

Kinetics and Mechanism of the Autoxidation of 2-Aminoethanethiol and Ethanethiol Catalyzed by Cobalt(II) 4,4',4'',4'''-Tetrasulfophthalocyanine in Aqueous Solution

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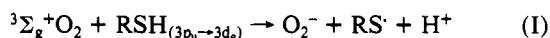
The kinetics of autoxidation of 2-aminoethanethiol to 2-aminoethyl disulfide and ethanethiol to ethyl disulfide as catalyzed by cobalt(II) 4,4',4'',4'''-tetrasulfophthalocyanine ($\text{Co}^{\text{II}}\text{TSP}$) were investigated. The following general rate law was found to hold for both substrates over the pH range 8.8–13.5: $\nu = -d[\text{RS}^-]/dt = k_{\text{obsd}}[\text{CoTSP}]_T[\text{RS}^-]$. Evidence for a mechanism that proceeds via a dimeric catalytic center that is bridged by the RS^- anion has been obtained. In the proposed mechanism, electron transfer from the $\text{Co}(\text{II})$ metal center to bound dioxygen was considered to be the rate-determining step. Hydrogen peroxide and mercaptan radical were identified as reaction intermediates in the autoxidation of both substrates. These intermediates react further to produce the corresponding disulfide, RSSR, as the final product of the autoxidation. k_{obsd} was found to be of the following general form: $k_{\text{obsd}} = (k_{31}K_{21} + (k_{32}K_{22}K'_1/a_{\text{H}^+}) + (k_{33}K_{23}K'_1K'_2/a_{\text{H}^+}{}^2))/[(1 + (K'_1/a_{\text{H}^+}) + (K'_1K'_2/a_{\text{H}^+}{}^2))(1 + (a_{\text{H}^+}/K'_1{}^2))]$, where k_{3i} and K_{2i} are the rate constants for the electron transfer and the equilibrium constants for substrate complexation of the i th catalytic center, respectively, K'_2 and K'_2 are the apparent acid dissociation constants of the pyrrole groups of $\text{Co}^{\text{II}}\text{TSP-RS}^-$ – $\text{Co}^{\text{II}}\text{TSP}$ and $\text{Co}^{\text{II}}\text{TSP-RS}^-$ – $\text{Co}^{\text{II}}\text{TSP}$, respectively, and K'_a is the apparent acid dissociation constant of $\text{RCH}_2\text{CH}_2\text{SH}$.

Introduction

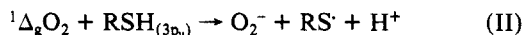
Autoxidation reactions of many inorganic and organic compounds are accelerated in the presence of first-row transition-metal ions and complexes in which the metal center has access to more than one stable oxidation state.^{1,2} A considerable amount of research has been directed toward determining the mechanisms of transition-metal catalysis in the reactions of O_2 with a wide variety of reduced sulfur compounds such as SO_2 ,³ H_2S ,⁴ and mercaptans, RSH ,⁵⁻⁸ in aqueous solution.

The catalytic properties of divalent and trivalent metal phthalocyanine, porphyrin, and Schiff base derivatives have been compared to those of catalase, peroxidase, oxidase, and oxygenase enzymes.⁹⁻¹³

The noncatalytic autoxidation of mercaptans¹⁴ may occur as follows:



or



In the first reaction, the half-filled π_g^* orbital of ground-state oxygen overlaps with an excited sulfur atom ($3p_u \rightarrow 3d_g$ transition) on the mercaptan, whereas in the second reaction, a direct overlap of empty π_g^* orbital of an excited single-state oxygen with the filled $3p_u$ orbital of the sulfur atom is required. However, both reactions have relatively large activation energies.

Cobalt(II) tetrasulfophthalocyanine ($\text{Co}^{\text{II}}\text{TSP}$) has been reported to be an effective catalyst for the autoxidation of 2-mercaptoethanol^{8,15} and cysteine.¹⁶ Simonov et al.¹⁷ proposed a linear free radical mechanism for the catalytic autoxidation of simple mercaptans, while Dolansky and Wagnerova⁵ have proposed an ordered ternary complex mechanism in which O_2 and RSH are simultaneously bound to the active catalytic center.

In our study⁸ of the autoxidation of 2-mercaptoethanol as catalyzed by $\text{Co}^{\text{II}}\text{TSP}$ we provided evidence for a mechanism that proceeds via a catalytic center that is bridged by the 2-mercaptoethanol anion. In the proposed mechanism, electron transfer from the $\text{Co}(\text{II})$ metal center to bound dioxygen was considered to be the rate-determining step, which was followed by the release of hydrogen peroxide and a mercaptan radical. These intermediates react further to produce disulfide, RSSR, as the final product of the autoxidation. Two additional 2-mercaptoethanol molecules are oxidized by H_2O_2 to give the disulfide. The kinetics and mechanism of the oxidation of 2-mercaptoethanol by H_2O_2 were also examined.¹⁸

The rapid catalytic autoxidation of 2-mercaptoethanol indicates that the $\text{Co}^{\text{II}}\text{TSP}$ should be an effective catalyst for the autoxidation of other mercaptans. Hence, we now report the results of our study on the kinetics and mechanism of the catalytic autoxidation of ethanethiol and 2-aminoethanethiol. Investigation of the kinetics of these substrates also allows us to explore the effect of substituents on the rates of autoxidation of $\text{RC}_2\text{H}_4\text{SH}$.

Experimental Procedures

Reagents. Reagent grade 2-aminoethanethiol (Aldrich 98%) was recrystallized twice before use, while ethanethiol (Aldrich 97%), which has a boiling point of 38 °C and an overwhelming odor detectable at the parts per trillion level, was used without further purification. Cobalt(II) 4,4',4'',4'''-tetrasulfophthalocyanine was synthesized according to the procedure described by Boyce et al.³ Buffers were prepared by using reagent grade sodium hydroxide (Mallinckrodt), sodium chloride (J. T. Baker), and sodium bicarbonate (Mallinckrodt). Purified water was obtained from a Milli-Q water purification system (Millipore) and had a resistivity of 18 MΩ cm. It was irradiated with intense UV light

(1) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidation of Organic Compounds*; Academic: New York, 1981.

(2) Hoffmann, M. R. *Environ. Sci. Technol.* **1980**, *14*, 1061.

(3) Boyce, S. D.; Hoffmann, M. R.; Hong, P. A.; Moberly, L. M. *Environ. Sci. Technol.* **1983**, *17*, 602.

(4) Hoffmann, M. R.; Lim, B. C. *Environ. Sci. Technol.* **1979**, *13*, 1406.

(5) Dolansky, J.; Wagnerova, D. M.; Veprek-Siska, J. *Collect. Czech. Chem. Commun.* **1976**, *43*, 2326.

(6) Schutten, J. H.; Zwart, J. J. *Mol. Catal.* **1979**, *5*, 109–123.

(7) Schutten, J. H.; Beelen, T. P. M. *J. Mol. Catal.* **1981**, *10*, 85–97.

(8) Leung, P. S.; Hoffmann, M. R. *Environ. Sci. Technol.*, in press.

(9) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139.

(10) Khan, M. M.; Martell, A. E. *Homogeneous Catalysis by Metal Complexes*; Academic: New York, 1974; pp 79–180.

(11) McLendon, G.; Martell, A. E. *Coord. Chem. Rev.* **1976**, *19*, 1–39.

(12) Ochiai, E. *J. Inorg. Nucl. Chem.* **1974**, *37*, 1503–1509.

(13) Boucher, L. J. In *Coordination Chemistry of Macrocyclic Compounds*; Melson, G. A., Ed.; Plenum: New York, 1979; pp 461–516.

(14) Koppenol, W. H.; Butler, J. *FEBS Lett.* **1977**, *83*, 1.

(15) Mass, T. A.; Kuijer, M. M.; Zwart, J. *Chem. Commun.* **1976**, 87.

(16) Kundo, N. N.; Keier, N. P.; Glezneva, G. V.; Manneva, E. K. *Kinet. Katal.* **1967**, *8*, 1325.

(17) Simonov, A. D.; Keier, N. P.; Kundo, N. N.; Manneva, E. K.; Glazneva, G. V. *Kinet. Katal.* **1973**, *14*, 988.

(18) Leung, P. K.; Hoffmann, M. R. *J. Phys. Chem.* **1985**, *89*, 5267.

TABLE I: Determination of the Stoichiometry of the Catalytic Autoxidation of 2-Aminoethanethiol by Co^{II}TSP^a

init O ₂ , mmol	final O ₂ , mmol	ΔO ₂ , ^a mmol	ΔS, ^b mmol	ΔS/ΔO ₂
5.98 × 10 ⁻²	5.7 × 10 ⁻²	2.8 × 10 ⁻³	1.1 × 10 ⁻²	3.9
5.93 × 10 ⁻²	5.7 × 10 ⁻²	2.6 × 10 ⁻³	1.1 × 10 ⁻²	4.2
5.86 × 10 ⁻²	2.1 × 10 ⁻²	3.7 × 10 ⁻²	1.6 × 10 ⁻¹	4.3
5.86 × 10 ⁻²	2.4 × 10 ⁻²	3.4 × 10 ⁻²	1.6 × 10 ⁻¹	4.7

^a Experimental conditions: $\mu = 0.4$ M, pH 9.7, $T = 25.5$ °C, $[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}} = 0.64$ μM . ^b ΔO_2 = amount of O₂ reacted. ^c ΔS = amount of 2-aminoethanethiol reacted.

before use to remove any trace organics that might be present.

Kinetics Measurements. Kinetics measurements were made on a Hewlett-Packard Model 8450 spectrophotometer. A minimum of 100 data points was collected for each kinetics experiment, and k_{obsd} was obtained from the average of at least three experiments. Data were analyzed on-line with a IBM-XT computer. Constant temperature was maintained at 25.5 °C with a Haake water bath. Sodium chloride stock solutions were added to the buffers to establish an ionic strength of 0.4 M. pH was determined with a Beckman Altex $\Phi 71$ pH meter and radiometer (GK2402B, Ag/AgCl reference system) combination pH electrode. Dissolved oxygen levels were established by dispersing N₂ and O₂ gas mixtures into the Co^{II}TSP-containing buffer. The reaction was monitored at 233 nm (the absorbance maximum for NH₃⁺C₂H₄S⁻(aq), NH₂C₂H₄S⁻(aq), and CH₃CH₂S⁻(aq)). Pseudo-first-order conditions of $[\text{O}_2] \gg [\text{RHS}]_{\text{T}} < 2.6 \times 10^{-4}$ M were employed for all kinetic runs.

Stoichiometry. Reaction stoichiometry with dissolved oxygen in excess was determined by measuring the residual oxygen after $\geq 99\%$ of the mercaptan had reacted in alkaline solution. Dissolved oxygen was analyzed by the azide modification iodometric method.¹⁹

Product Identification. The reaction products of the oxidation of 2-aminoethanethiol were identified by high-performance liquid chromatography (HPLC; Econosphere C18-5 Micron HPLC column mounted on a Hewlett-Packard 1084B HPLC); retention times were compared with standards (Aldrich). The solvent carrier was 15% methanol in deionized doubly distilled water. The oven temperature was set at 40 °C.

The reaction products of the oxidation of ethanethiol were identified by direct-injection GC (3% SP-1500 80/120 Carbowax B GC column mounted on a Hewlett-Packard 5880A GC equipped with a FID detector); retention times were compared with standards. The carrier gas was nitrogen. The temperatures of the injection port, the detector and the oven were set at 100, 150, and 200 °C, respectively. The hydroxide ion production was identified by continuously monitoring the pH of an unbuffered reaction solution.

Identification of Intermediates. Hydrogen peroxide was identified by a fluorescence method described by Lazrus et al.²⁰ A 1.6-mL sample was withdrawn from the reaction vessel at 60-s intervals, and the reaction was quenched by rapid neutralization to pH ≈ 7 with concentrated hydrochloric acid. The fluorescence reagent, which consisted of potassium hydrogen phthalate, (*p*-hydroxyphenyl)acetic acid, and peroxidase was added at that point to the sample. Immediately before the fluorescence measurement was made, sodium hydroxide was added to raise the pH above 10 to enhance the fluorescence intensity. The excitation wavelength was 350 nm, while the fluorescence intensity was measured at $\lambda = 400$ nm on a Shimadzu RF-540 spectrofluorophotometer.

The presence of radicals in the reactions of 2-aminoethanethiol and ethanethiol was determined by monitoring the formation of ascorbate radical in the reaction medium with ascorbic acid. Ascorbate is known to react with mercaptan radicals producing the corresponding ascorbate radical ($\text{RS}^\bullet + \text{AH}^- \rightarrow \text{A}^\bullet + \text{RS}^-$

TABLE II: Determination of the Stoichiometry of Catalytic Autoxidation of Ethanethiol by Co^{II}TSP

init O ₂ , mmol	final O ₂ , mmol	ΔO ₂ , ^a mmol	ΔS, ^b mmol	ΔS/ΔO ₂
5.45 × 10 ⁻²	2.28 × 10 ⁻²	3.17 × 10 ⁻²	1.35 × 10 ⁻¹	4.3
5.45 × 10 ⁻²	1.89 × 10 ⁻²	3.56 × 10 ⁻²	1.35 × 10 ⁻¹	3.8
5.45 × 10 ⁻²	1.79 × 10 ⁻²	3.66 × 10 ⁻²	1.35 × 10 ⁻¹	3.7

^a Experimental conditions: $\mu = 0.4$ M, pH 10, $T = 25$ °C, $[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}} = 0.64$ μM . ^b ΔO_2 = amount of O₂ reacted. ^c ΔS = amount of ethanethiol reacted.

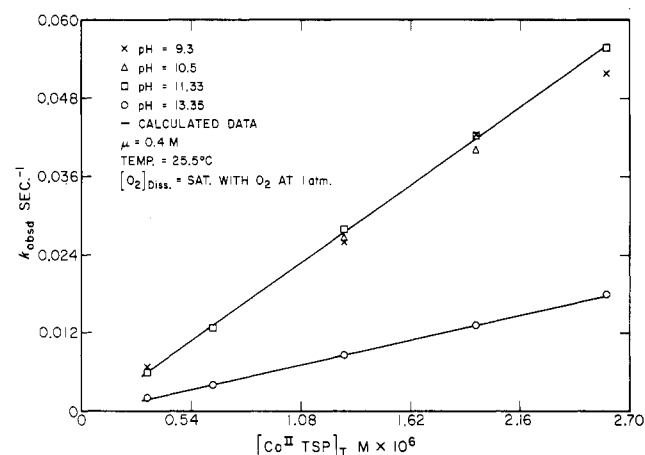
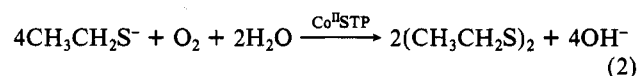
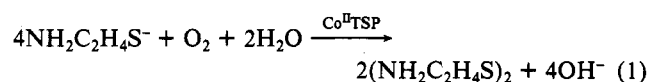


Figure 1. Determination of the reaction order with respect to $[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}}$ for 2-aminoethanethiol ($r^2 = 0.98$). The same linear dependence was observed for ethanethiol ($r^2 = 0.99$).

+ H⁺),^{21,22} which absorbs at $\lambda = 300$ nm with an extinction coefficient at 360 nm of $\epsilon_{360} = 3300$ cm⁻¹ M⁻¹.

Results

The results of the experiments to determine the reaction stoichiometries are given in Tables I and II. The average molar ratios of $[\text{O}_2]$ to $[\text{RCH}_2\text{CH}_2\text{SH}]$ for 2-aminoethanethiol and ethanethiol were found to be 4.4 and 3.9, respectively. The sole sulfur-containing products of the catalytic autoxidation of 2-aminoethanethiol and ethanethiol were determined to be 2-aminoethyl disulfide and ethyl disulfide, respectively. Thus, the overall stoichiometries are as follows:



Under pseudo-first-order conditions ($[\text{O}_2] \gg [\text{RCH}_2\text{CH}_2\text{SH}]_{\text{T}}$, T = total) plots of $\ln(A_t - A_\infty)$ versus t were linear ($r^2 \geq 0.999$) for 50–90% of the reaction. This linearity of the pseudo-first-order relationships for 2-aminoethanethiol and ethanethiol indicates that the rates of autoxidation are first order with respect to each mercaptan. The dependence of k_{obsd} on $[\text{O}_2]$ was determined at pH 9.3 and 13.0 for the 2-aminoethanethiol and at pH 11.0 and 13.0 for the ethanethiol. Results of these experiments showed that the rate of loss of $\text{RCH}_2\text{CH}_2\text{SH}$ was independent of the dissolved oxygen concentration between 10^{-4} and 10^{-3} M. Plots of k_{obsd} versus $[\text{CoTSP}]_{\text{T}}$ from 0.64 to 2.6 μM are shown in Figure 1 (2-aminoethanethiol and ethanethiol); they yield straight lines ($r^2 \geq 0.99$) at three different values of pH for each substrate. Double-log analysis of these data yields a reaction order of 1 for $[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}}$. Thus, the rate of autoxidation is first order in $[\text{RCH}_2\text{CH}_2\text{SH}]$ and $[\text{CoTSP}]_{\text{T}}$ but apparently zero order with respect to dissolved oxygen for both ethanethiol and 2-aminoethanethiol. Similar results were obtained for 2-mercaptoethanol.

(19) Standard Methods for the Examination of Water and Wastewater, 14th ed.; American Water Works Association: Washington, DC, 1975; p 443.

(20) Lazrus, A. L.; Kok, G. L.; Gitlin, S. N.; Lind, J. A. *Anal. Chem.* **1985**, *57*, 917.

(21) Redpath, J. L.; Wilson, R. L. *Int. J. Radiat. Biol.* **1973**, *23*, 51.

(22) Schuler, R. H. *Radiat. Res.* **1977**, *69*, 417.

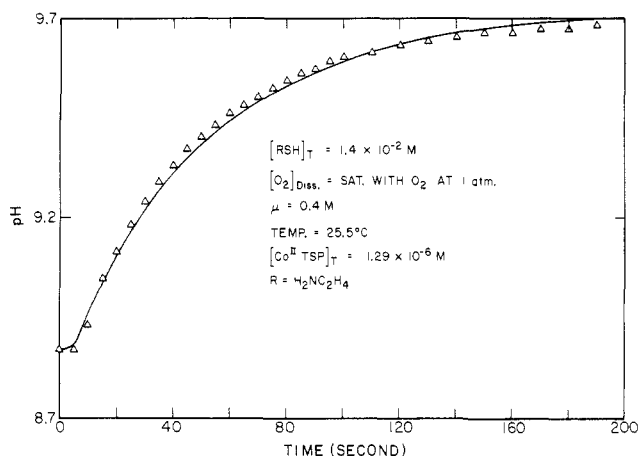


Figure 2. pH versus time during the course of the autoxidation of 2-aminoethanethiol in an unbuffered solution. A similar profile was observed for ethanethiol.

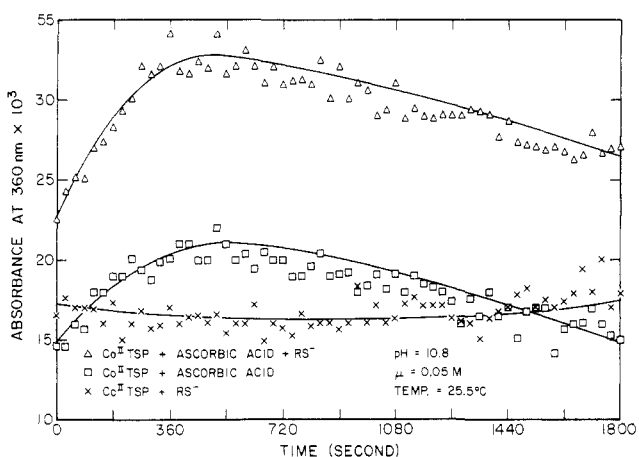
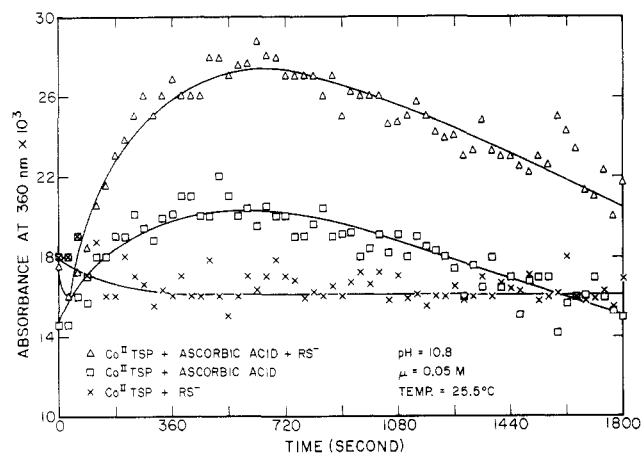


Figure 3. Absorbance versus time trace for the formation of ascorbate radical during the autoxidation of 2-aminoethanethiol (top) and ethanethiol (bottom).

In the absence of a buffer, the pH, as shown in Figure 2 (2-aminoethanethiol and ethanethiol), rose continuously during the course of reaction. The increase of pH indicates that hydroxide ion is a product of both catalytic autoxidations.

An oxidizing radical was found to be an intermediate of each reaction. Figure 3 (top, 2-aminoethanethiol; bottom, ethanethiol) shows the increase of absorbance at $\lambda = 360$ nm after the addition of ascorbic acid to the reaction mixture. Such an increase implies that the mercaptan radicals, $\text{NH}_2\text{C}_2\text{H}_4\text{S}^\cdot$ and $\text{CH}_3\text{CH}_2\text{S}^\cdot$, are the intermediates of the autoxidation of 2-aminoethanethiol and ethanethiol, respectively. Production of hydrogen peroxide, another reaction intermediate of the autoxidation of both mercaptans, is shown in Figure 4 for 2-aminoethanethiol. Therefore the overall

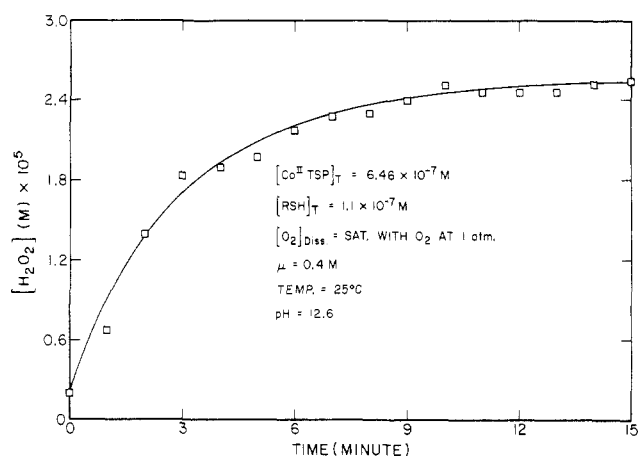


Figure 4. Hydrogen peroxide concentration versus time during the autoxidation of 2-aminoethanethiol.

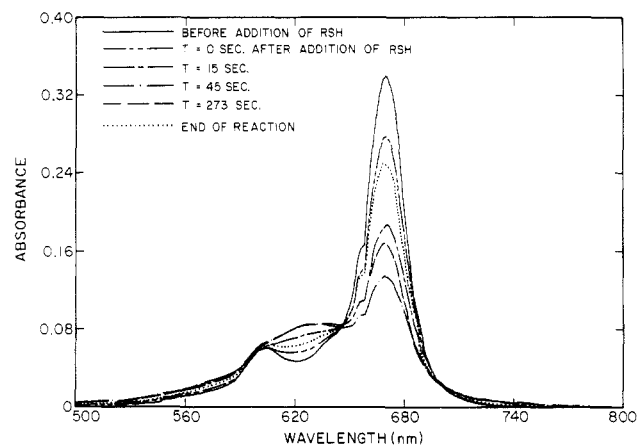
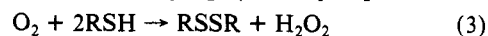


Figure 5. Changes in the visible spectrum of CoTSP during the autoxidation of ethanethiol at pH 13.4, $[\text{O}_2] = 1.0$ mM, and $[\text{Co}^{\text{II}}\text{TSP}] = 1.9$ μM . Similar changes in the spectrum of $\text{Co}^{\text{II}}\text{TSP}$ were observed during the oxidation of 2-aminoethanethiol.

1:4 stoichiometry of each mercaptan is given by the sum of eq 3 and 4, where R is either $\text{NH}_3^+\text{C}_2\text{H}_4$ or CH_3CH_2 .



The change of the visible spectra of $\text{Co}^{\text{II}}\text{TSP}$ during the course of reaction is shown in Figure 5. CoTSP has two characteristic peaks at $\lambda = 626$ nm and $\lambda = 668$ nm that correspond to a dimer and to the sum of a monomer plus an oxygenated monomer, respectively. The increase of absorption at $\lambda = 626$ nm and the concomitant decrease of absorption at $\lambda = 668$ nm after the addition of each thiol suggests that the dimer concentration is enhanced during the reaction. The resulting dimer is likely to be bridged by the anion of the corresponding mercaptan, which is similar to the structure proposed previously for 2-mercaptoethanol.⁸

The above kinetics information can be illustrated with the aid of the mechanism proposed in Figure 6. A similar mechanism has been proposed for the oxidation of 2-mercaptoethanol. The rates of disappearance of 2-aminoethanethiol and ethanethiol can be expressed as follows:

$$\nu^1 = -d[\text{NH}_2\text{C}_2\text{H}_4\text{SH}]_T/dt = 2(\nu_1^1 + \nu_2^1 + \nu_3^1 + \nu_4^1 + \nu_5^1 + \nu_6^1 + \nu_7^1) \quad (5)$$

where

$$\nu_1^1 = k_3[(\text{O}_2 - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_3^+ \text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_3^+ \text{C}_2\text{H}_4\text{S})^{-4}]$$

$$\nu_2^1 = k_{31}^1[(\text{O}_2 - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_3^+ \text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_2\text{C}_2\text{H}_4\text{S})^{-5}]$$

$$\begin{aligned} \nu_3^1 &= k_{31}^1 [(\cdot\text{O}_2\text{-Co}^{\text{II}}\text{TSP-NH}_2\text{C}_2\text{H}_4\text{S}^-\text{-Co}^{\text{II}}\text{TSP-NH}_3^+\text{C}_2\text{H}_4\text{S}^-)^{-5}] \\ \nu_4^1 &= k_{31}^1 [(O_2\text{-Co}^{\text{II}}\text{TSP-NH}_2\text{C}_2\text{H}_4\text{S}^-\text{-Co}^{\text{II}}\text{TSP-NH}_2\text{C}_2\text{H}_4\text{S}^-)^{-6}] \\ \nu_5^1 &= k_{32}^1 [(O_2\text{-Co}^{\text{II}}\text{TSP-NH}_2\text{C}_2\text{H}_4\text{S}^-\text{-Co}^{\text{II}}\text{TSP-NH}_2\text{C}_2\text{H}_4\text{S}^-)^{-7}] \\ \nu_6^1 &= k_{33}^1 [(O_2\text{-Co}^{\text{II}}\text{TSP-NH}_2\text{C}_2\text{H}_4\text{S}^-\text{-Co}^{\text{II}}\text{TSP-NH}_2\text{C}_2\text{H}_4\text{S}^-)^{-8}] \\ \nu_7^1 &= \text{rate of disappearance of mercaptan due to H}_2\text{O}_2 \\ k_{3i}^1 &= \text{rate constant of electron-transfer step of the } i\text{th} \\ &\quad \text{catalytic center} \end{aligned}$$

$$\nu^2 = -d[\text{CH}_3\text{CH}_2\text{SH}]_T/dt = 2(\nu_1^2 + \nu_2^2 + \nu_3^2 + \nu_4^2) \quad (6)$$

where

$$\begin{aligned} \nu_1^2 &= k_{31}^2 [(O_2\text{-Co}^{\text{II}}\text{TSP-CH}_3\text{CH}_2\text{S}^-\text{-Co}^{\text{II}}\text{TSP-CH}_3\text{CH}_2\text{S}^-)^{-6}] \\ \nu_2^2 &= k_{32}^2 [(O_2\text{-Co}^{\text{II}}\text{TSP-CH}_3\text{CH}_2\text{S}^-\text{-Co}^{\text{II}}\text{TSP-CH}_3\text{CH}_2\text{S}^-)^{-7}] \\ \nu_3^2 &= k_{33}^2 [(O_2\text{-Co}^{\text{II}}\text{TSP-CH}_3\text{CH}_2\text{S}^-\text{-Co}^{\text{II}}\text{TSP-CH}_3\text{CH}_2\text{S}^-)^{-8}] \\ \nu_4^2 &= \text{rate of disappearance of mercaptan due to H}_2\text{O}_2 \\ k_{3i}^2 &= \text{rate constant of electron-transfer step of } i\text{th catalytic center} \end{aligned}$$

The first, second, and third catalytic centers are formed by the combination of two protonated CoTSP monomers, a protonated Co^{II}TSP monomer and a deprotonated Co^{II}TSP monomer, two deprotonated CoTSP monomers, respectively.

Since $[\text{H}_2\text{O}_2]$ is very small, ν_5^1 and ν_6^1 can be neglected; therefore, eq 5 and 6 are respectively reduced to

$$\nu^1 = -d[\text{NH}_2\text{C}_2\text{H}_4\text{SH}]_T/dt = 2(\nu_1^1 + \nu_2^1 + \nu_3^1 + \nu_4^1 + \nu_5^1 + \nu_6^1) \quad (7)$$

$$\nu^2 = -d[\text{CH}_3\text{CH}_2\text{SH}]_T/dt = 2(\nu_1^2 + \nu_2^2 + \nu_3^2) \quad (8)$$

In the case of 2-aminoethanethiol, $[\text{NH}_2\text{C}_2\text{H}_4\text{SH}]_T = [\text{NH}_3^+\text{C}_2\text{H}_4\text{SH}] + [\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-] + [\text{NH}_2\text{C}_2\text{H}_4\text{S}^-]$. Expressing $[\text{NH}_2\text{C}_2\text{H}_4\text{SH}]_T$ in terms of $[\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-]$ allows eq 7 to be rewritten as follows:

$$\nu^1 = \frac{-d[\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-]}{dt} = \frac{2(\nu_1 + \nu_2 + \nu_3 + \nu_4 + \nu_5 + \nu_6)}{\left(1 + \frac{a_{\text{H}^+}}{K'_{a1}} + \frac{K'_{a2}}{a_{\text{H}^+}}\right)} \quad (9)$$

where K'_{a1} and K'_{a2} are the acid dissociation constants of $\text{NH}_3^+\text{CH}_2\text{CH}_2\text{SH}$ and $\text{NH}_3^+\text{CH}_2\text{CH}_2\text{S}^-$, respectively. Substitution of the corresponding equilibrium relationships for oxygen binding and for complexation of the substrate by the first catalytic center into ν_1^1 yields

$$\nu_1^1 = k_{31}^1 K_{21}^1 K_{21}^1 [(\text{Co}^{\text{II}}\text{TSP-NH}_3^+\text{C}_2\text{H}_4\text{S}^-\text{-Co}^{\text{II}}\text{TSP})^{-4}] [\text{O}_2] \times [\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-] \quad (10)$$

where K_{21}^1 and K_{21}^1 are the equilibrium constants for dioxygen binding and substrate complexation by the first catalytic center, respectively. Expressing the concentration of the first catalytic center in terms of the total concentration of catalyst, $[\text{Co}^{\text{II}}\text{TSP}]_T = 2\{[(\text{Co}^{\text{II}}\text{TSP-NH}_3^+\text{C}_2\text{H}_4\text{S}^-\text{-Co}^{\text{II}}\text{TSP})^{-4}] + [(\text{O}_2\text{-Co}^{\text{II}}\text{TSP-NH}_3^+\text{C}_2\text{H}_4\text{S}^-\text{-Co}^{\text{II}}\text{TSP})^{-4}] + [(\text{O}_2\text{-Co}^{\text{II}}\text{TSP-NH}_3^+\text{C}_2\text{H}_4\text{S}^-\text{-Co}^{\text{II}}\text{TSP-NH}_3^+\text{C}_2\text{H}_4\text{S}^-)^{-4}]\}$, yields

$$\nu_1^1 = \frac{k_{31}^1 K_{21}^1 K_{21}^1 [\text{Co}^{\text{II}}\text{TSP}]_T [\text{O}_2] [\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-]}{1 + K_{21}^1 [\text{O}_2] + K_{21}^1 K_{21}^1 [\text{O}_2] [\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-]} \quad (11)$$

The zero-order dependence on the dissolved oxygen concentration suggests that $K_{21}^1 [\text{O}_2] \gg K_{21}^1 K_{21}^1 [\text{O}_2] [\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-]$ and $K_{21}^1 [\text{O}_2] \gg 1$. The rate expression, ν_1^1 , can be reduced to the following:

$$\nu_1^1 = k_{31}^1 K_{21}^1 [\text{Co}^{\text{II}}\text{TSP}]_T [\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-] \quad (12)$$

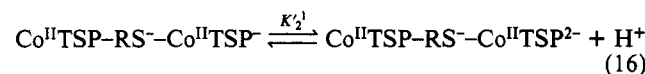
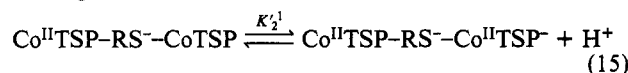
for which the reaction rate, ν_1^1 , is first order with respect to $[\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-]$ and $[\text{Co}^{\text{II}}\text{TSP}]_T$ and is independent of $[\text{O}_2]$. Similar expressions can be derived for ν_2^1 , ν_3^1 , ν_4^1 , ν_5^1 , and ν_6^1 . Thus, under the assumption that $K_{21}^1 [\text{O}_2] \gg K_{21}^1 K_{21}^1 [\text{O}_2] [\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-]$ and $K_{21}^1 [\text{O}_2] \gg 1$, the total rate of autoxidation becomes

$$\nu^1 = \{(\alpha_1 + \alpha_2\beta_2)[\text{C}]_{T1} + (\alpha_3\beta_2 + \alpha_4\beta_2^2) \times [\text{C}]_{T2} + \alpha_5\beta_2^2[\text{C}]_{T3} + \alpha_6\beta_2^2[\text{C}]_{T4}[\text{RS}^-]\} / (1 + \beta_1 + \beta_2) \quad (13)$$

where $\text{R} = \text{NH}_3^+\text{C}_2\text{H}_4$; $[\text{C}]_{Ti}$ = concentration of the catalyst in its respective form; $\alpha_1 = k_{31}^1 K_{21}^1$, $\alpha_2 = k_{32}^1 K_{21}^1$, $\alpha_3 = k_{33}^1 K_{21}^1$, $\alpha_4 = k_{31}^1 K_{21}^1$, $\alpha_5 = k_{32}^1 K_{21}^1$, $\alpha_6 = k_{33}^1 K_{21}^1$, $\beta_1 = a_{\text{H}^+}/K'_{a1}$, and $\beta_2 = K'_{a2}/a_{\text{H}^+}$. With the total catalyst concentration expressed as $[\text{Co}^{\text{II}}\text{TSP}]_T = [\text{Co}^{\text{II}}\text{TSP}]_{T1} + [\text{Co}^{\text{II}}\text{TSP}]_{T2} + [\text{Co}^{\text{II}}\text{TSP}]_{T3} + [\text{Co}^{\text{II}}\text{TSP}]_{T4}$, eq 13 can be rewritten as

$$\nu^1 = \{(\alpha_1 + \alpha_2\beta_2 + \alpha_3\beta_2 + \alpha_4\beta_2^2 + \alpha_5\beta_2^2\beta_3 + \alpha_6\beta_2^2\beta_3\beta_4) \times [\text{C}]_T [\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-] / \{1 + \beta_2(1 + \beta_3 + \beta_3\beta_4)\} \{1 + \beta_1 + \beta_2\}\} \quad (14)$$

where $\beta_3 = K'_{a1}/a_{\text{H}^+}$, $\beta_4 = K'_{a2}/a_{\text{H}^+}$, $[\text{C}]_T$ = total concentration of the catalyst, and K'_{a1} and K'_{a2} are the apparent acid dissociation constants of the pyrrole nitrogens of CoSTP, as shown in the following reactions:



In this case, k_{obsd}^1 is given by

$$k_{\text{obsd}}^1 = \{(\alpha_1 + \alpha_2\beta_2 + \alpha_3\beta_2 + \alpha_4\beta_2^2 + \alpha_5\beta_2^2\beta_3 + \alpha_6\beta_2^2\beta_3\beta_4) / \{1 + \beta_2(1 + \beta_3 + \beta_3\beta_4)\} \{1 + \beta_1 + \beta_2\}\} \quad (17)$$

Values of α_1 can be obtained by analyzing the kinetic data at pH ≤ 9.5 . In this pH range, the rate of autoxidation will be dominated by ν_1^1 , and k_{obsd}^1 will be reduced to

$$k_{\text{obsd}}^1 = k_{31}^1 K_{21}^1 / \left(1 + \frac{a_{\text{H}^+}}{K'_{a1}}\right) \quad (18)$$

and $k_{31}^1 K_{21}^1$ is calculated to be $(1.98 \pm 0.03) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. At $11.3 \leq \text{pH} \leq 12.1$, assuming that $\beta_2 \gg \beta_1 \gg 1$ and $\beta_3 \gg 1$, then eq 17 becomes

$$k_{\text{obsd}}^1 = (\alpha_5 + \alpha_6\beta_4) / (1 + \beta_4) \quad (19)$$

and $k_{32}^1 K_{21}^1$, $k_{33}^1 K_{21}^1$, and pK'_{a2} were calculated to be $(2.05 \pm 0.85) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, $(1.23 \pm 0.09) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, and 11.76 ± 0.27 , respectively. K'_{a1} and K'_{a2} values at $\mu = 0.4 \text{ M}$ were calculated from $K'_{a1} = 8.2$ and $K'_{a2} = 10.7$ at $\mu = 0.1 \text{ M}^{23}$ and the Davies equation.²⁴ Also, the constant value of k_{obsd}^1 at pH between 9.5 and 11 suggests that α_2 , α_3 , and α_4 are quite similar to α_1 or α_5 .

Similar assumptions and methods can be applied to the derivation of a rate expression for the catalytic autoxidation of ethanethiol. Under the same assumptions used for the 2-aminoethanethiol, the following rate expression for the ethanethiol is obtained:

$$\nu^2 = \left\{ \left(k_{31}^2 K_{21}^2 + k_{32}^2 K_{21}^2 \frac{K'_{a2}}{a_{\text{H}^+}} + k_{33}^2 K_{21}^2 \frac{K'_{a2} K'_{a2}}{a_{\text{H}^+}^2} \right) \times [\text{Co}^{\text{II}}\text{TSP}]_T [\text{CH}_3\text{CH}_2\text{S}^-] \right\} / \left\{ \left(1 + \frac{K'_{a2}}{a_{\text{H}^+}} + \frac{K'_{a2} K'_{a2}}{a_{\text{H}^+}^2} \right) \left(1 + \frac{a_{\text{H}^+}}{K'_{a1}} \right) \right\} \quad (20)$$

where k_{3i}^2 and K_{2i}^2 are the rate constant for the electron-transfer

(23) Felder, E.; Rescigno, C.; Radice, C. *Gazzetta* **1955**, *85*, 453.

(24) Stumm, W.; Morgan, J. J. *Aquatic Chemistry*, 2nd ed.; Wiley: New York, 1981; pp 134-137.

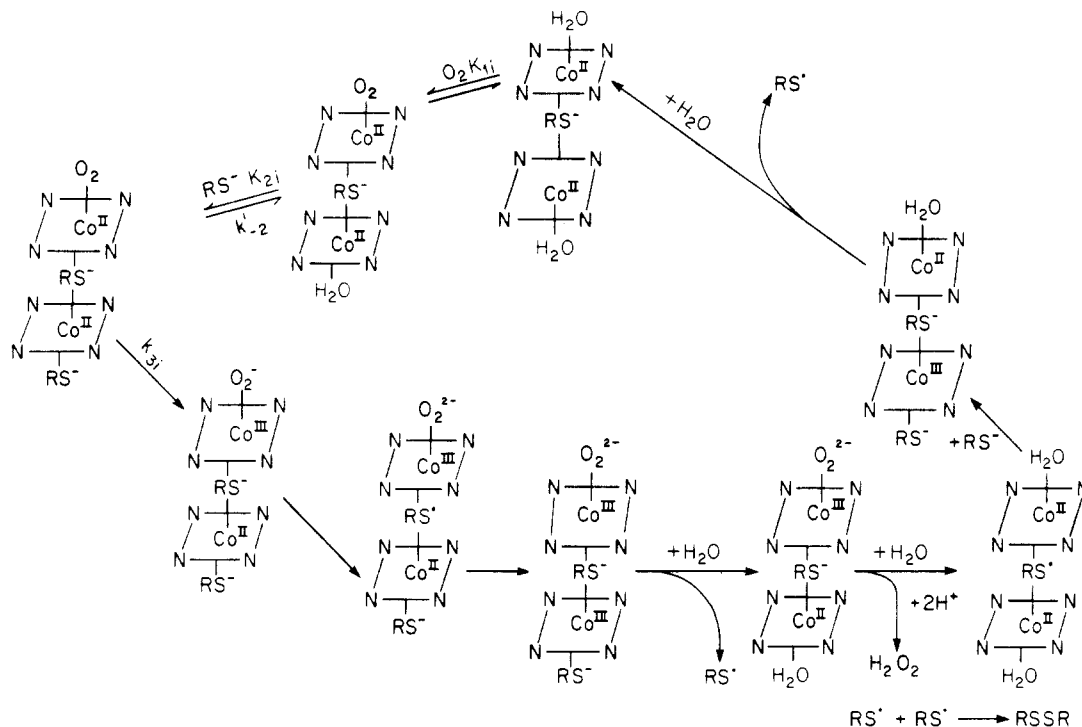


Figure 6. Schematic diagram of the proposed mechanism for the Co^{II} TSP-catalyzed autoxidation of RSH.

TABLE III: Comparison of k_{obsd} with k_{calcd} for the Catalytic Autoxidation of 2-Aminoethanethiol at Various pH Values^a

pH	$10^{-4}k_{\text{obsd}}, \text{M}^{-1} \text{s}^{-1}$	$10^{-4}k_{\text{calcd}}, \text{M}^{-1} \text{s}^{-1}$
8.83	1.61 ± 0.11	1.56
9.30	1.94 ± 0.16	1.82
10.50	2.02 ± 0.14	1.95
11.33	1.96 ± 0.19	1.79
12.06	1.1 ± 0.03	1.19
12.38	0.90 ± 0.02	0.92
12.54	0.80 ± 0.02	0.84
12.75	0.79 ± 0.01	0.75
12.91	0.68 ± 0.003	0.71
13.05	0.76 ± 0.02	0.68
13.35	0.62 ± 0.04	0.65

^a Experimental conditions: $\mu = 0.4 \text{ M}$, $T = 25.5^\circ \text{C}$, $[\text{O}_2] = 1 \text{ mM}$, $[\text{Co}^{\text{II}}\text{TSP}]_T = 0.64 \mu\text{M}$, buffer system = NaCl, NaHCO_3 , NaOH.

step and the equilibrium constant for substrate complexation by the i th catalytic center, respectively; $K_2^{\prime 2}$, $K_2^{\prime 2}$, and K_{a1}^{\prime} are the apparent acid dissociation constants of $\text{Co}^{\text{II}}\text{TSP-RS}^-$, $\text{Co}^{\text{II}}\text{TSP-RS}^-$, $\text{Co}^{\text{II}}\text{TSP-RS}^-$, and $\text{CH}_3\text{CH}_2\text{SH}$, respectively. k_{obsd} in this case is given by

$$k_{\text{obsd}}^2 = \frac{\left(k_{31}^2 K_{21}^2 + \frac{k_{32}^2 K_{22}^2 K_2^{\prime 2}}{a_{\text{H}^+}} + \frac{k_{33}^2 K_{23}^2 K_2^{\prime 2} K_2^{\prime 2}}{a_{\text{H}^+}^2} \right)}{\left(1 + \frac{K_2^{\prime 2}}{a_{\text{H}^+}} + \frac{K_2^{\prime 2} K_2^{\prime 2}}{a_{\text{H}^+}^2} \right) \left(1 + \frac{a_{\text{H}^+}}{K_{a1}^{\prime 2}} \right)} \quad (21)$$

The value of $k_{31}^2 K_{21}^2$ can be obtained by analyzing the experimentally observed rate constant at $\text{pH} \leq 10$. At this pH, assuming $1 \gg K_2^{\prime 2}/a_{\text{H}^+} \gg K_2^{\prime 2} K_2^{\prime 2}/a_{\text{H}^+}^2$, eq 21 reduces to

$$k_{\text{obsd}}^2 = k_{31}^2 K_{21}^2 / \left(1 + \frac{a_{\text{H}^+}}{K_{a1}^{\prime 2}} \right) \quad (22)$$

and $k_{31}^2 K_{21}^2$ is calculated to be $(2.99 \pm 0.22) \times 10^4 \text{ M}^{-1} \text{s}^{-1}$. At $\text{pH} \geq 12$, assuming that $K_2^{\prime 2}/a_{\text{H}^+} \gg 1$, eq 21 becomes

$$k_{\text{obsd}}^2 = \left(k_{32}^2 K_{22}^2 + k_{33}^2 K_{23}^2 \frac{K_2^{\prime 2}}{a_{\text{H}^+}} \right) / \left(1 + \frac{K_2^{\prime 2}}{a_{\text{H}^+}} \right) \quad (23)$$

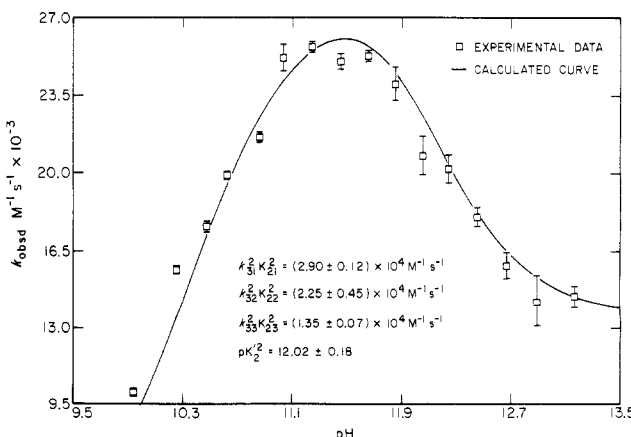
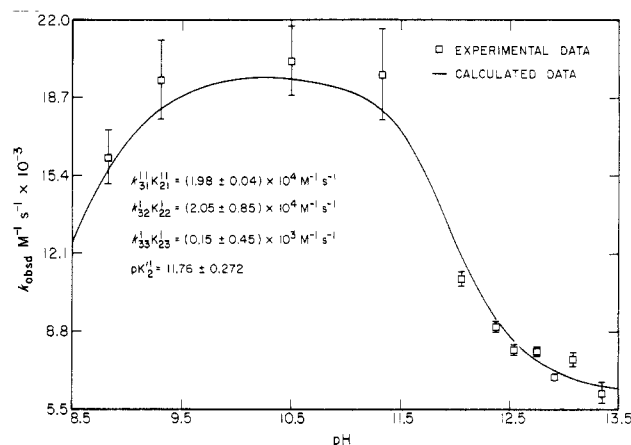


Figure 7. k_{obsd} versus pH for the catalytic autoxidation of 2-aminoethanethiol (top) and ethanethiol (bottom).

and $k_{32}^2 K_{22}^2$, $k_{33}^2 K_{23}^2$, and $pK_2^{\prime 2}$ was calculated to be $(2.75 \pm 0.45) \times 10^4 \text{ M}^{-1} \text{s}^{-1}$, $(1.35 \pm 0.07) \times 10^4 \text{ M}^{-1} \text{s}^{-1}$, and 12.02 ± 0.18 , respectively. $K_{a1}^{\prime 2}$ at $\mu = 0.4 \text{ M}$ was calculated from $K_{a1}^{\prime 2} = 10.6$ at infinite dilution²⁵ by using the Davies equation.²⁴

(25) Irving, R. J.; Neland, L.; Wadso, I. *Acta Chem. Scand.* **1964**, *18*, 769.

TABLE IV: Comparison of k_{obsd} with k_{calcd} for the Catalytic Autoxidation of Ethanethiol at Various pH Values^a

pH	$10^{-4}k_{\text{obsd}}, \text{M}^{-1} \text{s}^{-1}$	$10^{-4}k_{\text{calcd}}, \text{M}^{-1} \text{s}^{-1}$
9.98	1.00 ± 0.02	0.68
10.25	1.56 ± 0.01	1.12
10.47	1.76 ± 0.02	1.49
10.62	1.99 ± 0.02	1.74
10.86	2.16 ± 0.02	2.10
11.03	2.51 ± 0.06	2.31
11.24	2.56 ± 0.02	2.49
11.45	2.49 ± 0.03	2.58
11.65	2.52 ± 0.02	2.57
11.85	2.40 ± 0.07	2.45
12.05	2.08 ± 0.09	2.26
12.24	2.01 ± 0.06	2.04
12.45	1.80 ± 0.04	1.82
12.67	1.58 ± 0.05	1.65
12.89	1.42 ± 0.11	1.53
13.13	1.44 ± 0.04	1.44

^a Same experimental conditions as given in Table III.

Calculated values of the apparent second-order rate constants (k_{calcd}^1 and k_{calcd}^2) are compared to their respective experimental values in Tables III and IV and shown in Figure 7 for 2-aminoethanethiol (top) and ethanethiol (bottom). It was not possible to obtain an independent value of K'_2 for both mercaptans. Therefore, in the calculations, the assumption was made that K'_2 and K'_2 are approximately equal for both substrates. Since the fit for each substrate is fairly sensitive to its corresponding K'_2 value, the relatively good fits give indirect support to the assumption that $K'_2 = K'_2$ for both substrates.

Discussion

The mechanism proposed for the autoxidation of 2-aminoethanethiol and ethanethiol catalyzed by cobalt(II) 4,4',4'',4'''-tetrasulfophthalocyanine is the same as the mechanism proposed for the catalyzed autoxidation of 2-mercaptoethanol.⁸ The experimental data for the catalytic autoxidations show similarities in (1) the reaction orders of substrates, catalyst, and oxygen, (2) the reaction intermediates, namely, hydrogen peroxide and the corresponding mercaptan radical, (3) the stoichiometry of the overall reactions, and (4) the formation of corresponding disulfides and hydroxide ion as the final products. In addition, the change of the visible spectrum of Co^{II}TSP during the autoxidation was similar for all three mercaptans.

The mechanism presented above is similar in some respects to the mechanisms proposed previously by Dolansky et al.⁵ and Boyce et al.³ However, in our case, the binding of molecular oxygen precedes complexation of the substrate. At the relatively high pH of the system, the deprotonation of the pyrrole N's of the phthalocyanine ring and the hydrolysis of an apical water to give a hydroxide trans to the site open for oxygen binding favors O₂ addition. This pathway is consistent with the observed zero-order dependence on dissolved oxygen, which also suggests that the majority of the catalyst is present as an oxygenated adduct (i.e., [CoTSP]_T \approx oxygenated adduct). Another major difference between the mechanism proposed here and those of Dolansky et al. and Boyce et al. is that the catalytic center appears to be a dimer rather than a monomer.

The general spectral features of the oxygenated CoTSP complex have been reported previously by Gruen and Balgove.²⁶ As RS⁻ was added to the catalyst solution, significant changes in the CoTSP visible spectrum were observed; these were consistent with the formation of a dimer as the reactive species. A similar spectral change was also noted by Beelen et al.²⁷ in their study of the autoxidation of 2-mercaptoethanol catalyzed by CoTSP. According to the spectral changes shown in Figure 5, most of the catalyst dimerized within the first minute of reaction. This implies that [CoTSP]_T \approx 2[dimer] and that a half-order dependence

instead of a first-order dependence on [CoTSP]_T catalyst should be observed if a monomeric species were the principal reactive species.

According to the mechanism of Figure 6, several possible reactions can be considered as the rate-determining step. They are the binding of molecular oxygen, the complexation of the substrate by the oxygenated dimer, and the subsequent electron-transfer steps. However, it appears that one of the two sequential electron-transfer steps is most likely to be the rate-limiting step since a zero-order dependence on both the substrate at low ionic strength and dissolved oxygen at all ionic strengths was observed. Furthermore, both oxygen binding and substrate complexation should be fairly rapid ligand substitutions. The rate of ligand substitution for first-row transition metals is frequently independent of the nature of the ligand. The observed rates for each metal ion are similar to their corresponding water-exchange rates; therefore, the rate of ligand substitution for Co²⁺ should be close to its water-exchange rate. The water exchange rate for Co²⁺ is $\approx 10^5 \text{ M}^{-1} \text{ s}^{-1}$.²⁸ Thus, the characteristic rate constant for substrate complexation and dioxygen binding of the cobalt(II) centers should also be on the order of 10^5 . This value is an order of magnitude larger than our k_{obsd} values.

The observed independence of the rate of autoxidation on [O₂] requires both the rate of oxygenation to be fast and the equilibrium constant of the oxygenation to be quite large (i.e., $K_{\text{li}} \geq 10^3$). Jones et al.⁹ have argued that the binding of a fifth ligand in an apical coordination site of cobalt(II) porphyrin is a prerequisite for oxygenation. Therefore, the binding of the RS⁻ may result in an increase in both the rate and equilibrium constant of oxygenation. The bonding of oxygen to cobalt complexes can be explained in terms of σ donation of electrons from the sp² lone pair on dioxygen to d_{z²} orbital on the cobalt, coupled with the π -back-bonding from the cobalt d_{xy} or d_{yz} orbitals into the π^* dioxygen orbitals. The ligands coordinated trans to the O₂ could compete for the same π -electron density on the cobalt; therefore, the strength of the Co–O₂ bonding is very sensitive to the π -accepting or π -donating ability of the trans-axial ligands. Good π -electron acceptors will decrease the electron density on the metal, resulting a weaker Co–O₂ bond, whereas good π -electron donors will increase the electron density on the Co center available for π -back-bonding on O₂ and thereby stabilize the Co–O₂ bond. Several investigators have reported that the greater electron density on the metal results in a stronger metal–oxygen bond.^{29,30} Sulfur ligands³¹ are generally good π -donors, and therefore they should enhance the rate of oxygenation and strengthen the Co–oxygen bond. However, little thermodynamic data on the stability of mixed complexes of Co(II)–O₂ and mercaptans are available. This may be due to the relatively rapid oxidation of mercaptans to disulfides. The rate constants for dioxygen binding by a variety of bridged Co–chelate complexes have been reported to be large.⁹ In addition, Martell³² has shown a linear correlation of the sum of the basicities of the ligands bound to the cobalt metal center with the stabilities of the corresponding monobridged dioxygen–Co complexes. These macrocyclic cobalt(II) complexes show very large stability constants for oxygen binding that range from 10^5 to 10^{15} . Since the sum of the basicities ($\sum \text{p}K$) of the ligands on CoTSP–RS⁻ is >18 , it is plausible that the oxygenation equilibrium constant is at least greater than 10^3 and possibly $\geq 10^8$.

The catalytically active dimer probably consists of two CoTSP monomers linked by a single RCH₂CH₂S⁻ ligand at the metal center. Leung and Hoffmann⁸ have discussed the possibility of a μ -peroxo–binuclear CoTSP complex as the catalytically active dimer, and they discounted its importance based on kinetic and thermodynamic arguments. Formation of a μ -superoxo complex

(28) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 1188.

(29) McGinety, J.; Payne, N. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 6301.

(30) Terry, N. W.; Amma, E. L.; Vaska, L. *J. Am. Chem. Soc.* **1972**, *94*, 654.

(31) Klotz, I. M.; Klotz, T. A. *Science (Washington, D.C.)* **1955**, *121*, 477.

(32) Martell, A. E. *Acc. Chem. Res.* **1982**, *15*, 155.

(26) Gruen, L. C.; Balgove, R. *J. Aust. J. Chem.* **1973**, *26*, 319.

(27) Beelen, T. P. M.; da Costa Gomez, C. O.; Kuijter, M. *Recl.: J. R. Neth. Chem. Soc.* **1979**, *98*, 521.

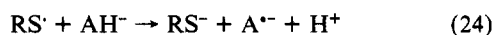
is too slow to be consistent with our kinetic observations.³³ It may be argued that the steric interaction between the two macrocyclic rings in our proposed RS⁻-bridged dimer would be too severe to allow dimerization to occur, but it has been shown that two CoTSP molecules can be bridged by the smaller N atom of an amino group.³⁴ Other dimeric forms of Co^{II}TSP are possible. They include a face-to-face dimer in which bonding occurs via π - π overlap of the delocalized 18-electron phthalocyanine ring system, a hydroxy-bridged dimer with a Co(II)-OH-Co(II) linkage (this becomes a possibility only at high pH), and a dimer in which the Co(II) metal center of one molecule interacts with the pyrrole N's of the other phthalocyanine complex.

A rate-limiting electron-transfer step has been proposed previously for the catalytic autoxidation of both SO₃²⁻ and H₂S by CoTSP. Hoffmann and Hong³⁵ have reported electron spin resonance (ESR) evidence for the formation of superoxide-like ternary CoTSP complex during the catalytic autoxidation of sulfite. Results from other ESR studies⁹ have also shown that superoxide-like Co complexes are formed during the course of catalytic autoxidation. Additional information obtained from magnetic susceptibility data and electron paramagnetic resonance (EPR) spectra shows that for low-spin d⁷ complexes, Co^{II}L₄B, where L₄ and B are the equatorial and axial ligands, respectively, there is only one unpaired electron, and more than 80% of the electron density resides in the π^* dioxygen orbital.⁹ Therefore, we believe that RCH₂CH₂S-Co^{II}TSP-RCH₂CH₂S-Co^{III}TSP-O₂⁻ is the principal reactive species in the catalytic cycle.

The effect of pH on the rate of autoxidation, as shown in Figure 7, suggests that the pyrrole nitrogens of Co^{II}TSP and its complexes remain protonated over the pH range investigated. Two possible acid-base equilibria can participate in the catalytic cycle to give the observed pH effect. They are the deprotonation of hydrogen ion either at the pyrrole nitrogens or at the bound water molecules in the open coordination sites.

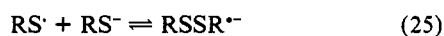
We estimate on the basis of potentiometric measurements that the pK_a of the bound water molecules on the dimer of H₂O-Co^{II}TSP-OH₂ is >>14.0. Since sulfur is a good electron donor, the incorporation of sulfur into the dimer would further enhance the electron density on the cobalt, and consequently the cobalt would withdraw less electron density from the bound water molecules. As a result, the hydrogen ion would be more difficult to deprotonate from the bound water molecules, and thereby the pK should be ≥ 14.7 . Berezin³⁶ has noted that protonation of metal phthalocyanine complexes occurs preferentially on the ring nitrogens. Since phthalocyanine is a highly conjugated macro-molecule, deprotonation of a single nitrogen would change the electron density on the ring and thereby could alter the electron density around the Co center and result in the change of the rate of electron transfer.

The observed production of ascorbate radicals during the course of the reaction provides strong evidence for the formation of RCH₂CH₂S⁻ (hereby shortened to RS⁻) as an intermediate. Ascorbate radicals may have been produced by one of two alternative pathways. The first pathway^{21,22} would be as follows:



$$k_{24} = 6.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

while the second and more likely pathway³⁷⁻³⁹ would be as follows:



$$k_{25} = 2.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

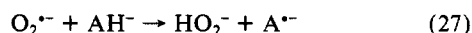
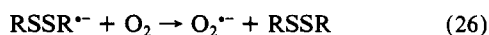


TABLE V: Correlation of Taft σ^* Values of R' Group on R'CH₂CH₂SH with the Apparent Rate Constant ($k_{\text{app}} = kK$) Values^a

R'	σ^*	$\log k_{\text{app}}/(\text{M}^{-1} \text{ s}^{-1})$
H	0.49	4.46
NH ₂	0.62	≈ 4.34
OH	1.34	4.18
NH ₃ ⁺	3.76	4.30

^a Linear relationship given by $\log k_{\text{app}} = -0.3\sigma^* + 4.57$.

In the former case, the ascorbate radical is formed directly, while in the latter case it is formed indirectly from RS⁻. Nonetheless, the corresponding mercaptan radicals appear to be intermediates of the catalyzed autoxidations.

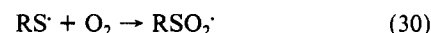
Several pathways may yield RSSR from RS⁻. They are first



and second a sequence that includes eq 25 and 26 as the initial reactions followed by



and third^{37,38,40,41}



$$k'_{31} = 2.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$



Given the above rate constants appropriate to the three pathways and the experimental conditions used in this study, we can estimate that eq 25-27 control the fate of RS⁻. With a small steady-state concentration of RS⁻, the rate of reaction 28 should be very slow, and it can be ignored as the primary route for the disappearance of RS⁻. Also, the subsequent reactions in the third sequence are expected to be relatively slow because of the low concentrations of the various radical intermediates. Thus, RS⁻ is more likely to react via reactions 25, 26, and 29 ($k'_{\text{obsd}} = 1.3 \times 10^6 \text{ s}^{-1}$) to give disulfide as the product.

The apparent rate constants, defined as the products of the rate constants for the rate-limiting electron-transfer steps and the complexation equilibrium constants of Co^{II}TSP dimer by the mercaptans (2-mercaptoethanol, 2-aminoethanethiol, and ethanethiol), were compared against the Taft σ^* values⁴² for the substituent groups. These data are given in Table V. The apparent rate constants and the Taft σ^* values show an inverse linear free energy relationship (LFER). The Taft σ^* value is a measure of the electron-withdrawing ability of the functional group; higher values of the Taft σ^* factor imply a stronger electron-withdrawing ability of the functional group. As can be seen in Table V, as the electron-withdrawing ability of the side group increases, the apparent rate constant decreases.

The LFER can be explained as follows: as the electron-withdrawing ability of the side group increases, the electron density on the sulfur atom will be drawn toward the substituent group. In the case of aliphatic compounds, HO⁻ and NH₂⁻ withdraw electron density inductively, whereas they donate electron density through a resonance mechanism in conjugated organic molecules. The consequences of the net electron withdrawal are 2-fold. First, the stability of the subsequent sulfur-cobalt bond will be decreased;

(33) Wagnerova, D. M.; Schwertnerova, E.; Veprek-Siska, J. *Collect. Czech. Chem. Commun.* **1974**, *39*, 1980.

(34) Przywarska-Boniecka, H.; Wojciechowski, W. *Mater. Sci.* **1975**, *1*, 27.

(35) Hoffmann, M. R.; Hong, A. P. K. *Sci. Total Environ.* **1987**, *64*, 99.

(36) Berezin, B. D. *Coordination Compounds of Porphyrins and Phthalocyanines*; Wiley: New York, 1981; p 66.

(37) Al-Thannon, A. A.; Barton, J. P.; Packer, J. E.; Sims, R. J.; Trumbore, C. N.; Winchester, R. V. *Int. J. Radiat. Phys. Chem.* **1974**, *6*, 223.

(38) Barton, J. P.; Packer, J. E. *Int. J. Radiat. Phys. Chem.* **1970**, *2*, 159.

(39) Cabelli, D. E.; Bleiski, H. J.; Benon, H. J. *J. Phys. Chem.* **1983**, *87*, 1809.

(40) Schenk, H. P. Diploma Thesis, Technical University of Berlin (FRG), 1982; pp 49, 67.

(41) Schäfer, K.; Bonifacic, M.; Bahnmann, D.; Asmus, K.-D. *J. Phys. Chem.* **1978**, *82*, 2777-2780.

(42) Perrin, D. D.; Dempsey, B.; Serjeant, E. P. *pK_a Prediction for Organic Acids and Bases*; Chapman & Hill: London, 1981; p 110.

TABLE VI: Correlation of Taft σ^* Values of R' Group on R'CH₂CH₂SH with the pK'_2 Values^a

R'	σ^*	pK'_2
H	0.49	12.02
NH ₂	0.62	11.76
OH	1.34	10.8

^a Linear relationship given by $pK'_2 = -1.2\sigma^* + 12.54$.

this should lead to a smaller value for the complexation equilibrium constant. Second, the decrease in the electron density available to the cobalt center results in a decrease of the rate constant for the rate-limiting electron-transfer step. The combination of these effects result in a lower apparent rate constant.

As indicated from Table V, $\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-$ did not fit the LFER. The apparent rate constant for $\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-$ should be smaller than the observed value. This anomaly probably arises from the effect of the positive charge on the amino group on the complexation equilibrium constant. The positive charge on the amino group may enhance stability of its complex with cobalt tetrasulfophthalocyanine. Since a higher value of Taft σ^* value implies a lower rate of electron transfer, the approximately equal values of the apparent rate constants for $\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-$ and $\text{NH}_2\text{C}_2\text{H}_4\text{S}^-$ suggest that the decrease of electron transfer is "balanced" by the increase of the stability constant for $\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-$ and $\text{Co}^{\text{II}}\text{TSP}$.

An additional LFER was observed between pK'_2 of $\text{Co}^{\text{II}}\text{TSP-RS-CO}^{\text{II}}\text{TSP}$ and the Taft δ^* value as shown in Table VI. This relationship can also be explained in terms of the effect of the side group of the mercaptan on the electron density of the cobalt center. As the electron density of the cobalt center is lowered by the stronger electron-withdrawing substituent of the mercaptan, the electron at the bonding orbital between the hydrogen and the pyrrole nitrogen of CoTSP molecule would be more drawn toward the cobalt center and consequently destabilize the bonding between the hydrogen ion and the pyrrole nitrogen. Therefore, the hydrogen ion more readily dissociates from the phthalocyanine ring, and thus a lower pK' value is observed.

Conclusion

Experimental data confirm our hypothesis that the autoxidation of structurally similar mercaptans proceed by similar mechanisms. The establishment of two linear free energy relationships enables us to predict the rate of autoxidation of other mercaptans.

The successful catalytic autoxidation of several mercaptans suggests that $\text{Co}^{\text{II}}\text{TSP}$ catalysis may be applied for the elimination of mercaptans and their associated odors from industrial wastes.

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Glossary

a_{H^+}	hydrogen ion activity, $\text{pH} \equiv -\log a_{\text{H}^+}$
A_t	absorbance (λ_{233}) at time = t
A_∞	absorbance (λ_{233}) at time = ∞

The following notation applies to the catalytic autoxidation of 2-aminoethanethiol:

k_{obsd}^1	observed rate constant
α_1	$k_{31}^1 K_{21}^1$
k_{31}^1	electron-transfer rate constant (s^{-1}) of the reaction $(\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{III}}\text{TSP} - \text{O}_2^-)^{-4} \rightarrow (\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{III}}\text{TSP} - \text{O}_2^-)^{-4}$
K_{21}^1	equilibrium constant (M^{-1}) of the reaction $(\text{O}_2 - \text{Co}^{\text{II}}\text{TSP} - \text{RS} - \text{Co}^{\text{II}}\text{TSP} - \text{OH}_2)^{-4} + \text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- \rightleftharpoons (\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{O}_2)^{-4} + \text{H}_2\text{O}$
α_2	$k_{31}^2 K_{21}^2$
k_{31}^2	electron-transfer rate constant (s^{-1}) of the reaction $(\text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{O}_2)^{-5} \rightarrow (\text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{III}}\text{TSP} - \text{O}_2^-)^{-5}$

K_{21}^{12}	equilibrium constant (M^{-1}) of the reaction $(\text{O}_2 - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{OH}_2)^{-4} + \text{NH}_2\text{C}_2\text{H}_4\text{S}^- \rightleftharpoons (\text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{O}_2)^{-5} + \text{H}_2\text{O}$
α_3	$k_{31}^3 K_{21}^3$
k_{31}^3	electron-transfer rate constant (s^{-1}) of the reaction $(\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{O}_2)^{-5} \rightarrow (\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{III}}\text{TSP} - \text{O}_2^-)^{-5}$
K_{21}^{13}	equilibrium constant (M^{-1}) of the reaction $(\text{O}_2 - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{OH}_2)^{-5} + \text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- \rightleftharpoons (\text{O}_2 - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{OH}_2)^{-5} + \text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- \rightleftharpoons (\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{O}_2)^{-5} + \text{H}_2\text{O}$
α_4	$k_{31}^4 K_{21}^4$
k_{31}^4	electron-transfer rate constant (s^{-1}) of the reaction $(\text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{O}_2)^{-6} \rightarrow (\text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{III}}\text{TSP} - \text{O}_2^-)^{-6}$
K_{21}^{14}	equilibrium constant (M^{-1}) of the reaction $(\text{O}_2 - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{OH}_2)^{-5} + \text{NH}_2\text{C}_2\text{H}_4\text{S}^- \rightleftharpoons (\text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{O}_2)^{-6} + \text{H}_2\text{O}$
α_5	$k_{32}^1 K_{22}^1$
k_{32}^1	electron-transfer rate constant (s^{-1}) of the reaction $(\text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{O}_2)^{-7} \rightarrow (\text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{III}}\text{TSP} - \text{O}_2^-)^{-7}$
K_{22}^1	equilibrium constant (M^{-1}) of the reaction $(\text{O}_2 - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{OH}_2)^{-6} + \text{NH}_2\text{C}_2\text{H}_4\text{S}^- \rightleftharpoons (\text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{O}_2)^{-7} + \text{H}_2\text{O}$
α_6	$k_{33}^1 K_{23}^1$
k_{33}^1	electron-transfer rate constant (s^{-1}) of the reaction $(\text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{O}_2)^{-8} \rightarrow (\text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{III}}\text{TSP} - \text{O}_2^-)^{-8}$
K_{23}^1	equilibrium constant (M^{-1}) of the reaction $(\text{O}_2 - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{OH}_2)^{-7} + \text{NH}_2\text{C}_2\text{H}_4\text{S}^- \rightleftharpoons (\text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{O}_2)^{-8} + \text{H}_2\text{O}$
β_1	a_{H^+}/K'_{a1}
K'_{a1}	apparent acid dissociation constant (M) of the acid-base equilibrium $\text{NH}_3^+\text{C}_2\text{H}_4\text{SH} \rightleftharpoons \text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- + \text{H}^+$
β_2	K'_{a2}/a_{H^+}
K'_{a2}	apparent acid dissociation constant (M) of the acid-base equilibrium $\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- \rightleftharpoons \text{NH}_2\text{C}_2\text{H}_4\text{S}^- + \text{H}^+$
K'_2	apparent acid dissociation constant (M) of the acid-base equilibrium $(\text{H}_2\text{O} - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{O}_2)^{-5} \rightleftharpoons (\text{H}_2\text{O} - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{OH}_2)^{-6} + \text{H}^+$
K_{11}^1	equilibrium constant (M^{-1}) of the reaction $(\text{H}_2\text{O} - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{OH}_2)^{-4} + \text{O}_2 \rightleftharpoons (\text{O}_2 - \text{Co}^{\text{II}}\text{TSP} - \text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{OH}_2)^{-4} + \text{H}_2\text{O}$

The following notation applies to the catalytic autoxidation of ethanethiol:

k_{obsd}^2	observed rate constant
k_{31}^2	electron-transfer rate constant (s^{-1}) of the reaction $(\text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{O}_2)^{-6} \rightarrow (\text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{III}}\text{TSP} - \text{O}_2^-)^{-6}$
K_{21}^2	equilibrium constant (M^{-1}) of the reaction $(\text{O}_2 - \text{Co}^{\text{II}}\text{TSP} - \text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{OH}_2)^{-5} + \text{HC}_2\text{H}_4\text{S}^- \rightleftharpoons (\text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{O}_2)^{-6} + \text{H}_2\text{O}$
k_{32}^2	electron-transfer rate constant (s^{-1}) of the reaction $(\text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{O}_2)^{-7} \rightarrow (\text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{III}}\text{TSP} - \text{O}_2^-)^{-7}$
K_{22}^2	equilibrium constant (M^{-1}) of the reaction $(\text{O}_2 - \text{Co}^{\text{II}}\text{TSP} - \text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{OH}_2)^{-6} + \text{HC}_2\text{H}_4\text{S}^- \rightleftharpoons (\text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{O}_2)^{-7} + \text{H}_2\text{O}$
k_{33}^2	electron-transfer rate constant (s^{-1}) of the reaction $(\text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{O}_2)^{-8} \rightarrow (\text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{III}}\text{TSP} - \text{O}_2^-)^{-8}$
K_{23}^2	equilibrium constant (M^{-1}) of the reaction $(\text{O}_2 - \text{Co}^{\text{II}}\text{TSP} - \text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{OH}_2)^{-7} + \text{HC}_2\text{H}_4\text{S}^- \rightleftharpoons (\text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{O}_2)^{-8} + \text{H}_2\text{O}$
K'_2	apparent acid dissociation constant (M) of the acid-base equilibrium $(\text{H}_2\text{O} - \text{Co}^{\text{II}}\text{TSP} - \text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{OH}_2)^{-5} \rightleftharpoons (\text{H}_2\text{O} - \text{Co}^{\text{II}}\text{TSP} - \text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{OH}_2)^{-6} + \text{H}^+$
K'_2	apparent acid dissociation constant (M) of the acid-base equilibrium $(\text{H}_2\text{O} - \text{Co}^{\text{II}}\text{TSP} - \text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{OH}_2)^{-6} \rightleftharpoons (\text{H}_2\text{O} - \text{Co}^{\text{II}}\text{TSP} - \text{HC}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP} - \text{OH}_2)^{-7} + \text{H}^+$
K'_{a2}	apparent acid dissociation constant (M) of the acid-base equilibrium $\text{HC}_2\text{H}_4\text{SH} \rightleftharpoons \text{HC}_2\text{H}_4\text{S}^- + \text{H}^+$

Registry No. $\text{Co}^{\text{II}}\text{TSP}$, 14285-59-7; 2-aminoethanethiol, 60-23-1; ethanethiol, 75-08-1.