Since the increase of pH above 12 appears to result in a decrease of the reaction rate, it would make sense to actually decrease the pH after extraction, at the same time adding some salt, such as NaCl, instead of NaOH, in order to increase the efficiency of catalysis. Obviously, this assumption takes into account only the rate of reaction (1) and disregards possible negative consequences of lowering the pH, such as an increase of thiol volatility and a decrease of its solubility in water.

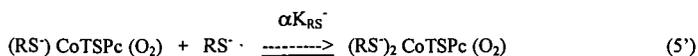
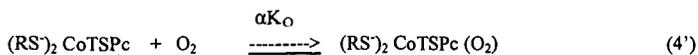
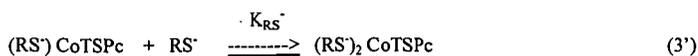
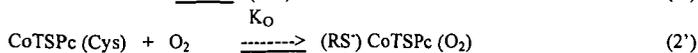
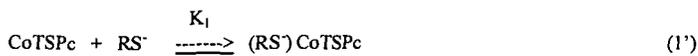
ACKNOWLEDGEMENTS

The authors thank Dr. A. K. Yatsimirsky (UNAM, Mexico) for valuable suggestions. The work was supported by NSF-EPSCoR through NSF grant # OSR-9452892.

REFERENCES

1. Basu, B.; Satapathy, S.; Bhatnagar A. K. *Catalysis Reviews*, **1993**, *35*, 571-609.
2. Dolinsky, J.; Wagnerova, D. M.; Veprek-Siska, J. *Coll. Czechoslovak. Chem. Commun.*, **1976**, *41*, 2326-2334.
3. Brouwer, W. M.; Piet, P.; German, A. L. *Journal of Molecular Catalysis*, **1984**, *22*, 297-308.
4. Leung, P.-S. K.; Hoffmann, M. R. *J. Phys. Chem.*, **1989**, *93*, 434-441.
5. Kozliak, E. I. *Preprints of ACS Division of Petroleum Chemistry*, **1996**, *41*, 628-631.
6. Gruen, L. C.; Blagrove, J. *Austral. J. Chem.*, **1973**, *26*, 319-325.
7. Weber, J. H.; Busch, D. H. *Inorganic Chemistry*, **1965**, *4*, 469-471.
8. Simonov, A. D.; Keyer, N. P.; Kundo, N. N.; Mamaeva, E. K.; Glazneva, E. V. *Kinetics and Catalysis (USSR)*, **1973**, *14*, 864-868.
9. Wagnerova, D. M.; Schwertnerova, E.; Veprek-Siska, J. *Coll. Czechoslovak. Chem. Commun.*, **1974**, *39*, 1980-1988.
10. Hong, A. P.; Chen, T.-C. *Environ. Sci. Technol.*, **1993**, *27*, 2404-2411.
11. Dubrovina, A. S.; Malkova, A. I.; Tupikov, V. I. *Coordination Chemistry (USSR)*, **1984**, *10*, 1207-1210.
12. Dolphin, D.; Halko, D. J.; Johnson, E. *Inorganic Chemistry*, **1981**, *20*, 4348-4351.
13. Shirai, H.; Tsiuki, H.; Masuda, E.; Koyama, T.; Hanabusa, K.; Kobayashi, N. *J. Phys. Chem.*, **1991**, *95*, 417-423.
14. Fomin, V. A.; Mazgarov, A. M.; Lebedev, N. N. *Petroleum Chemistry (USSR)*, **1979**, *18*, 298-306.
15. Skorobogaty, A.; Smith, T. D. *J. Mol. Catal.*, **1982**, *16*, 131-146.
16. Leo, A.; Hunch, C.; Elkins, D. *Chem. Rev.*, **1971**, *71*, 525-548.
17. Fomin, V. A.; Mazgarov, A. M. *Petroleum Chemistry (USSR)*, **1981**, *21*, 265-273.

Fig. 1. Suggested kinetic scheme of reaction (1).



Observed kinetic equation [obtained in (5)]:

$$v_0 = \frac{d[\text{O}_2]}{dt} = \frac{\alpha k_{\text{cat}} K_O K_{\text{Cys}} [\text{CoTSPc}] [\text{Cys}] [\text{O}_2]}{1 + K_O [\text{O}_2] + K_{\text{Cys}} [\text{Cys}] + \alpha K_O K_{\text{Cys}} [\text{Cys}] [\text{O}_2]} \quad (7')$$

Table 1. Kinetic parameters of reaction (1) at different pH

pH	K_O, M^{-1}	K_S, M^{-1}	α	$k_{\text{cat}}, \text{s}^{-1}$
7.8	$5.2 \cdot 10^4$	120	0.15	4.8
9.0	$2.7 \cdot 10^4$	90	0.33	9.4
9.5	$2.0 \cdot 10^4$	60	0.5	10.5
10.0	$3.5 \cdot 10^4$	80	0.6	4.6
12.2	$1.3 \cdot 10^4$	9	5.3	3.0

Table 2. Observed rate constants of CoDSPc-catalyzed autoxidation of alkyl mercaptides in 0.1 M aqueous solution at saturation with oxygen [k_{obs} (14)] vs. the distribution coefficient of the corresponding alcohol, ROH, between n-octanol and water, P_{ROH} (16).

Mercaptan	$k_{\text{obs}} \cdot 10^{-4}, \text{s}^{-1}$	P_{ROH}
Methyl thiol	0.9	0.2
Ethyl thiol	1.0	0.5
1-Propyl thiol	2.3	2.2
1-Butyl thiol	4.5	7.6
1-Pentyl thiol	11.7	29

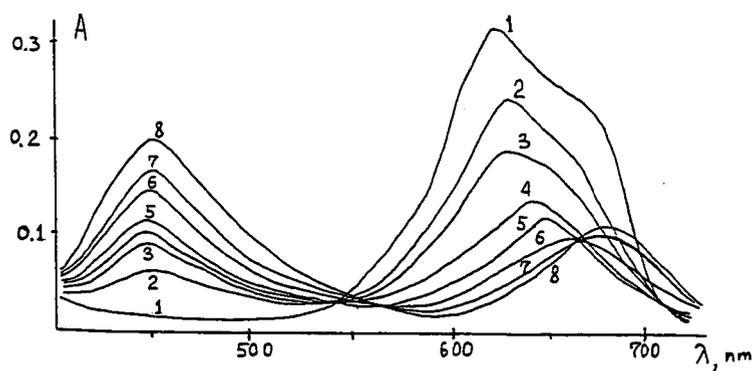


Fig. 2. Spectral changes occurring upon addition of the increased amounts of cysteine to the aqueous $8 \cdot 10^{-6}$ M solution of Co(II)TSPc in anaerobic conditions (pH 9.5, 0.1 M borate buffer, 0.5 M NaClO_4). 1. CoTSPc, no cysteine added; 2-7. Same solution with 10^{-4} , $2 \cdot 10^{-4}$, $5 \cdot 10^{-4}$, $5 \cdot 10^{-3}$, $5 \cdot 10^{-2}$, $5 \cdot 10^{-1}$ M cysteine, respectively; 8. Solution 1 with 10^{-2} M hydrazine, pH 13.

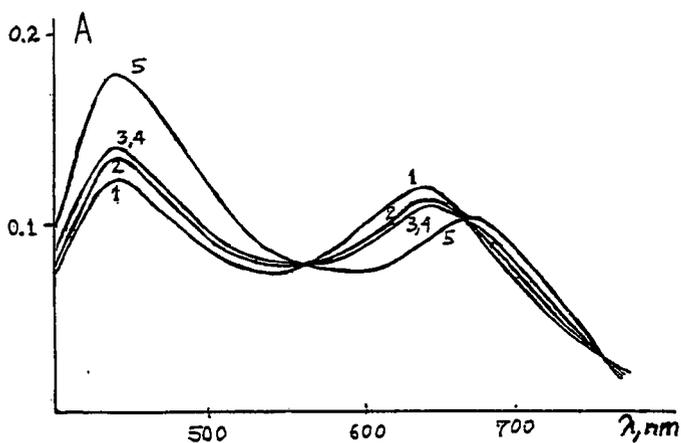


Fig. 3. Spectra of the complex of CoTSPc ($8 \cdot 10^{-6}$ M) with cysteine (10^{-2} M) at different pH: 1. 9.0; 2. 9.5; 3. 10.0; 4. 11.0; 5. 12.0, respectively.