

Co-PHTHALOCYANINE CATALYZED AUTOXIDATION OF
MERCAPTANS

Thesis by
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To My Parents
and
My Sister, Nancy.

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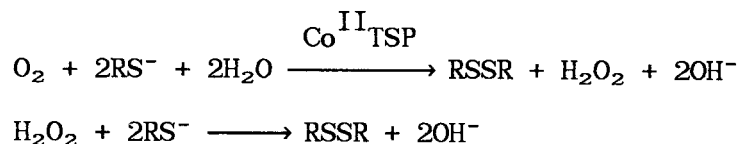
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ABSTRACT

The kinetics and mechanism of the autoxidation of 2-mercaptoethanol, 2-aminoethanethiol and ethanethiol catalyzed by Co(II)-4,4',4'',4'''-tetrasulfophthalocyanine, abbreviated as Co(II)TSP, has been examined. Kinetic data showed that the catalytic autoxidation of all three mercaptans proceeded via the same mechanism. The ultimate products of the autoxidation were found to be the corresponding disulfide (RSSR) and hydroxide ion. The kinetic data indicated that 50% to 80% of the disappearance of mercaptans was controlled by the catalytic cycle as opposed to oxidation by the intermediate, H₂O₂. The overall stoichiometry of the catalytic autoxidation is the sum of the following reactions:



Stoichiometric ratio of mercaptan to oxygen of 1:4 was found for each mercaptan.

When the mercaptan was added, a dimeric Co(II)TSP was formed by the bridging of the two Co(II)TSP monomers by mercaptan anion. This dimer is proposed as the catalytic center for the cycle. The electron transfer from Co(II) to bound O₂ forming a superoxide-like species is assumed to be the rate-determining step.

The experimental rate law for the autoxidation of each mercaptan was found to be

$$v = \frac{-d[\text{RS}^-]}{dt} = k_{\text{obsd}}[\text{CoTSP}]_T[\text{RS}^-]$$

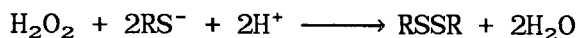
and an expression for k_{obsd} of each mercaptans was derived from the postulated mechanism.

The kinetics reveal that the catalytic cycle is sensitive to variations in pH. The pH dependence at $\text{pH} < 11$ can be easily explained by the acid-base equilibria of the mercaptan ($\text{RSH} \rightleftharpoons \text{RS}^- + \text{H}^+$). However, the pH dependence at $\text{pH} > 11$ suggests that the deprotonation of Co(II)TSP dimer must occur and that pK_1 of the dimer must be between 11 and 13.

The rate of autoxidation of mercaptans follows the relative order of ethanethiol $>$ 2-aminoethanethiol $>$ 2-mercaptoethanol. Linear free energy relationship (LFER) was established 1) between Taft σ^* value of the substituent group and the rate constant; 2) between Taft σ^* value and the pK_2 where K_2 is the apparent acid dissociation constant of the catalytic dimer.

The hydrogen peroxide produced from the catalytic cycle oxidizes the mercaptan anions giving the disulfide as the product. The

stoichiometry is found to be



The kinetics and mechanism for the oxidation of 2-mercaptoethanol by hydrogen peroxide have been examined. The rate expression for the oxidation is as follows:

$$v = - \frac{d[\text{RS}^-]}{dt} = k'_{\text{obsd}}[\text{H}_2\text{O}_2][\text{RS}^-]$$

k'_{obsd} depends on the apparent acid dissociation constants of $\text{HOC}_2\text{H}_4\text{SH}$, $\text{HOC}_2\text{H}_4\text{S}^-$ and H_2O_2 .

The kinetics and mechanism of reduction of Co(II)TSP by 2-mercaptoethanol under anoxic conditions were studied. Results from this study provide estimates of the rate of complexation of Co(II)TSP by 2-mercaptoethanol and the acid dissociation constant, K_{a_1} , of the bound water on the Co(II)TSP-RS-Co(II)TSP. Co(II)TSP was reduced to Co(I)TSP by 2-mercaptoethanol. The rate expression is given by

$$v = \frac{-d[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}}}{dt} = \frac{k_2 K_1 [\text{RSH}]_{\text{T}} [\text{Co}^{\text{II}}\text{TSP}]_{\text{T}}}{2 \left(1 + \frac{a_{\text{H}^+}}{K_{a_1}} + \frac{K_{a_2}}{a_{\text{H}^+}} \right) (1 + \alpha [\text{RSH}]_{\text{T}})}$$

where k_2 is the rate constant for the electron transfer step, and K_1

is the equilibrium constant for the complexation of CoTSP dimer with thioethanol. K_{a_1} and K_{a_2} are the apparent acid dissociation constants of $\text{HOC}_2\text{H}_4\text{SH}$ and $\text{HOC}_2\text{H}_4\text{S}^-$, respectively; and α is $K_1/(1 + a_{\text{H}^+}/K_{a_1} + K_{a_2}/a_{\text{H}^+})$. Results of this system further enhance the argument that the electron transfer step rather than the preceding mercaptan complexation step is the rate-determining step in the oxygenated system.

This study indicates that Co(II)TSP is a very effective catalyst for the autoxidation of mercaptans. pH is an important physiochemical parameter for the autoxidation, whereas the effect of dissolved O_2 concentration is rather insignificant. From a practical standpoint, use of the homogeneous catalyst is not very economical because of the relatively expensive recovery process. Solid-supported Co(II)TSP such as $(\text{SiO}_2)\text{-Co(II)TSP}$, $\text{TiO}_2\text{-Co(II)TSP}$, and polystyrene-divinyl benzene resin-Co(II)TSP contained in fixed bed reactors may be an economic alternative for mercaptan waste treatment. Nevertheless, the results of this study should provide useful insight into the design of a suitable hybrid system.

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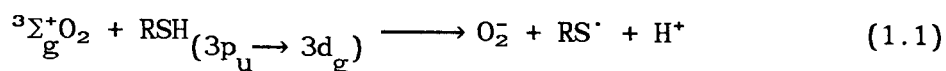
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CHAPTER ONE
INTRODUCTION

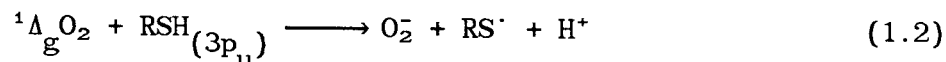
Hazardous chemical wastes pose a threat to human health and may cause significant ecological damage. They are generally difficult to remove from wastewater by conventional primary or secondary wastewater treatment. Frequently, hazardous wastes are stored in containers which leak and contaminate local environments such as groundwater. As the public concern about the control of hazardous waste, alternative methods for hazardous waste treatment such as incineration and reverse osmosis have been explored; however, these processes tend to be expensive and not totally reliable. For selected applications, oxidation of the chemical wastes by chlorine, ozone, hydrogen peroxide or molecular oxygen, has been employed for waste removal. With the exception of molecular oxygen which is readily available from atmosphere, these oxidants require special manufacturing and storage facilities which inevitably increase the overall cost of the processes; furthermore, these oxidants are listed as hazardous in their own right, and potentially explosive because of their relatively high reduction potentials. As a result, molecular oxygen is an attractive oxidant compared to chlorine, ozone and hydrogen peroxide.

Oxidation by molecular oxygen is often referred to "autoxidation". Autoxidation is technically described as the spontaneous oxidation which take place with molecular oxygen at moderate temperature ($\leq 150^{\circ}\text{C}$) without visible combustion (Hampel and Hawley, 1973). Thermodynamically, molecular oxygen can be considered

as a strong oxidant according to its reduction-potential ($O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $E^0 = 1.229$ volt); however, the rates of autoxidation are usually very slow. In general, autoxidation requires either excitation of molecular oxygen from its triplet ground state to an excited singlet state for reaction with singlet state reductants, or for the reductants to be excited to their triplet states to react with ground state molecular oxygen. For example, there are two possible reactions for the autoxidation of mercaptans (Koppenol, 1977). They are:



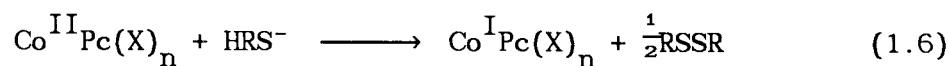
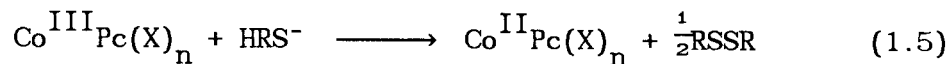
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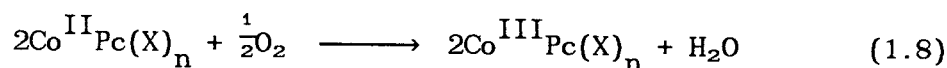
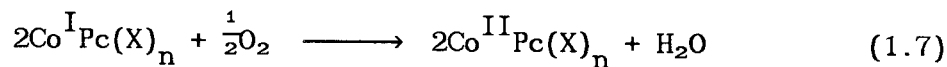


In the first reaction, the half-filled π_g^* orbital of ground state oxygen overlaps with the excited sulfur atom on the mercaptan; however, the second pathway requires a direct overlap of empty π_g^* orbital of an excited singlet state oxygen with the filled $3p_u$ orbital of the sulphur atom. Each mechanism requires a relatively large activation energy. Frequently, a catalyst is necessary to lower the activation energy. Transition metals, such as Cu(II), Co(II), Fe(II), Mn(II), Ni(II) and their complexes (Hoffmann, 1980; McAuley, 1970), are known to be effective catalysts for the autoxidation.

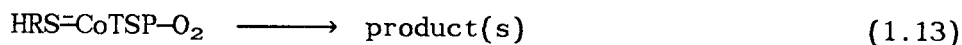
Metal phthalocyanine complexes are known to catalyze the autoxidation of selected organic compounds (Kropf, 1972) in non-aqueous solvents; however, these complexes are less effective catalysts in aqueous solution. The ineffectiveness of these catalysts is possibly due to their low solubilities in water. However, modification can be made to enhance solubility (Weber and Busch, 1965). Metal tetrasulfophthalocyanines are known to catalyze the autoxidation of H₂S (Hoffmann and Lim, 1979) and mercaptans (Anderson and Ward, 1976; Frame, 1981) in aqueous solution.

Cobalt tetrasulfophthalocyanine has been reported to be an effective catalyst for the autoxidation of 2-mercaptoethanol (Mass et al., 1976) and cysteine (Kundo et al., 1967). However, the reaction kinetics are understood only at a qualitative level. Simonov et al. (1973) proposed the following stoichiometric sequence for the catalytic autoxidation of simple mercaptans:





where $\text{Pc}(\text{X})_{\text{n}}$ represents for various water-soluble ligands including tetrasulfophthalocyanine (TSP) where $\text{X} \equiv \text{SO}_3^-$. However, Dolansky et al. (1976) have proposed the following mechanism:



Dolansky et al. (1973) proposed that molecular oxygen, CoTSP and the substrate form a ternary complex as indicated in equation 1.12, whereas Simonov (1973) did not consider the formation of a discrete Co(II)-dioxygen complex. No attempt has been made to describe the

stoichiometry, product distribution, reaction intermediates and the effect of physicochemical variable such as pH, ionic strength and temperature on the kinetics of the catalytic autoxidation of mercaptans in aqueous solution.

Mercaptans are the odorous constituent in sour refinery wastes. They can be detected at < parts per billion levels. In present day, mercaptans are first removed from the distillate by contacting it with a selective solvent such as monoethanamine. Subsequently, the mercaptans are removed from the solvent by contacting it with an aqueous alkaline solution (Anderson and Ward; 1976). The mercaptans in the aqueous alkaline solution are oxidized to disulfide by dissolved oxygen. However, this process is extremely slow. Frequently, metal chelate is added to accelerate the reaction. Co-tetrasulfophthalocyanine would be a good candidate to catalyze such reaction.

This thesis describes the research in investigation of the detail kinetics and mechanism of autoxidation of mercaptans catalyzed by Co(II) 4,4',4'',4'''-tetrasulfophthalocyanine and reaction of the intermediate dioxygen reduction product, H_2O_2 .

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CHAPTER TWO
THEORY AND BACKGROUND

Nomenclature and Nature of Oxygen

The terminology applied in this thesis, referring to different forms of oxygen, is the same as used by Jones et al. (1979) in his review on synthetic oxygen carriers. The term Molecular Oxygen is referred to the ground state (${}^3\Sigma_g^-$) of uncombined or free molecule of oxygen; whereas the term dioxygen is applied to O_2 in combined form with a covalent bond between the oxygen atoms. Metal-dioxygen refers to an oxygen molecule ligated to a metal center. Specifically, the terms, metal-superoxides and metal peroxide, are used for metal-dioxygen complexes in which the dioxygen resembles the superoxide ($O_2^- \cdot$) and peroxide (O_2^{2-}), respectively. The incorporation of O_2 into the metal center is referred to oxygenation; whereas deoxygenation is used for the reverse process.

Molecular oxygen is a paramagnetic molecule with a triplet ${}^3\Sigma_g^-$ ground state. Its next two excited states are in singlet forms, ${}^1\Delta_g$ and ${}^1\Lambda_g^+$, which are 94.3 and 156.9 kJ/mole (Jones et al., 1979) above the ground state, respectively. The ground state configuration is described as $(1s\sigma_g)^2 (1s\sigma_u^*)^2 (2s\sigma_g)^2 (2s\sigma_g^*) (2p\sigma_g)^2 (2p\pi_u)^4 (2p\pi_g^*)^1 (2p\pi_g^*)^1$. According to the configuration shown in Figure 2.1, the two unpaired electrons of O_2 occupy two antibonding π orbitals making the bond order of two. The addition of one or two electron(s) to fill the electron vacancies on the $2p\pi_g^*$ orbital results in the formation of superoxide ion ($O_2^- \cdot$) or peroxide anion (O_2^{2-}), respectively. The

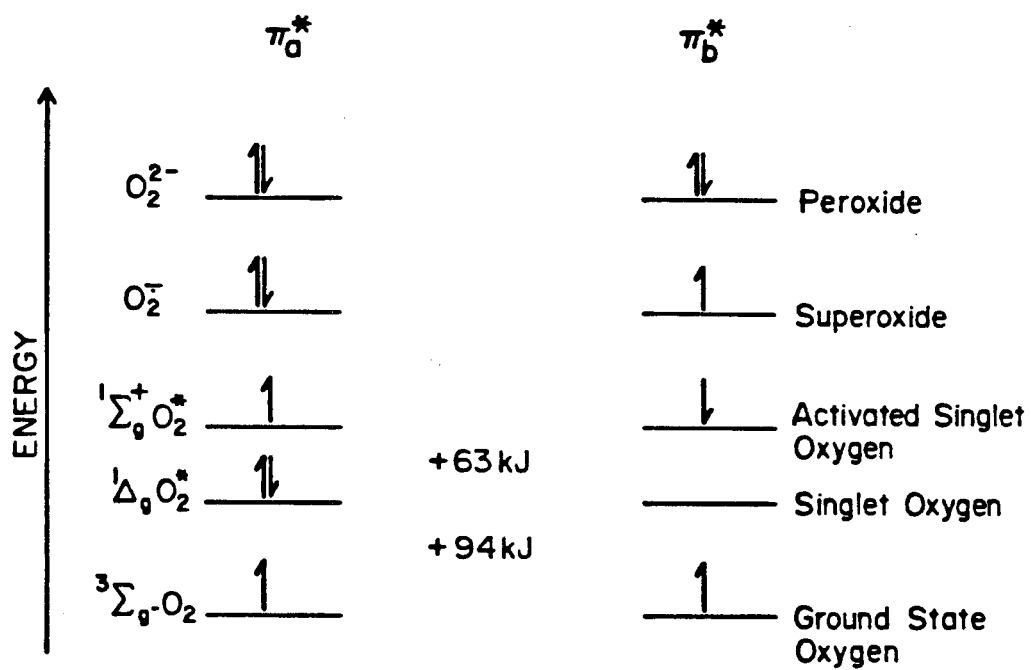


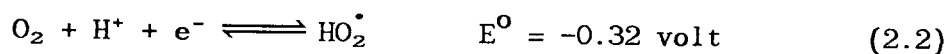
Figure 2.1: The energy level of Various Forms of Oxygen.

relative energy levels of the π^* orbitals for these two ions and molecular oxygen are shown in Figure 2.1.

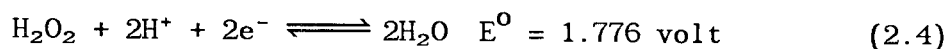
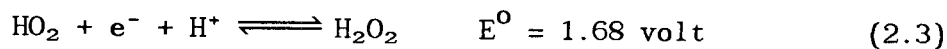
Molecular oxygen can accept up to 4 electron forming water as the ultimate reduction product. The overall process



where E^0 is 1.299 volts and ΔG^0 is -474.9 kJ/mole (Jones et al., 1979), is highly exothermic, making molecular oxygen as a powerful oxidant. However, the kinetics of the reduction do not proceed very rapidly because the initial step for the overall reduction is a one-electron process to form superoxide-like species with negative E^0 value (Jones et al., 1979):



The negative E^0 value of this single-electron transfer is the result of the large reduction of the O-O bond strength on going from O_2 to HO_2^\bullet . HO_2^\bullet may further react to form H_2O (Jones et al., 1979):



According to the above sequence, the overall rate of O_2 reduction is most-likely controlled by the production of superoxide. A summary of the reactions involving dioxygen with the corresponding physical and thermodynamic data are listed in Table 2.1.

Background and Chemistry of Mercaptans

Mercaptan is used to refer to any compounds in the form of RSH, where R denotes any organic groups. In the presence of oxygen, the RSH can be slowly oxidized to form disulfide. The reaction can be catalyzed by the presence of transition metals such as cobalt, copper, zinc, etc. (Cullis and Trimm, 1968). These highly odoriferous compounds can be detected in the subpart-per-million range. Mercaptans are normally present in oil refinery wastes. Co(II)-tetrasulfophthalocyanine has been shown to be an effective catalyst for the autoxidation of mercaptans (Zwart et al., 1977/78).

Nomenclature and Nature of Cobalt

In nature, cobalt is always found in association with nickel and quite often with arsenic. Smaltite ($CoAs_2$), and cobaltite ($CoAsS$) are the most important cobalt minerals. However, the major commercial sources of cobalt are the residues called "speisses", which are obtained from the smelting of arsenical ores of nickel, copper and lead.

TABLE 2.1: Physical and Thermodynamic Data of Dioxygen Species^a

	Bond Order	Sample Compound	O-O Distance Å	Bond Energy kcal/mol	$\nu_{\text{O-O}}$ cm ⁻¹
O_2^+	2.5	O_2AsF_6	1.123	149.4	1858
$\text{O}_2(^3\Sigma)$	2	O_2	1.207	117.2	1554.7
$\text{O}_2(^1\Delta)$	2	O_2	1.216	94.7	1483.5
O_2^-	1.5	KO_2	1.28		1145
O_2^{2-}	1	Na_2O_2	1.49	48.8	842

^a Data were obtained from Jones, et al., *Chemical Reviews* 1979, 79, 139.

Elemental cobalt is a hard, bluish-white metal with a melting point and a boiling point of $1,493^{\circ}\text{C}$ and $3,100^{\circ}\text{C}$, respectively (Cotton and Wilkinson, 1980). Although the reduction potential of $\text{Co}^{2+}/\text{Co}^0$ is -0.277 volt (Cotton and Wilkinson, 1980), the elemental metal is rather unreactive and dissolves very slowly in dilute acids. It does not combine directly with either nitrogen or hydrogen, and reacts with carbon, phosphorus, and sulfur only upon heating. Direct attack on the metal by molecular oxygen and water vapor occurs only at an elevated temperature, forming CoO .

Cobalt can exist in any oxidation state between $-I$ and $+V$. Among these possible oxidation states, the most common ones are the II and III states. Simple Binary Cobalt(II) and (III) salts such as $\text{Co}(II)$ oxide, $\text{Co}(II)$ halides and $\text{Co}(III)$ halides are commonly known. $\text{Co}(II)$ and $\text{Co}(III)$ can coordinate ligands to form a variety of complexes of variable geometry as given in Table 2.2. The most common configurations for these two oxidation states are the tetrahedral and octahedral complexes.

The electronic structure of these complexes is usually explained by molecular orbital theory, crystal field theory, and ligand field theory.

Chemistry of $\text{Co}(II)$ -4,4',4'',4'''-Tetrasulphthalocyanine

Phthalocyanine was first discovered as a by-product of the preparation of *o*-cyanobenzamide from phthalamide and acetic anhydride

TABLE 2.2: Oxidation States and Stereochemistry of Cobalt.^a

Oxidation State	Co-ordination Number	Geometry	Examples
Co ⁻¹ , d ¹⁰	4	Tetrahedral	Co(CO) ₄ ⁻ , Co(CO) ₃ NO
Co ⁰ , d ⁹	4	Tetrahedral	K ₄ [Co(CN) ₄], Co(PMe) ₄
Co ¹ , d ⁸	4	Tetrahedral	CoBr(PR ₃) ₃
	5 ^b	Tbp	[Co(CO) ₃ (PR ₃) ₂] ⁺ , HCo(PF ₃) ₄ [Co(NCMe) ₅] ⁺
	5	Sp	[Co(NCPh) ₅]ClO ₄
	6	Octahedral	[Co(bipy) ₃] ⁺
	2	Linear	Co[N(SiMe ₃) ₂] ₂
Co ² , d ⁷	4 ^b	Tetrahedral	[CoCl ₄] ²⁻ , CoBr ₂ (PR ₃) ₂
	5	Tbp	[Co(Me ₆ tren)Br] ⁺
	5	Sp	[CoClO ₄ (MePh ₂ AsO) ₄] ⁺
	6 ^b	Octahedral	[Co(CN) ₅] ³⁻ , [Co(CNPh) ₅] ²⁺ [Co(CN) ₆] ⁴⁻ , [Co(Cl) ₆] ⁴⁻ [Co(NH ₃) ₆] ²⁺
	8	Dodecahedral	(Ph ₄ As) ₂ [Co(NO ₃) ₄]
Co ³ , d ⁶	4	Tetrahedral	
	5	Sp	Co(corrole)Ph ₃
	6 ^b	Octahedral	[Coen ₂ Cl ₂] ⁺ , [Co(CN) ₆] ³⁻
Co ⁴ , d ⁵	4	Tetrahedral	Co(1-norbornyl)
	6	Octahedral	[CoF ₆] ²⁻
Co ⁵ , d ⁴	4	Tetrahedral	K ₃ CoO ₄

^a Data were obtained from Cotton & Wilkinson (1980).

^b Most common co-ordination number.

by Braun and Tcherniaev in 1907 (Moser and Thomas, 1983). Gradually, phthalocyanine became an important color agent for paint, plastics, printing inks and textile industries. Since its discovery, the x-ray spectra, absorption spectra, magnetic properties, catalytic activity, oxidation and reduction potentials, photoconductivity, solubility, photochemical activity, dielectric and semiconducting properties, and coordination chemistry of phthalocyanines have been examined. The catalytic activity, the absorption spectra, and the coordination chemistry of the Co(II)-tetrasulfophthalocyanine, abbreviated as Co(II)TSP, will be emphasized in this chapter.

Co(II)-tetrasulfophthalocyanine is a square-planar macro-molecule with Co^{2+} incorporated at the center of the plane. Its structure is shown in Figure 2.2. The phthalocyanine has been sulfonated to enhance its solubility in water. Metal-free phthalocyanine contains a total of forty π -electrons. Out of these forty π electrons, sixteen π electrons belong to the macro-ring, which are primarily linked through the nitrogen bridges on the molecule, while the other twenty-four π electrons are conjugated throughout the benzene rings. The π -electrons of the macro-ring do not strongly interact with the π -electrons of the benzene ring. In presence of transitional metal ions such as cobalt(II), four equivalent σ bonds ($\text{N} \rightarrow \text{M}$) with σ -electrons of the four inner nitrogen atoms of the phthalocyanine molecule are formed. The σ bonds are quite strong such that replacement of cobalt(II) center by other cations is unlikely. At the

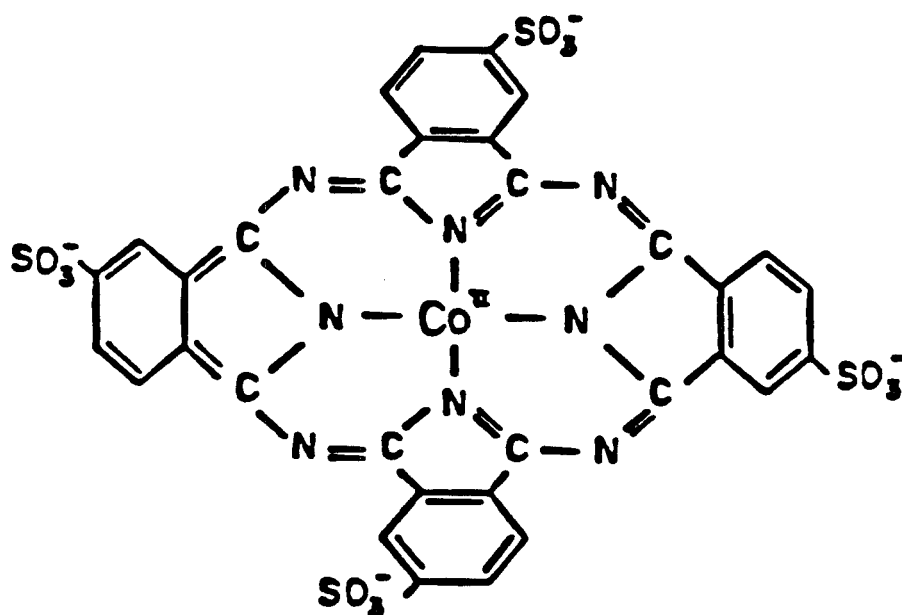
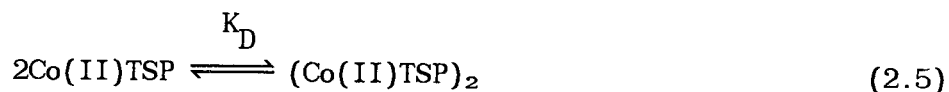


Figure 2.2: The Structure of Co(II)-4,4',4'',4'''-Tetrakisulfophthalocyanine.

same time, the electrons from filled metal d_{xy} , d_{xz} , d_{yz} orbitals form back-bonds with the phthalocyanine ligand. This effect is referred to as the dative π effect of coordination. The π back-bonding would further stabilize the complex. In this case, the cobalt metal center serves as the π -donor, whereas the phthalocyanine serves as the π -acceptor.

Co(II)-tetrasulfophthalocyanine is known to form dimers and higher degree polymers (Schelly et al., 1970). The dimerization constant for Co(II)TSP (K_D) for the following reaction



has been determined to be $6.17 \times 10^5 \text{ M}^{-1}$ at 38°C (Schelly et al., 1970). Typical UV-Visible spectrum of Co(II)TSP was shown in Figure 2.3. The spectrum is dominated by peaks around 350 nm and 700 nm. In the visible region, the first peak, which is attributed to the dimer, occurs around 626 nm, while the second peak, which is attributed to the monomer, occurs at 668 nm. However, the structure of the dimer is unclear. The monomers may be bridged by the hydroxide ion or linked together by the overlaps of the π orbitals on cofacial phthalocyanine rings. However, Abel et al. (1976) has suggested that water molecule play an important role in binding the monomers by hydrogen bonds.

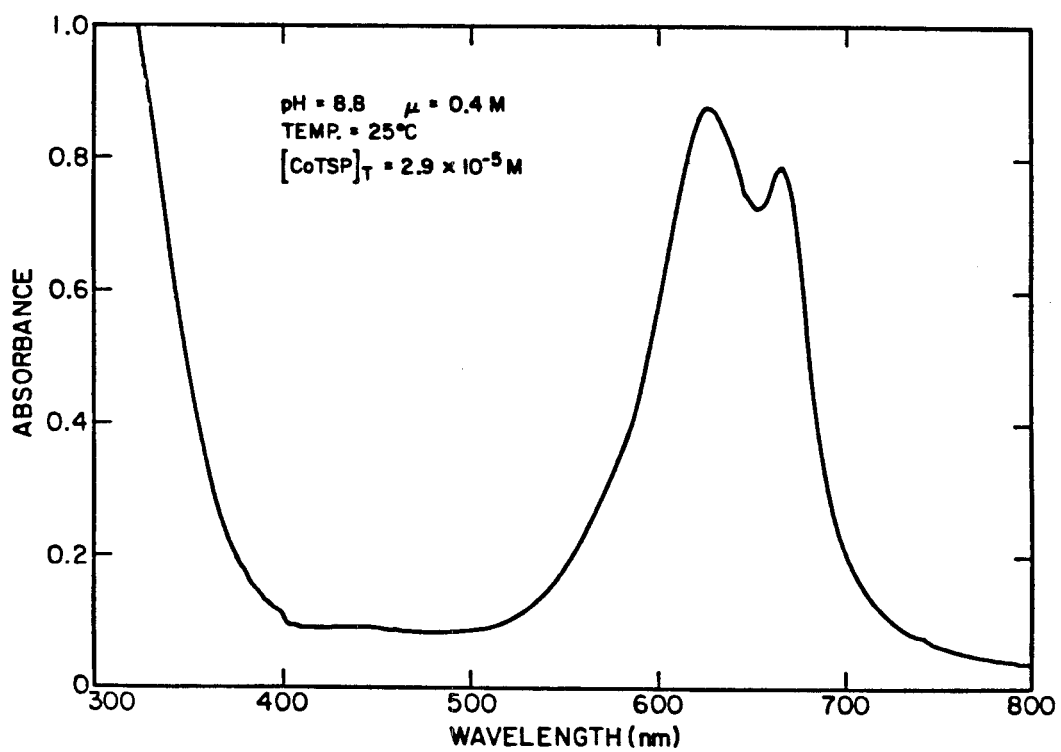


Figure 2.3: The Spectrum of Co(II)TSP under Deoxygenated Atmosphere.

In the case of the Co(II) center, four of the coordination sites are occupied by the phthalocyanine ligand. This leaves only the two trans-axial sites available for coordination of other ligands. These axial sites are known to be capable of binding with a variety of inorganic and organic ligands. The most common ligands includes H₂O (Przywarske-Boniecka and Krystyna, 1976), OH⁻ (Przywarske-Boniecka and Wojciechowski, 1975), Br⁻, pyridine, CN⁻, and imidazole (Przywarske-Boniecka and Krystna, 1976).

In addition to its ability to form complexes with the inorganic and organic ligands in the axial coordination sites, Co(II)-tetrasulfophthalocyanine is able to bind with molecular oxygen reversibly forming an oxygenated Co(II)TSP complex (Abel et al., 1971; Veprek-Siske et al., 1972). The formation of reversible cobalt(II) dioxygen complexes is the primary factor that determines the catalytic activity of Co(II)TSP in the autoxidation of a variety of inorganic and organic substrates. In addition to mercaptans, the autoxidation of substrates such as N₂H₄ (Wagnerova et al., 1973), H₂S (Hoffmann and Lim, 1979), HSO₃⁻ (Boyce et al., 1983), etc. have been shown to be effectively catalyzed by Co(II)-tetrasulfophthalocyanine in the concentration range of 10⁻⁸ M to 10⁻⁶ M with turn-over numbers in the range of 1000 to 150,000.

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CHAPTER THREE
KINETICS AND MECHANISM OF AUTOXIDATION OF 2-MERCAPTOETHANOL
CATALYZED BY Co(II)-4,4',4'',4'''-TETRASULFOPHTHALOCYANINE
IN AQUEOUS SOLUTION

NOTATIONS

k_{obsd}	Observed rate constant
k_{cald}	Calculated rate constant from equation 3.27
k_{31}	Electron-transfer rate constant (sec^{-1}) of reaction $\begin{aligned} &(\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2)^{-6} \longrightarrow \\ &(\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{III}}\text{TSP}-\text{O}_2)^{-6} \end{aligned}$
K_{21}	Equilibrium constant (M^{-1}) of reaction $\begin{aligned} &(\text{H}_2\text{O}-\text{Co}^{\text{II}}\text{TSP}-\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2)^{-5} + \text{HOC}_2\text{H}_4\text{S}^- \rightleftharpoons \\ &(\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2)^{-6} \end{aligned}$
k_{32}	Electron-transfer rate constant (sec^{-1}) of reaction $\begin{aligned} &(\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2)^{-7} \longrightarrow \\ &(\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{III}}\text{TSP}-\text{O}_2)^{-7} \end{aligned}$
K_{22}	Equilibrium constant (M^{-1}) of reaction $\begin{aligned} &(\text{H}_2\text{O}-\text{Co}^{\text{II}}\text{TSP}-\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2)^{-6} + \text{HOC}_2\text{H}_4\text{S}^- \rightleftharpoons \\ &(\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2)^{-7} \end{aligned}$
k_{33}	Electron-transfer rate constant (sec^{-1}) of reaction $\begin{aligned} &(\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2)^{-8} \longrightarrow \\ &(\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{III}}\text{TSP}-\text{O}_2)^{-8} \end{aligned}$
K_{23}	Equilibrium constant (M^{-1}) of reaction $\begin{aligned} &(\text{H}_2\text{O}-\text{Co}^{\text{II}}\text{TSP}-\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2)^{-7} + \text{HOC}_2\text{H}_4\text{S}^- \rightleftharpoons \\ &(\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2)^{-8} \end{aligned}$

- K_1 Apparent acid dissociation constant (M) of Acid-Base Equilibria $(\text{H}_2\text{O}-\text{Co}^{\text{II}}\text{TSP}-\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{H}_2\text{O})^{-5} \rightleftharpoons (\text{H}_2\text{O}-\text{Co}^{\text{II}}\text{TSP}-\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{H}_2\text{O})^{-6} + \text{H}^+$
- K_2 Apparent acid dissociation constant (M) of Acid-Base Equilibria $(\text{H}_2\text{O}-\text{Co}^{\text{II}}\text{TSP}-\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{H}_2\text{O})^{-6} \rightleftharpoons (\text{H}_2\text{O}-\text{Co}^{\text{II}}\text{TSP}-\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{H}_2\text{O})^{-7} + \text{H}^+$
- K_{a_1} Apparent acid dissociation constant (M) of Acid-Base Equilibria $\text{HOC}_2\text{H}_4\text{SH} \rightleftharpoons \text{HOC}_2\text{H}_4\text{S}^- + \text{H}^+$
- K_{a_2} Apparent acid dissociation constant (M) of Acid-Base Equilibria $\text{HOC}_2\text{H}_4\text{S}^- \rightleftharpoons ^-\text{OC}_2\text{H}_4\text{S}^- + \text{H}^+$
- K_{11} Equilibrium constant (M^{-1}) of reaction $(\text{H}_2\text{O}-\text{Co}^{\text{II}}\text{TSP}-\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{H}_2\text{O})^{-5} + \text{O}_2 \rightleftharpoons (\text{H}_2\text{O}-\text{Co}^{\text{II}}\text{TSP}-\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2)^{-5}$
- K_3 Equilibrium constant (M^{-1}) of reaction $\text{Co}^{\text{II}}\text{TSP}-\text{O}_2 + \text{HOC}_2\text{H}_4\text{S}^- \rightleftharpoons \text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2$
- K_4 Equilibrium constant of reaction $2(\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2) \rightleftharpoons \text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2-\text{Co}^{\text{II}}\text{TSP}=\text{SH}_4\text{C}_2\text{OH} + \text{O}_4$
- K_5 Apparent acid dissociation constant (M) of Acid-Base Equilibria $(\text{H}_2\text{O}-\text{Co}^{\text{II}}\text{TSP}-\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{H}_2\text{O})^{-5} \rightleftharpoons (\text{H}_2\text{O}-\text{Co}^{\text{II}}\text{TSP}-\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{OH})^{-6} + \text{H}^+$

a_{H^+}	Hydrogen ion activity
μ	Ionic strength (M)
$[\text{Co}^{\text{II}}_{\text{TSP}}]_{\text{T}}$	Total $\text{Co}^{\text{II}}_{\text{TSP}}$ concentration (M)
$[\text{Co}^{\text{II}}_{\text{TSP}}]_{\text{Ti}}$	Total i^{th} $\text{Co}^{\text{II}}_{\text{TSP}}$ catalytic center concentration (M)

Abstract

The kinetics and mechanism of catalytic autoxidation of 2-mercaptoethanol by Cobalt(II)-4,4',4'',4'''-tetrasulfophthalocyanine were investigated. At ionic strength, $\mu = 0.4$ M, the experimental rate law

$$v = \frac{-d[\text{RS}^-]}{dt} = k_{\text{obsd}}[\text{CoTSP}]_T[\text{RS}^-]$$

was found, with

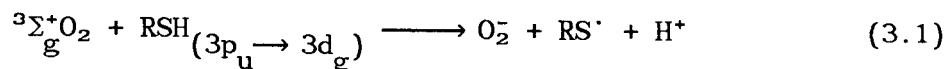
$$k_{\text{obsd}} = \frac{(k_{31}K_{21} + \frac{k_{32}K_{22}K_1'}{a_{\text{H}^+}} + \frac{k_{33}K_{23}K_1'K_2'}{a_{\text{H}^+}^2})}{(1 + \frac{K_1'}{a_{\text{H}^+}} + \frac{K_1'K_2'}{a_{\text{H}^+}^2})(1 + \frac{a_{\text{H}^+}}{K'_{a_1}} + \frac{K'_{a_2}}{a_{\text{H}^+}})}$$

where k_{3i} is the rate constant of the electron-transfer step of the i^{th} catalytic center; K_{1i} , K_{2i} are the equilibrium constants of oxygenation and substrate complexation of the i^{th} catalytic center, respectively; K_1' , K'_{a_1} , K'_{a_2} are the apparent acid dissociation constants of the catalyst, $\text{HOC}_2\text{H}_4\text{SH}$ and $\text{HOC}_2\text{H}_4\text{S}^-$ respectively; and a_{H^+} is the hydrogen ion activity. A non-linear least-squares fit of the experimental data to the above rate law gave values $k_{31}K_{21} = (1.5 \pm 0.05) \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$, $k_{32}K_{22} = (1.3 \pm 0.1) \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$, $k_{33}K_{23} =$

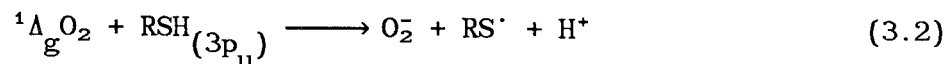
$(7.5 \pm 0.2) \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$, $\text{p}K_1 = 10.8$ and $\text{p}K_2^2 = 10.97$ at 25°C . The active catalytic center was determined to be a dimer that is bridged by 2-mercaptoethanol. Hydrogen peroxide and 2-mercaptoethanol radicals were identified as reaction intermediates; hydroxide ion and 2-hydroxyethyldisulfide were found as products.

Introduction

Autoxidation is described as the spontaneous oxidation which takes place with molecular oxygen at moderate temperature ($\leq 150^\circ\text{C}$) without visible combustion (Hampel and Hawley, 1973). Thermodynamically, O_2 is considered as a strong oxidant because of its high reduction-potential ($\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$; $E^0 = 1.229$ volt), however, rates of autoxidation are often slow. In general, autoxidation requires either excitation of molecular oxygen from its triplet ground state to an excited singlet state for reaction with singlet state reductants or for the reductants to be excited to their triplet states to react with ground state molecular oxygen. For example, there are two possible reactions for the autoxidation of mercaptans (Koppenol and Butler, 1977). They are:



or

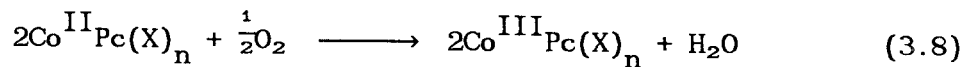
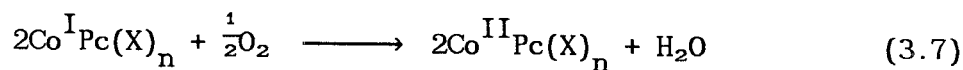
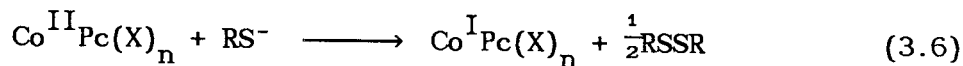
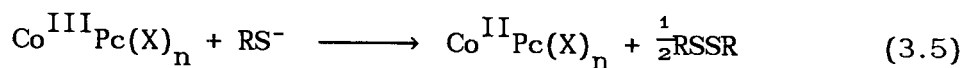
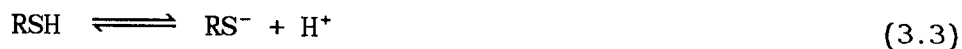


In the first reaction, the half-filled π_g^* orbital of ground state oxygen overlaps with the excited sulfur atom on the mercaptan, however, the second pathway requires a direct overlap of empty π_g^* orbital of an excited singlet state oxygen with the filled $3p_u$ orbital of the sulphur atom. Each mechanism requires a relatively large activation energy. Frequently, a catalyst is necessary to lower the activation energy. Transition metals, such as Cu(II), Co(II), Fe(II), Mn(II), Ni(II) and their complexes (Hoffmann, 1980; McAuley, 1970), are known to be effective catalysts for the autoxidation.

Metal phthalocyanine complexes are known to catalyze the autoxidation of selected organic compounds (Kropf, 1972) in non-aqueous solvents; however, these complexes are less effective catalysts in aqueous solution. The ineffectiveness of phthalocyanines as catalysts for organic autoxidations is most likely due to their low solubilities in water. However, the phthalocyanine ring can be easily modified by sulfonation to enhance solubility (Weber and Busch, 1965). Metal tetrasulfophthalocyanines are known to catalyze the autoxidation of H_2S (Hoffmann, 1979) and mercaptans (Anderson and Ward, 1976; Frame, 1981) in an aqueous solution.

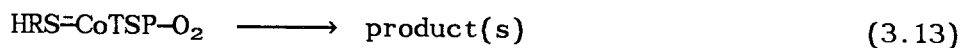
Cobalt(II) tetrasulfophthalocyanine, abbreviated as Co(II)TSP, has been reported to be an effective catalyst for the autoxidation of 2-mercaptoethanol (Mass et al., 1976) and cysteine (Kundo et al., 1967). However, the reaction kinetics are understood only at a

qualitative level. Simonov et al. (1973) proposed the following mechanism for the catalytic autoxidation of simple mercaptans:



where $\text{Pc}(\text{X})_n$ represents for various water-soluble ligands including tetrasulfophthalocyanine (TSP) where $\text{X} \equiv \text{SO}_3^-$. However, Dolansky and Wagnerova (Dolansky et al., 1976) have proposed the following mechanism:





Dolansky and Wagnerova et al. (1976) proposed that molecular oxygen, Co(II)TSP and the substrate form a ternary complex as indicated in equation 3.12, whereas Simonov did not consider the formation of a discrete Co(II)-dioxygen complex. No attempt has been made to describe the stoichiometry, product distribution, reaction intermediates and the effect of pH, ionic strength and temperature on the kinetics of the catalytic autoxidation of mercaptans in aqueous solution. This paper describes the detailed kinetics and mechanism of autoxidation of 2-mercaptoethanol catalyzed by Co(II)-4,4',4'',4'''-tetrasulfophthalocyanine. 2-mercaptoethanol and other mercaptans are often found in sour refinery wastes. The catalytic autoxidation of 2-mercaptoethanol and other mercaptans by Co(II)TSP may be used for the effective elimination of these malodorous compounds from aqueous wastes.

Experimental Procedure

Reagents: 2-mercaptoethanol stock solutions were prepared using redistilled 99% reagent grade 2-mercaptoethanol (Aldrich). Co(II)-4,4',4'',4'''-tetrasulfophthalocyanine, abbreviated as CoTSP, was synthesized by according to the procedure described by Boyce et al. (1983). Buffers were prepared using reagent grade sodium hydroxide (Mallinckrodt), sodium chloride (J.T.Baker), sodium bicarbonate (Mallinckrodt). Water used to prepare the buffers and reagent solutions was obtained from a Milli-Q water purification system (Millipore), had a resistivity of 18 M Ω cm, and was irradiated with ultra-violet light to remove any trace organics that may have been present.

Kinetic measurements: Kinetic measurements were made on Hewlett Packard Model 8450 Spectrophotometer. A minimum of 100 data points were collected for each kinetic measurement. At least three measurements were made for each value of k_{obsd} . Data were analyzed on-line with a IBM-XT Computer. Constant temperature was maintained at 25.5^oC with a Haake water bath. A sodium chloride stock solution was added into the appropriate buffer to establish the desired ionic strength (μ). pH was determined with a Beckman Altex Φ 71 pH meter and Radiometer Glass Electrode. Dissolved oxygen levels were established by dispersing N₂ and O₂ gas mixtures into the Co(II)TSP buffer. The reaction was monitored at 233 nm (the absorbance maximum for HOC₂H₄S⁻(aq)). Pseudo first-order conditions of $[O_2] \gg [HOC_2H_4SH]_{Tot} < 2.2 \times$

10^{-4} M were employed for all kinetic runs. The kinetics of autoxidation of 2-mercaptoethanol by Co(II)-4,4',4'',4'''-tetrasulfo-phthalocyanine were investigated at constant ionic strength ($\mu = 0.4$ M).

Stoichiometry: Reaction stoichiometry with dissolved oxygen in excess was determined by measuring the residual of dissolved oxygen after 99% of 2-mercaptoethanol had reacted in alkaline solution. Dissolved oxygen was analyzed by the Azide Modification Iodometric Method (Standard Methods for the Examination of water and Wastewater, 1975).

Product Identification: Reaction products were extracted into chloroform from the aqueous solution. The extracted sample was concentrated to dryness under a stream of N_2 gas. The residual was redissolved in 2 ml of chloroform and isolated by HPLC (Hewlett Packard 1084B). The solvent carrier was 15% methanol in deionized doubly distilled water. The oven temperature was set at $40^{\circ}C$.

Intermediate Identification: Hydrogen peroxide or peroxide ion was identified by the horseradish peroxidase fluorescence method (Lazrus et al., 1985). Samples (2 ml) were withdrawn from the reaction vessel at 60 second intervals and were immediately neutralized to $pH \approx 7$ with concentrated hydrochloric acid. After acidification, The fluorescence reagent, which consisted of KHphthalate, *p*-hydroxyphenylacetic acid and peroxidase, was added to the sample. Before the actual measurement was made, sodium hydroxide

was added to raise the pH ≥ 10 to enhance the fluorescence intensity. The excitation wavelength was 350 nm; the fluorescence intensity was measured at $\lambda = 400$ nm on a Shimadzu RF-540 Spectrofluorophotometer.

2-mercaptoethanol radical was identified by monitoring the formation of ascorbate radical in the reaction mixture with ascorbic acid. Ascorbate is known to react with mercaptan radical producing the corresponding ascorbate radical ($RS^{\cdot} + AH^- \longrightarrow A^{\cdot-} + RS^- + H^+$) (Redpath and Wilson, 1973; Schuler, 1977) which absorbs at $\lambda = 360$ nm with $\epsilon_{360} = 3300 \text{ cm}^{-1} \text{ M}^{-1}$.

Hydroxide Ion Identification: The hydroxide ion production was identified by continuously monitoring the pH of the unbuffered reaction solution.

Results

Under pseudo-first-order conditions ($[O_2] \gg [HOCH_2CH_2SH]_T$), plots of $\ln(A_t - A_\infty)$ vs. t were linear ($r^2 \geq 0.999$) for 50 to 90% of the reaction. This linearity of the pseudo-first-order relationship in mercaptoethanol indicates the rate of autoxidation is first order with respect to the thioethanol. Figure 3.1 compares the calculated exponential fit with the actual kinetic data. The dependence of k_{obsd} on $[O_2]$ was determined at both pH 10.5 and 13.0 (Figure 3.2). Results of these experiments showed an independence of the rate on the concentration of dissolved oxygen. Plots of k_{obsd} vs. $[CoTSP]_T$ from $0.64 \mu\text{M}$ to $2.6 \mu\text{M}$ as shown in Figure 3.3 yield straight lines ($r^2 \geq$

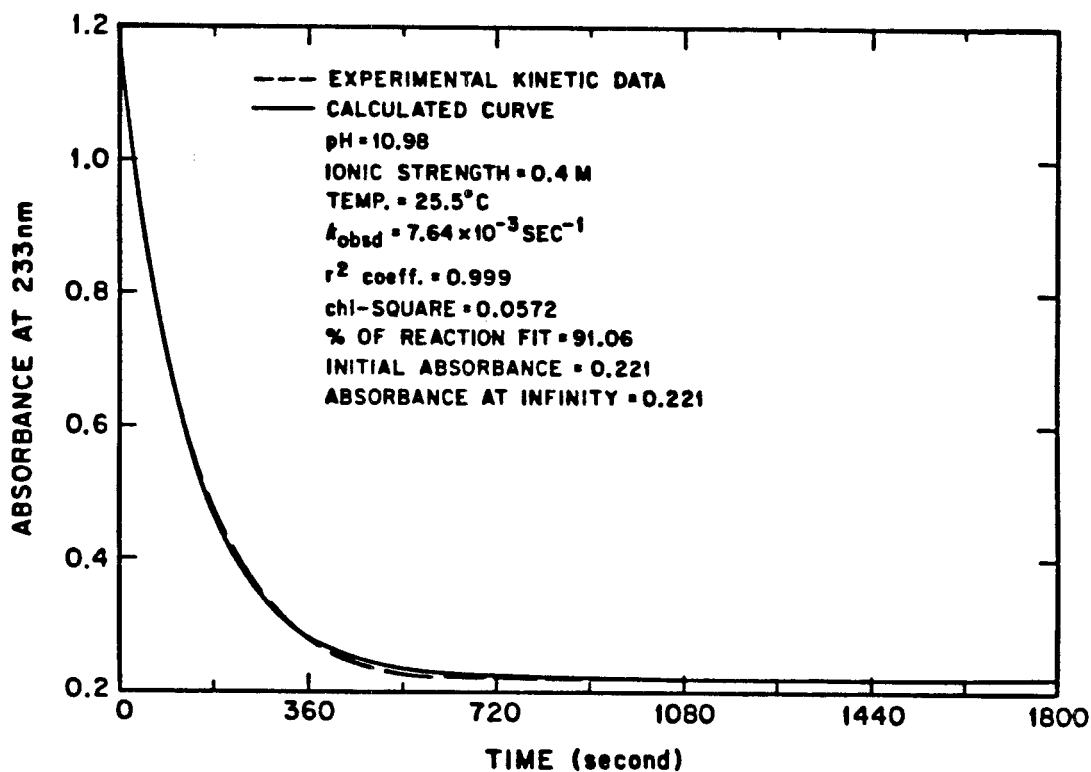


Figure 3.1: First Order Kinetic Plot of Autoxidation of 2-Mercaptoethanol catalyzed by Co(II)TSP.

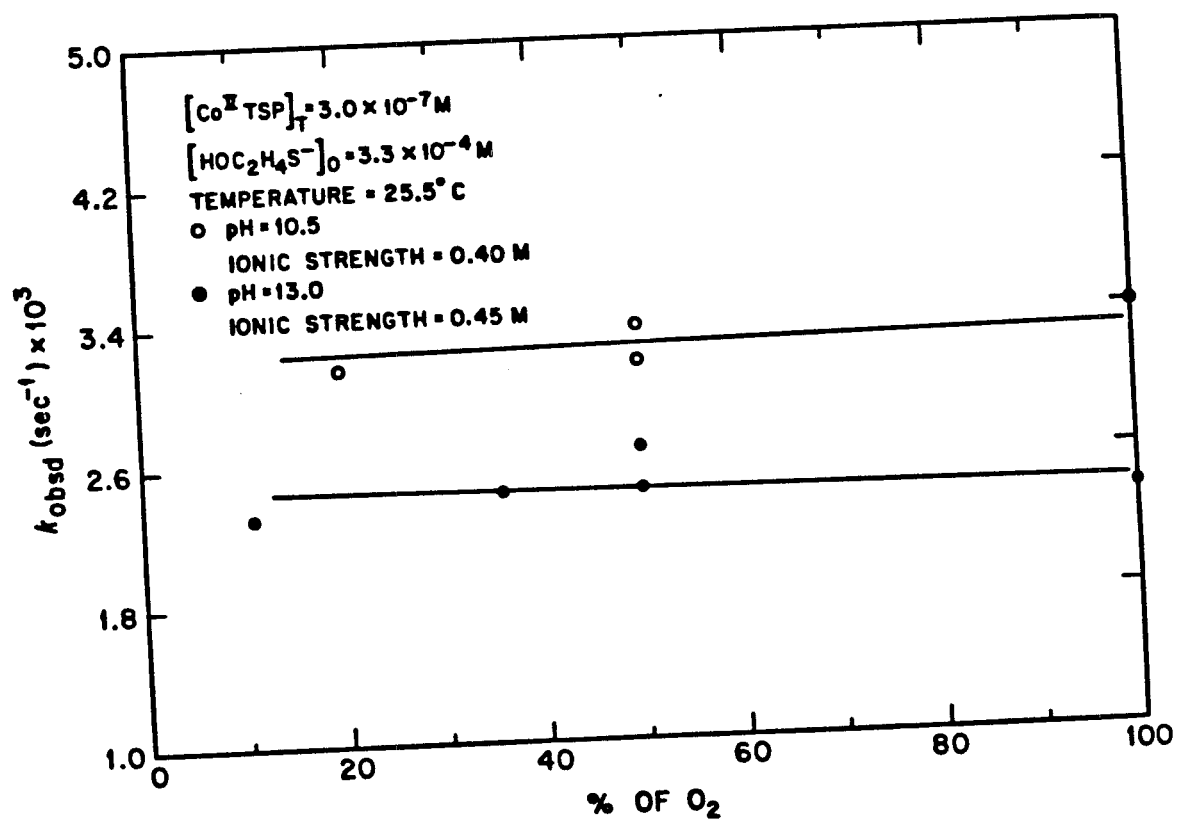


Figure 3.2: Determination of the Reaction Order of [O₂].

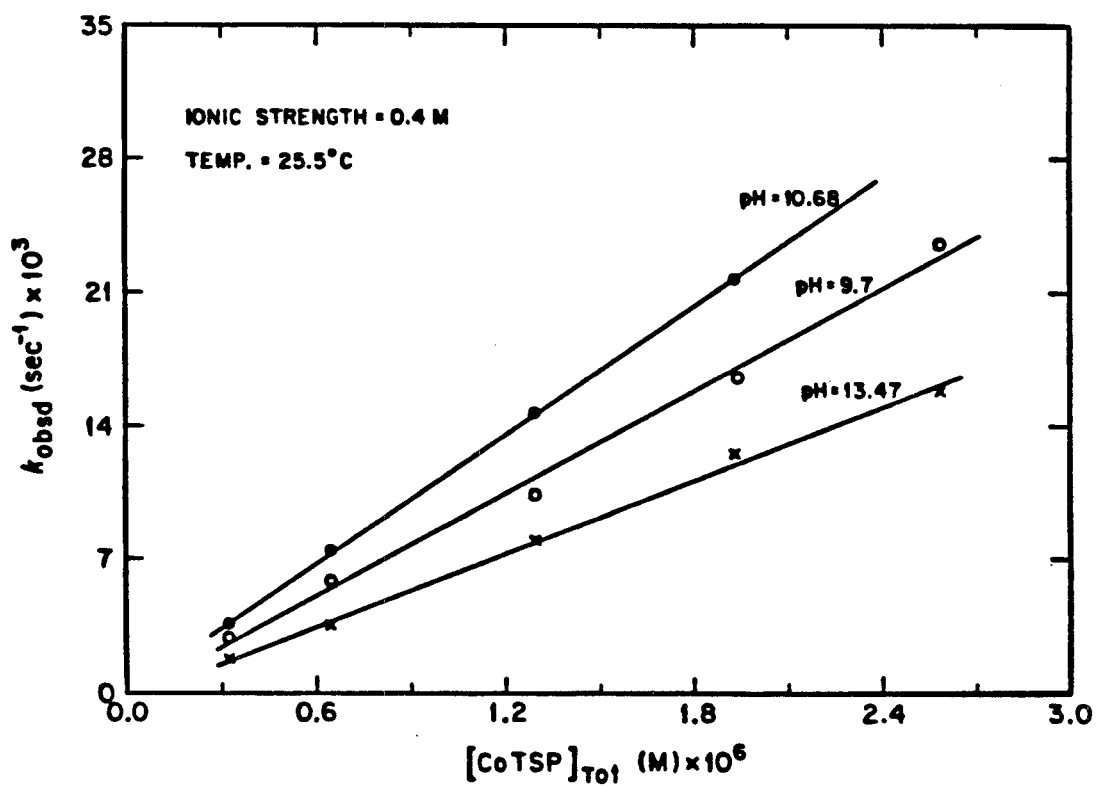
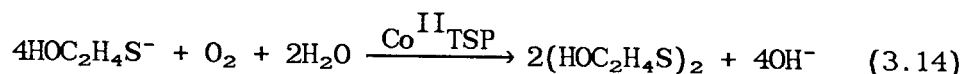


Figure 3.3: Determination of the Reaction Order of $[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}}$.

0.99) with slopes of $8795 \text{ M}^{-1}\text{s}^{-1}$, $11288 \text{ M}^{-1}\text{s}^{-1}$ and $7076 \text{ M}^{-1}\text{s}^{-1}$ at pH 9.7, 10.68 and 13.24, respectively. Thus, the rate of autoxidation is first order in both $\text{HOC}_2\text{H}_4\text{SH}$ and catalyst but apparent zero order with respect to dissolved oxygen.

In the absence of buffer, the pH, as shown in Figure 3.4, rose continuously during the course of reaction when $\text{pH}_0 \approx 10$. The increase of pH indicates that hydroxide ion is a reaction under these conditions.

The stoichiometry of the reaction, as listed on Table 3.1, was established to be 1 mole of oxygen to 4 moles of $\text{HOC}_2\text{H}_4\text{SH}$ as shown in equation 3.14, when dissolved oxygen was in excess. By comparison of chromatographic retention times with standards, the product of the catalytic autoxidation of 2-mercaptoethanol was determined to be 2-hydroxyethyldisulfide. Thus, the overall stoichiometry for $\text{pH} > 10$ is as follows:



Mercaptan radical was found to be an intermediate of the autoxidation. Figure 3.5 shows the increase of absorbance at $\lambda = 360$ nm after the addition of ascorbic acid into the reaction mixture. Such an increase implies that 2-mercaptoethanol radical, $\text{HOC}_2\text{H}_4\text{S}^\cdot$, is an intermediate of the reaction. Production of hydrogen peroxide, the other reaction intermediate, is shown in Figure 3.6. Therefore the

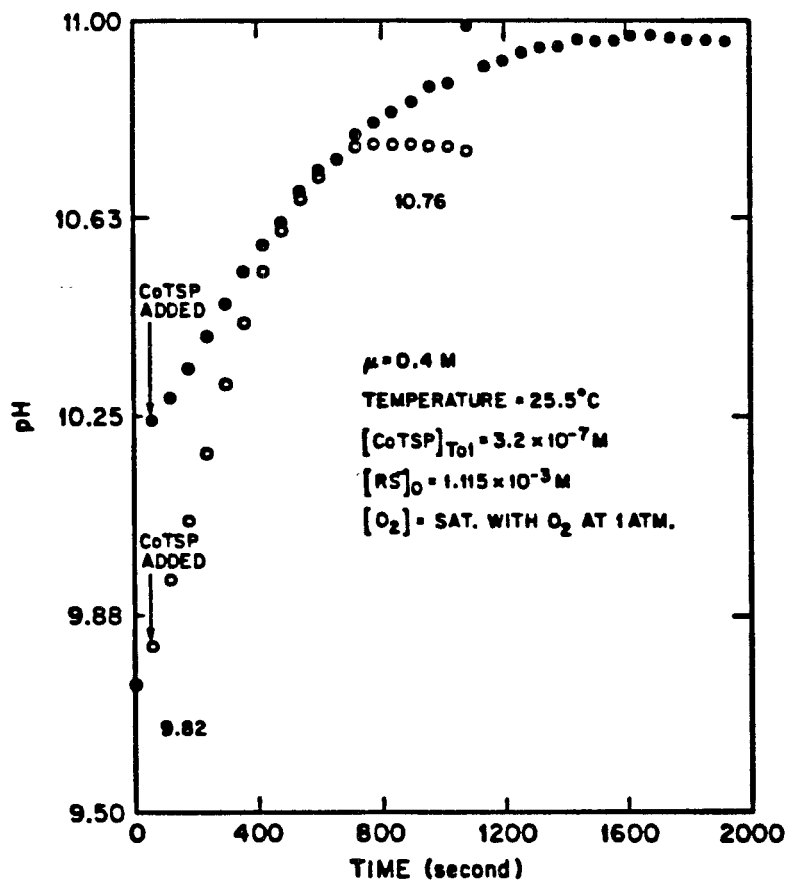


Figure 3.4: A Plot of pH vs time during the course of the Autoxidation of 2-Mercaptoethanol in unbuffered solution.

TABLE 3.1. Stoichiometry Determination of Catalytic Autoxidation of 2-Mercaptoethanol by Co(II)-4,4',4'',4'''-Tetrasulphthalocyanine.

Initial Oxygen m mole	Final Oxygen m mole	Amount of Oxygen Used m mole	Amount of Thiol Ethanol Reacted m mole	^a $\frac{\Delta S}{\Delta O_2}$
1.36×10^{-2}	6.8×10^{-3}	6.8×10^{-3}	3.2×10^{-2}	4.7
1.36×10^{-2}	6.4×10^{-3}	7.2×10^{-3}	3.2×10^{-2}	4.4
1.36×10^{-2}	6.5×10^{-3}	7.1×10^{-3}	3.2×10^{-2}	4.4
1.36×10^{-2}	5.9×10^{-3}	7.8×10^{-3}	3.2×10^{-2}	4.1

a S = Amount of 2-Mercaptoethanol reacted.

Experimental Conditions: $\mu = 0.01$ M, pH = 11.8, Temp. = 25°C

$[CoTSP]_T = 5.15 \times 10^{-6}$ M.

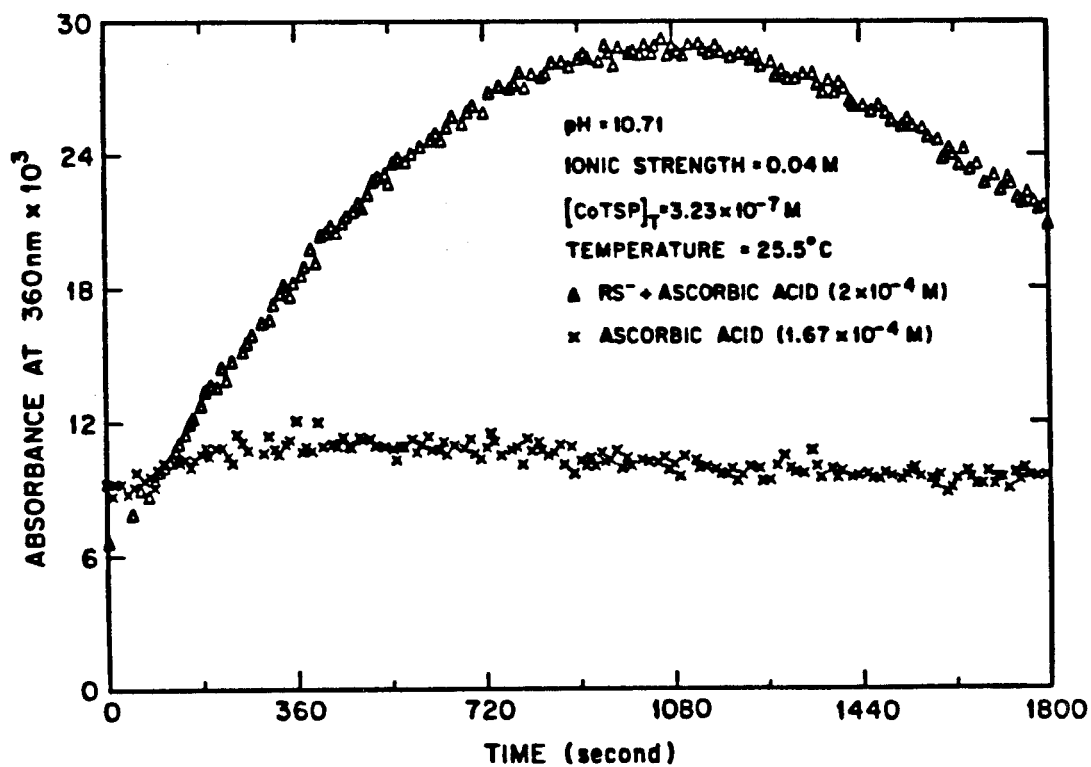


Figure 3.5: Formation of Ascorbate Radical during the Autoxidation of 2-Mercaptoethanol.

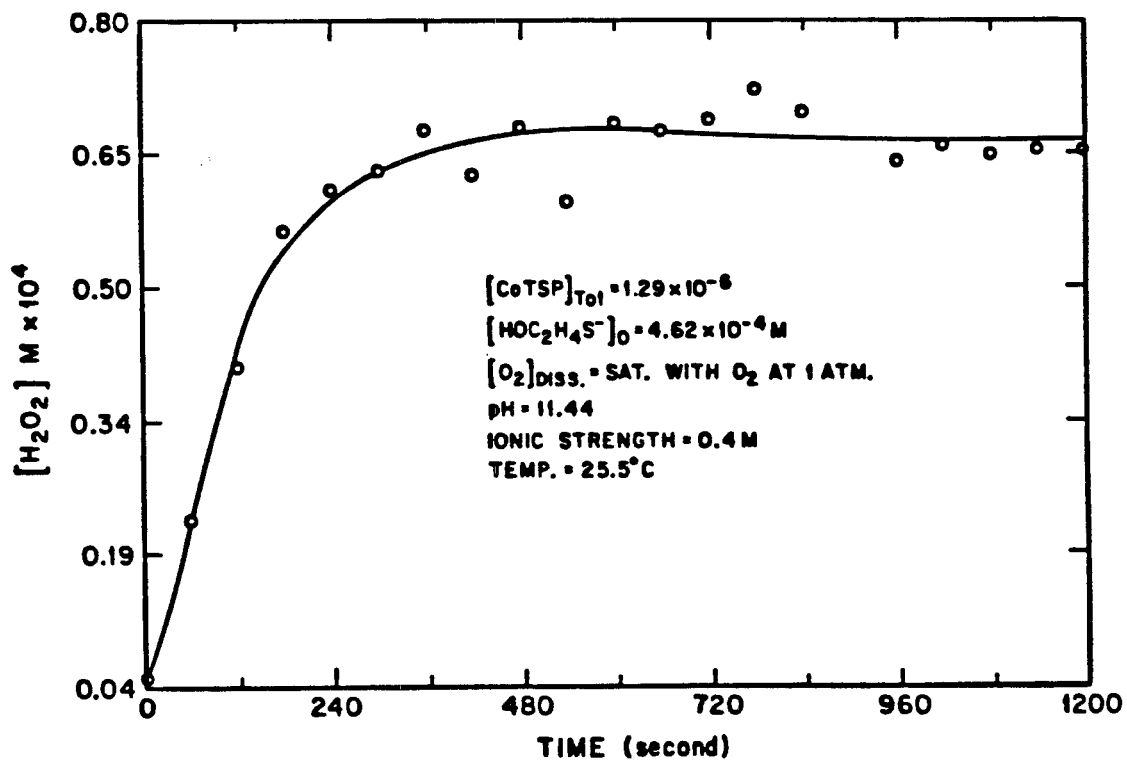
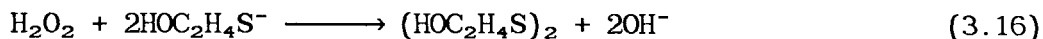


Figure 3.6: Hydrogen Peroxide vs time during the Autoxidation of 2-Mercaptoethanol.

overall 1:4 stoichiometry for pH > 10 is given by the sum of



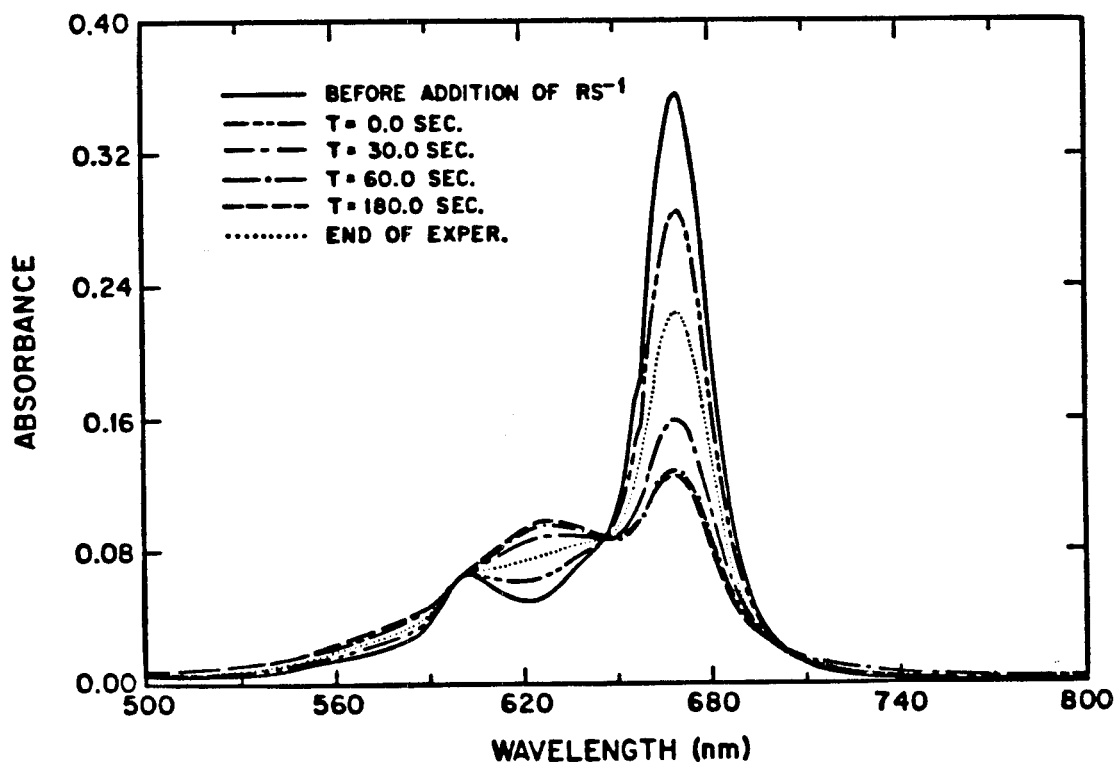
and



The detailed kinetics and mechanism of the oxidation of thioethanol by hydrogen peroxide have been reported by Leung and Hoffmann (*vide infra*, Chapter 4).

The change of the CoTSP spectrum in the visible region during the course of reaction is shown in Figure 3.7. Co(II)TSP 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 (Gruen and Blagrove, 1973). The increase of absorption at $\lambda = 626$ nm and the subsequent decrease of absorption at $\lambda = 668$ nm after the addition of the thioethanol suggests that the dimer concentration is enhanced during the reaction. The resulting dimer is likely to be bridged by the anion of 2-mercaptoethanol.

The above kinetic information can be explained with the aid of the mechanism proposed in Figure 3.8. According to this mechanism, the rate of disappearance of 2-mercaptoethanol is given by the sum of



Experimental Conditions: pH = 13.24, $\mu = 0.4$ M,
Temp. = 25.5°C,
 $[\text{Co}^{\text{II}}\text{TSP}]_T = 1.9 \times 10^{-6}$ M
 $[\text{O}_2]_{\text{Diss.}} = \text{Sat. with O}_2 \text{ at 1 Atm.}$

Figure 3.7: Changes in the Visible Spectrum of CoTSP During Autoxidation of 2-Mercaptoethanol.

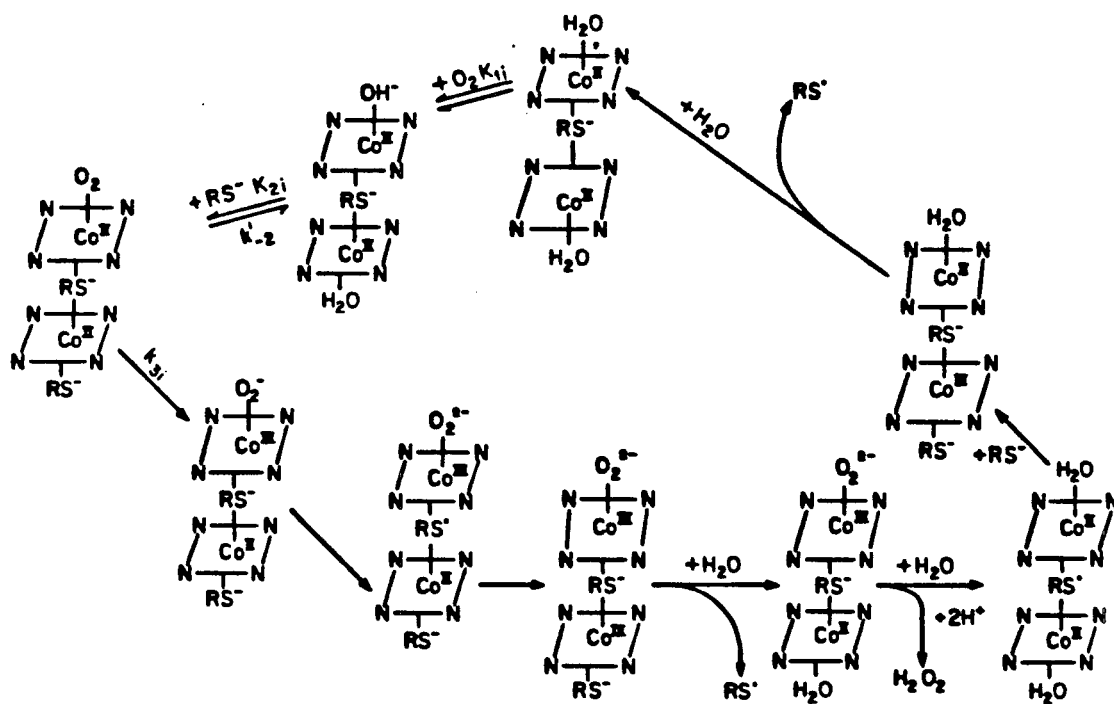


Figure 3.8: Schematic Diagram of the Proposed Mechanism of Autoxidation of 2-Mercaptoethanol.

three terms

$$v = \frac{-d[\text{RSH}]_T}{dt} = 2(v_1 + v_2 + v_3 + v_4) \quad (3.17)$$

where:

$$v_1 = k_{31}[(\text{O}_2\text{-Co}^{\text{II}}\text{TSP-RS}=\text{Co}^{\text{II}}\text{TSP-RS}^-)^{-6}]$$

$$v_2 = k_{32}[(\text{O}_2\text{-Co}^{\text{II}}\text{TSP-RS}=\text{Co}^{\text{II}}\text{TSP-RS}^-)^{-7}]$$

$$v_3 = k_{33}[(\text{O}_2\text{-Co}^{\text{II}}\text{TSP-RS}=\text{Co}^{\text{II}}\text{TSP-RS}^-)^{-8}]$$

$$v_4 = \text{rate of oxidation from H}_2\text{O}_2 \text{ cycle}$$

and k_{3i} = rate constant of the electron transfer step of i^{th} catalytic center.

The 1st, 2nd and 3rd catalytic centers are formed by the combination of two protonated monomers, a protonated monomer and a deprotonated monomer, two deprotonated monomers, respectively. Since $[\text{H}_2\text{O}_2]$ is very small, v_4 can be neglected, thereby, equation 3.17 becomes

$$v = 2(v_1 + v_2 + v_3) \quad (3.18)$$

Using the total concentration of thiol, $[\text{HOC}_2\text{H}_4\text{SH}]_T = [\text{HOC}_2\text{H}_4\text{SH}] + [\text{HOC}_2\text{H}_4\text{S}^-] + [^-\text{OC}_2\text{H}_4\text{S}^-]$, to express $[\text{RSH}]_T$ in term of $[\text{HOC}_2\text{H}_4\text{S}^-]$,

equation 3.18 can be written as follows:

$$v = \frac{-d[\text{RS}^-]}{dt} = \frac{2(v_1 + v_2 + v_3)}{\left(1 + \frac{a_{\text{H}^+}}{K'_{a_1}} + \frac{K'_{a_2}}{a_{\text{H}^+}}\right)} \quad (3.19)$$

Substitution of the corresponding equilibrium relationships for the binding of molecular oxygen and complexation of the substrate by the 1st catalytic center into v_1 yields

$$v_1 = k_{31}K_{11}K_{21}[(\text{Co}^{\text{II}}\text{TSP-RS}=\text{Co}^{\text{II}}\text{TSP})^{-5}][\text{O}_2][\text{RS}^-] \quad (3.20)$$

where K_{11} , K_{21} are the equilibrium constants for oxygen binding and substrate complexation by the 1st catalytic center, respectively. Expressing the concentration of the 1st catalytic center in term of the total concentration, $[\text{CoTSP}]_{\text{T1}} = 2([\text{Co}^{\text{II}}\text{TSP-RS}=\text{Co}^{\text{II}}\text{TSP})^{-5}] + [(\text{O}_2-\text{Co}^{\text{II}}\text{TSP-RS}=\text{Co}^{\text{II}}\text{TSP})^{-5}] + [(\text{O}_2-\text{Co}^{\text{II}}\text{TSP-RS}=\text{Co}^{\text{II}}\text{TSP-RS}^-)^{-6}]$, yields

$$v_1 = \frac{k_{31}K_{11}K_{21}[\text{CoTSP}]_{\text{T1}}[\text{O}_2][\text{RS}^-]}{2(1 + K_{11}[\text{O}_2] + K_{11}K_{21}[\text{O}_2][\text{RS}^-])} \quad (3.21)$$

If we assume $K_{11}[O_2] \gg K_{11}K_{21}[O_2][RS^-]$ and $K_{11}[O_2] \gg 1$, then the rate expression of 3.21 can be reduced to the following form

$$v_1 = \frac{1}{2}(k_{31}K_{21}[\text{CoTSP}]_{T1}[\text{RS}^-]) \quad (3.22)$$

which shows that the reaction rate should be first order with respect to both the $[\text{RS}^-]$ and $[\text{CoTSP}]_{T1}$; and that v_1 is independent of $[O_2]$. Similar expressions can be derived for both v_2 and v_3 . Thus, under the assumption that $K_{1i}[O_2] \gg K_{1i}K_{2i}[O_2][\text{RS}^-]$ and $K_{1i}[O_2] \gg 1$, the total rate of autoxidation becomes

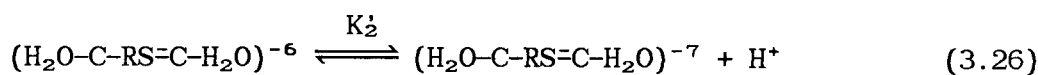
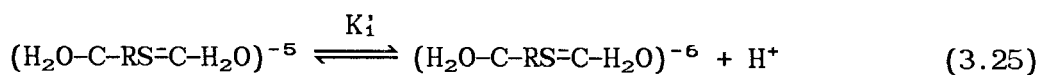
$$v = \frac{(k_{31}K_{21}[\text{CoTSP}]_{T1} + k_{32}K_{22}[\text{CoTSP}]_{T2} + k_{33}K_{23}[\text{CoTSP}]_{T3})[\text{RS}^-]}{(1 + \frac{a_{\text{H}^+}}{K'_{a1}} + \frac{K'_{a2}}{a_{\text{H}^+}})} \quad (3.23)$$

With the total catalyst concentration expressed as $[\text{CoTSP}]_T = [\text{CoTSP}]_{T1} + [\text{CoTSP}]_{T2} + [\text{CoTSP}]_{T3}$, equation 3.23 can be rewritten as

$$v = \frac{(k_{31}K_{21} + k_{32}K_{22}\frac{K_1}{a_{\text{H}^+}} + k_{33}K_{23}\frac{K_1K_2}{a_{\text{H}^+}^2})[\text{Co}^{\text{II}}\text{TSP}]_T[\text{RS}^-]}{(1 + \frac{K_1}{a_{\text{H}^+}} + \frac{K_1K_2}{a_{\text{H}^+}^2})(1 + \frac{a_{\text{H}^+}}{K'_{a1}} + \frac{K'_{a2}}{a_{\text{H}^+}})} \quad (3.24)$$

where k_{3i} , K_{2i} are the rate constants for the slow electron transfer

steps and the equilibrium constants of substrate complexation by the i^{th} catalytic center, respectively; K'_{a_1} and K'_{a_2} are the apparent acid dissociation constants of $\text{HOC}_2\text{H}_4\text{SH}$ and $\text{HOC}_2\text{H}_4\text{S}^-$, respectively, whereas K_i and K'_2 are the apparent acid dissociation constants of reaction 3.25 and 3.26.



where $\text{C} = \text{Co}^{\text{II}}\text{TSP}$; $\text{R} = \text{HOC}_2\text{H}_4$

k_{obsd} in this case is given by

$$k_{\text{obsd}} = \frac{\left(k_{31}K_{21} + \frac{k_{32}K_{22}K_i}{a_{\text{H}^+}} + \frac{k_{33}K_{23}K_iK'_2}{a_{\text{H}^+}^2} \right)}{\left(1 + \frac{K_i}{a_{\text{H}^+}} + \frac{K_iK'_2}{a_{\text{H}^+}^2} \right) \left(1 + \frac{a_{\text{H}^+}}{K'_{a_1}} + \frac{K'_{a_2}}{a_{\text{H}^+}} \right)} \quad (3.27)$$

Values of K'_{a_2} , $k_{32}K_{21}$ and $k_{33}K_{23}$ can be obtained by analyzing the kinetic data at $\text{pH} \leq 10$ and at $\text{pH} \geq 12$. At $\text{pH} \leq 10$, assuming that 1

$$\gg \frac{K_i}{a_{\text{H}^+}} \gg \frac{K_i^2}{a_{\text{H}^+}^2} \text{ and } \left(1 + \frac{a_{\text{H}^+}}{K'_{a_1}} + \frac{K'_{a_2}}{a_{\text{H}^+}} \right) \simeq \left(1 + \frac{a_{\text{H}^+}}{K'_{a_1}} \right), \text{ equation 3.27}$$

reduces to

$$k_{obsd} = \frac{k_{31}K_{21}}{\left(1 + \frac{a_{H^+}}{K'_{a_1}}\right)} \quad (3.28)$$

and $k_{31}K_{21}$ is calculated to be $1.5 \times 10^4 \text{ M}^{-1}\text{sec}^{-1}$. At $\text{pH} \geq 12$,

assuming, the $\frac{K_1K_2'}{a_{H^+}^2} \gg \frac{K_1}{a_{H^+}} \gg 1$, equation 3.27 becomes

$$k_{obsd} = \frac{k_{33}K_{23}}{\left(1 + \frac{a_{H^+}}{K'_{a_1}} + \frac{K'_{a_2}}{a_{H^+}}\right)} \quad (3.29)$$

and $\text{p}K'_{a_2}$ and $k_{33}K_{23}$ are calculated to be 13.5 ± 0.3 and $7.5 \times 10^3 \text{ M}^{-1}\text{sec}^{-1}$ at $\mu = 0.4 \text{ M}$ and $T = 25.5^\circ\text{C}$, respectively.

The constants, $k_{32}K_{22}$ and K_1' , were obtained by the nonlinear least-squares analysis of the following function (Bevington, 1969):

$$\phi = \sum_{i=1}^n [(k_{obsd} - k_{calc})\text{wts}(i)]^2 \quad (3.30)$$

$$\text{wts}(i) = \sigma(i)^{-1} \quad (3.31)$$

$\sigma(i)$ = sample standard deviation of data point i

The constants $k_{31}K_{21}$ and $k_{33}K_{23}$ were further refined by the same function, while the values of k_{cald} were determined according to equation 24. Values obtained by this method were $k_{31}K_{21} = (1.5 \pm 0.05) \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$, $k_{32}K_{22} = (1.3 \pm 0.1) \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$, $k_{33}K_{23} = (7.5 \pm 0.2) \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$, $K_1 = (1.68 \pm 0.8) \times 10^{-11} \text{ M}$, $K_2 = 1.05 \times 10^{-11} \text{ M}$ at 25.5°C . Values of the calculated pseudo first-order rate constants (k_{cald}) are compared to the experimental values in Table 3.2 and shown in Figure 3.9.

Discussion

The mechanism presented above is similar in some respects to the mechanisms proposed previously by Dolansky et al. (1976) and Boyce et al. (1983). However, in our case, the binding of molecular oxygen precedes complexation of the substrate. 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. $[\text{CoTSP}]_T \cong \text{oxygenated adduct}$). Another major difference between the mechanism proposed herein and those proposed previously by Dolansky et al. (1976) and Boyce et al. (1983) is that the catalytic center appears to be a dimer rather than the monomer.

The general spectral features of the oxygenated CoTSP complex have been reported previously by Gruen and Balgrove (1973). As RS^- was added to the catalyst solution, significant changes in the CoTSP

TABLE 3.2. Comparison of k_{obsd} with k_{cald} at various pH.

pH	$k_{obsd} \times 10^{-3} (M^{-1}s^{-1})$	$k_{cald} \times 10^{-3} (M^{-1}s^{-1})$
9.17	5.04 ± 0.5	5.29
9.38	7.3 ± 0.2	7.04
9.60	9.15 ± 0.1	8.90
9.79	10.1 ± 0.1	10.35
10.19	12.1 ± 0.05	12.38
10.36	12.7 ± 0.2	12.71
10.49	12.4 ± 0.3	12.73
10.74	11.8 ± 0.1	12.23
10.98	11.4 ± 0.4	11.22
12.14	7.2 ± 0.5	7.38
12.48	6.5 ± 0.2	6.75
12.80	5.52 ± 0.2	5.96
13.04	5.51 ± 0.1	5.17
13.24	5.01 ± 0.05	4.37

Experimental Conditions : $\mu = 0.4$ M, Temperature = 25.5°C,

$[O_2]_{Diss}$ = Saturated with pure O_2 gas at 1 atmosphere,

$[CoTSP]_T = 6.4 \times 10^{-7}$ M, Buffer system = NaCl, $NaHCO_3$, NaOH.

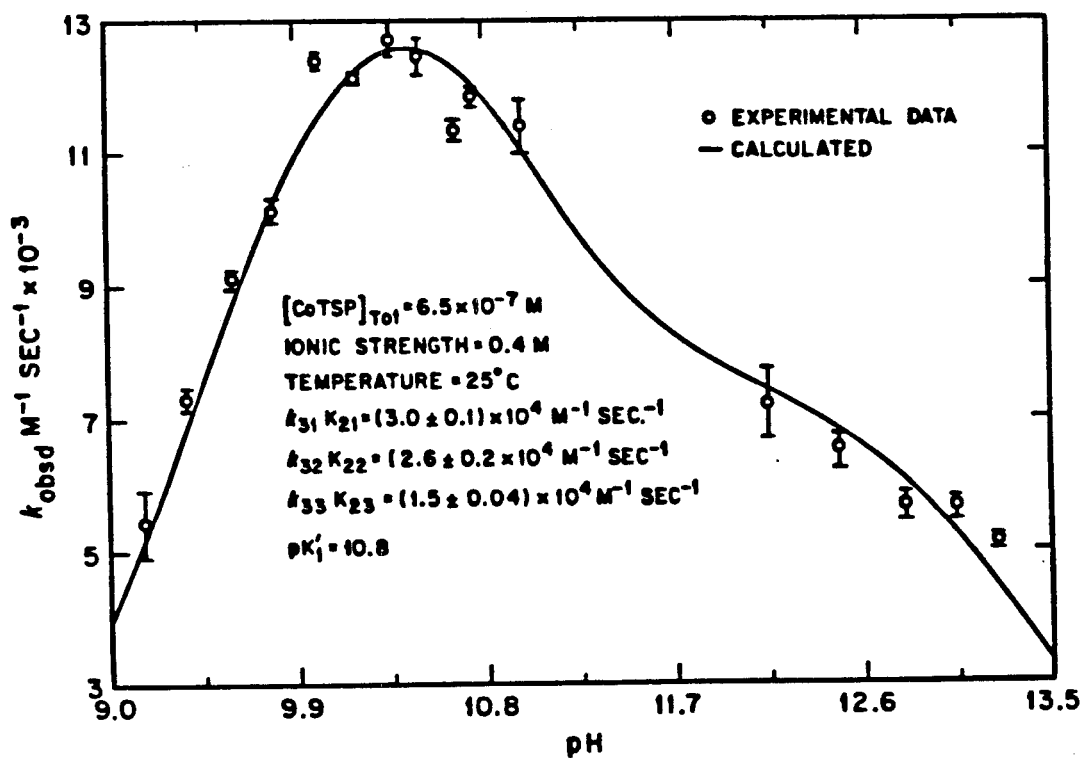


Figure 3.9: pH Dependence of Autoxidation of 2-Mercaptoethanol.

visible spectrum were observed; these were consistent with the formation of a dimer as the reactive species. This spectral change was also noted by Beelen et al. (1979) in their study of the autoxidation of 2-mercaptoethanol as catalyzed by CoTSP. According to the spectral changes shown in Figure 3.7, the majority of catalyst dimerized within the first minute of reaction. This implies that $[\text{CoTSP}]_{\text{T}} \cong 2[\text{Dimer}]$ and that a half-order dependence instead of a first-order dependence on $[\text{CoTSP}]_{\text{T}}$ catalyst should be observed if a monomeric species is the principal reactive species.

According to the mechanism of Figure 3.8, three possible reactions can be considered as the rate determining step. They are the binding of molecular oxygen, the complexation of the substrate by oxygenated dimer and the subsequent electron transfer step. However, it appears that electron transfer is most likely to be the rate limiting step since a zero-order dependence on both the substrate at low ionic strength and the 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 1st 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 Co^{2+} should be close to its water exchange rate. The water exchange rate for Co^{2+} is $\approx 10^5$ (Cotton and Wilkinson, 1980). 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 large than k_{obsd} values.

The observed independence of the rate of autoxidation on $[O_2]$ requires both the rate of oxygenation to be fast and the equilibrium constant of the oxygenation to be quite large (i.e., $K_{1i} \geq 10^3$). Jones et al. (Jones et al., 1979) have argued that the binding of a fifth ligand in an apical coordination Co(II) porphyrin is 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 sp^2 lone pair on dioxygen to d_{z^2} orbital on the cobalt, coupled with the π -back bonding from the cobalt d_{xz} or d_{yz} orbitals into the π^* dioxygen orbitals. The ligands co-ordinated trans to the O_2 could compete for the same π -electron density on the cobalt; therefore, the strength of the Co- O_2 bonding is very sensitive on 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- O_2 bonds, whereas, a good π -electron donors will increase the electron density on the Co center available for π -back bonding on O_2 and thereby promote the stabilization of the Co- O_2 bond. Several investigators have reported that the greater electron density on the metal results a stronger metal oxygen bond (McGinnety et al., 1969;

Terry et al., 1972). Sulfur ligands (Klotz and Klotz, 1955) 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 is available. This may be due to the relatively rapid oxidation of mercaptans to disulfides. The rate constants for dioxygen binding by a variety bridged Co-chelate complexes have been reported to be large (Jones et al., 1979). In addition, Martell (1982) 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 (Table 3.3). All of these complexes shows a very large stability constants for oxygen binding that range from 10⁵ to 10¹⁵. Since the sum of the basicities of the ligands on CoTSP-RS⁻ > 18, it is highly plausible that the oxygenation equilibrium constant is greater than 10³.

The catalytically active dimer probably consists of two CoTSP monomers linked by a single RS⁻ ligand at the metal center. However, two different molecules can be considered as possible monomeric bridges. The first possibility involves a dioxygen bridge to yield μ -peroxo-binuclear CoTSP center, while the other would be the binuclear complex bridge by the thioethanol. Assuming that the former

TABLE 3.3. Correlation of Oxygenation Equilibrium Constant of Monobridged Dioxygen Cobalt Complexes with Basicities of Ligands.^a

Ligands	ΣpK^b	$\log K_{O_2}$
TEP ^c	35.8	15.8
EPYDEN ^d	30.6	14.7
4-IMDIEN ^e	29.1	12.6
PYDIEN ^f	21.6	11.4
TRPY(PHEN) ^g	≈ 13	6.3
TRPY(BPY) ^h	≈ 12	5.4

a Data obtained from Martell, A.E.; Acc. Chem. Res., 1982, 15, 155-162.

b ΣpK = sum of the basicities of ligands bound to Co metal center.

c TEP = tetraethylenepentamine.

d EPYDEN = 2,6-bis(5-(1,4-diazahexyl))pyridine.

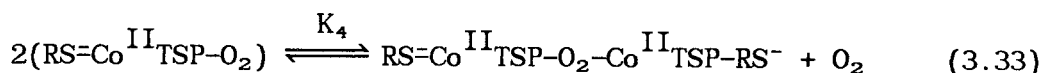
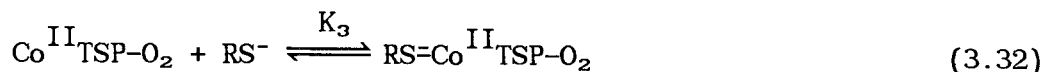
e 4-IMDIEN = 1,9-bis(4-imidazolyl)-2,5,8-triazanonane.

f PYDIEN = 1,9-bis(2-pyridyl)-2,5,8-triazanonane.

g TRPY(PHEN) = 2',5'-bis(2-pyridyl)pyridine(1,1-phenanthroline).

h TRPY(BPY) = 2',5'-bis(2-pyridyl)pyridine(2,2'-bipyridyl).

dimer is the reactive species, the reaction cycle would be as follows:

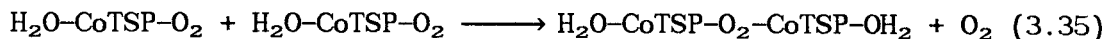


According to the above mechanism, the following rate law will be obtained:

$$v = k'_{\text{obsd}} \frac{[\text{CoTSP}]_{\text{Tot}}^2 [\text{RS}^-]^2}{[\text{O}_2](1 + K_3[\text{RS}^-])^2} \quad (3.34)$$

where K_3 and K_4 are the equilibrium constants of reaction 3.32 and 3.33, respectively. According to the equation 3.34, the rate should be second order in $[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}}$ and reciprocal first order in $[\text{O}_2]$. If $1 \gg K_3[\text{RS}^-]$ or $K_3[\text{RS}^-] \gg 1$, either a reciprocal second-order dependence or a zero-order dependence on $[\text{RS}^-]$ should be observed. However, these predicted kinetic orders for the substrate, catalyst and dioxygen do not agree with the experimental observations. Wagnerova et al. (1974) have studied the oxygenation of Co(II)TSP in alkaline solution ($\text{pH} > 12$) and observed that the peak at 670 nm was the only peak in the spectrum after five days of oxygenation and that the peak normally attributed to the dimer at 630 nm was not observed

over a five-day period. This implies that the reaction



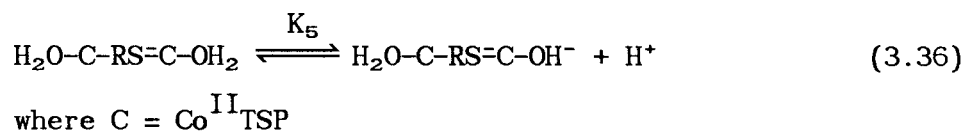
was extremely slow. Since the bonding of RS^- at the trans to dioxygen should enhance the rate of oxygenation, the rate of the formation of corresponding binuclear oxygenated adduct would be even slower. Formation of a μ -superoxo complex is too slow to be consistent with our kinetic observations. Also, a cobalt phthalocyanine dimer with NH_2 bridge through Co metal has been synthesized and reported by Przywarska-Boniecka and Wojciechowski (1975). Since the size sulfur atom is larger than the nitrogen atom, the distance between two Co(II)TSP molecules of the sulfur-bridged dimer should be greater than the distance for the nitrogen-bridged dimer. Thus, the steric interference between two Co(II)TSP molecules should be reduced. We believe that formation of thioethanol bridged dimer is essential to catalytic activity in this system.

Thioethanol may bridge the two Co^{2+} centers either through sulfur or oxygen. However, sulfur should preferably serve as the bridging site due to its better electron donating ability and higher polarizability than oxygen.

A rate-limiting electron transfer step has been proposed previously for the catalytic autoxidation of both SO_3^{2-} and H_2S by CoTSP . Hoffmann and Hong (1985) have reported ESR evidence for the

formation of superoxide-like ternary CoTSP complex during the catalytic autoxidation of sulfite. Results from other ESR studies (Jones et al., 1979) have also shown that superoxide-like Co complexes are formed during the course of catalytic autoxidation. Additional information obtained from magnetic susceptibility data and EPR spectra shows that for low-spin d^7 complexes, $\text{Co(II)L}_4(\text{B})$, where L_4 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 (Jones et al., 1979). Therefore, we believed that $\text{RS=Co}^{\text{II}}\text{TSP-RS=Co}^{\text{III}}\text{TSP-O}_2^-$ is the principal reactive species in the catalytic cycle.

The effect of pH on the rate of autoxidation, as shown in Figure 3.8, suggests that the pyrrole nitrogens are protonated in Co(II)TSP . 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 (reaction 3.25 and 3.26) or at the bound water molecules (reaction 3.36).



According to Chapter 5, the pK_a of the bound water molecules on the dimer $\text{H}_2\text{O-(Co}^{\text{II}}\text{TSP)-OH}_2$ was determined to be $\gg 14.7$. Since sulfur is a good electron donor, the incorporation of sulfur onto the dimer

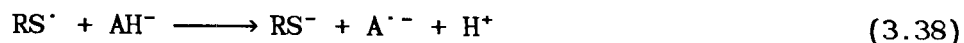
would further enhance the electron density on the cobalt and consequently, the cobalt would withdraw less electron density from the bound water molecules. As a result, the hydrogen ion would be more difficult to deprotonate from the bound water molecules and thereby the pK_5 should be ≥ 14.7 . Thus, the effect of reaction 3.36 is ignored for the autoxidation. Berezin (1981) has noted that protonation of metal phthalocyanine complexes occurs preferentially on the ring nitrogens. Since phthalocyanine is a highly conjugated macromolecule, 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. If the Co(II)TSP is deprotonated, k_{obsd} would be as given by

$$k_{obsd} = \frac{k_{31}K_{21}}{\left(1 + \frac{a_{H^+}}{K'_{a_1}} + \frac{K'_{a_2}}{a_{H^+}}\right)} \quad (3.37)$$

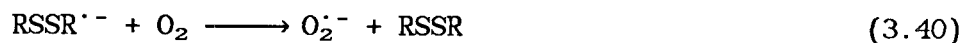
According to equation 3.37, the observed pH dependence is determined by the deprotonation of HOC_2H_4SH and $HOC_2H_4S^-$; however, pK'_{a_2} for the 2-mercaptoethanol, which was estimated to be > 13 by titration is too high to yield the observed dependence. The estimated value of pK'_{a_2} is reasonable since the pK'_a of the OH group of ethanol is ≈ 15 (Stewart, 1985). Thus, deprotonation of a pyrrole nitrogen is likely. The

values of pK_1 and pK_2 were determined to be 10.8 and 10.97, respectively. These values agree well with the pK_a 's for deprotonation of primary, secondary and tertiary amines (Perrin et al., 1981).

The observed production of ascorbate radical during the course of the reaction provides strong evidence for the formation of RS^\cdot as an intermediate. Ascorbate radical may have been produced by one of two alternative pathways. The first pathway (Redpath and Wilson, 1973; Schuler, 1977) may have been



while the second pathway (Al-Thannon et al., 1974; Barton and Packer, 1970; Cabelli et al., 1983) may have been as follows:



In the former case, the ascorbate radical is formed directly while in the latter case it is formed indirectly from RS^\cdot . Nonetheless, the

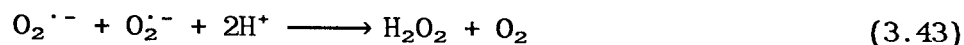
thioethanol radical is undoubtedly an intermediate of the catalyzed autoxidation.

Several pathways may yield RSSR from RS^\cdot . They are:

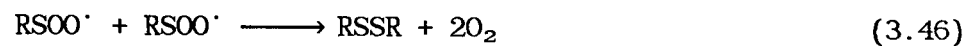
first,



and second, a sequence that includes equations 3.39 and 3.40 as the initial reactions followed by:



and third, (Al-Thannon et al., 1974; Barton and Packer, 1970)



The relative importance of these three alternative pathways has not been well established. However, with a small steady-state concentration of RS^\cdot , the rate of reaction 3.42 should be very slow, thereby it can be ignored as the primarily route for the disappearance

of RS^{\cdot} . Also, the subsequent reactions in the third sequence are expected to be relatively slow because of the small concentrations of the various radical intermediates. Thus, RS^{\cdot} is more likely to react via eqns. 3.39, 3.40 and 3.43 to give disulfide as the product.

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CHAPTER FOUR
KINETICS AND MECHANISM OF THE OXIDATION OF 2-MERCAPTOETHANOL
BY HYDROGEN PEROXIDE IN AQUEOUS SOLUTION

NOTATIONS

- k_1 Rate constant ($M^{-1} \text{ sec}^{-1}$) of reaction
 $\text{HOC}_2\text{H}_4\text{S}^- + \text{H}_2\text{O}_2 \longrightarrow \text{HOC}_2\text{H}_4\text{SOH} + \text{OH}^-$
- k_2 Rate constant ($M^{-1} \text{ sec}^{-1}$) of reaction
 $\text{HOC}_2\text{H}_4\text{S}^- + \text{HO}_2^- \longrightarrow \text{HOC}_2\text{H}_4\text{SO}^- + \text{OH}^-$
- K' Apparent acid dissociation constant (M) of Acid-Base
Equilibra $\text{H}_2\text{O}_2 \rightleftharpoons \text{HO}_2^- + \text{H}^+$
- K'_{a_1} Apparent acid dissociation constant (M) of Acid-Base
Equilibra $\text{HOC}_2\text{H}_4\text{SH} \rightleftharpoons \text{HOC}_2\text{H}_4\text{S}^- + \text{H}^+$
- K'_{a_2} Apparent acid dissociation constant (M) of Acid-Base
Equilibra $\text{HOC}_2\text{H}_4\text{S}^- \rightleftharpoons \text{OC}_2\text{H}_4\text{S}^- + \text{H}^+$
- k_4 Rate constant ($M^{-1} \text{ sec}^{-1}$) of reaction
 $\text{HOC}_2\text{H}_4\text{SOH} + \text{HOC}_2\text{H}_4\text{S}^- \longrightarrow \text{HOC}_2\text{H}_4\text{SSH}_4\text{C}_2\text{OH}$
- $[\text{H}_2\text{O}_2]_T$ Total hydrogen peroxide concentration
- a_{H^+} Hydrogen ion activity

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**Kinetics and Mechanism of the Oxidation of 2-Mercaptoethanol by Hydrogen Peroxide in
Aqueous Solution**

Ping-Sang K. Leung and Michael R. Hoffmann

Kinetics and Mechanism of the Oxidation of 2-Mercaptoethanol by Hydrogen Peroxide in Aqueous Solution

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The kinetics of oxidation of 2-mercaptoethanol by H_2O_2 to 2-hydroxyethyl disulfide in aqueous solution has been studied. Over the pH range 9 to 13, the rate law for the oxidation of 2-mercaptoethanol was found to be

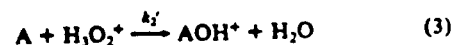
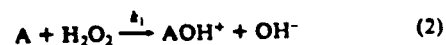
$$r = \frac{-d[\text{RS}^-]}{dt} = \frac{[\text{H}_2\text{O}_2]_T[\text{RS}^-]}{\left(1 + \frac{K'}{a_{\text{H}^+}}\right)\left(1 + \frac{a_{\text{H}^+}}{K'_{a1}} + \frac{K'_{a2}}{a_{\text{H}^+}}\right)}(k_1 + K'k_2/a_{\text{H}^+})$$

where R is HOC_2H_4 , K' is the apparent acid dissociation constant of H_2O_2 , K'_{a1} and K'_{a2} are the apparent acid dissociation constants of $\text{HOC}_2\text{H}_4\text{SH}$ and $\text{HOC}_2\text{H}_4\text{S}^-$, respectively, and a_{H^+} is the hydrogen ion activity. A nonlinear least-squares fit of experimental data to the above rate law gave values of $k_1 = 12.64 \pm 0.54 \text{ M}^{-1} \text{ s}^{-1}$ and $k_2 = 0.93 \pm 0.39 \text{ M}^{-1} \text{ s}^{-1}$ at 20 °C. The rate law and other data indicate that the reaction proceeds via a nucleophilic displacement by thioethanol on hydrogen peroxide with the formation of $\text{HOCH}_2\text{CH}_2\text{SOH}$ as an intermediate.

Introduction

The kinetics of oxidation of a variety of reductants such as hydrogen sulfide,¹ aqueous sulfur dioxide,² thiourea,³ substituted thioureas,³ thioxane,⁴ thiocyanate,^{5,6} and halides⁷ by hydrogen peroxide in aqueous solution have been studied. In general, two-term rate laws of overall second and third order have been

observed. A common mechanism for the acid-catalyzed nucleophilic attack of reductant A on H_2O_2 is as follows:

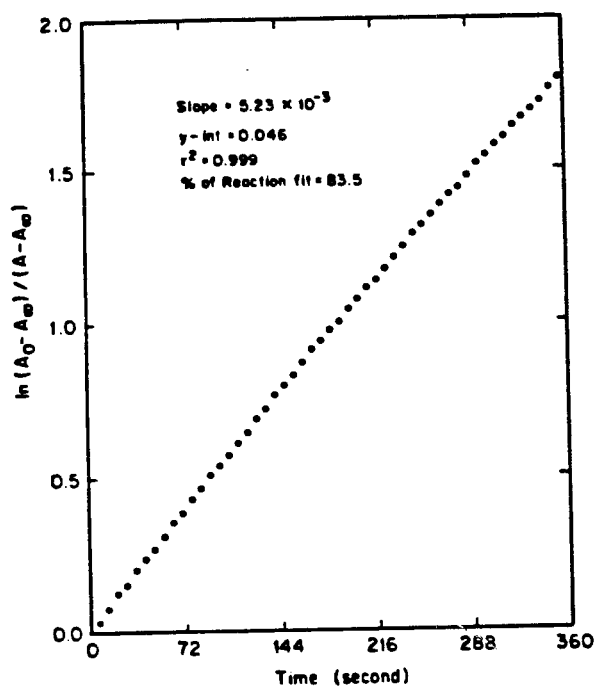


where A denotes the nucleophile. This mechanism gives a rate expression of the following form:

$$r = k_1[\text{H}_2\text{O}_2][\text{A}] + k_2K[\text{H}_2\text{O}_2][\text{H}^+][\text{A}] \quad (5)$$

In the above mechanism, the oxygen-oxygen bond of hydrogen peroxide is cleaved heterolytically with the release of either hy-

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A_0 = Initial Absorbance = 1.208
 A = Absorbance at time t
 A_∞ = Absorbance at infinity = 0.03

EXPERIMENTAL CONDITIONS:

pH = 10.43
 μ = 0.10 M
 Temp = 20.5 °C
 $[EDTA] = 1 \times 10^{-5}$ M
 $[H_2O_2]_0 = 4.52 \times 10^{-4}$ M
 $[RS]_0 = 2.9 \times 10^{-5}$ M

Figure 1. First-order kinetic plot of the oxidation of 2-mercaptoethanol by H_2O_2 .

dioxide ion or water as the leaving group. The "hydroxy intermediate" subsequently reacts with either a second molecule of A to form a dimer as the final product or with an additional H_2O_2 via a different pathway.¹

According to Edwards⁸ the nucleophilic reactivity of RS^- toward H_2O_2 should exceed that of CN^- , $S_2O_3^{2-}$, and $(NH_2)_2CS$, respectively. With this in mind, we decided to examine in detail the kinetics of the reaction of 2-mercaptoethanol (RSH) in a pH domain where $pH > pK_{a1}$. Furthermore, we have observed hydrogen peroxide as an intermediate during the oxidation of 2-mercaptoethanol and sulfur dioxide⁹ by O_2 catalyzed by 4,4',4''-tetrasulfocobalt(II)phthalocyanine. Mercaptans such as 2-mercaptoethanol are odorous constituents of sour refinery wastes. Catalytic autoxidation or oxidation by H_2O_2 of mercaptans may be used for odor and wastewater quality control.

Experimental Procedure

Stock solutions were prepared from redistilled 99% reagent grade 2-mercaptoethanol (Aldrich) and 3.23% hydrogen peroxide (Mallinckrodt). Buffer solutions were prepared with reagent grade sodium hydroxide (Mallinckrodt), sodium chloride (J. T. Baker), sodium bicarbonate (Mallinckrodt), and 18 M Ω -cm resistivity water (Millipore). Ionic strength was held constant at $\mu = 0.1$ M with NaCl.

TABLE I: Kinetic Data for Oxidation of 2-Mercaptoethanol by Hydrogen Peroxide in Carbonate Buffer at 20 °C^a

pH	k_{obsd}	k_{intd}	% diff
12.61	0.31 ± 0.02	0.28	8.34
12.32	0.55 ± 0.04	0.65	-18.28
12.09	1.36 ± 0.12	1.24	8.60
11.10	8.20 ± 0.13	7.71	5.89
10.76	9.20 ± 0.18	9.62	-4.67
10.58	9.95 ± 0.10	10.20	-2.51
10.43	10.96 ± 0.46	10.45	4.67
10.26	10.38 ± 0.29	10.47	-0.89
10.14	9.97 ± 0.06	10.31	-3.44
9.98	10.17 ± 0.05	9.92	2.45
4.8	b	3.73×10^{-4}	

^a 1.53×10^{-4} M $\leq [H_2O_2] \leq 3.057 \times 10^{-4}$ M and $[HOC_2H_4S^-]$ is at least tenfold less than $[H_2O_2]$. ^b Very small.

TABLE II: Stoichiometry Determination of the Oxidation of 2-Mercaptoethanol by Hydrogen Peroxide

H_2O_2 used, mmol	initial RS^- , mmol	RS^- unreacted, mmol	RS^- reacted, mmol	$\Delta[RS^-]/\Delta[H_2O_2]$
0.24	0.73	0.20	0.53	2.24
0.24	0.73	0.22	0.51	2.13
0.24	0.73	0.20	0.53	2.19

Pseudo-first-order kinetic data were obtained with a Hewlett Packard Model 8450 spectrophotometer linked to a DEC MINC 23 minicomputer. A minimum of four data sets was obtained for each value of k_{obsd} . Constant temperature was maintained at 20 °C with a Haake HK2 circulating water bath, while pH was determined with a Beckman Altex Φ 71 pH meter and Radiometer glass electrodes. EDTA was used (10 μ M) to minimize the influence of trace-metal catalysis (i.e., Fenton's reagent). For $pH \geq 9.4$ the reaction was monitored at $\lambda = 233$ nm (the absorbance maximum for $HOC_2H_4S^-(aq)$, the $pK_{a1} = 9.4^{10}$), whereas when $pH \leq 9.4$, the reaction was monitored at $\lambda = 220$ nm.

Stoichiometry was established by determination of the residual 2-mercaptoethanol after 99% of hydrogen peroxide had reacted in alkaline solution. 2-Mercaptoethanol was analyzed by titration with I_2 .^{11,12} Hydrogen peroxide was standardized according to the method given by Wilson and Wilson.¹¹

Reaction products were extracted into chloroform, concentrated by evaporation under nitrogen, and analyzed by HPLC (HP1080B) using deionized doubly distilled water with 15% of methanol as the solvent carrier.

Results

Pseudo-first-order plots, $([H_2O_2] \gg [HOC_2H_4SH])$, Figure 1) of $\ln(A_0 - A_\infty)/(A - A_\infty)$ vs. t were linear ($r^2 \geq 0.999$) for up to 85% of the reaction which indicates that the reaction is, in fact, first order with respect to 2-mercaptoethanol. The dependence of k_{obsd} on $[H_2O_2]$ was determined at pH 10.4. A plot of k_{obsd} vs. $[H_2O_2]$ ($d \log k_{obsd}/d \log [H_2O_2] = 1.0$) up to (1.2 mM) yields a straight line ($r^2 \geq 0.99$) with a slope of 10.96 ± 0.45 M⁻¹ s⁻¹ and an intercept of zero, as shown in Figure 2. Thus, the rate of disappearance of 2-mercaptoethanol is first order in both H_2O_2 and HOC_2H_4SH . k_{obsd} exhibits a pH dependency as shown in Figure 3 and Table I. For the pH range of 10.4 to 12, $1/k_{obsd}$ vs. $1/a_{H^+}$ was linear with $r^2 = 0.99$, $d(1/k_{obsd})/d(1/a_{H^+}) = 5.31 \times 10^{-13}$ and $1/k_{obsd} = 0.078$. At pH 4.8 and $pH \geq 13$, the oxidation rate was negligible. In the absence of buffer, the pH rose continuously during the course of reaction (Figure 4), whereas a variation of ionic strength over the range of 0.05 M $< \mu < 0.4$ M had no effect on the rate of reaction.

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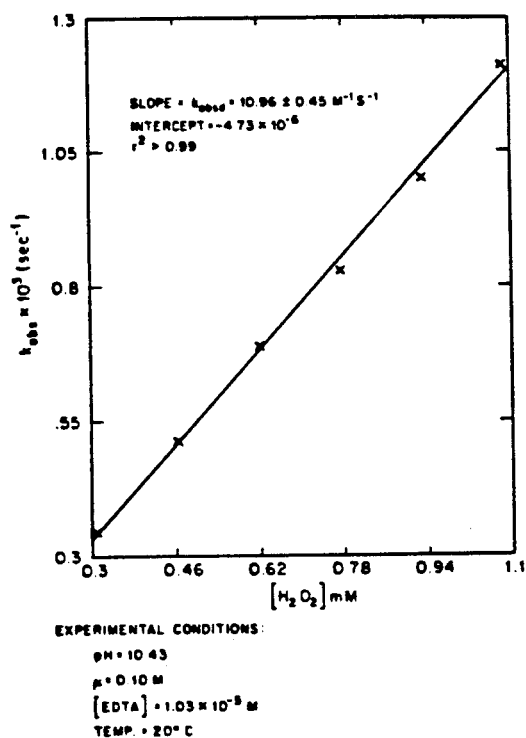


Figure 2. Hydrogen peroxide dependence analysis of the oxidation of 2-mercaptoethanol by H₂O₂.

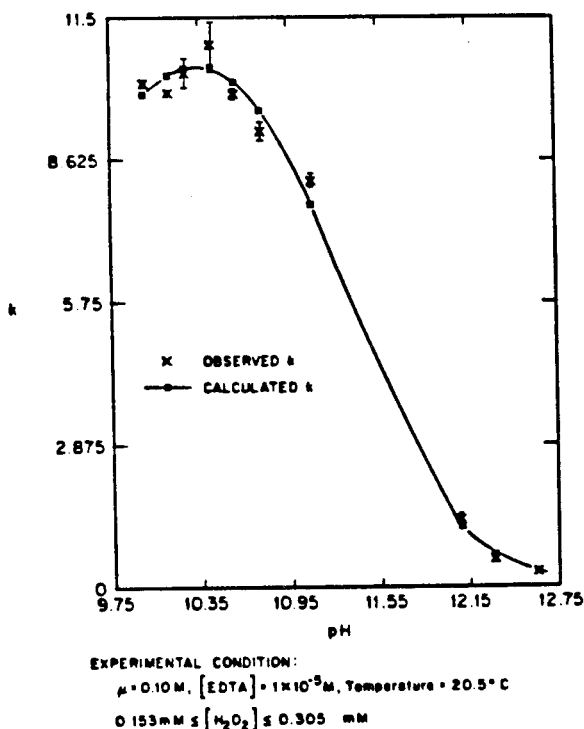


Figure 3. pH dependence analysis of the oxidation of 2-mercaptoethanol by H₂O₂.

The stoichiometry (Table II) was established to be 1 mol of H₂O₂ to 2 mol of HOC₂H₄SH (eq 6). The sole oxidation product was determined to be 2-hydroxyethyl disulfide by HPLC analysis. Thus, the overall reaction is

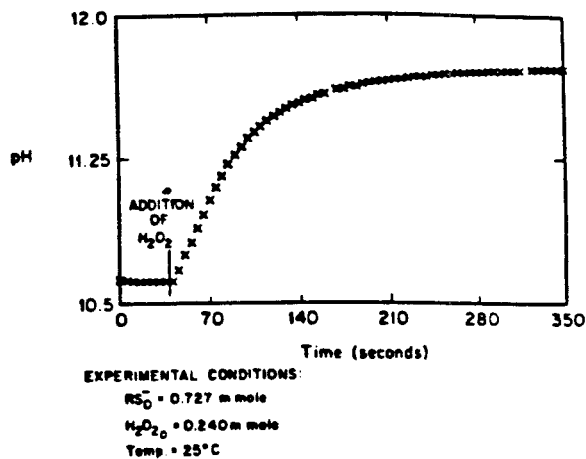
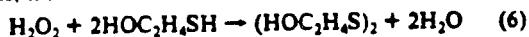
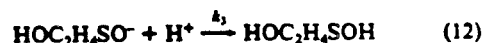


Figure 4. Evidence for the formation of OH⁻ on the oxidation of 2-mercaptoethanol by H₂O₂.

The above kinetic information is consistent with the following mechanism:



This mechanism is similar to the general mechanism for nucleophilic displacements on H₂O₂ as discussed by Hoffmann and Edwards.³ According to this mechanism, the rate of disappearance of the 2-mercaptoethanol is given by

$$r = -d[\text{RSH}]_T/dt = k_1[\text{H}_2\text{O}_2][\text{HOC}_2\text{H}_4\text{S}^-] + k_2[\text{HO}_2^-][\text{HOC}_2\text{H}_4\text{S}^-] + k_4[\text{HOC}_2\text{H}_4\text{SOH}][\text{HOC}_2\text{H}_4\text{S}^-] \quad (14)$$

where

$$[\text{RSH}]_T = [\text{HOC}_2\text{H}_4\text{SH}] + [\text{HOC}_2\text{H}_4\text{S}^-] + [\text{OC}_2\text{H}_4\text{S}^-]$$

If we assume that $k_4[\text{HOC}_2\text{H}_4\text{SOH}] \ll k_1[\text{H}_2\text{O}_2]$ and $k_2[\text{HO}_2^-]$, the rate expression reduces to

$$r = [\text{HOC}_2\text{H}_4\text{S}^-]\{k_1[\text{H}_2\text{O}_2] + k_2[\text{HO}_2^-]\} \quad (15)$$

Expressing the concentration of H₂O₂ and 2-mercaptoethanol in terms of their total concentrations, $[\text{H}_2\text{O}_2]_T = [\text{H}_2\text{O}_2] + [\text{HO}_2^-]$ and $[\text{HOC}_2\text{H}_4\text{SH}]_T = [\text{HOC}_2\text{H}_4\text{SH}] + [\text{HOC}_2\text{H}_4\text{S}^-] + [\text{OC}_2\text{H}_4\text{S}^-]$, yields

$$r = \frac{-d[\text{HOC}_2\text{H}_4\text{S}^-]}{dt} = [\text{H}_2\text{O}_2]_T[\text{HOC}_2\text{H}_4\text{S}^-] \left(\frac{k_1 + K'k_2/a_{\text{H}^+}}{\left(1 + \frac{K'}{a_{\text{H}^+}}\right)\left(1 + \frac{a_{\text{H}^+}}{K'_{a1}} + \frac{K'_{a2}}{a_{\text{H}^+}}\right)} \right) \quad (16)$$

where K' is the apparent acid dissociation constant for H₂O₂; K'_{a1}

is the apparent acid dissociation constant for 2-mercaptoethanol; K'_{a2} is the apparent acid dissociation constant for $\text{HOC}_2\text{H}_4\text{S}^-$. k_{obsd} in this case is given by

$$k_{\text{obsd}} = \left(k_1 + \frac{K'K_2}{a_{\text{H}^+}} \right) / \left(1 + \frac{K'}{a_{\text{H}^+}} \right) \left(1 + \frac{a_{\text{H}^+}}{K'_{a1}} + \frac{K'_{a2}}{a_{\text{H}^+}} \right) \quad (17)$$

Initial values for the constants of eq 17 can be obtained by analyzing kinetic data over the pH range of 10.4 to 12. The observed linear behavior between $1/a_{\text{H}^+}$ and $1/k_{\text{obsd}}$ over this pH range requires that $k_1 \gg k_2K'/a_{\text{H}^+}$ and $1 \gg a_{\text{H}^+}/K'_{a1} \gg K'_{a2}/a_{\text{H}^+}$. Given these constraints, eq 17 reduces to

$$k_{\text{obsd}} = k_1 / \left(1 + \frac{K'}{a_{\text{H}^+}} \right) \quad (18)$$

or

$$\frac{1}{k_{\text{obsd}}} = \frac{1}{k_1} + \frac{K'}{a_{\text{H}^+}(k_1)} \quad (19)$$

where $k_1 = 12.82 \text{ M}^{-1} \text{ s}^{-1}$ and $\text{p}K' = 11.18$ at $\mu = 0.1 \text{ M}$ and $T = 20^\circ \text{C}$.

The variation of k_1 with temperature at pH 10.4 gave $\Delta H_1^\ddagger = 46.5 \pm 0.09 \text{ kJ/mol}$ and $\Delta S_1^\ddagger = -65.5 \pm 5.3 \text{ J/(deg}\cdot\text{mol)}$. The temperature dependence of $K' = K(\gamma_{\text{HO}_2^-})^{-1}$ can be determined from the thermodynamic data of Evan and Uri¹³ and the appropriate value of $\gamma_{\text{HO}_2^-}$ determined from the Davies equation.¹⁴

The constants k_2 and K'_{a2} were obtained by the nonlinear least-squares analysis of the following function:¹⁵

$$\Phi = \sum_{i=1}^n [(k_{\text{obsd}} - k_{\text{calcd}}) \text{wts}(i)]^2 \quad (20)$$

$$\text{wts}(i) = \sigma(i)^{-1} \quad (21)$$

$\sigma(i)$ = sample standard deviation of data point i

The constants k_1 and K' were further refined by the same function, while the values of k_{calcd} were determined according to eq 17. Values obtained by this method were $k_1 = 12.64 \pm 0.54 \text{ M}^{-1} \text{ s}^{-1}$, $\text{p}K' = 11.45 \pm 0.19$, $\text{p}K'_{a2} = 11.92 \pm 0.56$. k_2 was calculated as $0.93 \pm 0.39 \text{ M}^{-1} \text{ s}^{-1}$. Calculated values of pseudo-first-order rate constant (k_{calcd}) are compared to the experimental values in Table I and shown in Figure 3.

Discussion

The mechanism presented above is similar to the generalized mechanism for nucleophilic displacements on H_2O_2 as discussed by Hoffmann and Edwards.³ However, in this study, the acid-catalyzed term is unimportant. Equations 7, 8, and 9 are pre-equilibria that give HO_2^- , $\text{HOC}_2\text{H}_4\text{S}^-$, and $^-\text{OC}_2\text{H}_4\text{S}$, respectively. The slow rate of oxidation above and below the pH range of 9 to 12 indicates that $\text{HOC}_2\text{H}_4\text{S}^-$ is the reactive mercaptan species for the rate-determining steps of eq 10 and 11. $\text{HOC}_2\text{H}_4\text{S}^-$ reacts with H_2O_2 and HO_2^- , respectively, via nucleophilic displacements in which hydroxide serves as the leaving group. The rapid decrease of oxidation rate above pH 10.5 indicates that H_2O_2 is clearly more reactive than HO_2^- . The value of k_1 for thioethanol oxidation is consistent with those reported for other mercaptides.¹⁶

Large negative values of ΔS^\ddagger are generally observed for reactions between singly charged ions and neutral molecules; this has been attributed to bond formation between substrate and nucleophile before departure of the leaving group.¹⁷ Some typical

TABLE III: Some Kinetic Data for Oxidations by Peroxides^a

R	N ^b	k_1^c	$\Delta H_1^\ddagger, \text{m}$	$\Delta S_1^\ddagger, \text{m}$	E_{rxn}	H	ref
H	i	16.24	47	-65	1.98	11.07	o
H	g	0.094	56	-75	2.22	0.43	3
H	h	0.086	56	-80	2.21		3
H	f	0.07-	62	-59	2.18	0.55	3
H	$\text{S}_2\text{O}_3^{2-}$	0.025			1.68	3.60	24, 25
H	I^-	0.011	54	-67	1.22	-9.00	7
H	c	2.6×10^{-3}	54	-113			4
H	b	2.2×10^{-3}					26
H	SCN^-	5.2×10^{-3}	62	-105	0.99	1.06	5, 6
H	d	5.3×10^{-5}	73	-71			27
H	e	4.6×10^{-5}					28
H	NO_2^-	5×10^{-7}			0.90	5.09	8
H	Br^-	3.8×10^{-7}	86	-46	0.67	-6.00	7
H	Cl^-	1.8×10^{-9}	96	-54	0.40	-3.00	7
t-Bu ^d	b	1.4×10^{-4}	59	-121			4
t-Bu ^d	c	1.4×10^{-4}	56	-130			29

^aAll data are for ROOH oxidation of N at 25 °C in aqueous solution. ^bN is bis(2-hydroxyethyl)sulfide. ^cN is thioxane. ^dN is the thiocyanatopentaamminecobalt(III) sulfide. ^eN is the thiocyanatopentaamminecobalt(III) cation. ^fN is the thiocyanatobis(ethylenediamine)cobalt(III) cation. ^gN is thiourea. ^hN is N,N' -dimethylthiourea. ⁱN is N,N' -diethylthiourea. ^jN is $\text{HOC}_2\text{H}_4\text{S}$. ^kt-Bu = $(\text{CH}_3)_3\text{C}$. ^lN = nucleophile. ^m k_1 in $\text{M}^{-1} \text{ s}^{-1}$. ⁿ ΔH^\ddagger in kJ mol^{-1} . ^o ΔS^\ddagger in $\text{J mol}^{-1} \text{ K}^{-1}$. ^pThis study.

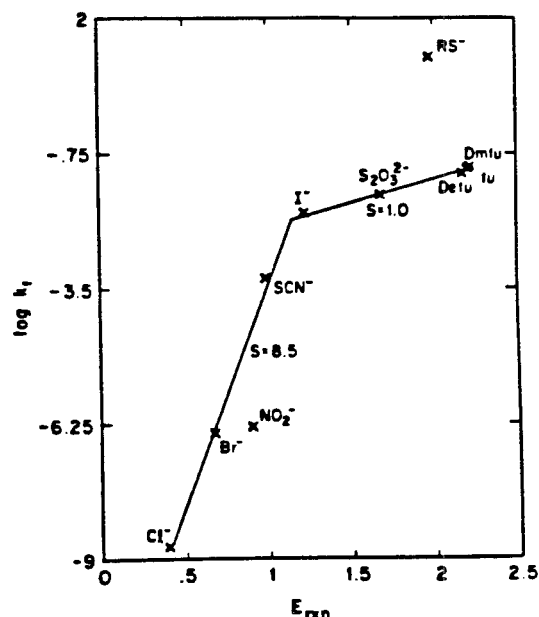


Figure 5. Linear free energy relationship.

values of ΔS^\ddagger for nucleophilic displacements on peroxides are given in Table III.

The order of nucleophilic reactivity as listed in Table III is similar to the order predicted by Edwards and Pearson¹⁸ (i.e., $\text{RS}^- > \text{R}_3\text{P} > \text{C}_6\text{H}_5\text{S}^- \sim \text{SCN}^- > \text{SO}_3^{2-} > \text{OH}^- > \text{S}_2\text{O}_3^{2-} > \text{SC}(\text{NH}_2)_2 > \text{SCN}^- > \text{Br}^- > \text{Cl}^-$), with the exception of the relative order of $\text{S}_2\text{O}_3^{2-}$ and $\text{SC}(\text{NH}_2)_2$.

Three important factors have been considered by Edwards and Pearson¹⁸ in determination of nucleophilic reactivity. They are basicity, polarizability, and the α effect.¹⁸ In Figure 5, a linear free energy relationship of $\log k_1$ vs. the E_{rxn}° ($E_{\text{rxn}}^\circ = E_{\text{H}_2\text{O}_2}^\circ - E_{\text{N}}^\circ$), where $E_{\text{H}_2\text{O}_2}^\circ$ is the electrode potential for the half-reaction of $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = 2\text{H}_2\text{O}$, and E_{N}° is the electrode potential of the nucleophile (N) for the half-reaction of $(\text{N})_2 + 2\text{e}^- = 2\text{N}$, shows that there are two independent linear free energy relationships for the nucleophiles listed in Table III. The reduction

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potential of 2-hydroxyethyl disulfide to 2-mercaptoethanol ($E_0 = -0.22$ V) can be calculated from the half-wave potential reported by Stricks et al.¹⁹ The thioureas, $S_2O_3^{2-}$, and I^- appear to cluster as a distinct group exhibiting a slope of 1.0, while Cl^- , Br^- , and SCN^- cluster as another distinct group with a steeper slope of 8.5. However, 2-mercaptoethanol does not appear to correlate with either group of nucleophiles.

A linear free energy relationship of the following form can be written:

$$\log k_1 = \frac{2.3SRT}{nF} \log K_{\text{reac}} + C \quad (22)$$

where S is the slope, C is the intercept and K_{reac} ($\log K_{\text{reac}} = nFE_{\text{ox}}/2.3RT$) is the equilibrium constant of the overall reaction. Equation 22 is similar in form to the Edwards equation²⁰

$$\log (k_1/k_0) = \alpha E_n + \beta H \quad (23)$$

where k_0 corresponds to the rate constant for water as a nucleophile, E_n is a nucleophilic constant characteristic of the particular electron donor, H is the relative basicity of the donor to protons which has been defined at $H = \text{pH}_a + 1.74$, and α and β are the substrate constants. E_n , which depends on the polarizability,²¹ is calculated from the electrode potential of the nucleophile.

Comparison of eq 22 to 23 suggests that E_{reac} should be comparable to E_n , that S is equivalent to the substrate constant, and that C can be equated to $(\beta H + \log k_0)$.

The minimal contribution (i.e., $\alpha E_n \gg \beta H$) of the basicity term to relative reactivity and the existence of two apparently inde-

pendent linear free energy domains as shown in Figure 5 may be explained within the context of Pearson's HSAB theory.²² The observed order of nucleophilic reactivity should be similar to the order of softness of bases. The relative order of softness for various nucleophiles is thiourea $> SO_3^{2-} > SCN^- > I^- > Br^- > NO_2^- > Cl^- > F^-$ which is similar to the observed order to nucleophilic reactivity. Since H_2O_2 is soft center,²³ polarizability rather than basicity should be the more important factor. Thiosulfate and I^- are considered as soft bases, whereas Cl^- , Br^- , F^- , and NO_3^- are considered to be hard bases. As a consequence, the former group will have higher polarizabilities and hence greater nucleophilic reactivities than the latter group. The departure of 2-mercaptoethanol from this correlation implies that its rate of the oxidation also depends strongly on its basicity. The relative basicity of 2-mercaptoethanol ($H = 11.1$) is significantly higher than all other nucleophiles listed in Table III. This indicates that the addition of 2-mercaptoethanol to hydrogen peroxide is energetically more favorable than the other listed sulfur compounds.

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CHAPTER FIVE
KINETICS AND MECHANISM OF REDUCTION OF Co(II)-4,4',4'',4'''-
TETRASULFOPHTHALOCYANINE BY 2-MERCAPTOETHANOL
UNDER ANOXIC CONDITIONS

NOTATIONS

- k_2 Electron-transfer rate constant (sec^{-1}) of reaction
 $\text{HOC}_2\text{H}_4\text{S}=(\text{Co}^{\text{II}}\text{TSP})_2 \longrightarrow \text{Co}^{\text{I}}\text{TSP} + \text{Co}^{\text{II}}\text{TSP} + \text{HOC}_2\text{H}_4\text{S}^{\cdot}$
- K_1 Equilibrium constant (M^{-1}) of reaction
 $(\text{Co}^{\text{II}}\text{TSP})_2 + \text{HOC}_2\text{H}_4\text{S}^- \rightleftharpoons \text{HOC}_2\text{H}_4\text{S}=(\text{Co}^{\text{II}}\text{TSP})_2$
- K_{a_1} Apparent acid dissociation constant (M) of Acid-Base
 Equilibrium $\text{HOC}_2\text{H}_4\text{SH} \rightleftharpoons \text{HOC}_2\text{H}_4\text{S}^- + \text{H}^+$
- K_{a_2} Apparent acid dissociation constant (M) of Acid-Base
 Equilibrium $\text{HOC}_2\text{H}_4\text{S}^- \rightleftharpoons ^-\text{OC}_2\text{H}_4\text{S}^- + \text{H}^+$
- K_{D} Dimerization equilibrium constant (M^{-1}) of reaction
 $2(\text{Co}^{\text{II}}\text{TSP}) \rightleftharpoons (\text{Co}^{\text{II}}\text{TSP})_2$
- K_3 Equilibrium constant (M^{-1}) of reaction
 $\text{Co}^{\text{II}}\text{TSP} + \text{HOC}_2\text{H}_4\text{S}^- \rightleftharpoons \text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}$
- k_4 Electron-transfer rate constant (sec^{-1}) of reaction
 $\text{HOC}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP} \longrightarrow \text{Co}^{\text{I}}\text{TSP} + \text{HOC}_2\text{H}_4\text{S}^{\cdot}$
- k' Rate constant (see equation 5.22)
- k'' Rate constant (see equation 5.22)
- K_{a} Apparent acid dissociation constant (M) of Acid-Base
 Equilibrium $\text{H}_2\text{O}-(\text{Co}^{\text{II}}\text{TSP})_2-\text{OH}_2 \rightleftharpoons \text{H}_2\text{O}-(\text{Co}^{\text{II}}\text{TSP})_2-\text{OH}^- + \text{H}^+$

a_{H^+}	Hydrogen ion activity
$[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}}$	Total $\text{Co}^{\text{II}}\text{TSP}$ concentration (M)
$[\text{RSH}]_{\text{T}}$	Total 2-mercaptoethanol concentration (M)
$[\text{Co}^{\text{I}}\text{TSP}]_{\text{T}}$	Total $\text{Co}^{\text{I}}\text{TSP}$ concentration (M)

Abstract

The kinetics and mechanism of reduction of Co(II)-4,4',4'',4'''-tetrasulfophthalocyanine by 2-mercaptoethanol under anoxic conditions were investigated and the following rate law was found:

$$v = \frac{-d[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}}}{dt} = \frac{k_2 K_1 [\text{RSH}]_{\text{T}} [\text{Co}^{\text{II}}\text{TSP}]_{\text{T}}}{2\left(1 + \frac{a_{\text{H}^+}}{K_{\text{a}_1}} + \frac{K_{\text{a}_2}}{a_{\text{H}^+}}\right) (1 + \alpha [\text{RSH}]_{\text{T}})}$$

where k_2 is a rate constant for the rate-limiting electron transfer step, and K_1 is the equilibrium constant for the complexation of CoTSP dimer with thioethanol; K_{a_1} and K_{a_2} are the apparent acid dissociation constants of $\text{HOC}_2\text{H}_4\text{SH}$ and $\text{HOC}_2\text{H}_4\text{S}^-$, respectively; α is $K_1 / (1 + a_{\text{H}^+} / K_{\text{a}_1} + K_{\text{a}_2} / a_{\text{H}^+})$; and a_{H^+} is the hydrogen ion activity. Calculation of the experimental data to the above rate law gave $k_2 = 228 \pm 3.8 \text{ s}^{-1}$ and $K_1 = 117 \pm 2.5 \text{ M}^{-1}$ at 27°C and at ionic strength, $\mu = 0.4 \text{ M}$.

Introduction

In the absence of oxygen, vitamin $\text{B}_{12\text{a}}$ (aquocobalamin), a cobalt corrin complex, can be reduced from its Co(III) to Co(I) states by sodium borohydride in two different stages (Johnson et al., 1963). Initially, the Co(III), $\text{B}_{12\text{a}}$, is reduced to Co(II), $\text{B}_{12\text{r}}$, producing a brown solution; subsequently the Co(II) is further reduced to Co(I),

B₁₂S (Johnson et al., 1963). A similar sequence of reactions with cobalt(III)-dimethyl-glyoxime was also reported by Schrauzer and Kratel (1965).

Reduction of Co(II) phthalocyanine to Co(I) phthalocyanine has been reported by Day (1968) and Busch et al. (1964). Day (1968) reported that with the addition of sodium borohydride, a yellow solution was obtained under anoxic conditions. Busch et al. (1964) also described the reduction of Co(II)-tetrasulfophthalocyanine to Co(I)-tetrasulfophthalocyanine by reductants such as borohydride, sulfide and hydrazine all in the absence of oxygen. The spectrum of the yellow solution has been shown to be in good agreement with the spectrum of the reduced solution reported by Day (1968) and the Co(I)-phthalocyanine obtained from the controlled-potential reduction of Co(II)-phthalocyanine. Magnetic studies of the resulting Co-tetrasulfophthalocyanine solution suggested that Co(I)-tetrasulfophthalocyanine is the primary product of the reduction. However, the kinetics and the mechanism of the reduction have not been examined in detail. In this chapter we address the kinetics and mechanism of the reduction of Co(II)-4,4',4'',4'''-tetrasulfophthalocyanine, abbreviated as Co(II)TSP, by 2-mercaptoethanol in aqueous solution in the absence of oxygen.

This study would also provide additional information on the mechanism of the autoxidation of 2-mercaptoethanol catalyzed by Co(II)-4,4',4'',4'''-tetrasulfophthalocyanine. The mechanism of the

catalytic autoxidation of 2-mercaptoethanol involves the complexation of Co(II)-tetrasulfophthalocyanine by 2-mercaptoethanol prior to the rate-determining electron transfer step in the catalytic cycle. This study would give an estimate of the rate of complexation and provide additional information on the actual rate-limiting step.

Experimental Procedure

Reagents: 2-mercaptoethanol stock solutions were prepared using redistilled 99% reagent grade 2-mercaptoethanol (Aldrich). Co(II)-4,4',4'',4'''-tetrasulfophthalocyanine was synthesized according to the procedure described by Boyce et al. (1983). Buffers were prepared using reagent grade sodium hydroxide (Mallinckrodt), sodium chloride (J.T. Baker) and sodium bicarbonate (Mallinckrodt). Water used to prepare the buffers and reagent solutions was obtained from a Milli-Q water purification system (Millipore), with a resistivity of 18 M Ω -cm. The water was irradiated with ultra-violet light to remove any trace organics that may have been present. The irradiated water was deoxygenated three times under vacuum/nitrogen cycle. All the reagent solutions were stored under nitrogen in a glove box (Vacuum Atmosphere Models HE-63P and HE-493) to prevent any oxygen contamination.

Kinetic measurements: Kinetic measurements were made on Dionex Durrum Rapid Kinetics System Series D-100 Stopped-flow spectrophotometer. The stopped-flow apparatus was placed inside a glove-box to ensure oxygen-free experimental conditions. The uv-visible light

source and the monochromator were located outside the glove box to prevent overheating, and the monochromator was connected to the reaction cell by optical fiber (Polymicro Technologies). The signal was collected by a Gould Biomation (Model 2805) and was subsequently digitized and transferred to a MINC-Mini computer. The schematic diagram of the instrumental setup is shown in Figure 5.1. Five hundred and twelve data points were collected for each kinetic measurement. At least three measurements were made for each value of k_{obsd} . Data on the MINC-Minc computer was transferred to and analyzed with a IBM-XT computer. Constant temperature was maintained at 27°C with Haake FK2 water bath. Sodium chloride stock solutions were added to appropriate buffers to establish constant ionic strength at 0.4 M. The pH of each reagent was determined with a Beckman Altex ϕ 71 pH meter and Radiometer Glass Electrode. The reaction was monitored at 444 nm which its absorbance is linearly proportional to the $[Co^I TSP]_T$. Pseudo-first-order conditions with $[HOC_2H_4SH]_T (> 10^{-4} M) \gg [CoTSP]_T (= 6.4 \times 10^{-6} M)$ were employed for all kinetic runs.

Results

During the course of reaction, the color of the solution changes from blue to yellow which is consistent to the color changes reported by Busch (1964). The spectra of the original blue solution and the final yellow solution were recorded and are shown in Figure 5.2. The spectrum of the blue Co(II)TSP solution shows two distinct peaks at

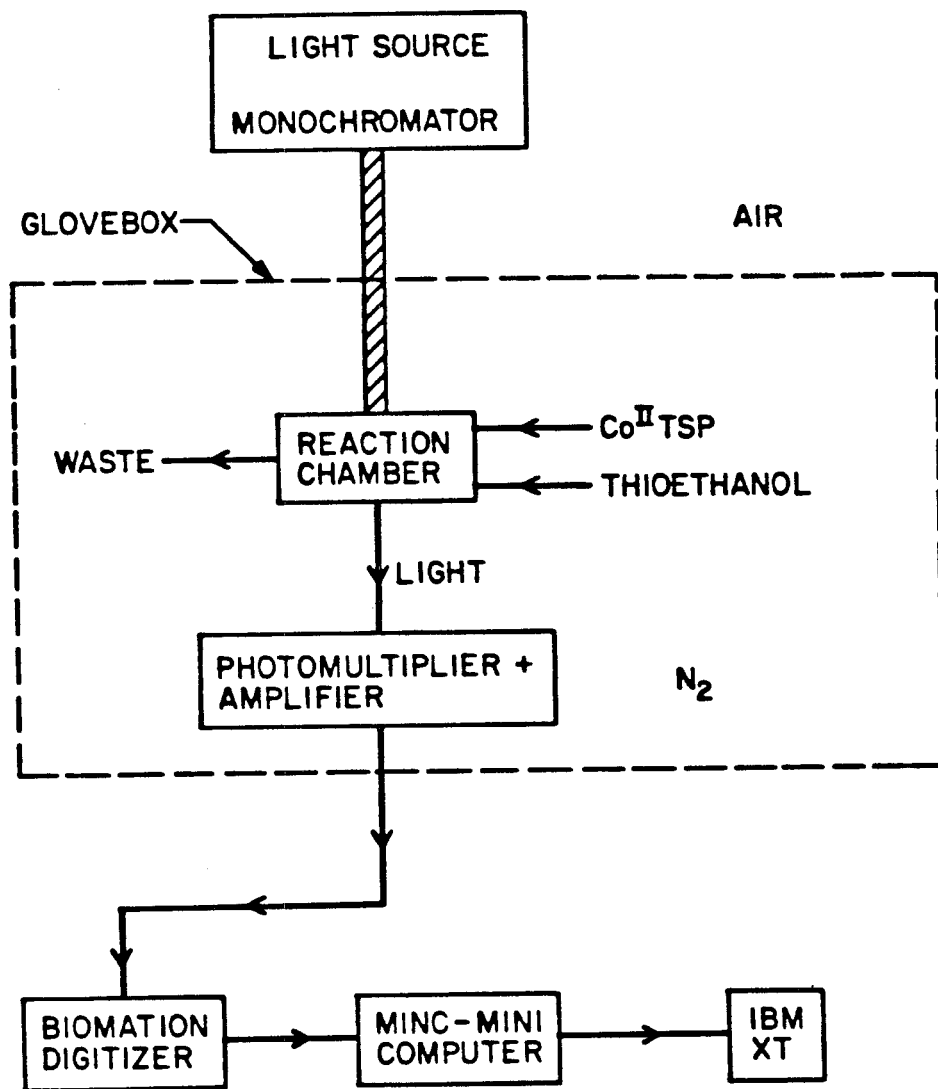


Figure 5.1: Schematic Diagram of the Instrumental Setup of Stopped-flow Spectrophotometer.

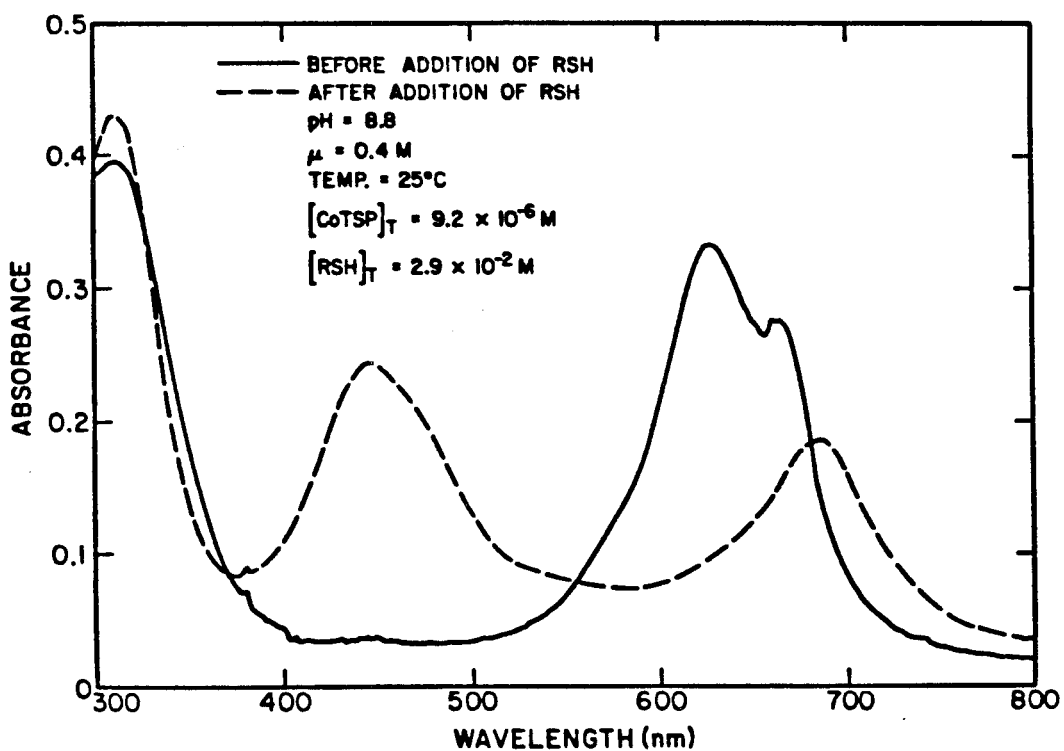


Figure 5.2: Changes of CoTSP Spectrum during its Reduction by 2-Mercaptoethanol.

624 nm and 664 nm which corresponds to the dimer and monomer of the Co(II)-tetrasulfophthalocyanine, respectively (Gruen and Blagrove, 1973). Figure 5.2 shows that the concentration of the dimeric species was significant. Calculation from the dimerization constant at 38°C suggests that > 70% of total Co(II)TSP is in the dimeric form. When RS⁻ was added, both peaks of the original spectrum disappeared and two other peaks at 444 nm and 688 nm arose. The spectrum of the yellow solution was found to be consistent with the spectrum of Co(I) phthalocyanine reported by Day (1968). If oxygen gas was bubbled through the yellow solution, the characteristic blue color rapidly returned. This observation indicated that Co(II)-tetrasulfophthalocyanine had been reversibly reduced to Co(I)-tetrasulfophthalocyanine.

Under pseudo-first-order conditions, plots of $\ln(A_t - A_\infty)$ vs. t were linear ($r^2 \geq 0.995$) for 75 to 90% of the reaction. This linearity indicates the rate of reduction is first order with respect to the Co-(II)tetrasulfophthalocyanine. Figure 5.3 compares the experimental kinetic data with the calculated exponential curve. The dependence of k_{obsd} on $[\text{HOC}_2\text{H}_4\text{SH}]_T$ was determined at pH 11.5. A straight line plot of k_{obsd} vs $[\text{HOC}_2\text{H}_4\text{SH}]_T$ from 3.89×10^{-4} M to 1.56×10^{-3} M is shown in Figure 5.4 (slope = $13113 \text{ M}^{-1}\text{s}^{-1}$). Thus, the rate of reduction of Co(II)-4,4',4'',4'''-tetrasulfophthalocyanine by thioethanol is first order in both Co-tetrasulfophthalocyanine and 2-mercaptoethanol over the concentration range studied. However, as

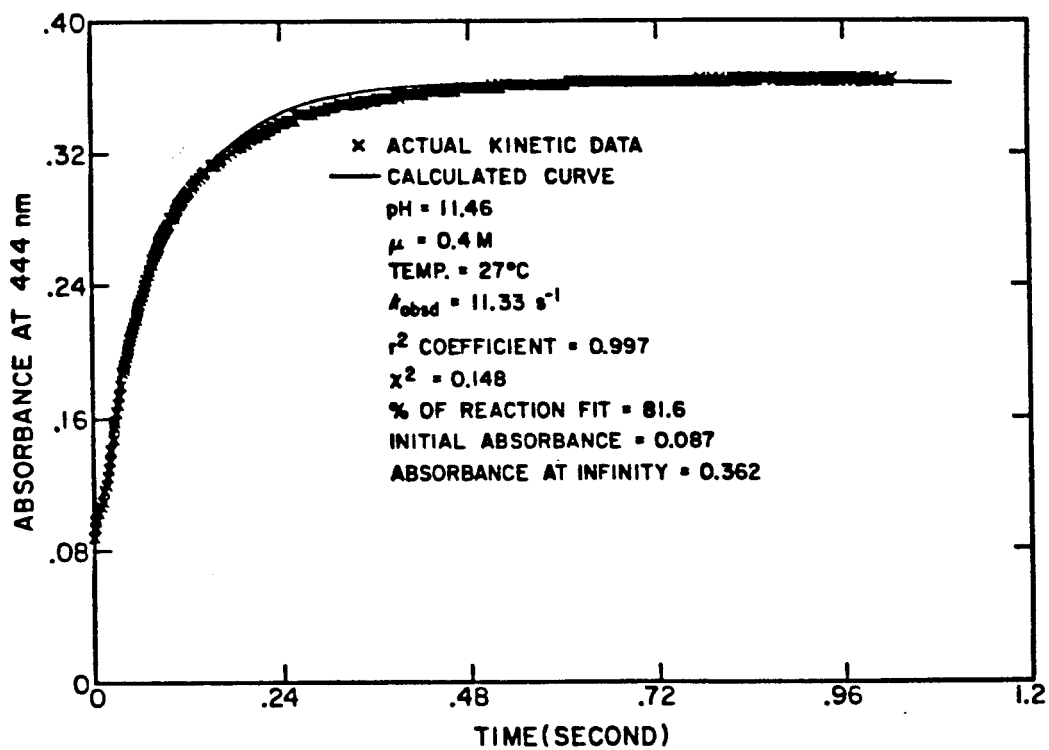


Figure 5.3: First-order Kinetic Plot of the Reduction of Co(II)TSP by 2-Mercaptoethanol.

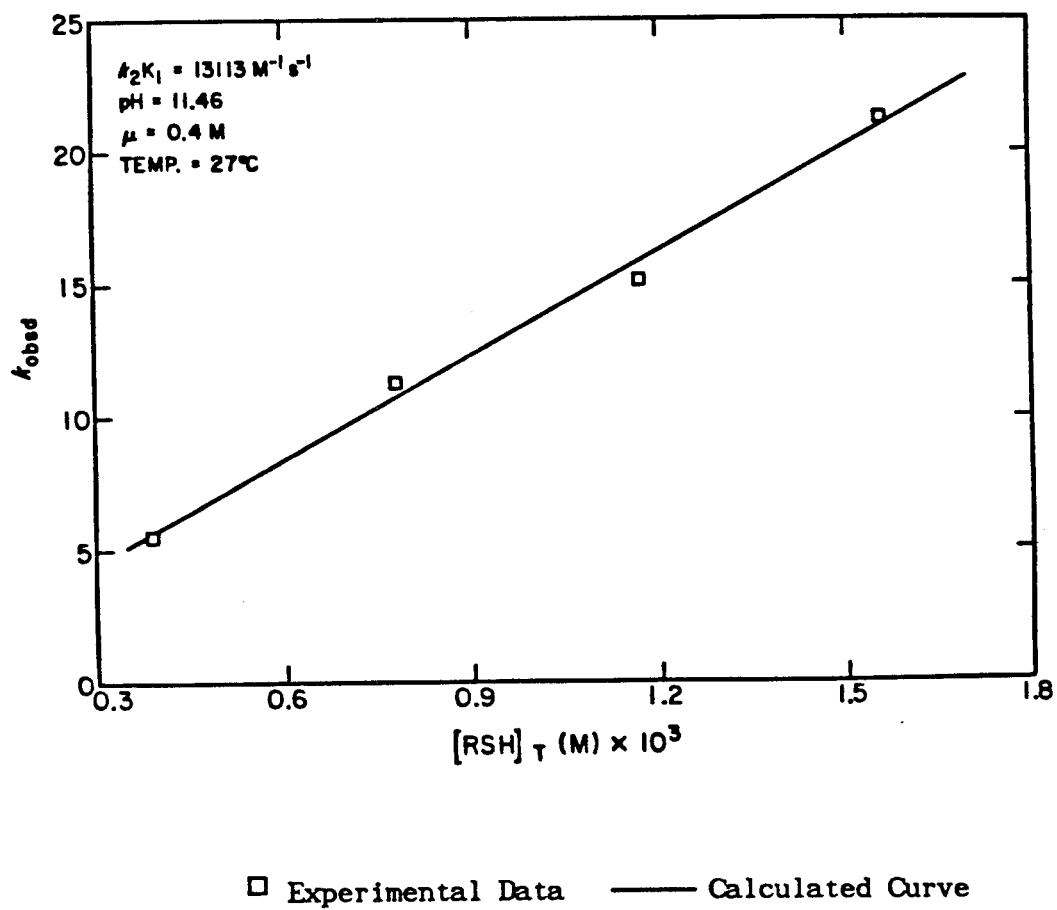
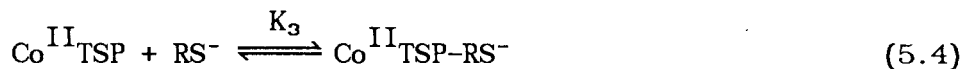
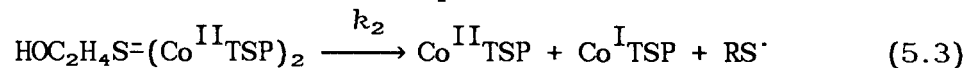
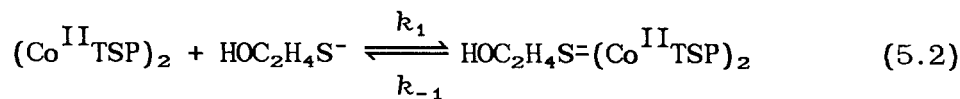
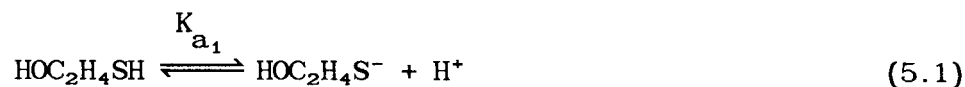


Figure 5.4: Determination of Reaction Order for low concentration of 2-Mercaptoethanol.

the concentration of the 2-mercaptoethanol was increased beyond 1.56×10^{-3} M, the dependence k_{obsd} on the thioethanol concentration gradually changed from first-order to zero-order, yielding a saturation curve which levels off at about 115 s^{-1} , as shown in Figure 5.5.

The effect of pH on the rate of reduction was investigated at low 2-mercaptoethanol concentration. The experimental data are shown in Figure 5.6. According to Figure 5.6, the rate of reduction is independent of pH above 10.5. This independence suggests that the RS^- bridged dimer is not the reactive dimeric species.

The above kinetic information can be explained with the aid of the following mechanism:



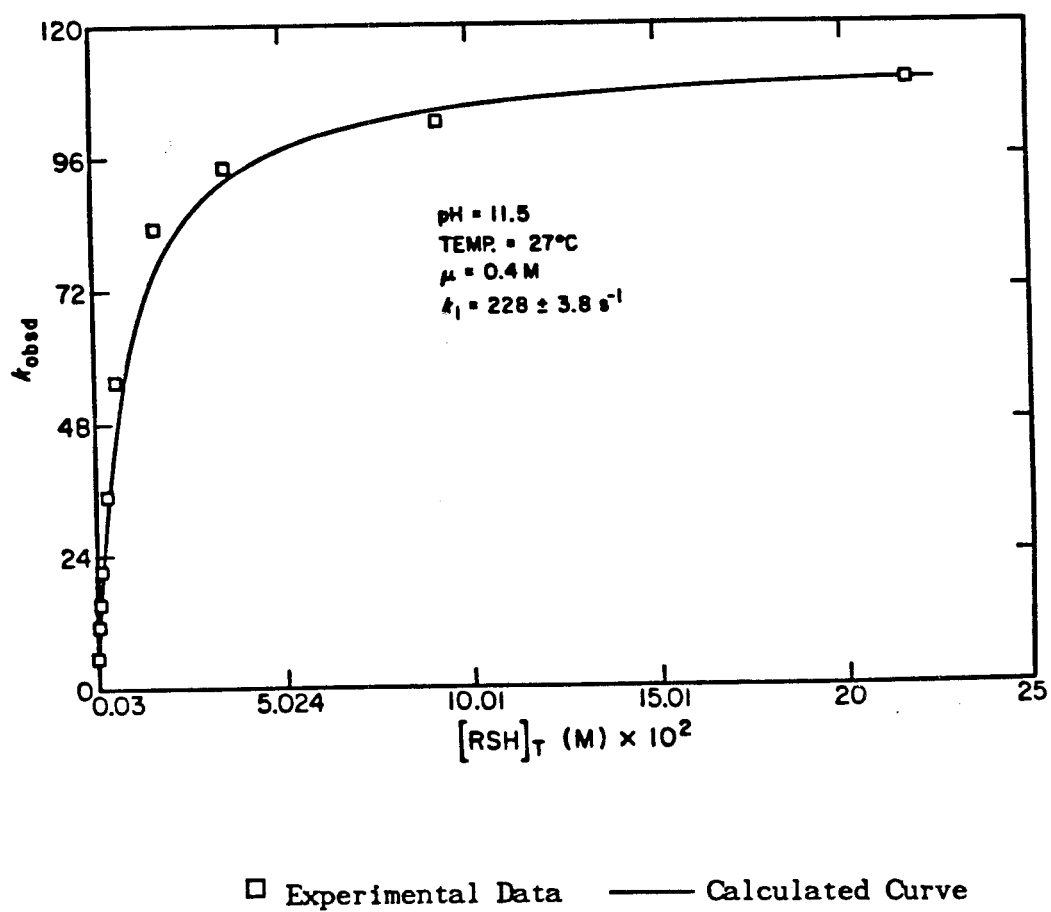
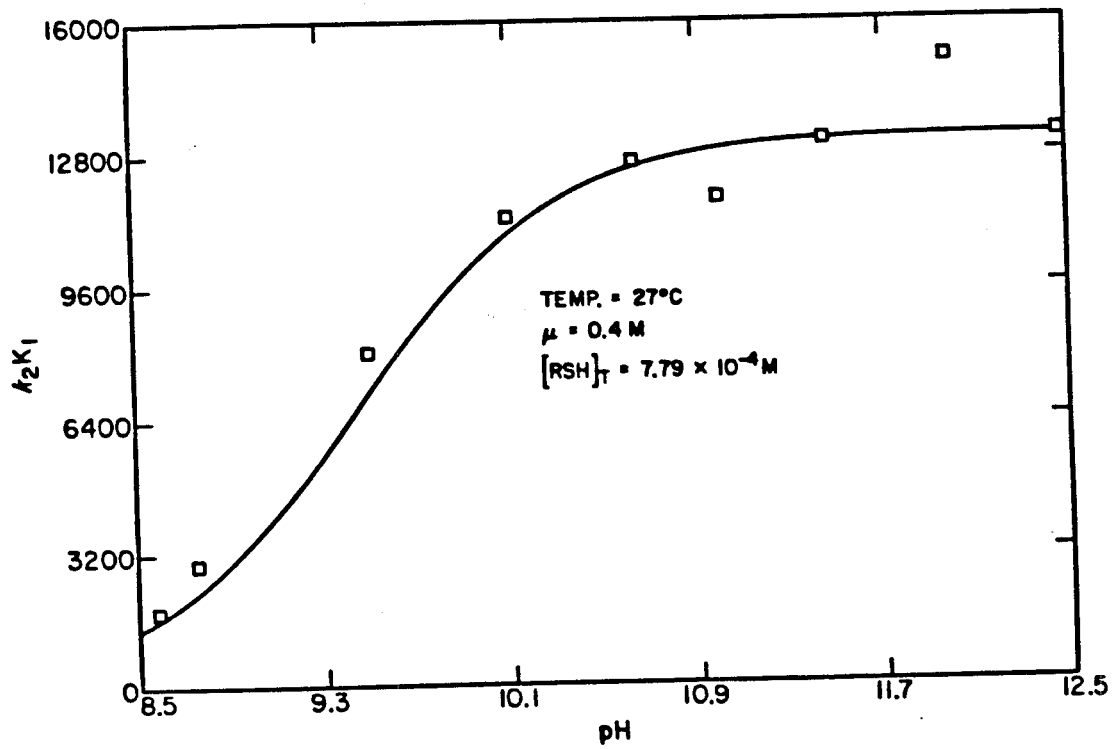


Figure 5.5: The reduction rate dependence on the 2-Mercaptoethanol.



□ Experimental Data — Calculated Curve

Figure 5.6: pH Dependence of the rate of Co(II)TSP reduction.

According to this mechanism, the rate of appearance of Co(I)-4,4',4'',4'''-tetrasulfophthalocyanine is given by the expression

$$v = \frac{d[\text{Co}^{\text{I}}\text{TSP}]_{\text{T}}}{dt} = k_2[\text{RS}=\text{Co}^{\text{II}}\text{TSP}-\text{Co}^{\text{II}}\text{TSP}] + k_4[\text{RS}=\text{Co}^{\text{II}}\text{TSP}] \quad (5.6)$$

where k_2 and k_4 are the rate constants for the electron transfer from the bound thioethanolate to the metal center of dimer and monomer, respectively. Substitution of the appropriate equilibrium relationships for complexation of thioethanol by Co(II)-tetrasulphthalocyanine yields

$$v = \{k_2K_1[(\text{Co}^{\text{II}}\text{TSP})_2] + k_4K_3[\text{Co}^{\text{II}}\text{TSP}]\}[\text{RS}^-] \quad (5.7)$$

where K_1 ($K_1=k_1/k_{-1}$) and K_3 ($K_3=k_3/k_{-3}$) are the equilibrium constants for the complexation of thioethanol to the Co(II)TSP dimer and Co(II)TSP monomer, respectively. However, the observed first-order dependence on $[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}}$ suggests that either that $k_2K_1[(\text{Co}^{\text{II}}\text{TSP})_2] \gg k_4K_3[\text{Co}^{\text{II}}\text{TSP}]$ or the reverse is true. Assuming that the term involving $(\text{Co}^{\text{II}}\text{TSP})_2$ dominates the rate expression (see discussion later) equation 5.7 becomes

$$v = k_2K_1[(\text{Co}^{\text{II}}\text{TSP})_2][\text{RS}^-] \quad (5.8)$$

Using the Co(II)-tetrasulfophthalocyanine total concentration expressed as $[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}} \cong 2[(\text{Co}^{\text{II}}\text{TSP})_2] + 2[\text{HOC}_2\text{H}_4\text{S}=(\text{Co}^{\text{II}}\text{TSP})_2]$, equation 5.8 can be rewritten as follows:

$$v = \frac{d[\text{Co}^{\text{I}}\text{TSP}]_{\text{T}}}{dt} = \frac{k_2 K_1 [\text{Co}^{\text{II}}\text{TSP}]_{\text{T}} [\text{HOC}_2\text{H}_4\text{S}^-]}{2(1 + K_1 [\text{HOC}_2\text{H}_4\text{S}^-])} \quad (5.9)$$

Expressing the concentration of $\text{HOC}_2\text{H}_4\text{S}^-$ in term of its total concentrations as $[\text{HOC}_2\text{H}_4\text{SH}]_{\text{T}}$ ($[\text{HOC}_2\text{H}_4\text{SH}]_{\text{T}} = [\text{HOC}_2\text{H}_4\text{SH}] + [\text{HOC}_2\text{H}_4\text{S}^-] + [-\text{OC}_2\text{H}_4\text{S}^-]$) gives

$$v = \frac{k_2 K_1 [\text{Co}^{\text{II}}\text{TSP}]_{\text{T}} [\text{HOC}_2\text{H}_4\text{SH}]_{\text{T}}}{2(1 + \frac{a_{\text{H}^+}}{K_{a_1}} + \frac{K_{a_2}}{a_{\text{H}^+}})(1 + \alpha [\text{HOC}_2\text{H}_4\text{SH}]_{\text{T}})} \quad (5.10)$$

where a_{H^+} is the activity of hydrogen ion and α is $K_1/(1 + a_{\text{H}^+}/K_{a_1} + K_{a_2}/a_{\text{H}^+})$. When $1 \gg \alpha [\text{HOC}_2\text{H}_4\text{SH}]_{\text{T}}$ then equation 5.10 becomes

$$v = \frac{1}{2} k_2 \alpha [\text{Co}^{\text{II}}\text{TSP}]_{\text{T}} [\text{HOC}_2\text{H}_4\text{SH}]_{\text{T}} \quad (5.11)$$

Therefore when the concentration of thioethanol is low, the rate of Co(I)TSP formation would show a first-order dependence on the both $[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}}$ and $[\text{2-mercaptoethanol}]_{\text{T}}$. On the other hand, when the

concentration of thioethanol is high, the rate expression becomes

$$v = \frac{1}{2}k_2[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}} \quad (5.12)$$

and the rate should be independent of the thioethanol concentration and the observed rate constant should reach a maximum value (equivalent to $\frac{1}{2}k_2$). These predictions were actually observed. Values of k_2 and K_1 were calculated from the k_{obsd} data in Figure 5.5 as $228 \pm 3.8 \text{ sec}^{-1}$ and $117 \pm 2.5 \text{ M}^{-1}$, respectively.

Since the effect of pH on the rate of reduction was investigated at a relatively low 2-mercaptoethanol concentration, the rate of reduction is governed by Equation 5.11. According to Equation 5.11, k_{obsd} is given by

$$k_{\text{obsd}} = \frac{k_2K_1}{2\left(1 + \frac{a_{\text{H}^+}}{K_{a_1}} + \frac{K_{a_2}}{a_{\text{H}^+}}\right)} \quad (5.13)$$

Since $K_{a_1} = 10^{-9.4}$ (Martell and Smith, 1977) and $K_{a_2} < 10^{-13.5}$ (Chapter 3), then between pH 10.5 and 12.5, the denominator of Equation 5.13 is approximately 2 and $k_{\text{obsd}} = \frac{1}{2}k_2K_1$. The experimental k_{obsd} and the calculated k_{obsd} are listed in Table 5.1 and shown in Figure 5.6.

TABLE 5.1. Comparison of k_{obsd} with k_{cald} of Reduction of Co(II)TSP by 2-Mercaptoethanol at various pH.

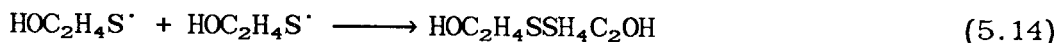
pH	$k_{obsd} \times 10^{-4}(\text{M}^{-1}\text{sec}^{-1})$	$k_{cald} \times 10^{-4}(\text{M}^{-1}\text{sec}^{-1})$
8.59	0.18 ± 0.005	0.16
8.76	0.29 ± 0.01	0.23
9.50	0.80 ± 0.01	0.71
10.10	1.12 ± 0.01	1.09
10.64	1.26 ± 0.01	1.25
11.00	1.17 ± 0.01	1.30
11.46	1.31	1.32
11.99	1.50 ± 0.05	1.33
12.47	1.32 ± 0.02	1.33

Experimental Conditions : $\mu = 0.4 \text{ M}$, Temperature = 27°C ,
 $[\text{RSH}]_{\text{T}} = 7.8 \times 10^{-4} \text{ M}$, Buffer system = NaCl, NaHCO_3 , NaOH.

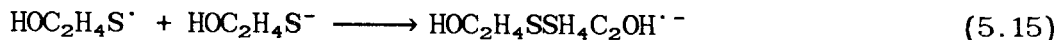
Discussion

As can be seen in Figure 5.2, the dimer is the major Co(II) species at the start of the reaction. The dimerization constant, K_D , is $6.17 \times 10^5 \text{ M}^{-1}$ at 38°C by (Schelly et al., 1970); its value increases as the temperature decreases. An estimate of the [dimer] can be made from the reported K_D value. Under our experimental conditions of total Co(II)TSP ($6.46 \times 10^{-6} \text{ M}$), 70% of the total Co(II) is calculated to be in dimeric form at 38°C . This percentage is probably higher since our experimental temperature was 27°C and not 38°C . Therefore, >70% of the total Co(II) concentration at the start of solution is in dimeric form.

The initial part of the mechanism described here is a simple two-step system. The first step is a rapid equilibrium complexation of the Co(II)-tetrasulfophthalocyanine dimer with RS^- and the second reaction is the rate-determining electron transfer from the bound thioethanolate to the Co(II). The products of this two-step mechanism are assumed to be the mixed Co(I)-Co(II)-tetrasulfophthalocyanine dimer and 2-mercaptoethanol radical. The 2-mercaptoethanol radical would further react through the following sequence of reactions



OR



to give 2-hydroxyethyl disulfide as the final product.

In addition to the proposed mechanism, the following reaction sequence is possible:



According to this mechanism, the rate law is

$$v = k_4 K_3 K_D^{-1/2} [\text{RS}^-] [\text{Co}^{\text{II}}\text{TSP}]_T^{1/2} \quad (5.19)$$

and the rate of reduction show a half-order dependence on the $[\text{Co}^{\text{II}}\text{TSP}]_T$. A simple exponential kinetics should not be observed. This contradicts the observed behavior and therefore, this mechanism is not highly probable.

The assumption that $k_2 K_1 [\text{RS}^-] [\text{Co}^{\text{II}}\text{TSP-Co}^{\text{II}}\text{TSP}] \gg k_4 K_3 [\text{RS}^-] [\text{Co}^{\text{II}}\text{TSP}]$ was made to derive the final form of the rate expression. This assumption can be justified by the observed first-order dependence on $[\text{Co}^{\text{II}}\text{TSP}]_T$. Let's suppose that the

inequality does not hold, then substitution of following relationships

$$[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}} \cong 2[(\text{Co}^{\text{II}}\text{TSP})_2] \quad (5.20)$$

$$[\text{Co}^{\text{II}}\text{TSP}] = K_{\text{D}}^{-1/2}[(\text{Co}^{\text{II}}\text{TSP})_2]^{1/2} \quad (5.21)$$

into Equation 5.7 yields

$$v = k'[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}} + k''[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}}^{1/2} \quad (5.22)$$

In the case that $k_4K_3[\text{Co}^{\text{II}}\text{TSP}] \gg k_2K_1[(\text{Co}^{\text{II}}\text{TSP})_2]$, the rate law is

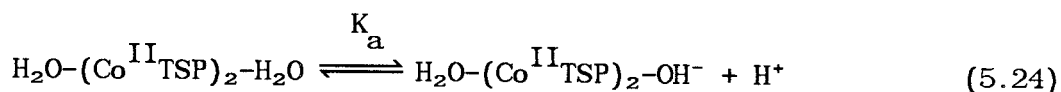
$$v = k''[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}}^{1/2} \quad (5.23)$$

and a half-order dependence on $[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}}$ is predicted. According to either Equation 5.22 and Equation 5.23, the first-order dependence on $[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}}$ should not be observed. Therefore, the inequality must hold in order to observe the first-order dependence on $[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}}$.

The effect of pH on the rate of reduction can be explained by the equilibrium partition between $\text{HOC}_2\text{H}_4\text{S}^-$ and $\text{HOC}_2\text{H}_4\text{SH}$. As the pH of the solution increases from 8.8 to a pH beyond the pK_{a_1} (9.4) of the 2-mercaptoethanol (Martell and Smith, 1977), the concentration of RS^- increases significantly, therefore, resulting in an increase in the rate of reduction. However, at $\text{pH} \geq 10.5$, thioethanol is completely deprotonated and the rate of reduction is consequently independent of

pH. This pH dependence also reveals that the 2-mercaptoethanol anion is probably the reactive form of the reductant.

The approximately equal values of the observed rate constants at $\text{pH} \geq 10.5$ suggests that the pK_a of reaction 5.24



must be $\gg 14.7$. If the rxn. 5.24 actually participates in the reaction, then $[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}} \cong (1 + K_a/a_{\text{H}^+})[\text{Co}^{\text{II}}\text{TSP}]_{\text{D}}$. At $\text{pH} > 10.5$, k_{obsd} can be written as

$$k_{\text{obsd}} = \frac{k_2 K_1}{2(1 + \frac{K_a}{a_{\text{H}^+}})} \quad (5.25)$$

According to Equation 5.25, a noticeable pH dependence should be observed between 10.5 and 12.47 if $\text{pK}_a < 14.5$. The lack of an observed pH dependence in that pH region thereby suggests that the pK_a must be $\gg 14.5$.

The observed rate of reduction can be used to make an estimation on the lower-bound value of rate constants, k_1 and k_{-1} . As indicated

before, the observed rate of reduction is written as:

$$v = \frac{d[\text{Co}^{\text{I}}\text{TSP}]}{dt} = k_2[(\text{Co}^{\text{II}}\text{TSP})_2\text{-RS}^-] = k_{\text{obsd}}[(\text{Co}^{\text{II}}\text{TSP})_2][\text{RS}^-] \quad (5.26)$$

The rate of the complexation of Co(II)TSP and $\text{HOC}_2\text{H}_4\text{S}^-$ can be written as follows:

$$v_1 = k_1[(\text{Co}^{\text{II}}\text{TSP})_2][\text{HOC}_2\text{H}_4\text{S}^-] \quad (5.27)$$

Since the electron transfer step is the rate determining step in the mechanism, the rate of complexation should be significantly greater than the observed rate of reduction, (i.e., $v_1 \gg v$). This inequality indicates that $k_1 \gg k_{\text{obsd}}$ and thus $k_1 \gg 1.3 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$. This lower-bound estimate is in agreement with the rate constant of ligand exchange of uncomplexed Co(II) which is given by Cotton and Wilkinson (1980). In addition, a lower-bound inequality for k_{-1} is estimated to be $\gg 1 \times 10^2 \text{ s}^{-1}$ from the inequality $k_1 \gg 1.3 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ and the calculated K_1 ($1.15 \times 10^2 \text{ M}^{-1}$).

The estimate on the rate of complexation in this paper supports the electron transfer step rather than the substrate complexation step to be the rate limiting step in the mechanism of the autoxidation of 2-mercaptoethanol catalyzed by Co(II)-4,4',4'',4'''-tetrasulfophthalocyanine. As described in Chapter 3, two possible steps can be chosen

as the rate limiting step. They are the complexation of 2-mercaptoethanol to the dimer and the electron-transfer from Co metal center to bound dioxygen. As the thioethanol in both aerobic and anaerobic conditions is complexed to dimeric species, their complexation rates should be quite similar. Therefore, the comparison of k_1 with the k_{obsd} values ($\cong 10^4 \text{ M}^{-1}\text{s}^{-1}$) of the corresponding catalytic autoxidation indicates that the complexation of 2-mercapoethanol to the catalytic dimer in the oxygenated system is unlikely to be the rate-determining step. This conclusion strengthens the proposition that electron transfer from Co(II) to dioxygen is the rate-limiting step in catalytic autoxidation.

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CHAPTER SIX
KINETICS AND MECHANISM OF AUTOXIDATION OF 2-AMINOETHANETHIOL
AND ETHANETHIOL CATALYZED BY
Co(II)-4,4',4'',4'''-TETRASULFOPHTHALOCYANINE
IN AQUEOUS SOLUTION

NOTATIONS

a_{H^+} Hydrogen ion activity

The following notations are applied to catalytic autoxidation of 2-aminoethanethiol.

k_{obsd}^1 Observed rate constant

α_1 $k_{31}^{11}K_{21}^{11}$

k_{31}^{11} Electron-transfer rate constant (sec^{-1}) of reaction
 $(\text{NH}_3^+\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{NH}_3^+\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2)^{-4} \longrightarrow$
 $(\text{NH}_3^+\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{NH}_3^+\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{III}}\text{TSP}-\text{O}_2^-)^{-4}$

K_{21}^{11} Equilibrium constant (M^{-1}) of reaction
 $(\text{O}_2-\text{Co}^{\text{II}}\text{TSP}-\text{RS}=\text{Co}^{\text{II}}\text{TSP}-\text{OH}_2)^{-4} + \text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- \rightleftharpoons$
 $(\text{NH}_3^+\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{NH}_3^+\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2)^{-4}$

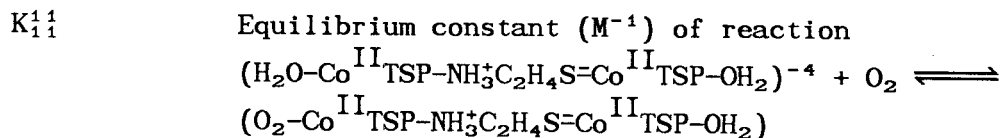
α_2 $k_{31}^{12}K_{21}^{12}$

k_{31}^{12} Electron-transfer rate constant (sec^{-1}) of reaction
 $(\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{NH}_3^+\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2)^{-5} \longrightarrow$
 $(\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{NH}_3^+\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{III}}\text{TSP}-\text{O}_2^-)^{-5}$

K_{21}^{12} Equilibrium constant (M^{-1}) of reaction
 $(\text{O}_2-\text{Co}^{\text{II}}\text{TSP}-\text{NH}_3^+\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{OH}_2)^{-4} + \text{NH}_2\text{C}_2\text{H}_4\text{S}^- \rightleftharpoons$
 $(\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{NH}_3^+\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2)^{-5}$

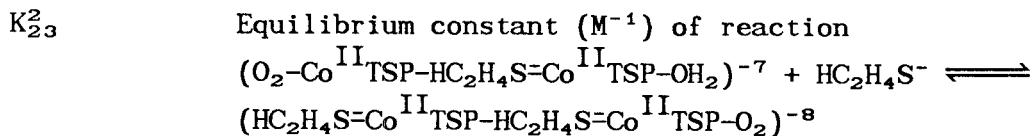
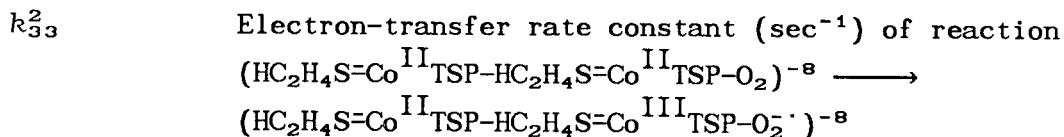
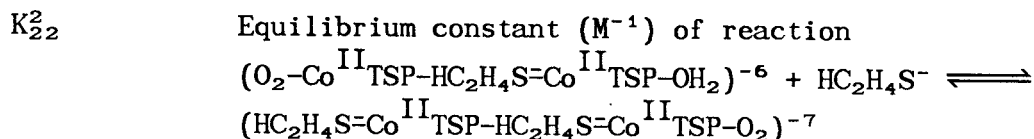
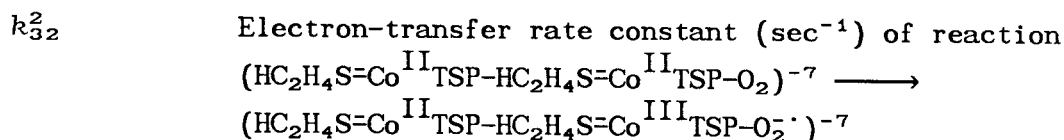
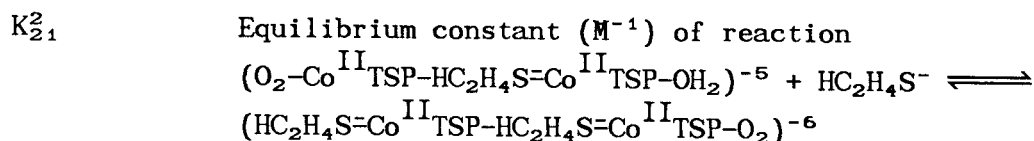
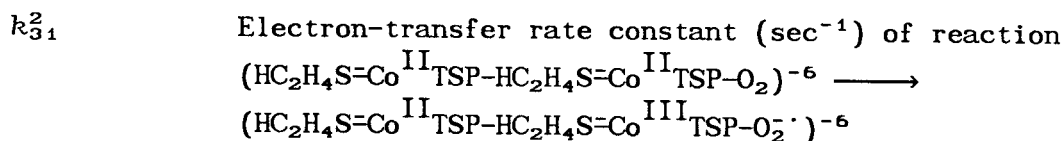
- α_3 $k_{31}^{13}K_{21}^{13}$
- k_{31}^{13} Electron-transfer rate constant (sec^{-1}) of reaction
 $(\text{NH}_3^+\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{III}}\text{TSP}-\text{O}_2)^{-5} \longrightarrow$
 $(\text{NH}_3^+\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2^-)^{-5}$
- K_{21}^{13} Equilibrium constant (M^{-1}) of reaction
 $(\text{O}_2-\text{Co}^{\text{II}}\text{TSP}-\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{OH}_2)^{-5} + \text{NH}_3^+\text{C}_2\text{H}_4\text{S}^- \rightleftharpoons$
 $(\text{NH}_3^+\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2)^{-5}$
- α_4 $k_{31}^{14}K_{21}^{14}$
- k_{31}^{14} Electron-transfer rate constant (sec^{-1}) of reaction
 $(\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2)^{-6} \longrightarrow$
 $(\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{III}}\text{TSP}-\text{O}_2^-)^{-6}$
- K_{21}^{14} Equilibrium constant (M^{-1}) of reaction
 $(\text{O}_2-\text{Co}^{\text{II}}\text{TSP}-\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{OH}_2)^{-5} + \text{NH}_2\text{C}_2\text{H}_4\text{S}^- \rightleftharpoons$
 $(\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2)^{-6}$
- α_5 $k_{32}^1K_{22}^1$
- k_{32}^1 Electron-transfer rate constant (sec^{-1}) of reaction
 $(\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2)^{-7} \longrightarrow$
 $(\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{III}}\text{TSP}-\text{O}_2^-)^{-7}$
- K_{22}^1 Equilibrium constant (M^{-1}) of reaction
 $(\text{O}_2-\text{Co}^{\text{II}}\text{TSP}-\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{OH}_2)^{-6} + \text{NH}_2\text{C}_2\text{H}_4\text{S}^- \rightleftharpoons$
 $(\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2)^{-7}$

α_6	$k_{33}^1 K_{23}^1$
k_{33}^1	Electron-transfer rate constant (sec^{-1}) of reaction $(\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2)^{-8} \longrightarrow$ $(\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{III}}\text{TSP}-\text{O}_2)^{-8}$
K_{23}^1	Equilibrium constant (M^{-1}) of reaction $(\text{O}_2-\text{Co}^{\text{II}}\text{TSP}-\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{OH}_2)^{-7} + \text{NH}_2\text{C}_2\text{H}_4\text{S}^- \rightleftharpoons$ $(\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{O}_2)^{-8}$
β_1	a_{H^+}/K_{a_1}'
K_{a_1}'	Apparent acid dissociation constant (M) of 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_{a_2}'/a_{H^+}
K_{a_2}'	Apparent acid dissociation constant (M) of 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_{i_1}'	Apparent acid dissociation constant (M) of Acid-Base Equilibrium $(\text{H}_2\text{O}-\text{Co}^{\text{II}}\text{TSP}-\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{OH}_2)^{-5} \rightleftharpoons$ $(\text{H}_2\text{O}-\text{Co}^{\text{II}}\text{TSP}-\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{OH}_2)^{-6} + \text{H}^+$
K_{i_2}'	Apparent acid dissociation constant (M) of Acid-Base Equilibrium $(\text{H}_2\text{O}-\text{Co}^{\text{II}}\text{TSP}-\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{OH}_2)^{-6} \rightleftharpoons$ $(\text{H}_2\text{O}-\text{Co}^{\text{II}}\text{TSP}-\text{NH}_2\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP}-\text{OH}_2)^{-7} + \text{H}^+$



The following notations are applied to catalytic autoxidation of ethanethiol.

k_{obsd}^2 Observed rate constant



K_i^2 Apparent acid dissociation constant (M) of Acid-Base
Equilibrium $(H_2O-Co^{II}TSP-HC_2H_4S-Co^{II}TSP-OH_2)^{-5} \rightleftharpoons$
 $(H_2O-Co^{II}TSP-HC_2H_4S-Co^{II}TSP-OH_2)^{-6} + H^+$

K_2^2 Apparent acid dissociation constant (M) of Acid-Base
Equilibrium $(H_2O-Co^{II}TSP-HC_2H_4S-Co^{II}TSP-OH_2)^{-6} \rightleftharpoons$
 $(H_2O-Co^{II}TSP-HC_2H_4S-Co^{II}TSP-OH_2)^{-7} + H^+$

$K_{a_2}^2$ Apparent acid dissociation constant (M) of Acid-Base
Equilibrium $HC_2H_4SH \rightleftharpoons HC_2H_4S^- + H^+$

Abstract

The autoxidation of 2-aminoethanethiol and ethanethiol as catalyzed by Co(II)-4,4',4'',4'''-tetrasulfophthalocyanine were examined. Both substrates appear to follow the same mechanism. Dimeric species bridged by RS⁻ appear to be the active catalytic centers for both substrates. H₂O₂ and mercaptan radical were found to be significant reaction intermediates in the autoxidation of both substrates. Hydroxide ion and the corresponding disulfide were identified as the primary products. At ionic strength, μ = 0.4 M, the following general rate law was hold for both substrates over pH range of 8.8 to 13.5

$$v = \frac{-d[RS^-]}{dt} = k_{obsd}[CoTSP]_T[RS^-]$$

For 2-aminoethanethiol k_{obsd}^1 is as follow:

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

where $\alpha_1 = k_{31}^1 K_{21}^1$, $\alpha_2 = k_{31}^2 K_{21}^2$, $\alpha_3 = k_{31}^3 K_{21}^3$, $\alpha_4 = k_{31}^4 K_{21}^4$, $\alpha_5 = k_{32}^1 K_{22}^2$, $\alpha_6 = k_{33}^1 K_{23}^1$, $\beta_1 = a_{H^+}/K_{a1}'$, $\beta_2 = K_{a2}'/a_{H^+}$, $\beta_3 = K_{i1}^1/a_{H^+}$ and $\beta_4 = K_{i2}^1/a_{H^+}$; k_{3i}^1 and K_{2i}^1 are the rate constants for the electron transfer and the equilibrium constants for substrate complexation of

the i^{th} catalytic center with the substrate, $\text{NH}_2\text{CH}_2\text{CH}_2\text{S}^-$, respectively; K_i^1 , $K_{a_1}^1$ and $K_{a_2}^1$ are the apparent acid dissociation constants of the catalytic center, $\text{NH}_3^+\text{CH}_2\text{CH}_2\text{SH}$ and $\text{NH}_3^+\text{CH}_2\text{CH}_2\text{S}^-$, respectively; and a_{H^+} is the hydrogen ion activity. For the ethanethiol, k_{obsd}^2 has the following form

$$k_{\text{obsd}}^2 = \frac{\left(k_{31}^2 K_{21}^2 + \frac{k_{32}^2 K_{22}^2 K_i^2}{a_{\text{H}^+}} + \frac{k_{33}^2 K_{23}^2 K_i^2 K_2^2}{a_{\text{H}^+}^2} \right)}{\left(1 + \frac{K_i^2}{a_{\text{H}^+}} + \frac{K_i^2 K_2^2}{a_{\text{H}^+}^2} \right) \left(1 + \frac{a_{\text{H}^+}}{K_{a_1}^2} \right)}$$

where k_{3i}^2 and K_{2i}^2 are the rate constants for the electron-transfer and the equilibrium constants for substrate complexation of the i^{th} catalytic center, respectively; K_i^2 , K_2^2 and $K_{a_1}^2$ are the apparent acid dissociation constants of the $\text{Co}^{\text{II}}\text{TSP-RS}=\text{Co}^{\text{II}}\text{TSP}$, $\text{Co}^{\text{II}}\text{TSP-RS}=\text{Co}^{\text{II}}\text{TSP}$ and $\text{CH}_3\text{CH}_2\text{SH}$, respectively. Evaluation of the experimental data for each substrate gave values of $k_{31}^1 K_{21}^1 = (1.98 \pm 0.04) \times 10^4 \text{ M}^{-1}\text{s}^{-1}$, $k_{32}^1 K_{22}^1 = (2.05 \pm 0.8) \times 10^4 \text{ M}^{-1}\text{s}^{-1}$, $k_{33}^1 K_{23}^1 = (6.15 \pm 0.45) \times 10^3 \text{ M}^{-1}\text{s}^{-1}$, $\text{p}K_2^1 = 11.76 \pm 0.27$, $k_{31}^2 K_{21}^2 = (2.99 \pm 0.22) \times 10^4 \text{ M}^{-1}\text{s}^{-1}$, $k_{32}^2 K_{22}^2 = (2.75 \pm 0.44) \times 10^4 \text{ M}^{-1}\text{s}^{-1}$, $k_{33}^2 K_{23}^2 = (1.35 \pm 0.07) \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ and $\text{p}K_2^2 = 12.02 \pm 0.18$. Similar values of k_{obsd} for 2-aminoethanethiol at pH between 9.3 to 11 suggested that values of $k_{31}^{12} K_{21}^{12}$, $k_{31}^{13} K_{21}^{13}$ and $k_{31}^{14} K_{21}^{14}$ are all similar to those for $k_{31}^1 K_{21}^1$ or $k_{32}^1 K_{22}^1$.

Introduction

The kinetics and mechanism of autoxidation of 2-mercaptoethanol as catalyzed by Co(II)-4,4',4'',4'''-tetrasulfophthalocyanine, abbreviated as Co(II)TSP, have been studied and described in Chapter 3. Evidence was provided for a mechanism that proceeds via catalytic center that is bridged by the 2-mercaptoethanol anion. The structure of the proposed catalytic center is shown in Figure 6.1. In this mechanism, the electron transfer from the Co(II) metal center to dioxygen was proposed as the rate-determining step which was followed by the release of hydrogen peroxide and mercaptan radical. These intermediates react further to produce disulfide, RSSR, as the final product of the autoxidation. Two additional 2-mercaptoethanol molecules are oxidized to give the disulfide. The kinetics and mechanism of the oxidation of 2-mercaptoethanol by hydrogen peroxide have been examined and reported by Leung and Hoffmann (1985). The combination of the catalytic cycle for autoxidation and the hydrogen peroxide pathway gives the overall stoichiometric ratio of O₂ to 2-mercaptoethanol of 1:4.

The rapid catalytic autoxidation indicates that the CoTSP should be an effective catalyst for the autoxidation of other mercaptans. Therefore, we have examined the kinetics and mechanism of the CoTSP catalyzed autoxidation of two additional mercaptans, ethanethiol and 2-aminoethanethiol. The choice of these substrates provides an

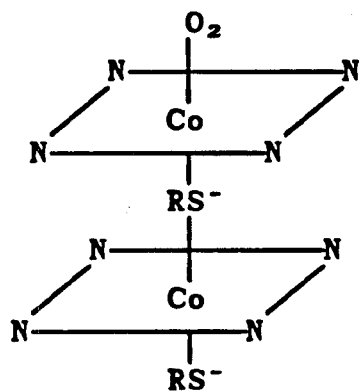


Figure 6.1: The Proposed Structure of the Co(II)TSP Dimer Bridged by Mercaptan Anion.

opportunity to investigate the effect of substituents on the rates of autoxidation of R-C₂H₄SH.

Experimental Procedures

Reagents: Reagent grade of 2-aminoethanethiol (Aldrich 98%) recrystallized twice and ethanethiol (Aldrich 97%) without further purification were used to prepare stock solutions. Co(II)-4,4',-4'',4'''-tetrasulfophthalocyanine, abbreviated as CoTSP, was synthesized according to the procedure described by Boyce et al. (1983). Buffers were prepared using reagent grade sodium hydroxide (Mallinckrodt), sodium chloride (J.T.Baker), sodium bicarbonate (Mallinckrodt). Water, which was used to prepare the buffers and reagent solutions, was obtained from a Milli-Q water purification system (Millipore), and had a resistivity of 18 MΩ-cm. It was irradiated with UV light before use to remove any trace residual organics that might be present.

Kinetic measurements: Kinetic measurements were made on Hewlett Packard Model 8450 Spectrophotometer. A minimum of 100 data points were collected for each kinetic experiment and k_{obsd} is the average of at least three experiments. Data were analyzed on-line with a IBM-XT computer. Constant temperature was maintained at 25.5⁰C with Haake water bath. Sodium chloride stock solutions were added into the buffers to establish an ionic strength of 0.4 M. pH was determined with a Beckman Altex ϕ 71 pH meter and Radiometer Glass Electrode.

Dissolved oxygen levels were established by dispersing N_2 and O_2 gas mixtures into the CoTSP buffer. The reaction was monitored at 233 nm (the absorbance maximum for both $NH_3^+C_2H_4S^-$ (aq), $NH_2C_2H_4S^-$ (aq) and $HCH_2CH_2S^-$ (aq)). Pseudo-first-order conditions of $[O_2] \gg [mercaptan]_T < 2.6 \times 10^{-4} M$ 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 Titration Method (Standard Method for the Examination of Water and Wastewater, 1975).

Product Identification: Reaction product of the autoxidation of 2-aminoethanethiol was identified by injecting the solution directly into a Econosphere C18 5 Micron HPLC column mounted on Hewlett Packard 1084B HPLC and comparing the retention times with standards. The solvent carrier was 15% methanol in deionized doubly-distilled water. The oven temperature was set at $40^\circ C$.

The reaction product of the autoxidation of ethanethiol was identified by injecting the solution directly into a 3% SP-1500 80/120 Carbo-pack B GC column mounted on a Hewlett Packard 5880A GC equipped with a Flame Ionization Detector and comparing the retention times with the standard. The carrier gas was nitrogen. The temperatures of the injection port, the detector and the oven were set at 100, 150 and $200^\circ C$, respectively.

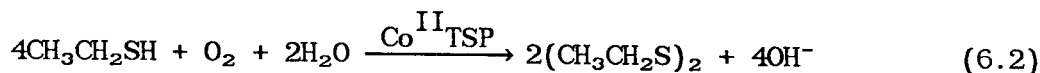
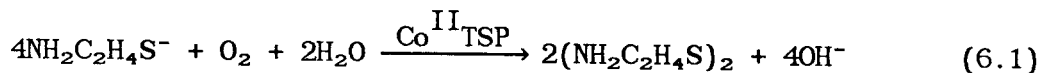
Intermediate Identification: Hydrogen peroxide or peroxide ion was identified by a fluorescence method described by Lazrus et al. (1985). A 1.6 ml sample was withdrawn from the reaction vessel at 60 second intervals and the reaction was quenched by rapid neutralization to $\text{pH} \approx 7$ with concentrated hydrochloric acid. The fluorescence reagent, which consisted of KHphthalate, *p*-hydroxy-phenylacetic 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 in order 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 existence of radicals in the reactions of 2-aminoethanethiol and ethanethiol was detected by monitoring the formation of ascorbate radical in the reaction mixture with ascorbic acid. Ascorbate is known to react with mercaptan radicals producing the corresponding ascorbate radical ($\text{RS}^\cdot + \text{AH}^- \longrightarrow \text{A}^{\cdot-} + \text{RS}^- + \text{H}^+$) (Redpath and Willson, 1973; Schuler, 1977) which absorbs at $\lambda = 300$ nm with an extinction coefficient at 360 nm of $\epsilon_{360} = 3300 \text{ cm}^{-1} \text{ M}^{-1}$.

Hydroxide Ion Identification: The hydroxide ion production was identified by continuously monitoring the pH of an unbuffered reaction solution.

Results

The results of the experiments to determine the reaction stoichiometries, are given in Table 6.1 and 6.2. The average molar ratios of $[O_2]$ to [mercaptan] for 2-aminoethanethiol and ethanethiol were found to be 4.4 and 3.9, respectively, which are both rounded off to 1:4 as in equation 6.1 and 6.2, when dissolved oxygen was in excess. The sulfur products of the catalytic autoxidation of 2-aminoethanethiol and ethanethiol were determined to be 2-aminoethyldisulfide and ethyldisulfide, respectively. Thus, the overall stoichiometries for both mercaptans are as follows:



Under pseudo-first-order conditions ($[O_2] \gg [mercaptan]_T$), plots of $\ln(A_t - A_\infty)$ vs. t were linear ($r^2 \geq 0.999$) for 50 to 90% of the reaction for both mercaptans. This linearity of the pseudo first-order relationships for 2-aminoethanethiol and ethanethiol indicates that the rate of autoxidation is first order with respect to mercaptan. In Figure 6.2a and 6.2b, the calculated exponential fits are compared with the actual kinetic data. The dependence of k_{obsd} on $[O_2]$ was determined at pH 9.3 and pH 13.0 for the 2-aminoethanethiol

TABLE 6.1. Stoichiometry Determination of Catalytic Autoxidation of 2-Aminoethanethiol by Co(II)-4,4',4'',4'''-Tetrasulfo-phthalocyanine.

Initial Oxygen mmole	Final Oxygen mmole	Amount of Oxygen Used mmole	Amount of 2-Aminoethanethiol Reacted mmole	$\frac{\Delta S^1}{\Delta O_2}$
5.98×10^{-2}	5.7×10^{-2}	2.8×10^{-2}	1.1×10^{-2}	4.0
5.93×10^{-2}	5.7×10^{-2}	2.6×10^{-2}	1.1×10^{-2}	4.4
5.86×10^{-2}	2.1×10^{-2}	3.7×10^{-2}	1.6×10^{-1}	4.4
5.86×10^{-2}	2.4×10^{-2}	3.4×10^{-2}	1.6×10^{-1}	4.8

¹ S = Amount of 2-Aminoethanethiol reacted.

Experimental Conditions: $\mu = 0.4M$, pH = 9.7, Temperature = 25.5°C
 $[Co^{II}TSP]_T = 6.46 \times 10^{-7} M$.

TABLE 6.2: Stoichiometry Determination of Catalytic Autoxidation of Ethanethiol by CO(II)-4,4',4'',4'''-Tetrasulfophthalocyanine.

Initial Oxygen mmole	Final Oxygen mmole	Amount of Oxygen Used mmole	Amount of Ethanethiol Reacted mmole	$\frac{\Delta S^1}{\Delta O_2}$
5.45×10^{-2}	2.28×10^{-2}	3.17×10^{-2}	1.35×10^{-1}	4.25
5.45×10^{-2}	1.89×10^{-2}	3.56×10^{-2}	1.35×10^{-1}	3.78
5.45×10^{-2}	1.79×10^{-2}	3.66×10^{-2}	1.35×10^{-1}	3.68

¹ ΔS = Amount of Ethanethiol reacted.

Experimental Conditions: $\mu = 0.4$ M, pH = 10, Temperature = 25°C,
 $[Co^{II}TSP]_T = 6.46 \times 10^{-7}$ M.

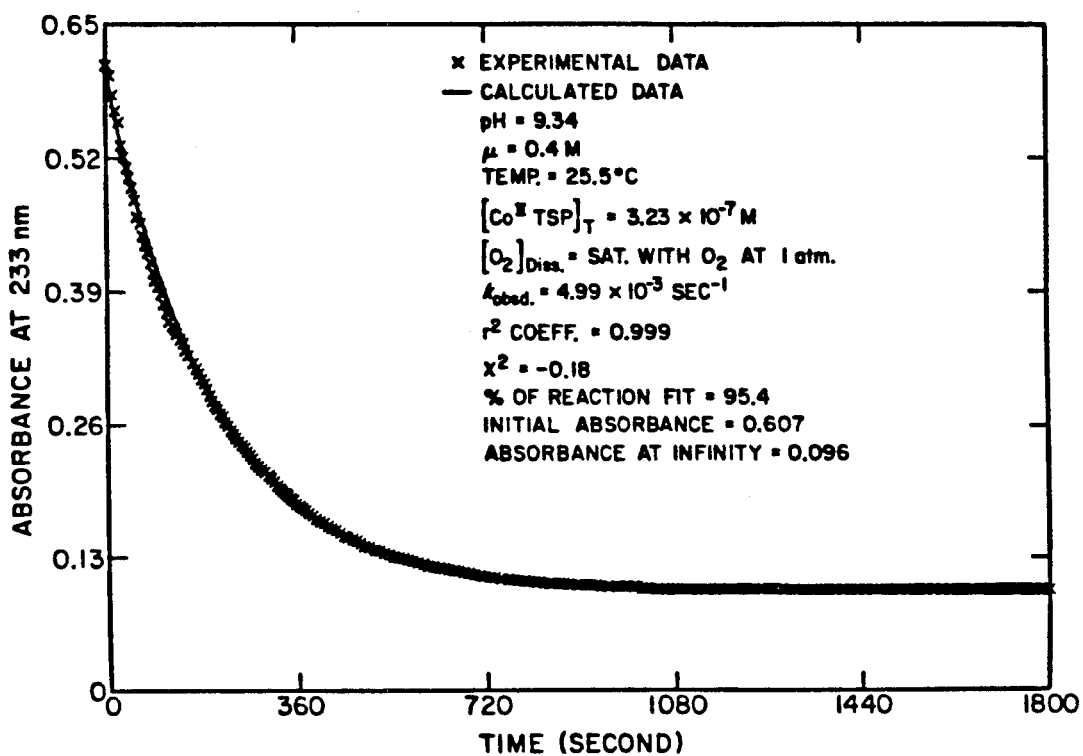


Figure 6.2a: First Order Kinetic Plot of Autoxidation of 2-Aminoethanethiol catalyzed by Co(II)TSP.

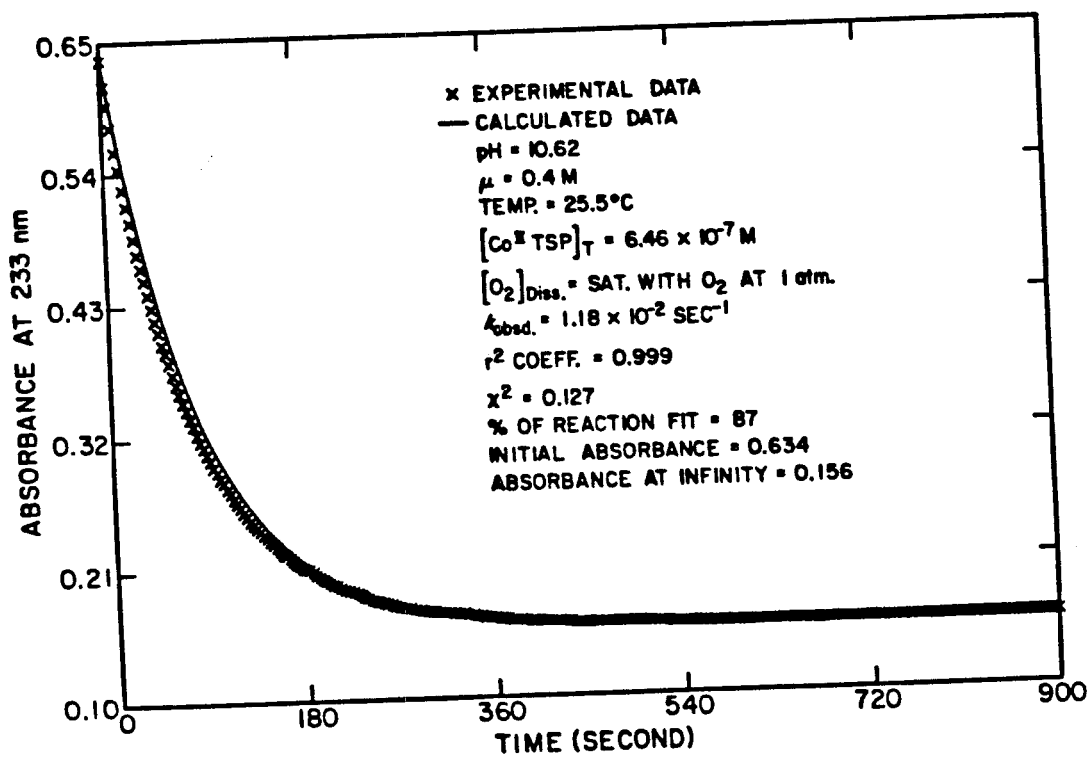


Figure 6.2b: First Order Kinetic Plot of Autoxidation of Ethanethiol catalyzed by Co(II)TSP.

and at pH 11.0 and pH 13.0 for the ethanethiol. Results of these experiments showed that the rate of loss of mercaptan was independent of dissolved oxygen concentration between $2 \times 10^{-4}\text{M}$ and 10^{-3}M (Figure 6.3a and 6.3b). Plots of k_{obsd} vs. $[\text{CoTSP}]_{\text{T}}$ from $0.64 \mu\text{M}$ to $2.6 \mu\text{M}$, are shown in Figure 6.4a (2-aminoethanethiol) and 6.4b (ethanethiol), and yielded straight lines ($r^2 \geq 0.99$) at 3 different values of pH for each substrate. For 2-aminoethanethiol, the slopes are $2.06 \times 10^4 \text{M}^{-1}\text{s}^{-1}$, $2.09 \times 10^4 \text{M}^{-1}\text{s}^{-1}$, $2.22 \times 10^4 \text{M}^{-1}\text{s}^{-1}$, and $7.01 \times 10^3 \text{M}^{-1}\text{s}^{-1}$ at pH 9.3, 10.5, 11.3 and 13.35, respectively. For ethanethiol, the slopes are $1.37 \times 10^4 \text{M}^{-1}\text{s}^{-1}$, $2.72 \times 10^4 \text{M}^{-1}\text{s}^{-1}$ and $1.87 \times 10^4 \text{M}^{-1}\text{s}^{-1}$ at pH 9.94, 11.1, and 13.17, respectively. Thus, the rate of autoxidation is first order in [mercaptan] and $[\text{CoTSP}]_{\text{T}}$ but apparently zero-order with respect to dissolved oxygen for both ethanethiol and 2-aminoethanethiol.

In the absence of a buffer, the pH, as shown in Figure 6.5a (2-aminoethanethiol) and 6.5b (ethanethiol), rose continuously during the course of reaction. The increase of pH indicates that hydroxide ion is a product of both catalytic autoxidations.

Mercaptan radical was found to be an intermediate of the autoxidation of each mercaptan. Figure 6.6a (2-aminoethanethiol) and 6.6b (ethanethiol) show the increase of absorbance at $\lambda = 360 \text{nm}$ after the addition of ascorbic acid to the reaction mixture. Such an increase implies that the mercaptan radicals, $\text{NH}_2\text{C}_2\text{H}_4\text{S}'$ and $\text{CH}_3\text{CH}_2\text{S}'$, are the intermediates of the autoxidation of 2-aminoethanethiol and

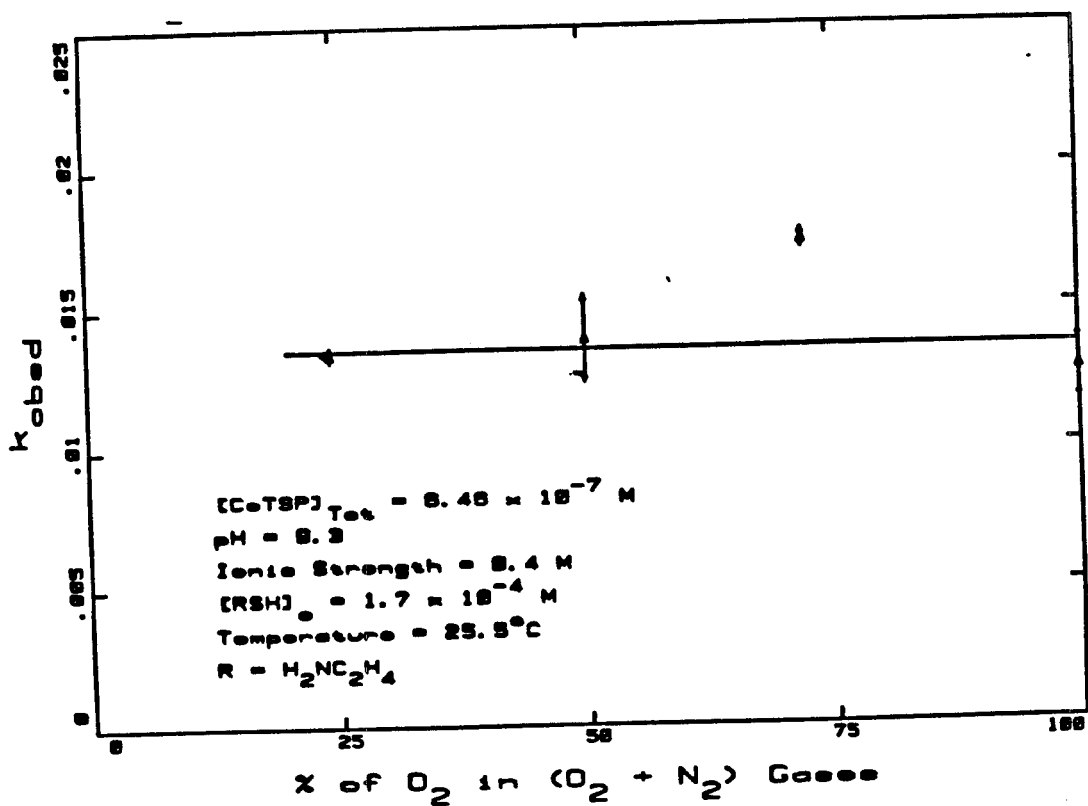


Figure 6.3a: Determination of the Reaction Order of [O₂] of Autoxidation of 2-Aminoethanethiol.

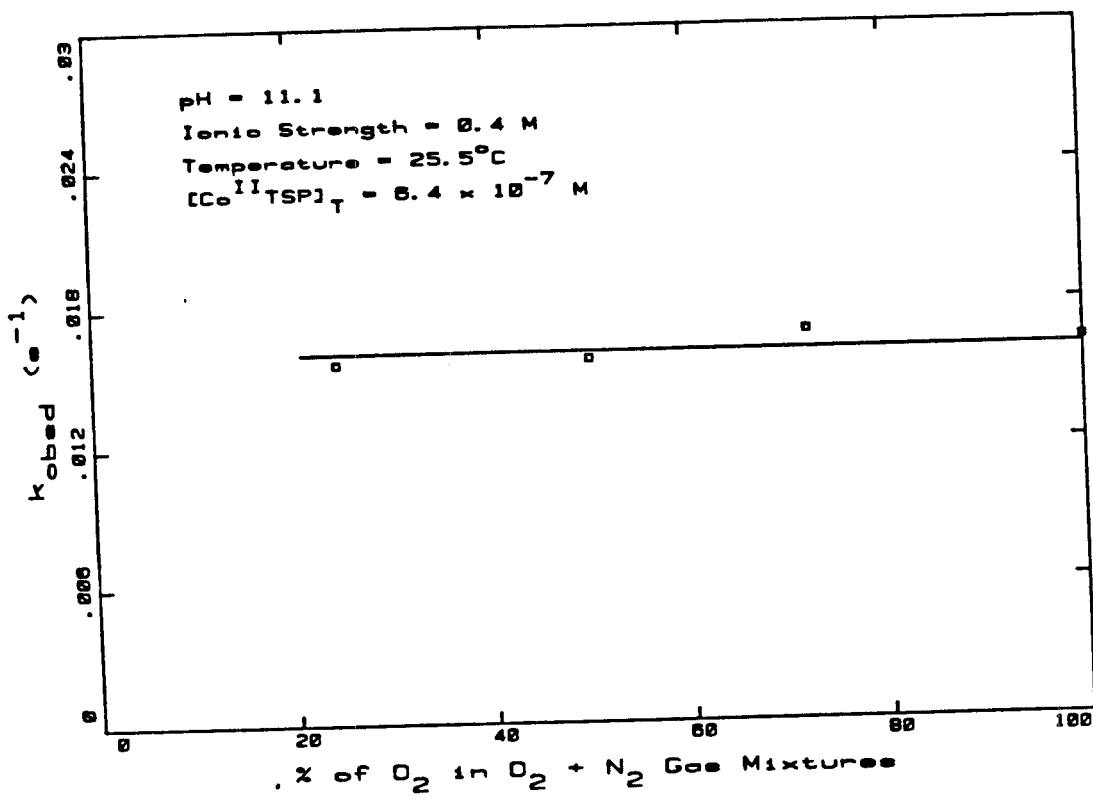


Figure 6.3b: Determination of the Reaction Order of [O₂] of Autoxidation of Ethanethiol.

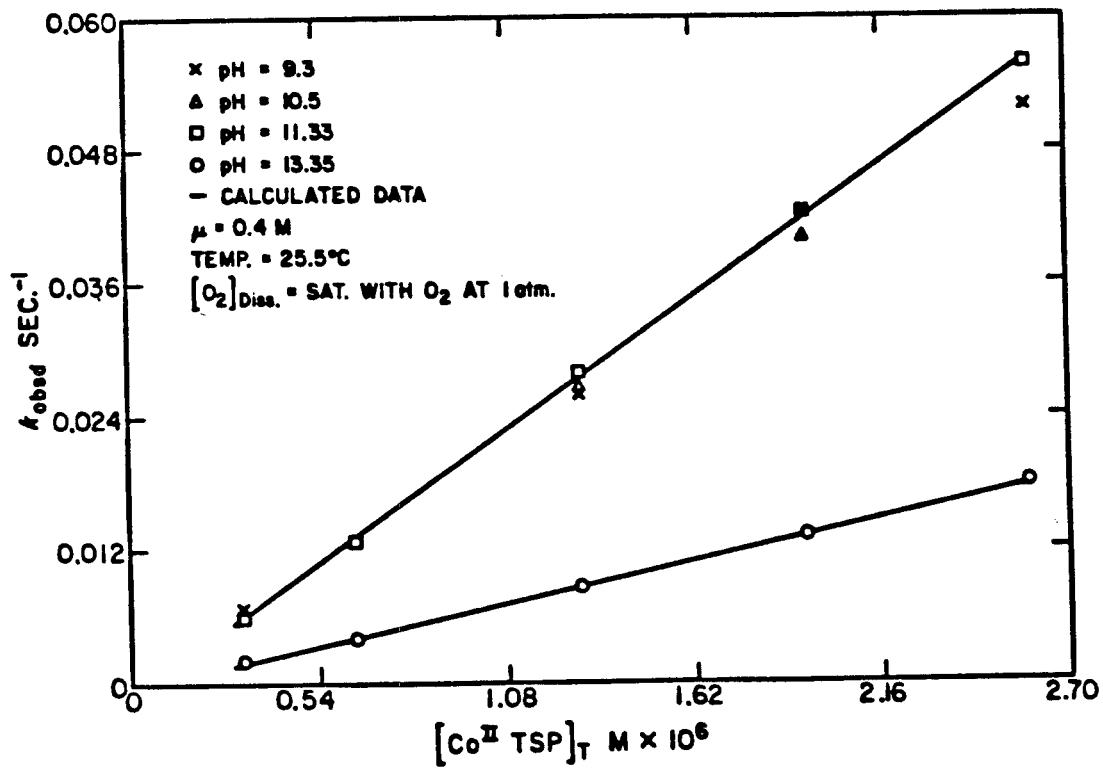


Figure 6.4a: Determination of the Reaction Order of $[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}}$ of Autoxidation of 2-Aminoethanethiol.

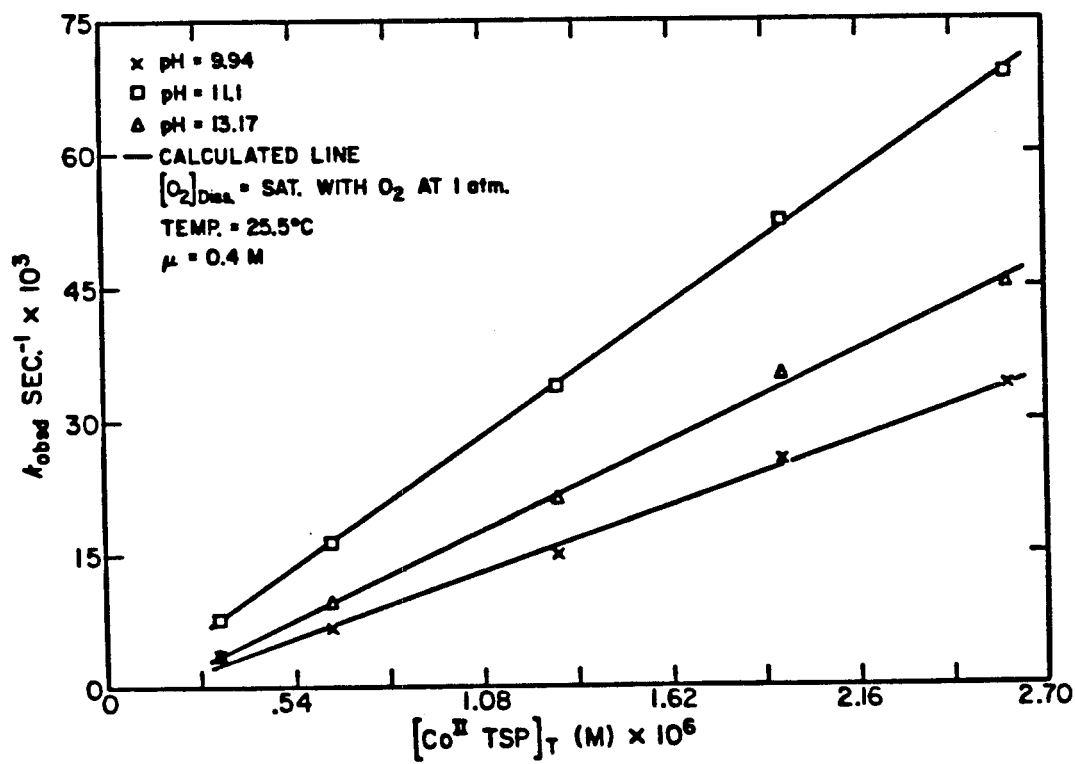


Figure 6.4b: Determination of the Reaction Order of $[Co^{II} TSP]_T$ of Autoxidation of Ethanethiol.

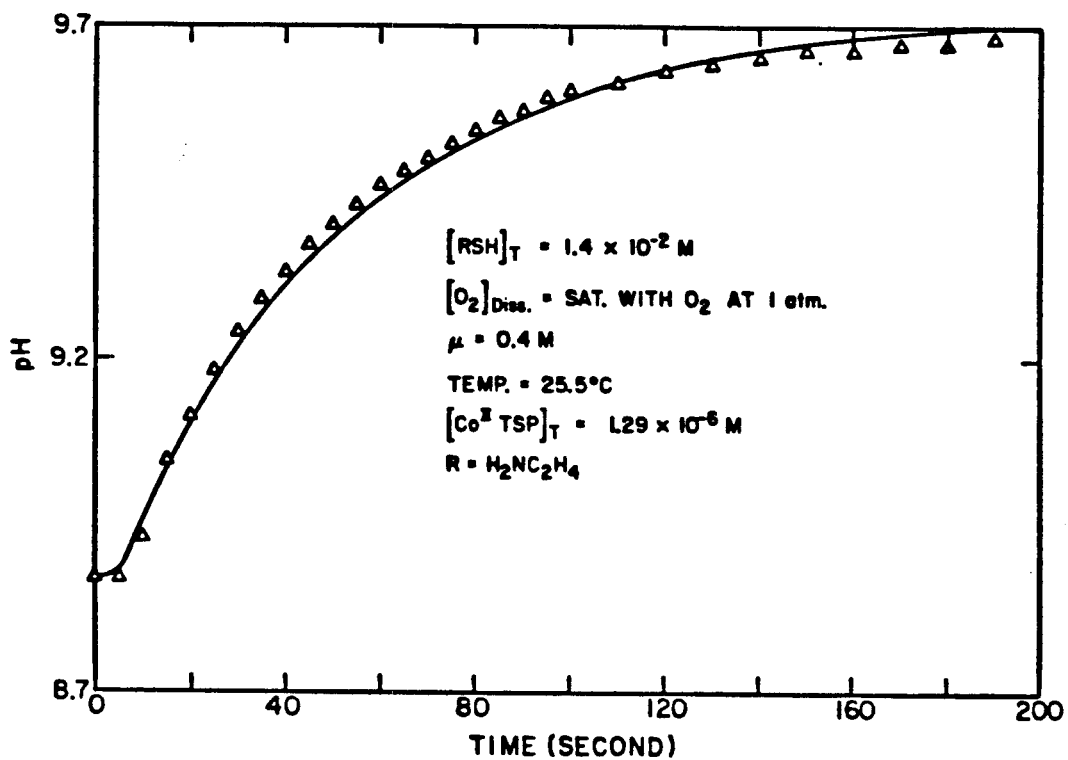


Figure 6.5a: A Plot of pH vs time during the course of the Autoxidation of 2-Aminoethanethiol in unbuffered solution.

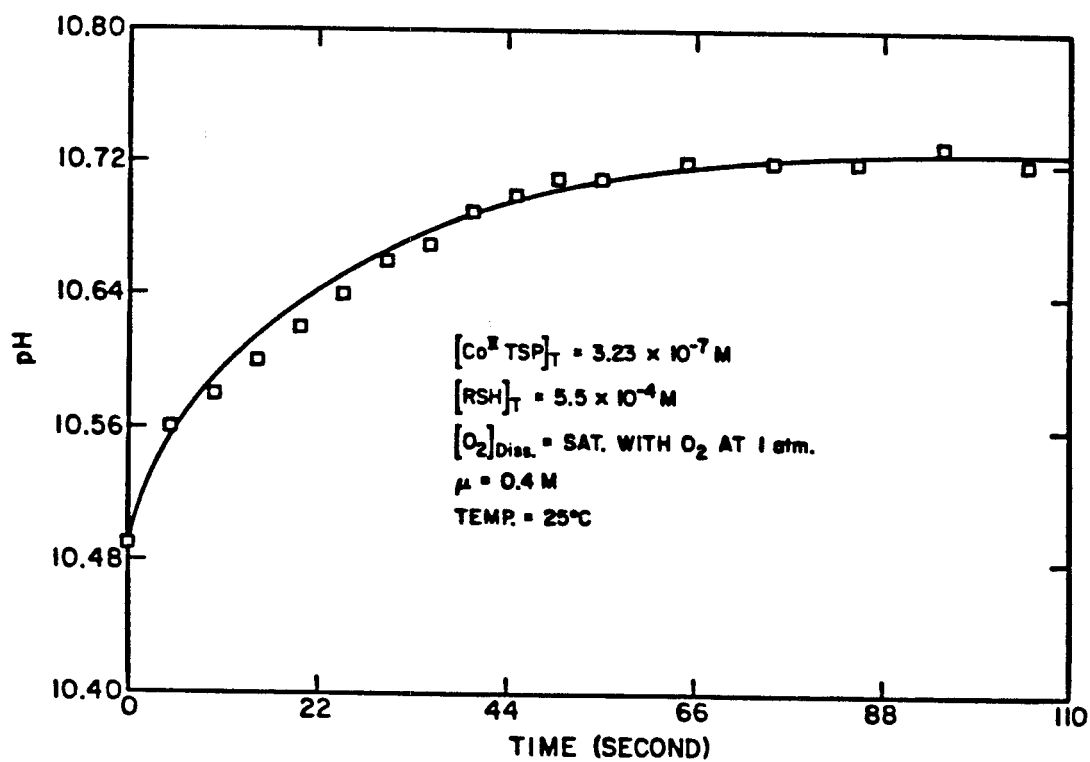


Figure 6.5b: A Plot of pH vs time during the course of the Autoxidation of Ethanethiol in unbuffered solution.

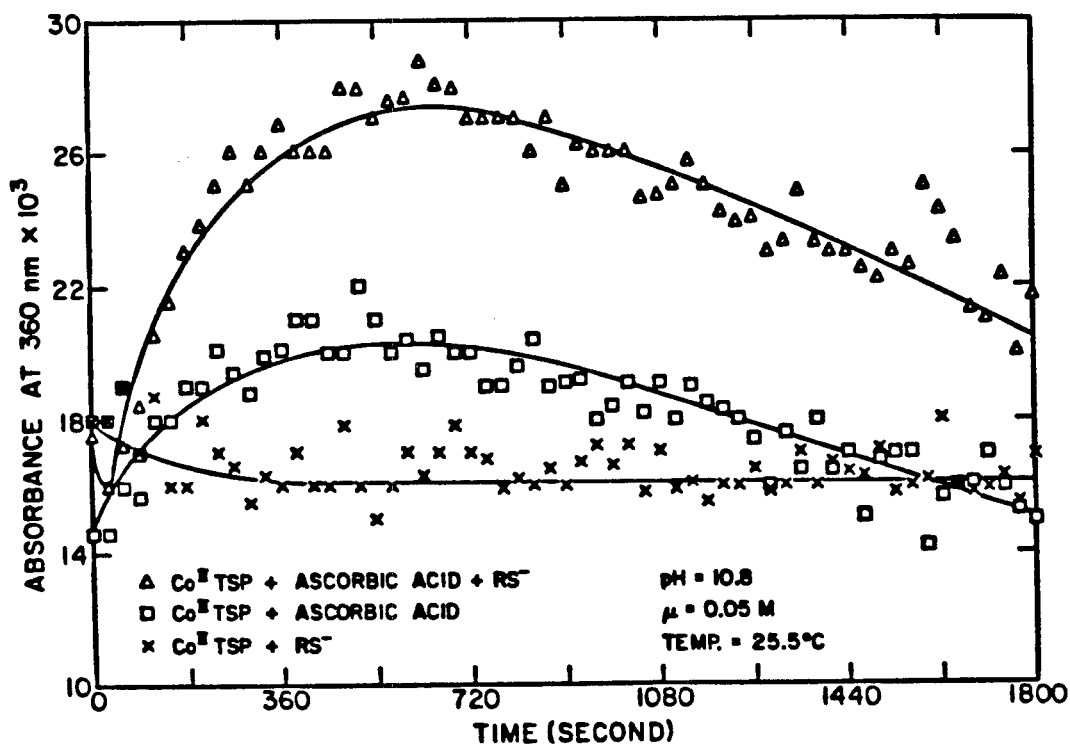


Figure 6.6a: Formation of Ascorbate Radical during the Autoxidation of 2-Aminoethanethiol.

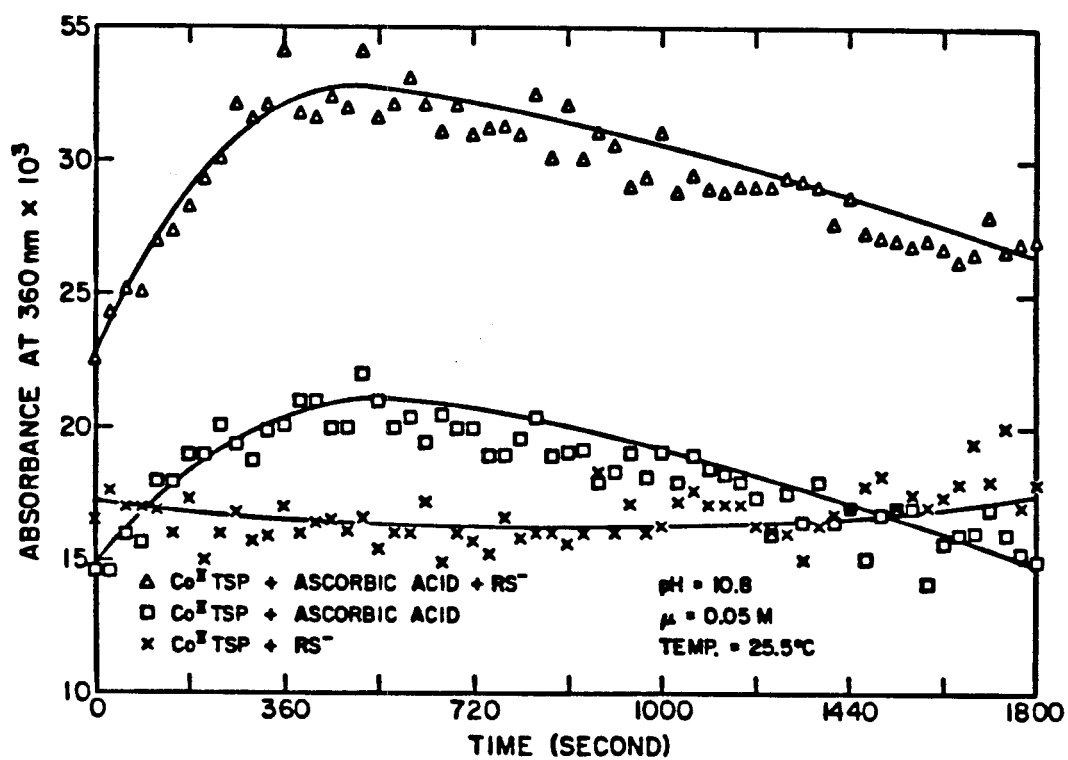
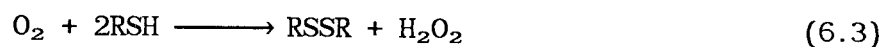
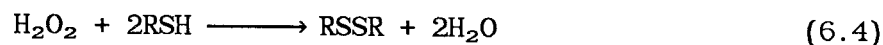


Figure 6.6b: Formation of Ascorbate Radical during the Autoxidation of Ethanethiol.

ethanethiol, respectively. Production of hydrogen peroxide, another reaction intermediate of the autoxidation of both mercaptans, is shown in Figure 6.7a (2-aminoethanethiol) and 6.7b (ethanethiol). Therefore the overall 1:4 stoichiometry of each mercaptan is given by the sum of



and



where R is either $\text{NH}_3^+\text{C}_2\text{H}_4$ or CH_3CH_2 .

The change of the CoTSP spectrum in the visible region of the spectrum during the course of reaction is shown in Figure 6.8a and 6.8b. 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 subsequent decrease of absorption at $\lambda = 668$ nm after the addition of each thiols suggests that the dimer concentration is enhanced. The resulting dimer is likely to be bridged by the anion of the corresponding mercaptan which is similar to the structure in Figure 6.1.

The above kinetic and thermodynamic information can be explained with the aid of the mechanism proposed in Figure 6.9. According to this mechanism and the stoichiometries of reaction 6.3 and reaction 6.4, the rates of disappearance of 2-aminoethanethiol and ethanethiol

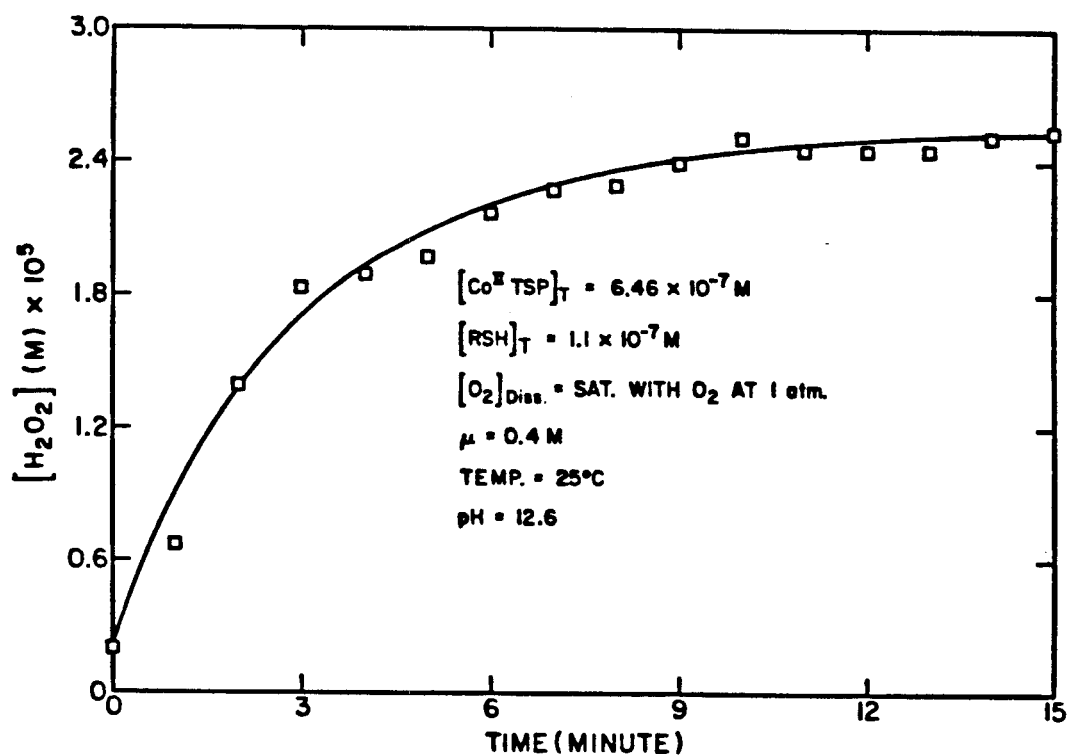


Figure 6.7a: Hydrogen Peroxide vs time during the Autoxidation of 2-Aminoethanethiol.

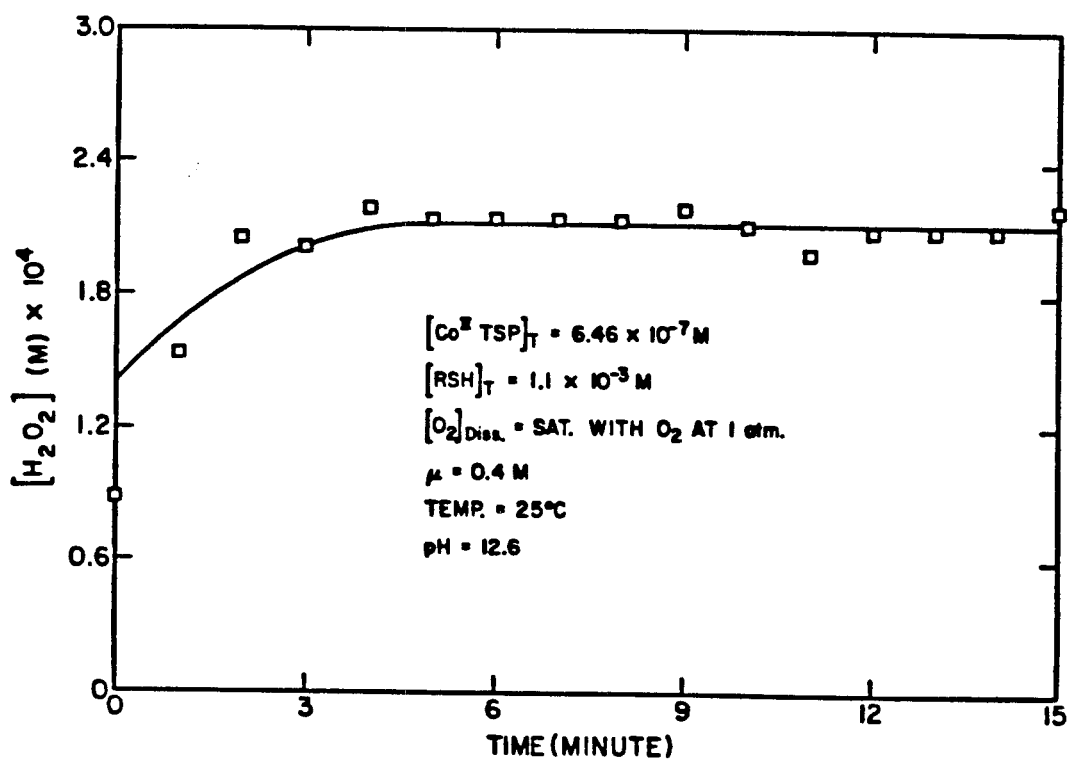
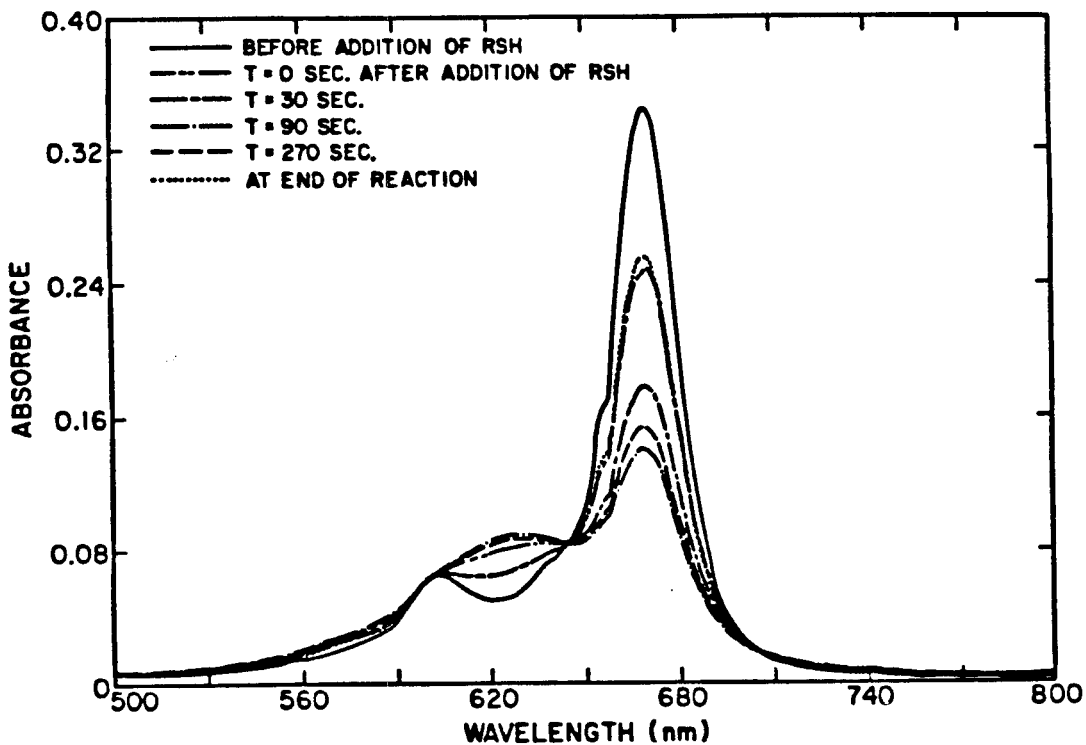


Figure 6.7b: Hydrogen Peroxide vs time during the Autoxidation of Ethanethiol.



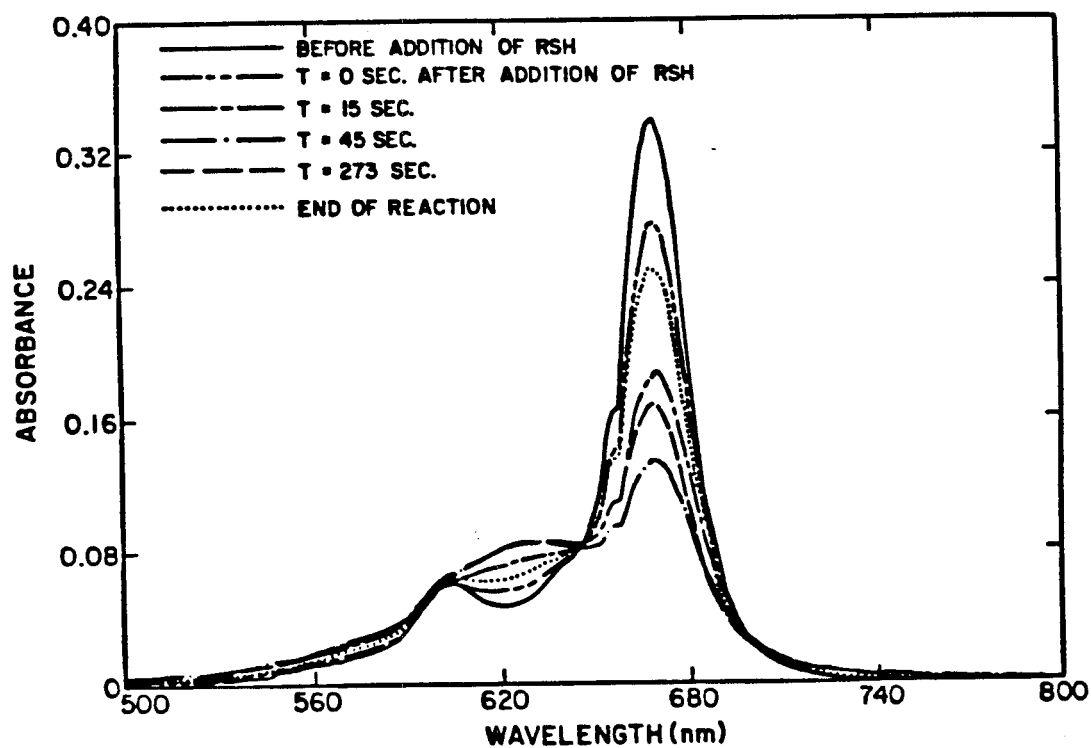
Experimental Conditions: pH = 13.38, $\mu = 0.4$ M.

Temp. = 25.5°C.

$[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}} = 1.9 \times 10^{-6}$ M

$[\text{O}_2]_{\text{Diss.}} = \text{Sat. with O}_2 \text{ at 1 Atm.}$

Figure 6.8a: Changes in the Visible Spectrum of CoTSP During Autoxidation of 2-Aminoethanethiol.



Experimental Conditions: pH = 13.17, $\mu = 0.4$ M.
Temp. = 25.5°C.
 $[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}} = 1.9 \times 10^{-6}$ M
 $[\text{O}_2]_{\text{Diss.}} = \text{Sat. with O}_2 \text{ at 1 Atm.}$

Figure 6.8b: Changes in the Visible Spectrum of CoTSP During Autoxidation of Ethanethiol.

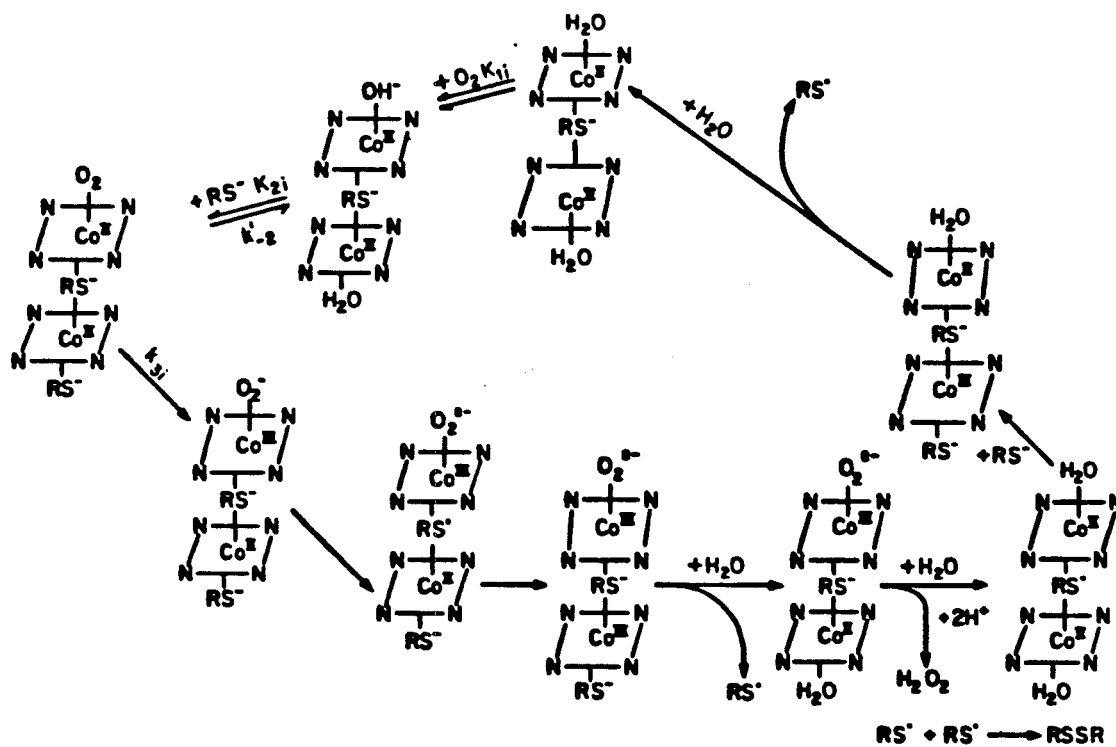


Figure 6.9: Schematic Diagram of the Proposed Mechanism of Autoxidation of 2-Aminoethanethiol and Ethanethiol.

are given by the Equations 6.5 and 6.6, respectively

$$v^1 = \frac{-d[\text{NH}_2\text{C}_2\text{H}_4\text{SH}]_T}{dt} = 2(v_1^1 + v_2^1 + v_3^1 + v_4^1 + v_5^1 + v_6^1 + v_7^1) \quad (6.5)$$

where $v_1^1 = k_{31}^{11}[(\text{O}_2\text{-Co}^{\text{II}}\text{TSP-NH}_3^+\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP-NH}_3^+\text{C}_2\text{H}_4\text{S}^-)^{-4}]$;

$$v_2^1 = k_{31}^{12}[(\text{O}_2\text{-Co}^{\text{II}}\text{TSP-NH}_3^+\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP-NH}_2\text{C}_2\text{H}_4\text{S}^-)^{-5}]$$
;

$$v_3^1 = k_{31}^{13}[(\text{O}_2\text{-Co}^{\text{II}}\text{TSP-NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP-NH}_3^+\text{C}_2\text{H}_4\text{S}^-)^{-5}]$$
;

$$v_4^1 = k_{31}^{14}[(\text{O}_2\text{-Co}^{\text{II}}\text{TSP-NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP-NH}_2\text{C}_2\text{H}_4\text{S}^-)^{-6}]$$
;

$$v_5^1 = k_{32}^1[(\text{O}_2\text{-Co}^{\text{II}}\text{TSP-NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP-NH}_2\text{C}_2\text{H}_4\text{S}^-)^{-7}]$$
;

$$v_6^1 = k_{33}^1[(\text{O}_2\text{-Co}^{\text{II}}\text{TSP-NH}_2\text{C}_2\text{H}_4\text{S}^- - \text{Co}^{\text{II}}\text{TSP-NH}_2\text{C}_2\text{H}_4\text{S}^-)^{-8}]$$
;

v_7^1 = rate of disappearance of mercaptan due to H_2O_2 .

k_{3i}^1 = rate constant of electron transfer step of its i^{th} respective catalytic center

$$v^2 = \frac{-d[\text{CH}_3\text{CH}_2\text{SH}]_T}{dt} = 2(v_1^2 + v_2^2 + v_3^2 + v_4^2) \quad (6.6)$$

where $v_1^2 = k_{31}^2[(\text{O}_2\text{-Co}^{\text{II}}\text{TSP-CH}_3\text{CH}_2\text{S}^- - \text{Co}^{\text{II}}\text{TSP-CH}_3\text{CH}_2\text{S}^-)^{-6}]$;

$$v_2^2 = k_{32}^2[(\text{O}_2\text{-Co}^{\text{II}}\text{TSP-CH}_3\text{CH}_2\text{S}^- - \text{Co}^{\text{II}}\text{TSP-CH}_3\text{CH}_2\text{S}^-)^{-7}]$$
;

$$v_3^2 = k_{33}^2[(\text{O}_2\text{-Co}^{\text{II}}\text{TSP-CH}_3\text{CH}_2\text{S}^- - \text{Co}^{\text{II}}\text{TSP-CH}_3\text{CH}_2\text{S}^-)^{-8}]$$
;

v_4^2 = rate of disappearance of mercaptan due to H_2O_2 ;

k_{3i}^2 = rate constant of electron transfer step of i^{th} catalytic center.

The 1st, 2nd and 3rd catalytic centers are formed by the combination of two protonated monomers, a protonated monomer and a deprotonated monomer, two deprotonated monomers, respectively.

As the concentration of hydrogen peroxide, the intermediate produced from the catalytic cycle, is expected to be very low, the contribution of v_7^1 and v_4^2 to its respective rate expression would be very small and they can be eliminated from the total rate expression. Thus, Equations 6.5 and 6.6 become

$$v^1 = \frac{-d[\text{NH}_2\text{C}_2\text{H}_2\text{SH}]_T}{dt} = 2(v_1^1 + v_2^1 + v_3^1 + v_4^1 + v_5^1 + v_6^1) \quad (6.7)$$

$$v^2 = \frac{-d[\text{CH}_3\text{CH}_2\text{SH}]_T}{dt} = 2(v_1^2 + v_2^2 + v_3^2) \quad (6.8)$$

respectively.

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 Equation 6.20 to be written as follows:

$$v^1 = \frac{-d[\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-]}{dt} = \frac{2(v_1 + v_2 + v_3 + v_4 + v_5 + v_6)}{\left(1 + \frac{a_{\text{H}^+}}{K'_{a_1}} + \frac{K'_{a_2}}{a_{\text{H}^+}}\right)} \quad (6.9)$$

where K'_{a_1} and K'_{a_2} 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 1st catalytic center into v_1^1 yields

$$v_1^1 = k_{31}^{11}K_{11}^{11}K_{21}^{11}[(\text{Co}^{\text{II}}\text{TSP-NH}_3^+\text{C}_2\text{H}_4\text{S}=\text{Co}^{\text{II}}\text{TSP})^{-4}][\text{O}_2][\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-] \quad (6.10)$$

where K_{11}^{11} , K_{21}^{11} are the equilibrium constants for dioxygen binding and substrate complexation by the 1st catalytic center, respectively. Expressing the concentration of the 1st catalytic center in terms of the total concentration, $[\text{Co}^{\text{II}}\text{TSP}]_{\text{T1}} = 2([\text{CoTSP-NH}_3^+\text{C}_2\text{H}_4\text{S}=\text{CoTSP})^{-4}] + [(\text{O}_2-\text{CoTSP-NH}_3^+\text{C}_2\text{H}_4\text{S}=\text{CoTSP})^{-4}] + [(\text{O}_2-\text{CoTSP-NH}_3^+\text{C}_2\text{H}_4\text{S}=\text{CoTSP-NH}_3^+\text{C}_2\text{H}_4\text{S}^-)^{-4}]$ yields

$$v_1^1 = \frac{k_{31}^{11}K_{11}^{11}K_{21}^{11}[\text{Co}^{\text{II}}\text{TSP}]_{\text{T1}}[\text{O}_2][\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-]}{(1 + K_{11}^{11}[\text{O}_2] + K_{11}^{11}K_{21}^{11}[\text{O}_2][\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-])} \quad (6.11)$$

The zero-order dependence on the dissolved oxygen concentration suggests that $K_{11}^{11}[\text{O}_2] \gg K_{11}^{11}K_{21}^{11}[\text{O}_2][\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-]$ and $K_{11}^{11}[\text{O}_2] \gg 1$. The rate expression, v_1^1 , can be reduced to the following:

$$v_1^1 = (k_{31}^{11}K_{21}^{11}[\text{Co}^{\text{II}}\text{TSP}]_{\text{T1}}[\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-]) \quad (6.12)$$

for which the reaction rate, v_1^1 , is first order with respect to both the $[\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-]$ and $[\text{Co}^{\text{II}}\text{TSP}]_{\text{T1}}$; and is independent of $[\text{O}_2]$. Similar

expressions can be derived for v_2^1 , v_3^1 , v_4^1 , v_5^1 and v_6^1 . Thus, under the assumption that $K_{11}^1[O_2] \gg K_{11}^1 K_{21}^1 [O_2][NH_3^+C_2H_4S^-]$ and $K_{11}^1[O_2] \gg 1$, the total rate of autoxidation becomes

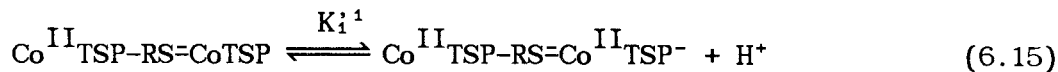
$$v^1 = \frac{\{(\alpha_1 + \alpha_2 \beta_2)[C]_{T1} + (\alpha_3 \beta_2 + \alpha_4 \beta_2^2)[C]_{T2} + \alpha_5 \beta_2^2 [C]_{T3} + \alpha_6 \beta_2^2 [C]_{T4}\} [RS^-]}{(1 + \beta_1 + \beta_2)} \quad (6.13)$$

where $R = NH_3^+C_2H_4$; $[C]_{Ti}$ = concentration of the catalyst in its respective form; $\alpha_1 = k_{31}^1 K_{21}^1$, $\alpha_2 = k_{31}^2 K_{21}^2$, $\alpha_3 = k_{31}^3 K_{21}^3$, $\alpha_4 = k_{31}^4 K_{21}^4$, $\alpha_5 = k_{32}^1 K_{22}^2$, $\alpha_6 = k_{33}^1 K_{23}^1$, $\beta_1 = a_{H^+}/K_{a1}^1$ and $\beta_2 = K_{a2}^1/a_{H^+}$. With the total catalyst concentration expressed as $[Co^{II}TSP]_T = [Co^{II}TSP]_{T1} + [Co^{II}TSP]_{T2} + [Co^{II}TSP]_{T3} + [Co^{II}TSP]_{T4}$, Equation 6.13 can be rewritten as

$$v^1 = \frac{\{\alpha_1 + \alpha_2 \beta_2 + \alpha_3 \beta_2 + \alpha_4 \beta_2^2 + \alpha_5 \beta_2^2 \beta_3 + \alpha_6 \beta_2^2 \beta_3 \beta_4\} [C]_T [NH_3^+C_2H_4S^-]}{\{1 + \beta_2(1 + \beta_3 + \beta_3 \beta_4)\} \{1 + \beta_1 + \beta_2\}} \quad (6.14)$$

where $\beta_3 = K_1^1/a_{H^+}$; $\beta_4 = K_2^1/a_{H^+}$; $[C]_T$ = total concentration of the catalyst; K_1^1 and K_2^1 are the apparent acid dissociation constants of

the peripheral nitrogen of CoTSP, as shown in the following reactions,



and k_{obsd}^1 in this case is given by

$$k_{\text{obsd}}^1 = \frac{\{\alpha_1 + \alpha_2\beta_2 + \alpha_3\beta_2 + \alpha_4\beta_2^2 + \alpha_5\beta_2\beta_3 + \alpha_6\beta_2^2\beta_3\beta_4\}}{\{1 + \beta_2(1 + \beta_3 + \beta_3\beta_4)\} \{1 + \beta_1 + \beta_2\}} \quad (6.17)$$

Values of α_1 can be obtained by analyzing the kinetic data at $\text{pH} \leq 9.5$. At $\text{pH} \leq 9.5$, the rate of autoxidation will be dominated by v_1^1 , k_{obsd}^1 will be reduced to

$$k_{\text{obsd}}^1 = \frac{k_3^1 K_2^1}{\left(1 + \frac{a_{\text{H}^+}}{K_1^1 a_1}\right)} \quad (6.18)$$

and $k_3^1 K_2^1$ is calculated to be $(1.98 \pm 0.03) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. At $12.06 \leq \text{pH} \leq 11.3$, assuming that $\beta_2 \gg \beta_1 \gg 1$ and $\beta_3 \gg 1$, then Equation 6.17

becomes

$$k_{obsd}^1 = (\alpha_5 + \alpha_6\beta_4)/(1 + \beta_4) \quad (6.19)$$

and $k_{32}^1K_{22}^1$, $k_{33}^1K_{23}^1$ and pK_2^1 were calculated to be $(2.05 \pm 0.85) \times 10^4$ $M^{-1}s^{-1}$, $(1.23 \pm 0.09) \times 10^4$ $M^{-1}s^{-1}$ and 11.76 ± 0.27 , respectively. K'_{a_1} and K'_{a_2} values at $\mu = 0.4$ M were calculated from $K'_{a_1} = 8.2$ and $K'_{a_2} = 10.7$ at $\mu = 0.1$ M (Felder et al., 1955) and Davies equation (Stumm and Morgan, 1981). 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:

$$v^2 = \frac{(k_{31}^2K_{21}^2 + k_{32}^2K_{22}^2 \frac{K_1^2}{a_{H^+}} + k_{33}^2K_{23}^2 \frac{K_1^2K_2^2}{a_{H^+}^2}) [Co^{II}TSP]_T [CH_3CH_2S^-]}{(1 + \frac{K_1^2}{a_{H^+}} + \frac{K_1^2K_2^2}{a_{H^+}^2}) (1 + \frac{a_{H^+}}{K'_{a_1}})} \quad (6.20)$$

where k_{3i}^2 and K_{2i}^2 are the rate constant for electron transfer step and the equilibrium constant for substrate complexation by the i^{th} catalytic center, respectively; K_1^2 , K_2^2 and K'_{a_1} are the apparent acid dissociation constants of $Co^{II}TSP-RS=Co^{II}TSP$, $Co^{II}TSP-RS=Co^{II}TSP^-$ and

CH₃CH₂SH, respectively. k_{obsd}^2 in this case is given by

$$k_{obsd}^2 = \frac{\left(k_{31}^2 K_{21}^2 + \frac{k_{32}^2 K_{22}^2 K_1'^2}{a_{H^+}} + \frac{k_{33}^2 K_{23}^2 K_1'^2 K_2'^2}{a_{H^+}^2} \right)}{\left(1 + \frac{K_1'^2}{a_{H^+}} + \frac{K_1'^2 K_2'^2}{a_{H^+}^2} \right) \left(1 + \frac{a_{H^+}}{K_{a1}'^2} \right)} \quad (6.21)$$

The value of $k_{31}^2 K_{21}^2$ can be obtained by analyzing the experimentally

observed rate constant at $pH \leq 10$. At this pH, assuming $1 \gg \frac{K_1'^2}{a_{H^+}} \gg$

$\frac{K_1'^2 K_2'^2}{(a_{H^+})^2}$, Equation 6.21 reduces to

$$k_{obsd}^2 = \frac{k_{31}^2 K_{21}^2}{\left(1 + \frac{a_{H^+}}{K_{a1}'^2} \right)} \quad (6.22)$$

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 $pH \geq$

12, assuming that $\frac{K_1}{a_{H^+}} \gg 1$, Equation 6.21 becomes

$$k_{obsd}^2 = \frac{k_{32}^2 K_{22}^2 + k_{33}^2 K_{23}^2 \frac{K_2'^2}{a_{H^+}}}{\left(1 + \frac{K_2'^2}{a_{H^+}}\right)} \quad (6.23)$$

and $k_{32}^2 K_{22}^2$, $k_{33}^2 K_{23}^2$ and $pK_2'^2$ 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. $K_{a_1}'^2$ at $\mu = 0.4 \text{ M}$ was calculated from $K_{a_1}'^1 = 10.6$ at infinite dilution (Irving et al., 1964) and Davies equation (Stumm and Morgan, 1981).

Calculated values of the pseudo-first-order rate constants (k_{cald}^1 and k_{cald}^2) are compared to their respective experimental values in Table 6.3 and 6.4 and shown in Figure 6.10a and 6.10b for 2-aminoethanethiol and ethanethiol, respectively. It was not possible to obtain an independent value of K_1' of both mercaptans. Therefore, in the calculations, the assumption was made that K_1' and K_2' are approximately equal for both substrates. Since the fit for each substrate is fairly sensitive to its corresponding K_1' value, the reasonably good fit gives indirect support to the assumption that $K_1' \cong K_2'$ for both substrates.

TABLE 6.3: Comparison of k_{obsd} with k_{cald} of Catalytic Autoxidation of 2-Aminoethanethiol at various pH.

pH	$k_{obsd} \times 10^{-4} (M^{-1}s^{-1})$	$k_{cald} \times 10^{-4} (M^{-1}s^{-1})$
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

Experimental Conditions : $\mu = 0.4$ M, Temperature = $25.5^{\circ}C$,

$[O_2]_{Diss}$ = Saturated with O_2 at 1 atm.,

$[Co^{II}TSP]_T = 6.4 \times 10^{-7}$ M, Buffer system = NaCl, $NaHCO_3$, NaOH.

TABLE 6.4: Comparison of k_{obsd} with k_{cald} of Catalytic Autoxidation of Ethanethiol at various pH.

pH	$k_{obsd} \times 10^{-4} (M^{-1}s^{-1})$	$k_{cald} \times 10^{-4} (M^{-1}s^{-1})$
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

Experimental Conditions : $\mu = 0.4$ M, Temperature = 25.5°C,

$[O_2]_{Diss} =$ Saturated with O_2 at 1 atm.,

$[Co^{II}_{TSP}]_T = 6.4 \times 10^{-7}$ M, Buffer system = NaCl, $NaHCO_3$, NaOH.

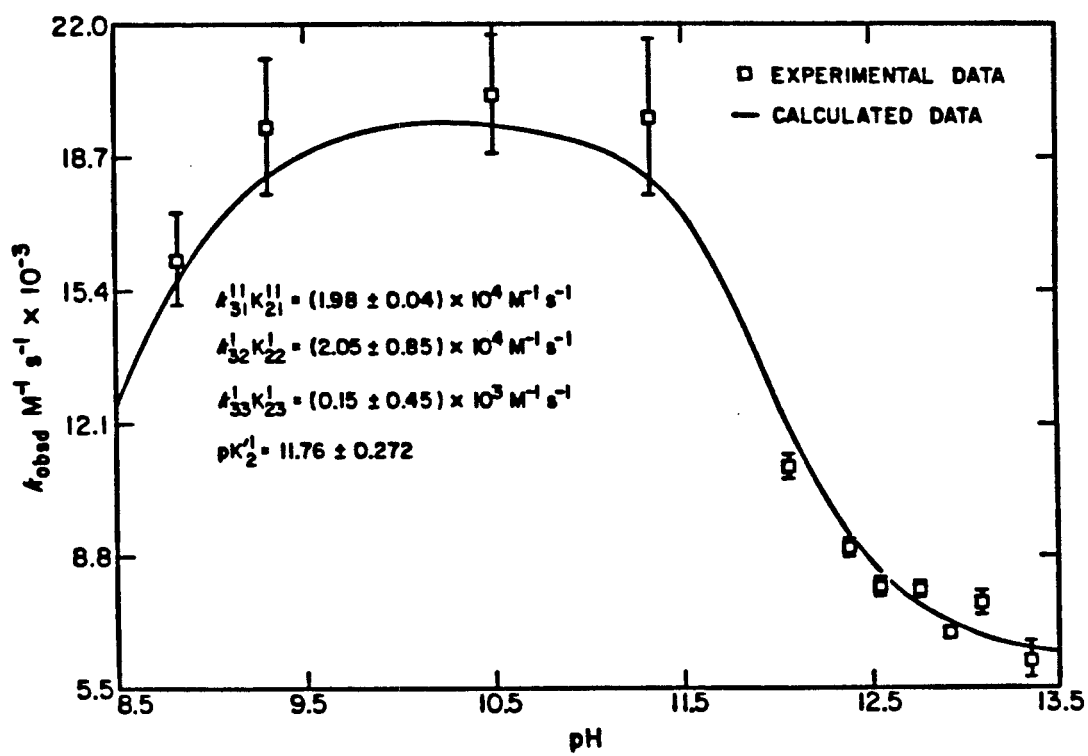


Figure 6.10a: pH Dependence of Autoxidation of 2-Aminoethanethiol.

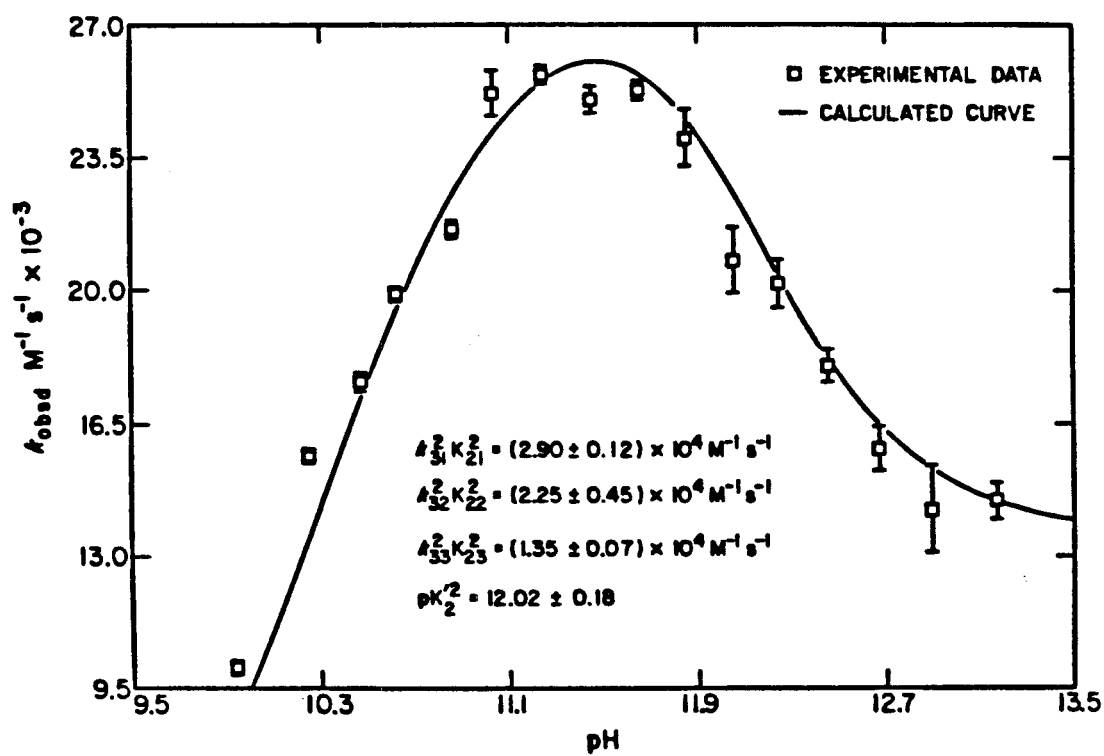


Figure 6.10b: pH Dependence of Autoxidation of Ethanethiol.

Discussion

The kinetics and mechanism of the autoxidation of 2-aminoethanethiol and ethanethiol catalyzed by Co(II)-4,4',4'',4'''-tetrasulfophthalocyanine appear to be the same as the mechanism proposed for the catalyzed autoxidation of 2-mercaptoethanol. The experimental data for the catalytic autoxidation show similarities in 1) the reaction orders of substrates, catalyst and oxygen; 2) reaction intermediates, which were found to be hydrogen peroxide and mercaptan radical; 3) stoichiometry of the overall reaction; and 4) the formation of disulfide 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; this suggests that the dimer is bridged by the corresponding mercaptan anion to give the active catalytic center for the catalytic cycle.

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-amionethanethiol and ethanethiol), were compared with the Taft σ^* value (Perrin et al., 1981) for the substituent groups. These data are listed in Table 6.5 and plotted in Figure 6.11. The apparent rate constants and the Taft σ^* value 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

TABLE 6.5. Correlation of Taft σ^* Values of R' Group on R'CH₂CH₂SH with the Apparent Rate Constant ($k_{app} = kK$) Values.

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

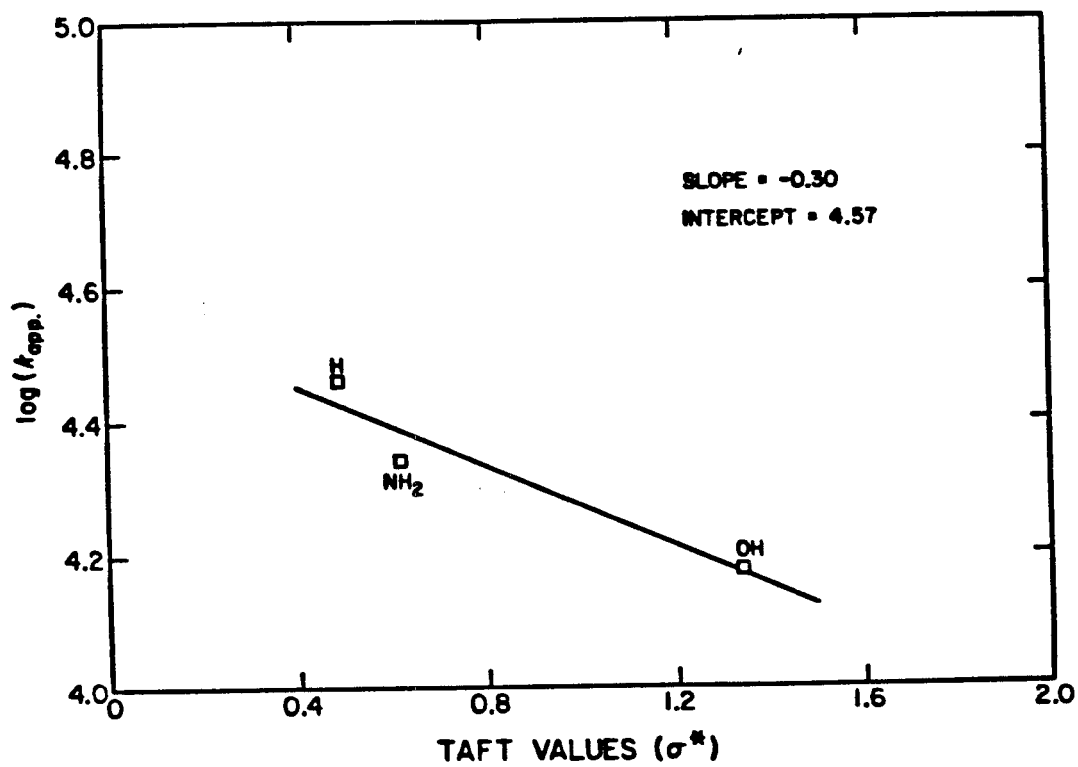


Figure 6.11: Linear Free Energy Relationship between Taft σ^* Value and $\log k_{app.}$

withdrawing ability of the functional group. As can be seen in Table 6.5, 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 more toward the substituent group which this withdrawal has two various effects. First, the stability of the subsequent sulfur-cobalt bond will be decreased; this should lead to a smaller value for the complexation equilibrium constant. Second, the decrease of the electron density available to the cobalt center results in a lower electron density on the cobalt center; this causes 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 6.5, $\text{NH}_3^+\text{C}_2\text{H}_4\text{S}^-$ 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 Co-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 $\text{NH}_2\text{C}_2\text{H}_4\text{S}^-$ suggests 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 Co(II)TSP.

An additional LFER was observed between pK'_2 of $\text{Co}^{\text{II}}\text{TSP-RS}=\text{Co}^{\text{II}}\text{TSP}$ and the Taft σ^* value as shown in Table 6.6 and Figure 6.12. 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 lower by the stronger electron withdrawing substituent of the mercaptan, the electron at the bonding orbital between the hydrogen and the peripheral nitrogen of CoTSP molecule would be more drawn toward the cobalt center and consequently destabilize the bonding between the hydrogen ion and the peripheral nitrogen. Therefore, the hydrogen ion more readily dissociates from the phthalocyanine ring and thus a lower pK' value is observed.

Conclusion

Due to the structural similarity of the mercaptans, it is expected that the catalytic autoxidations of 2-aminoethanethiol and ethanethiol would proceed via the same mechanism as the catalytic autoxidation of 2-mercaptoethanol. The establishment of two linear free energy relationships enables us to predict the rate of autoxidation of other mercaptans. Comparison of the calculated apparent rate constant from the linear free energy relationship to its observed apparent rate constant of the catalytic autoxidation of benzylethanethiol was attempted. An attempt was made to 1) test the predictions of the LFER and 2) determine its sensitivity of the

TABLE 6.6. Correlation of Taft σ^* Values of R' Group on R'CH₂CH₂SH with the pK₂' Values.

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

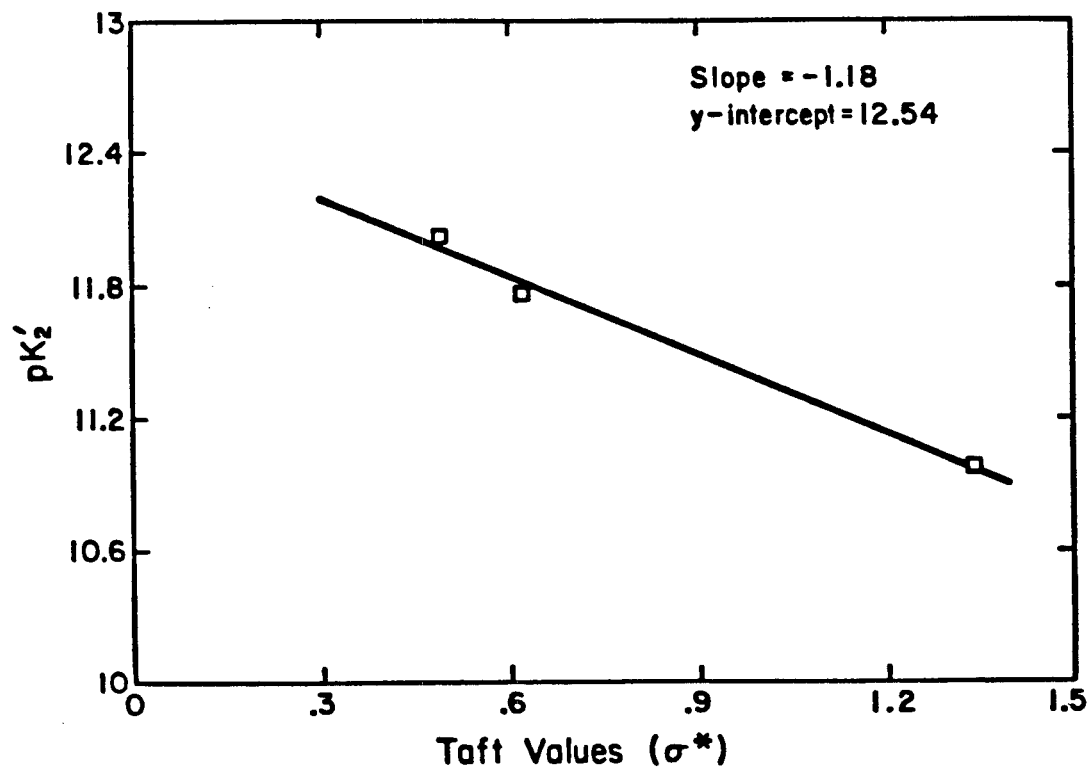


Figure 6.12: Linear Free Energy Relationship between Taft σ^* Value and pK'_2 .

reaction to steric effects by including the benzylethanethiol in the series, $H > NH_2 > C_6H_5 > OH$. However, the aqueous solution of benzylethanethiol rapidly clouded during autoxidation due to the formation of the insoluble disulfide. Consequently, the experiments with benzylethanethiol could not be performed with UV-VIS spectrophotometry.

The successful catalytic autoxidation of several mercaptans suggests that $Co^{II}TSP$ catalysis may be applied for the elimination of mercaptans and their associated odors. However, research is still required to investigate the kinetics and mechanism of the autoxidation of mercaptans catalyzed by hybrid $Co(II)$ -4,4',4'',4'''-tetrasulphthalocyanine complexes such as (SiO_2) -CoTSP, TiO_2 -CoTSP and polystyrene-divinyl benzene resins-CoTSP in order to make the process more economically attractive.

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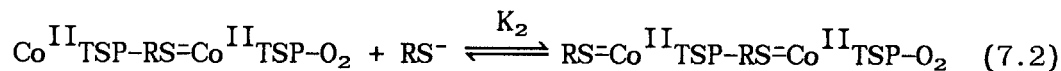
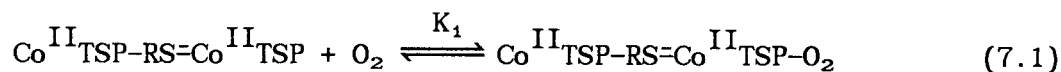
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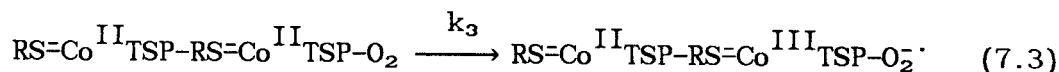
CHAPTER SEVEN
SUMMARY, CONCLUSIONS AND
SUGGESTIONS FOR FUTURE RESEARCH

Catalytic Autoxidation of Mercaptans

The kinetics and mechanism of the autoxidation of 2-mercaptoethanol, 2-aminoethanethiol and ethanethiol catalyzed by Co(II)-4,4',4'',4'''-tetrasulfophthalocyanine, abbreviated as Co(II)TSP, have been examined. Kinetic data showed that the catalytic autoxidation of all three mercaptans proceeded via the same mechanism. The ultimate products of the autoxidation were found to be the corresponding disulfide (RSSR) and hydroxide ion. The kinetic data indicated that 50% to 80% of the disappearance of mercaptans was controlled by the catalytic cycle as opposed to oxidation by the intermediate, H₂O₂.

Catalytic Cycle: The detailed mechanism of the catalytic cycle is shown in Figure 3.7. When the mercaptan was added, a dimeric Co(II)TSP was formed by the bridging of the two Co(II)TSP monomers by mercaptan anion. This dimer is proposed as the catalytic center for the cycle. The initial two steps of the catalytic cycle involve the complexation of O₂ and RS⁻ onto two apical sites of the same Co(II)TSP dimer, as shown in reaction 7.1 and reaction 7.2. The subsequent electron transfer from Co(II) to O₂ forming a superoxide-like species, as shown in reaction 7.3, is assumed to be the rate-determining step.





The observed zero-order dependence in oxygen for all three cases suggests that the rate of binding of O₂ is high and that most of the catalyst is in oxygenated form.

The experimental rate law for the autoxidation of each mercaptan was found to be

$$v = \frac{-d[\text{RS}^-]}{dt} = k_{\text{obsd}}[\text{CoTSP}]_{\text{T}}[\text{RS}^-] \quad (7.4)$$

and an expression for k_{obsd} of each mercaptans was derived from the posulated mechanism. For 2-mercaptoethanol, k_{obsd} is

$$k_{\text{obsd}} = \frac{\left(k_{31}K_{21} + \frac{k_{32}K_{22}K_1}{a_{\text{H}^+}} + \frac{k_{33}K_{23}K_1K_2}{a_{\text{H}^+}^2} \right)}{\left(1 + \frac{K_1}{a_{\text{H}^+}} + \frac{K_1K_2}{a_{\text{H}^+}^2} \right) \left(1 + \frac{a_{\text{H}^+}}{K'_{a_1}} + \frac{K'_{a_2}}{a_{\text{H}^+}} \right)} \quad (7.5)$$

where k_{3i} is the rate constant of the electron-transfer step of the i^{th} catalytic center; K_{1i} , K_{2i} are the equilibrium constants of oxygenation and substrate complexation of the i^{th} catalytic center, respectively; K_1 , K'_{a_1} , K'_{a_2} are the apparent acid dissociation constants of the catalyst, $\text{HOC}_2\text{H}_4\text{SH}$ and $\text{HOC}_2\text{H}_4\text{S}^-$, respectively, and

a_{H^+} is the hydrogen ion activity.

For 2-aminoethanethiol k_{obsd} is given by

$$k_{obsd} = \frac{\{\alpha_1 + \alpha_2\beta_2 + \alpha_3\beta_2 + \alpha_4\beta_2^2 + \alpha_5\beta_2\beta_3 + \alpha_6\beta_2^2\beta_3\beta\}}{\{1 + \beta_2(1 + \beta_3 + \beta_3\beta_4)\} \{1 + \beta_1 + \beta_2\}} \quad (7.6)$$

where $\alpha_1 = k_{31}^1 K_{21}^1$, $\alpha_2 = k_{31}^2 K_{21}^2$, $\alpha_3 = k_{31}^3 K_{21}^3$, $\alpha_4 = k_{31}^4 K_{21}^4$, $\alpha_5 = k_{32}^1 K_{22}^2$, $\alpha_6 = k_{33}^1 K_{23}^1$, $\beta_1 = a_{H^+}/K_{a1}'$, $\beta_2 = K_{a2}'/a_{H^+}$, $\beta_3 = K_i^1/a_{H^+}$ and $\beta_4 = K_2^1/a_{H^+}$; k_{3i}^1 and K_{2i}^1 are the rate constant of the electron transfer step and the equilibrium constant of substrate complexation of i^{th} catalytic centre with substrate $NH_2CH_2CH_2S^-$, respectively; K_i^1 , K_{a1}' and K_{a2}' are the apparent acid dissociation constants of the catalytic center, $NH_3^+CH_2CH_2SH$, and $NH_3^+CH_2CH_2S^-$, respectively. For the ethanethiol, k_{obsd} has the following form:

$$k_{obsd} = \frac{\left(k_{31}^2 K_{21}^2 + \frac{k_{32}^2 K_{22}^2 K_i^2}{a_{H^+}} + \frac{k_{33}^2 K_{23}^2 K_i^2 K_2^2}{a_{H^+}^2} \right)}{\left(1 + \frac{K_i^2}{a_{H^+}} + \frac{K_i^2 K_2^2}{a_{H^+}^2} \right) \left(1 + \frac{a_{H^+}}{K_{a1}'} \right)} \quad (7.7)$$

where k_{3i}^2 is the rate constant of the electron-transfer step of i^{th} catalytic center and K_{2i}^2 are the equilibrium constant of substrate complexation of i^{th} catalytic center; K_i^2 , K_2^2 and K_{a1}^2 are the

apparent acid dissociation constants of the $\text{Co}^{\text{II}}\text{TSP-RS}=\text{Co}^{\text{II}}\text{TSP}$, $\text{Co}^{\text{II}}\text{TSP-RS}=\text{Co}^{\text{II}}\text{TSP}^-$ and $\text{CH}_3\text{CH}_2\text{SH}$, respectively.

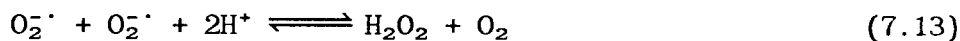
The kinetics reveal that the catalytic cycle is sensitive to variations in pH. The pH dependence at $\text{pH} < 11$ can be easily explained by the acid-base equilibria of the mercaptan ($\text{RSH} \rightleftharpoons \text{RS}^- + \text{H}^+$). However, the pH dependence at $\text{pH} > 11$ suggests that the deprotonation of $\text{Co}(\text{II})\text{TSP}$ dimer, as shown in reaction 7.12, must occur and that pK_i of the dimer must be between 11 and 13.



During each catalytic cycle, hydrogen peroxide and mercaptan radical are formed as intermediates. The overall stoichiometry for the catalytic cycle can be written as follows:



The mercaptan radical subsequently reacts through two pathways to give the corresponding disulfide as the final product. These pathways are:



However, the most likely pathway for the experimental conditions appears to be the second because $[RS^-] \gg [RS^*]$.

A linear free energy relationship was established between the Taft σ^* values

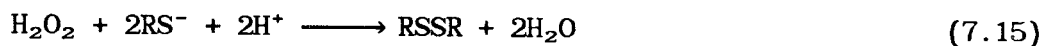
$$\log k_{app} = S(\sigma^*) + C \quad (7.14)$$

where S = slope; C = constant

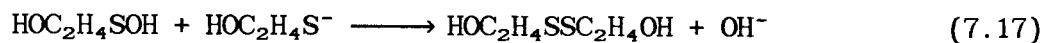
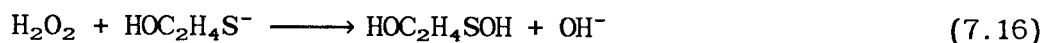
of R (OH, NH₂, H) , and the apparent rate constant, k_{app} , a product of the rate-limiting electron transfer rate constant and the equilibrium constant of the complexation of Co(II)TSP dimer by mercaptan. The negative slope of linear free energy relationship indicates that as the Taft σ^* value increases, the k_{app} decreases. The Taft σ^* value is a measure of electron withdrawing ability of the group. The decrease of electron density available to cobalt would have two different effects. First, the stability of the Co-sulfur bond would be lower which consequently reduces the value of the equilibrium constant. Second, as the electron density on cobalt contracts, the rate of electron transfer may decrease. The combination of these two effect causes the k_{app} to decrease. This would explain the apparent inverse linear free energy relationship (LFER) between the Taft σ^* value and the $\log k_{app}$. The deviation of NH₃⁺ from this relationship suggests that electrostatic effects may be important for charged side-group.

Another inverse linear free energy relationship between the Taft σ^* value of side-groups, OH, NH₂, H, and the negative log of the apparent acid dissociation constant of the Co^{II}TSP-RS-Co^{II}TSP dimer, pK_2^{\dagger} , was found. A similar explanation can be applied here. As the electron density on the sulfur decreases due to electron withdrawn by the side-group, there is a decrease of electron density on the cobalt. The cobalt may then draw electron from the phthalocyanine ring. Subsequently, the electron between the H and the peripheral nitrogen on the ring is moved toward the ring with the result that the H⁺ ion is easier to dissociate from the Co(II)TSP molecule. Thus, the value of pK_2^{\dagger} is lower.

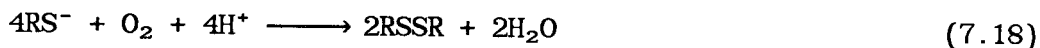
Hydrogen Peroxide Sequence: The hydrogen peroxide produced from the catalytic cycle oxidizes the mercaptan anions giving the disulfide as the product. The stoichiometry is found to be



The kinetics and mechanism for the oxidation of 2-mercaptoethanol by hydrogen peroxide have been examined and described in Chapter 4. The proposed mechanism is



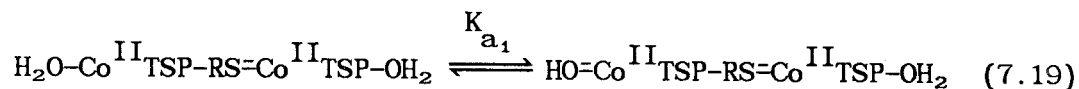
Combining the stoichiometries of the catalytic cycle and the hydrogen peroxide sequence, the overall stoichiometry of the catalytic autoxidation is



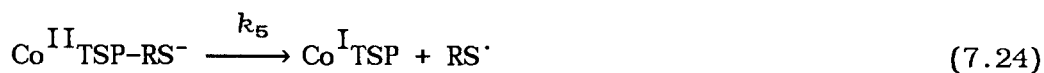
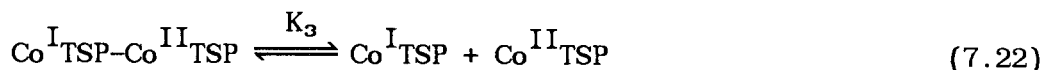
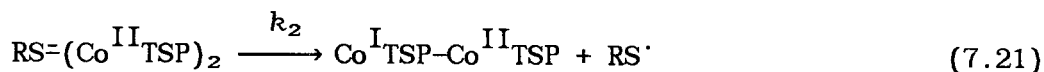
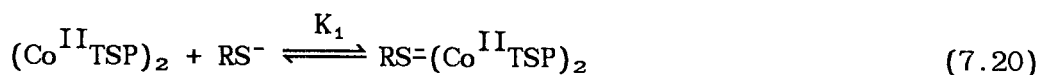
The proposed mechanism for autoxidation predicts hydrogen peroxide and mercaptan radical as intermediates, and that the disulfide and the water are the final products of autoxidation. Also, the pH is predicted to rise during the course of reaction in an unbuffered solution provided $\text{pH}_0 > 10$. All of these effects have been experimentally observed (except for the production of H_2O) for all three mercaptans. Furthermore, the stoichiometry of 1 mole of oxygen to 4 moles of mercaptan was found for all three thiols.

The Reduction of Co(II)TSP by 2-mercaptoethanol under Anoxic conditions

The kinetics and mechanism of reduction of Co(II)TSP by 2-mercaptoethanol under anoxic conditions were studied. Results from this study provide estimates of the rate of complexation of Co(II)TSP by 2-mercaptoethanol and the acid dissociation constant, K_{a_1} , of the bound water on the Co(II)TSP-RS=Co(II)TSP, as shown in reaction 7.19.



The rate of formation of Co(I)TSP showed a first order dependence in both total Co(II)TSP concentration and 2-mercaptoethanol concentration $< 1.6 \times 10^3$ M. However, as the 2-mercaptoethanol concentration was increased beyond 1.6×10^3 M, the dependence on the thioethanol gradually changed from first-order to zero-order and the rate of reduction gradually reached a maximum value yielding a saturation curve. Spectral changes indicate that the dimer is the active species. During the reduction, the original blue color of the solution changes to yellow indicating that the Co(II)TSP is indeed reduced to Co(I)TSP. Introduction of oxygen gas into the yellow solution restores the blue color. The return of the blue color suggests that the Co(II)TSP was reversibly reduced to Co(I)TSP. The kinetic and spectral information suggested the following mechanism for the Co(II)TSP reduction:

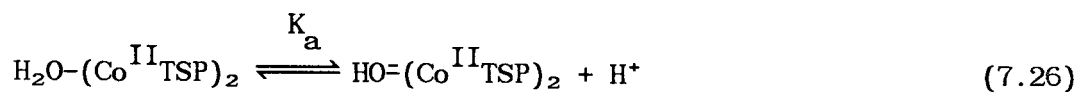


According to this mechanism, the rate expression is given by

$$v = \frac{-d[\text{Co}^{\text{II}}\text{TSP}]_{\text{T}}}{dt} = \frac{k_2 K_1 [\text{RSH}]_{\text{T}} [\text{Co}^{\text{II}}\text{TSP}]_{\text{T}}}{2\left(1 + \frac{a_{\text{H}^+}}{K_{\text{a}_1}} + \frac{K_{\text{a}_2}}{a_{\text{H}^+}}\right) (1 + \alpha [\text{RSH}]_{\text{T}})} \quad (7.25)$$

where k_2 is the rate constant for the electron transfer step, and K_1 is the equilibrium constant for the complexation of CoTSP dimer with thioethanol. K_{a_1} and K_{a_2} are the apparent acid dissociation constants of $\text{HOC}_2\text{H}_4\text{SH}$ and $\text{HOC}_2\text{H}_4\text{S}^-$, respectively, and α is $K_1 / (1 + a_{\text{H}^+} / K_{\text{a}_1} + K_{\text{a}_2} / a_{\text{H}^+})$.

The rate is independent of pH between 11 and 12.47 suggesting that the apparent acid dissociation constant, $\text{p}K_{\text{a}}$, of reaction 7.26 must be $\gg 14.7$. This implies that the apparent acid dissociation constant, K_{a_1} , of the dimer in the oxygenated system (reaction 7.19) must be even greater than 14.7 because of the further stabilization of the H^+ on water by indirect electron density donating effect by the bridging RS^- . This estimate supports the assumption that the observed pH effect in the oxygenated system is due to deprotonation at a peripheral nitrogen on the phthalocyanine ring rather than on the bound water molecule.



The rate constant for complexation in reaction 7.20 was estimated to be $\gg 10^4 \text{ M}^{-1}\text{s}^{-1}$. Since thioethanol is complexed to the dimer of Co(II)TSP in the oxygenated system, its rate of complexation should be quite similar i.e. it should be $\gg 10^4 \text{ M}^{-1}\text{s}^{-1}$. This estimate further enhances the argument that the electron transfer step rather than the preceding mercaptan complexation step is the rate-determining step in the oxygenated system.

Practical Applications

This study indicates that Co(II)TSP is a very effective catalyst for the autoxidation of mercaptans. Mercaptans are ubiquitous found in oil refinery wastes. They are normally removed from the distillate by contacting it with a selective solvent such as monoethanoamine. The mercaptans are subsequently removed from monoethanoamine by extraction with an aqueous alkaline solution (Anderson and Ward; 1976), in which they are oxidized to disulfide by dissolved oxygen. However, this process is extremely slow. Frequently, metal complexes such as cobalt phthalocyanine are used to catalyze the oxidation under strongly alkaline conditions. From a practical standpoint, use of the homogeneous catalyst is not very economical because of the relatively expensive recovery process. Solid-supported Co(II)TSP such as $(\text{SiO}_2)\text{-Co(II)TSP}$, $\text{TiO}_2\text{-Co(II)TSP}$, and polystyrene-divinyl benzene resin-Co(II)TSP contained in fixed bed

reactors may be an economic alternative for mercaptan waste treatment. Nevertheless, the results of this study should provide useful insight into the design of a suitable hybrid system.

Future Research

Future research should be focused on the following areas:

1. Further investigation of the linear free energy relationship between the Taft σ^* values of the substituent groups on the mercaptan and the apparent rate constant, k_{app} is warranted.
2. The kinetics and mechanisms of the reduction of Co(II)TSP by 2-aminoethanethiol and ethanethiol should be examined and compared with the mechanism proposed for 2-mercaptoethanol. In addition, linear free energy relationships should be established between the electron transfer constant or the equilibrium complexation constant and the Taft value.
3. As the mechanism for the homogeneous catalytic autoxidation of mercaptans in aqueous solution is better understood, the kinetics and mechanism of the autoxidation of mercaptans as catalyzed by hybrid complexes of Co(II)TSP, such as silica gel-Co(II)TSP, or metal-oxide-Co(II)-TSP can be examined. Recently, Hong et al. (1986) have shown that Co(II)TSP anchored on titanium dioxide (a semiconductor) is a potent photocatalyst. Such photochemical properties could further enhance the rate of autoxidation of mercaptans. However, a detailed study of the kinetics and mechan-

ism of the heterogeneous catalytic systems is still required. The mechanism deduced for the homogeneous system can be a useful for interpretation of the heterogeneous reaction system.

4. The oxidation of 2-aminoethanethiol and ethanethiol by hydrogen peroxide should be examined to verify the assumption that in the catalytic autoxidation, the contribution to the observed rate of disappearance of mercaptans by hydrogen peroxide is negligible.

References

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Hong, A.P.; Bahnemann, D.W.; Hoffmann, M.R.; Submitted to *J. Amer. Chem. Soc.*, 1986.

APPENDIX A
THE EFFECT OF IONIC STRENGTH, INERT ANION AND CATION
ON THE KINETICS OF CATALYTIC AUTOXIDATION
OF 2-MERCAPTOETHANOL

Purpose

The effects of ionic strength and inert anions and cations on the rate of catalytic autoxidation of 2-mercaptoethanol were examined in order to determine the relative importance of electrostatic and cage effects on catalysis by Co(II)TSP.

Experimental Procedure

Reagents: 2-mercaptoethanol stock solutions were prepared using redistilled 99% reagent grade 2-mercaptoethanol (Aldrich). Co(II)-4,4',4'',4'''-tetrasulfophthalocyanine, abbreviated as CoTSP, was synthesized by according to the procedure described by Boyce et al. (1983). Buffers were prepared using reagent grade sodium hydroxide (Mallinckrodt), sodium chloride (J.T.Baker), sodium bicarbonate (Mallinckrodt). Water used to prepare the buffers and reagent solutions was obtained from a Milli-Q water purification system (Millipore), had a resistivity of 18 M Ω -cm, and was irradiated with ultra-violet light to remove any trace organics that may have been present.

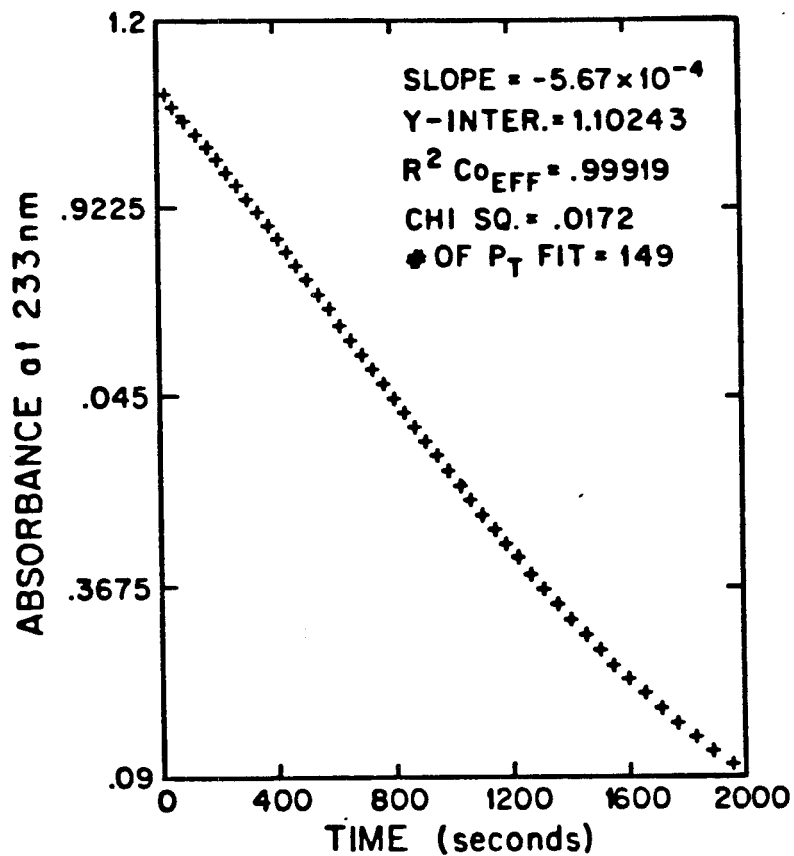
Kinetic measurements: Kinetic measurements were made on Hewlett Packard Model 8450 Spectrophotometer. A minimum of 100 data points were collected for each kinetic measurement. At least three measurements were made for each value of k_{obsd} . Data were analyzed on-line with a IBM-XT Computer. Constant temperature was maintained

at 25.5°C with a Haake water bath. Sodium chloride or approximate inert salt stock solutions were added into the appropriate buffer to establish the desired ionic strength (μ). pH was determined with a Beckman Altex Φ 71 pH meter and Radiometer Glass Electrode. Dissolved oxygen levels were established by dispersing N₂ and O₂ gas mixtures into the Co(II)TSP buffer. The reaction was monitored at 233 nm (the absorbance maximum for HOC₂H₄S⁻ (aq)). Pseudo first-order conditions of [O₂] \gg [HOC₂H₄SH]_T < 2.2 x 10⁻⁴ M were employed for all kinetic runs.

Results

The variation of ionic strength over a range of 0.01 M $\leq \mu \leq$ 0.5 M has a significant effect on the kinetics of autoxidation. The dependence on 2-mercaptoethanol is changed dramatically from first order at $\mu \geq$ 0.2 M to zero order at $\mu \leq$ 0.05 M (Figure A.1), while the dependence on [Co^{II}TSP]_T remains the same (Figure A.2). The apparent rate of the oxidation increases as the ionic strength increases.

The effect of inert anions and cations in the buffer medium were examined. Fluoride, Cl⁻, and ClO₄⁻ were selected to investigate the effects of variation in anion. Figure A.3 indicates that the inert anion does not affect the rate of autoxidation. The Group I cations, Li⁺, Na⁺, K⁺, were chosen to examine the effects of a variation in cation. The results, listed in Table A.1, show that the k_{obsd} is



EXPERIMENTAL CONDITIONS:

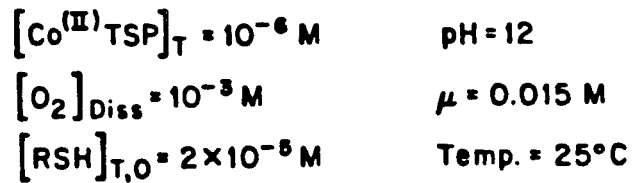
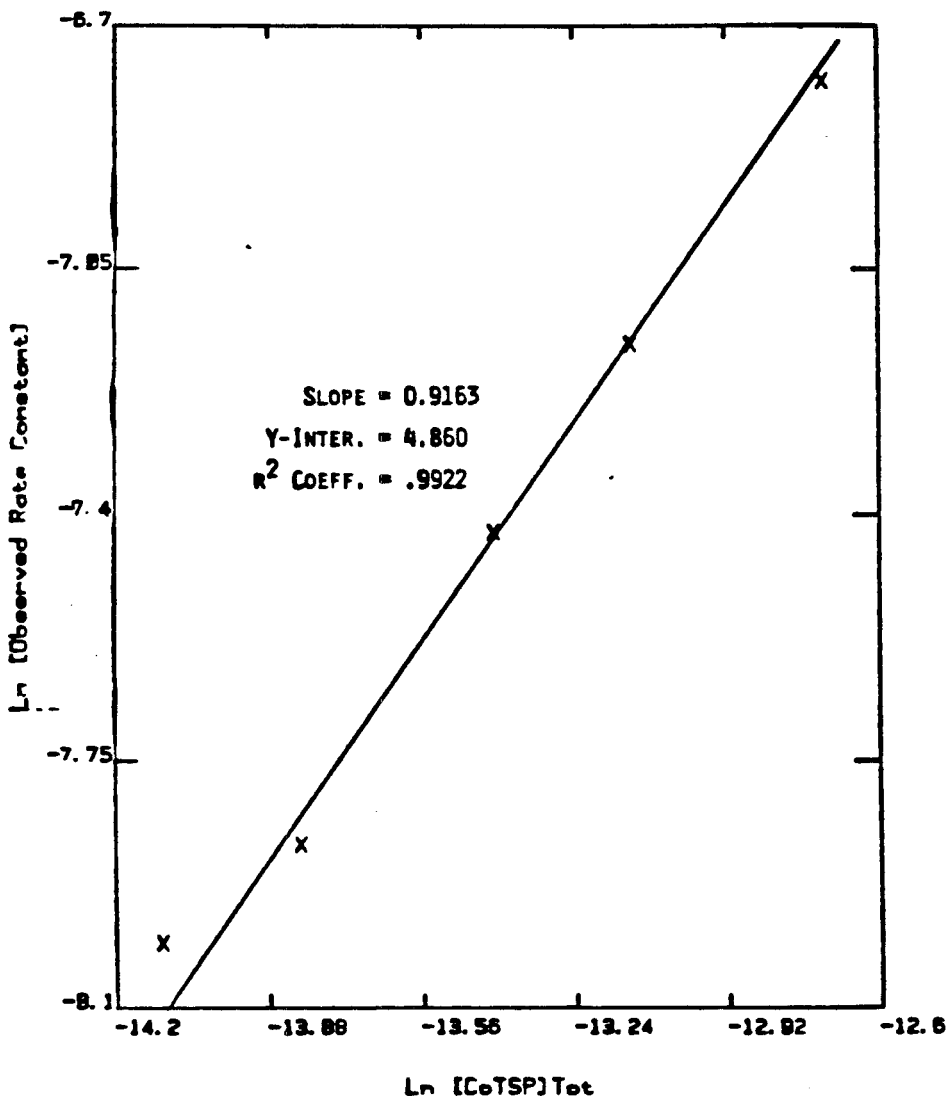
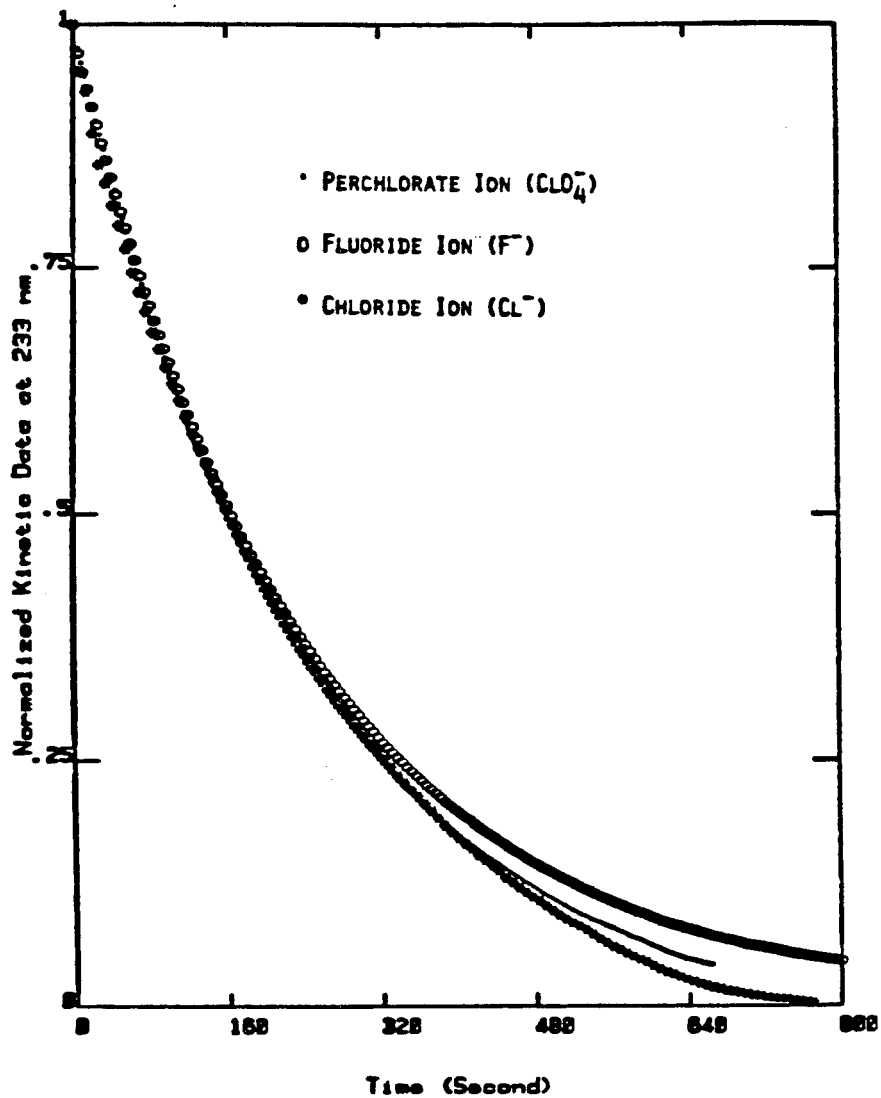


Figure A.1: Rate of Catalytic Autoxidation of 2-Mercaptoethanol by Co(II)TSP at $\mu = 0.015 \text{ M}$.



Experimental Conditions: pH = 12, $\mu = 0.015$ M, Temp. = 25°C,
Buffer NaCl, NaOH,
 $[\text{RSH}]_T = 2 \times 10^{-5}$ M
 $[\text{O}_2]_{\text{Diss}} = \text{Sat. with O}_2 \text{ at 1 atm.}$

Figure A.2: Reaction Order of $[\text{Co}^{\text{II}}\text{TSP}]_T$ at $\mu = 0.015$ M.



Experimental Conditions: pH = 12, $\mu = 0.015$ M, Temp. = 25°C .
Inert Cation = Na^+
 $[\text{CoTSP}]_T = 5 \times 10^{-6}$ M,
 $[\text{RSH}]_T = 2 \times 10^{-5}$ M
 $[\text{O}_2]_{\text{Diss.}} = \text{Sat. with O}_2 \text{ at 1 atm.}$

Figure A.3: The Effect of Anion on the Rate of Catalytic Autoxidation of 2-Mercaptoethanol

Table A.1. Effect of Cations on the Rate of Autoxidation of 2-mercaptoethanol catalyzed by Co(II)-4,4',4'',4'''-Tetrasulfophthalocyanines.

Cation	$p^cH = 13.6$ $k_{obsd} (M^{-1}sec^{-1})$	hydration ^a radius (A^0)	hydration ^a number
Li ⁺	$(3.3 \pm 0.2) \times 10^4$	3.40	25.3
Na ⁺	$(4.7 \pm 0.1) \times 10^4$	2.76	16.6
K ⁺	$(7.6 \pm 0.1) \times 10^4$	2.32	10.5

^a Data obtained from Cotton & Wilkinson, "Advanced Inorganic Chemistry", Fourth Edition, John Wiley & Sons, 1980, page 255.

inversely proportional to the size, hydration number, hydration radius of the cation.

Discussions

As presented in Chapter 3, the rate expression for catalytic autoxidation for the each of the catalytic centers is given by the following relationship:

$$v_i = \frac{k_{3i} K_{1i} K_{2i} [\text{CoTSP}]_{Ti} [\text{O}_2] [\text{RS}^-]}{2(1 + K_{1i} [\text{O}_2] + K_{1i} K_{2i} [\text{O}_2] [\text{RS}^-])} \quad (\text{A.1})$$

where k_{3i} , K_{1i} , K_{2i} are the rate constants of the electron transfer steps, the equilibrium constants for oxygenation, and the equilibrium constants for substrate complexation for each catalytic center, respectively. Both the observed zero-order and first-order dependence with respect to 2-mercaptoethanol at $\mu = 0.05 \text{ M}$ and 0.4 M , respectively, can be obtained from Equation A.1 under different conditions. Zero-order dependence on 2-mercaptoethanol results when $K_{1i} K_{2i} [\text{O}_2] [\text{RS}^-] \gg K_{1i} [\text{O}_2] \gg 1$ such that $K_{2i} [\text{RS}^-] \gg 1$; whereas a first-order dependence results, when $K_{1i} [\text{O}_2] \gg K_{1i} K_{2i} [\text{O}_2] [\text{RS}^-] \gg 1$ such that $1 \gg K_{2i} [\text{RS}^-]$. When $[\text{HOC}_2\text{H}_4\text{SH}]_0$ is held constant, the value of K_{2i} must change by a factor of 10^2 as the ionic strength is varied. Expressing K_{2i} in term of its intrinsic constant and the appropriate

activity coefficients, the conditions for a zero-order dependence can be written as:

$$K'_{2i} \frac{\gamma_{ai, \mu_1} \gamma_{[RS^-], \mu_1}}{\gamma_{bi, \mu_1}} [RS^-] \gg 1 \quad (\mu_1 \leq 0.04 \text{ M}) \quad (\text{A.2})$$

while those for a first-order dependence can be written as:

$$1 \gg K'_{2i} \frac{\gamma_{ai, \mu_2} \gamma_{[RS^-], \mu_2}}{\gamma_{bi, \mu_2}} [RS^-] \quad (\mu_2 \geq 0.3 \text{ M}) \quad (\text{A.3})$$

where K'_{2i} is the intrinsic equilibrium constant of i^{th} catalytic center; $\gamma_{[RS^-], j}$, $\gamma_{a_i, j}$, $\gamma_{b_i, j}$ are the activity coefficients of $\text{HOC}_2\text{H}_4\text{S}^-$, the dimeric forms of $(\text{O}_2\text{-Co}^{\text{II}}\text{TSP-RS-Co}^{\text{II}}\text{TSP-RS}^-)$ and $(\text{O}_2\text{-Co}^{\text{II}}\text{TSP-RS-Co}^{\text{II}}\text{TSP})$ at ionic strength, j , respectively. Since the values of K'_{2i} and $[RS^-]$ are constant, the activity coefficient quotient must exhibit a 100-fold decrease as the ionic strength changes from 0.05 M to 0.4 M to be consistent with a change in reaction order. However, the activity coefficients for the individual species cannot be calculated from the Davies' Equation (Stumm and Morgan, 1981) to establish the likelihood of this change because the applicability of Davies' Equation is limited to the relatively small ions. However, qualitatively the two-order of magnitude change in the value of K'_{2i} can be explained by considering the interaction of the

catalysts and RS^- with the cationic electrolytes at various ionic strengths. As ionic strength increases, the concentration of cations surrounding RS^- and the catalyst will also increase. Such an increase of concentration of cation around the substrate and the catalyst may have two significant effects. First, the extent of ion-pairing between RS^- and its counterion may increase substantially; and second, the size of the cages for RS^- and the catalytic dimer would increase significantly. These combined effects would make it more difficult for the RS^- to approach the Co(II) center resulting in an increase of ΔG for substrate binding.

The independence of the observed rate on the anionic electrolytes indicates that the cage effect of anion is insignificant. Since CoTSP is negatively charged due to the four sulfonate groups on its periphery, the molecule is surrounded mainly by cations. Thus the effect of a change in the anion is rather small. On the other hand, when different metal cations in Group I of Periodic Table, (i.e., Li^+ , Na^+ , K^+), were used as counterions for the buffer, the rate of autoxidation increased in the relative order of $Li^+ < Na^+ < K^+$. This order is inversely related to the hydration radii and hydration numbers of the cations (Cotton and Wilkinson, 1980). As the hydration radius and hydration number increases, the hydration layer for the corresponding cationic electrolyte thickens. This increase in hydration layer enlarges the thickness of the cages for both catalyst and thioethanol anion. Therefore, ΔG of the complexation between the

substrate and the catalyst increases, (i.e., becomes less negative) which results a smaller value of K_{2i} and consequently a slower rate of catalytic autoxidation.

References

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Cotton, F.A.; Wilkinson, G.; "Advanced Inorganic Chemistry", Fourth Edition, John Wiley & Sons, New York, 1980, pp. 255.

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APPENDIX B

PROGRAM TO INTERFACE HP8450 UV/VISIBLE

SPECTROPHOTOMETER TO IBM XT/AT

```
10 DIM C$(150,2),D(150),DAT$(410)
20 KEY OFF:COLOR 7,1,1:CLS:COLOR 4,7:LOCATE 5,5:PRINT "This
  program is used to transfer data from HP 8450A
  Spectrophotometer.";
30 LOCATE 15,9:COLOR 20,7:PRINT " INSERT";:COLOR 4,7:PRINT
  " Raw Data Disk into Drive A,"::COLOR 20,7:PRINT
  "Strike";:COLOR 4,7
40 PRINT " <RET> Key when done";
50 A$=INKEY$:IF A$="" GOTO 50
55 IF A$=CHR$(13) GO TO 60 ELSE GO TO 50
60 I=0:COLOR 7,1,1:CLS
70 I=I+1:INPUT "Enter File Name; At END Hit <RET>":C$(I,1)
80 IF C$(I,1)="" GOTO 250
90 P8=LEN(C$(I,1)):P9=INSTR(C$(I,1),"."):IF P9>9 THEN PRINT
  "Illegal Format for File Name";:I=I-1:GOTO 70
100 IF P9=0 THEN C$(I,2)=C$(I,1)+"R":GOTO 130
110 IF (P8-P9)>3 THEN PRINT "Illegal Format for File
  Name";:I=I-1:GOTO 70
120 C$(I,2)=MID$(C$(I,1),1,P9-1)+"R"+MID$(C$(I,1),P9,(P8-P9+1))
130 INPUT "Is this a kinetic file";Y$
140 IF Y$="y" GOTO 190
150 IF Y$="Y" GOTO 190
160 IF Y$="N" GOTO 240
170 IF Y$="n" GOTO 240
180 GOTO 130
190 INPUT "Starting Time";stime:input "Time interval";itime:input
  "Final Time";ftime:D(I)=(ftime-stime)/itime+1
200 IF D(I)<>INT(D(I)) THEN GOTO 230
210 IF D(I)<1 THEN 230
215 print "There are ";d(I);" Data Point in this kinetic file"
220 PRINT ""':PRINT ""':GOTO 70
230 PRINT "The input must be in INTEGER, Please try again";:GOTO
  190
240 D(I)=401:PRINT ""':PRINT ""':GOTO 70
250 CLS:I=I-1
260 OPEN "COM1:9600,N,8,1" AS #1
270 FOR J=1 TO I
280 CLS:Q$=STR$(J):Q1=LEN(Q$)-1:Q$=RIGHT$(Q$,Q1):TEST$="C:
  PRO"+Q$+".dat":OPEN TEST$ FOR OUTPUT AS #2:OPEN C$(J,2)
  FOR OUTPUT AS #3
290 LOCATE 5,8:PRINT "Transfer # ";J;
300 LOCATE 12,8:PRINT "Go to spectrophotometer, enter 'DISPLAY to
  DEVICE 31'"
310 LOCATE 15,8:PRINT "Set Wavelength from 200 to 800 for
  transferring Spectrum"
320 LOCATE 24,8:PRINT "File transferring is ";C$(J,1);
330 FOR J1=1 TO D(J)
```

```
340 INPUT #1,DAT$(J1)
350 NEXT J1
360 FOR J1=1 TO D(J):PRINT #2,DAT$(J1):PRINT #3,DAT$(J1):NEXT J1
370 CLOSE #2,#3
380 CLS:LOCATE 25,1:PRINT "The List from spectrophotometer";
390 LOCATE 1,1
400 FOR J1=1 TO (D(J)-1) STEP 10
410 PRINT DAT$(J1)
420 NEXT J1
430 PRINT DAT$(D(J))
440 NEXT J
450 CLS:COLOR 20,7:LOCATE 13,10:PRINT " INSERT";:COLOR 4,7:PRINT
  " the Processed Data Disk; ";:COLOR 20,7:PRINT "STRIKE";:
  COLOR 4,7
460 PRINT " <RET> Key when Done";
470 A$=INKEY$:IF A$="" GOTO 470
475 IF A$=CHR$(13) THEN 480 ELSE GO TO 470
480 COLOR 7,1,1:CLS:COLOR 20,7:LOCATE 25,35:PRINT " Processing
  Data ";:COLOR 7,1
490 SP$=SPACES$(70)
500 FOR J=1 TO I
510 LOCATE 10,10:PRINT SP$;:LOCATE 10,10:PRINT "Processing data
  for file ";CS$(J,1);
520 Q$=STR$(J):Q1=LEN(Q$)-1:Q$=RIGHT$(Q$,Q1):TEST$="C:PRO"+Q$+
  ".dat":OPEN TEST$ FOR INPUT AS #2:OPEN CS$(J,1) FOR OUTPUT AS
  #3
530 INPUT #2,DATA1$
540 P8=INSTR(DATA1$,"L"):IF P8>0 THEN P8=1
550 PRINT #3,P8:P5=P8
560 IF P8=0 THEN P8=INSTR(DATA1$,"t") ELSE P8=INSTR(DATA1$,"L")
570 P9=INSTR(DATA1$,"="):P7=LEN(DATA1$):P4=P9-P8-1:
  X=VAL(MID$(DATA1$,P8+1,P4)):Y=VAL(MID$(DATA1$,P9+1,P7-P9))
580 PRINT #3,X
590 PRINT #3,Y
600 FOR J1=2 TO D(J)
610 INPUT #2,DATA1$
620 IF P5=0 THEN P8=INSTR(DATA1$,"t") ELSE P8=INSTR(DATA1$,"L")
630 P9=INSTR(DATA1$,"="):P7=LEN(DATA1$):X=VAL(MID$(DATA1$,P8+1,
  P9-P8-1)):Y=VAL(MID$(DATA1$,P9+1,P7-P9))
640 PRINT #3,X
650 PRINT #3,Y
660 NEXT J1
670 CLOSE #2:CLOSE #3
680 NEXT J
690 CLOSE #1
700 COLOR 7,1,1:CLS:LOCATE 15,10:INPUT "Do you want to transfer
  more file";Y$
710 IF Y$="y" GOTO 10
```



```
720 IF Y$="Y" GOTO 10
730 IF Y$="n" GOTO 760
740 IF Y$="N" GOTO 760
750 GOTO 700
760 CLS:END
```

APPENDIX C
COMPUTER PROGRAM TO ANALYZE KINETIC DATA

```
10 DIM X(800),Y(800),FX(800),FY(800),TX(800),TY(800),YINDEX(3)
20 KEY OFF:SCREEN 0:CLS:LOCATE 10,10:PRINT "Position the paper on
the printer, STRIKE any key when done.";
30 A$=INKEY$:IF A$="" GOTO 30
40 CLS:COLOR 7,0,0:LOCATE 10,10:INPUT "File Name to be analyzed";
FILE$
50 SP$=SPACE$(70)
60 OPEN FILE$ FOR INPUT AS #1
70 INPUT #1,C:IF C=1 THEN PRINT "The data in this file cannot be
analyzed by this program.":CLOSE:GOTO 1880
80 I=1
90 IF EOF(1) GOTO 130
100 INPUT #1,X(I)
110 INPUT #1,Y(I)
120 I=I+1:GOTO 90
130 I=I-1:CLOSE
140 J1=I-59:J2=I
150 IF I<120 THEN CLS:PRINT "The file does not have enough data
point to calculate the infinity":GOTO 320
160 AVERAGE=0:FOR J=J1 TO J2:AVERAGE=AVERAGE+Y(J1):NEXT J
170 AVERAGE=AVERAGE/(J2-J1+1):STD=0:FOR J=J1 TO J2:
STD=STD+(AVERAGE-Y(J1))^2: NEXT J
180 STD=SQR(STD/(J2-J1)):CLS:PRINT "The Average of last ";
(J2-J1+1);" Y-VALUE IS ";AVERAGE
190 PRINT "Its standard deviation is ";STD
200 PRINT "":PRINT "":INPUT "Do you want to use this average for
the infinity value";Y$
210 IF Y$="y" THEN INFIN=AVERAGE:GOTO 410
220 IF Y$="Y" THEN INFIN=AVERAGE:GOTO 410
230 IF Y$="n" THEN CLS:GOTO 260
240 IF Y$="N" THEN CLS:GOTO 260
250 GOTO 200
260 PRINT "":PRINT "":PRINT "ENTER 1 FOR RECALCULATING THE
INFINITY BY THE PROGRAM";
270 PRINT "ENTER 2 FOR INPUT FROM THE USER";
280 PRINT "":PRINT "":INPUT "ENTER YOUR CHOICE";Q
290 IF Q=1 THEN CLS:GOTO 370
300 IF Q=2 THEN CLS:GOTO 320
310 LOCATE 20,10:PRINT "INCORRECT RESPONSE, PLEASE TRY
AGAIN";:LOCATE 10,10:PRINT SP$:GOTO 260
320 CLS:IF J2<15 THEN PRINT "There are ";J2;" Data
Points":XCUS=J2:J20=1:XCU=2:LOCATE 2,12:PRINT "X",,," Y":
GOTO 350
330 XCU=1:LOCATE XCU,10:PRINT "The Last 15 Data Points are ";
340 LOCATE 2,12:PRINT "X",,," Y":;J20=I-14:XCU=2:XCUS=15
350 FOR XCU=1 TO XCUS:XCU=XCU+1:LOCATE XCU,10:PRINT X(J20),
Y(J20);:J20=J20+1:NEXT XCU1
```

```
360 LOCATE 20,10:INPUT "INPUT Y-VALUE AT INFINITY ";INFIN:
    GOTO 410
370 PRINT "There are ";I;" data points in the file."
380 INPUT "Input the starting data point # for infinity
    calculation";J1
390 INPUT "Input the final data point # for infinity
    calculation";J2
400 GOTO 160
410 YINDEX(1)=-1:YINDEX(2)=-1:XMIN=X(1):XMAX=X(1):YMIN=Y(1):
    YMAX=Y(1)
420 FOR J=1 TO I:IF X(J)>XMAX THEN XMAX=X(J)
430 IF XMIN>X(J) THEN XMIN=X(J)
440 IF Y(J)>YMAX THEN YMAX=Y(J)
450 IF YMIN>Y(J) THEN YMIN=Y(J)
460 FX(J)=X(J):FY(J)=Y(J):NEXT J
470 J1=I:COL=3:J2=1:YMAX9=YMAX
480 Y19=ABS(YMAX-INFIN):Y18=ABS(YMIN-INFIN):IF Y19>Y18 THEN
    Y20=Y19 ELSE Y20=Y18
490 GOSUB 3210
500 J=1:LOCATE 25,1:PRINT " ";CHR$(27);CHR$(25);" - LEFT
    ";:LOCATE 25,13:PRINT " ";CHR$(26);CHR$(24);" - RIGHT
    ";:LOCATE 25,26
510 PRINT " <RET> - END";
520 LOCATE 24,25:PRINT " <S> - SELECT ";
530 LOCATE 22,10:PRINT " ";:LOCATE
    22,10:PRINT " STARTING POINT SELECTION ";:XINDEX=1:GOTO 550
540 LOCATE 22,10:PRINT " ";:LOCATE
    22,10:PRINT " FINAL POINT SELECTION ";:XINDEX=2
550 PY=160-(FY(J)-YMIN)*YINC:PX=20+(FX(J)-XMIN)*XINC:PY=INT(PY):
    PX=INT(PX)
560 PY1=PY-5:PY2=PY+5:IF PY2>160 THEN PY2=158
570 IF PY1<5 THEN PY1=7
580 LINE (PX,PY1)-(PX,PY2),1
590 LOCATE 23,1:PRINT " ";:LOCATE 23,1:PRINT
    "INDEX AT PT # ";J;
600 LOCATE 24,1:PRINT " ";:LOCATE
    24,1:PRINT "X=";X(J);" Y=";Y(J);
610 A$=INKEY$: IF A$="" GOTO 610
620 IF LEN(A$)=2 GOTO 770
630 IF A$="1" THEN 530
640 IF A$="2" THEN 540
650 IF A$="S" THEN YINDEX(XINDEX)=J
660 IF A$="s" THEN YINDEX(XINDEX)=J
670 IF A$=CHR$(13) GOTO 690
680 GOTO 610
690 IF YINDEX(1)=-1 THEN LOCATE 23,1:PRINT SPACES(39):LOCATE
    23,1:PRINT "Starting Data Point has not been chosen";:
    GOTO 720
```

```
700 IF YINDEX(2)=-1 THEN LOCATE 23,1:PRINT SPACES$(39):LOCATE
    23,1:PRINT "Final Data Point has not been selected";:GOTO 720
710 GOTO 890
720 LOCATE 24,1:PRINT SPACES$(39);:LOCATE 24,1:PRINT "STRIKE any
    key to continue";
730 A$=INKEY$:IF A$="" GOTO 730
740 LOCATE 22,1:PRINT SPACES$(39);:LOCATE 23,1:PRINT SPACES$(39)
750 IF YINDEX(1)=-1 THEN XINDEX=1 ELSE XINDEX=2
760 LOCATE 23,1:PRINT SPACES$(39);:LOCATE 24,1:PRINT SPACES$(39);:
    LOCATE 24,25:PRINT " <S> - SELECT";
765 IF XINDEX=1 GOTO 530
766 IF XINDEX=2 GOTO 540
770 J8=J:A$=RIGHT$(A$,1):IF ASC(A$)=75 THEN J=J-1:GOTO 820
780 IF ASC(A$)=77 THEN J=J+1:GOTO 820
790 IF ASC(A$)=72 THEN J=J+10:GOTO 820
800 IF ASC(A$)=80 THEN J=J-10:GOTO 820
810 GOTO 610
820 IF J<1 THEN J=1
830 IF J>J1 THEN J=J1
840 LINE (PX,PY1)-(PX,PY2),0:IF J8=1 THEN LINE (PX,PY1)-
    (PX,PY2),3:GOTO 880
850 IF J8<6 THEN LINE (20,5)-(20,160),3
860 IF J8=J1 THEN LINE (PX,PY1)-(PX,PY2),3:GOTO 880
870 IF J8>(J1-6) THEN LINE (300,5)-(300,160),3
880 PSET (PX,PY),3:GOTO 550
890 SCREEN 2:SCREEN 0:SP$=SPACES$(79)
900 LOCATE 5,10:PRINT " SELECTION
    MATHEMATICAL FORMULA"
910 LOCATE 7,10:PRINT "      0                                Y = S*X +
    C (ZERO ORDER KINETICS)"
920 LOCATE 8,10:PRINT "      1                                ln (Y) =
    S*X + C (FIRST ORDER KINETICS)"
930 LOCATE 9,10:PRINT "      2                                1/Y = S*X
    + C (SECOND ORDER KINETICS)";
940 LOCATE 16,2 :INPUT "ENTER SELECTION OF MATHEMATICAL MODEL FOR
    WHICH DATA WILL BE CORRELATED ";S$
950 IF S$="" THEN 1000
960 IF S$="0" THEN CLS:GOTO 1010
970 IF S$="1" THEN CLS:GOTO 1010
980 IF S$="2" THEN CLS:GOTO 1010
990 GOTO 1000
1000 COLOR 4,7:LOCATE 20,10:PRINT "INCORRECT SELECTION, PLEASE
    TRY AGAIN";:COLOR 7,0:LOCATE 16,2:PRINT SP$;:GOTO 900
1010 COLOR 7,0:LOCATE 10,10:PRINT SP$:LOCATE 10,10:INPUT "SELECT
    r^2 coefficient (0 to 1)";R
1020 IF R>1 THEN GOTO 1050
1030 IF R<0 THEN GOTO 1050
1040 CLS:GOTO 1060
```

```
1050 COLOR 4,7:LOCATE 20,10:PRINT "INCORRECT RESPONSE, PLEASE TRY
AGAIN";:GOTO 1010
1060 COLOR 7,0:LOCATE 10,10:PRINT SP$:LOCATE 10,10:INPUT "Input
Decrement Interval (INTEGER)";DE
1070 IF DE<>INT(DE) THEN COLOR 4,7:LOCATE 20,10:PRINT "INCORRECT
RESPONSE, PLEASE TRY AGAIN";:GOTO 1060
1075 IF DE=0 THEN COLOR 4,7:LOCATE 20,10:PRINT "INCORRECT
RESPONSE, PLEASE TRY AGAIN";:GOTO 1060
1080 IF S$="0" THEN CLS:GOTO 1110
1090 IF S$="1" THEN CLS:GOTO 1940
1100 IF S$="2" THEN CLS:GOTO 2460
1110 N=YINDEX(1):N1=YINDEX(2)
1120 FOR I1=N TO N1:TX(I1)=X(I1):TY(I1)=Y(I1):NEXT I1:GOSUB 2980
1130 IF FLAG$="N" THEN 1820
1140 FOR J=N TO I
1150 TY(J)=SLOPE*X(J)+INTERCEPT:IF INFIN>TY(J) THEN TY(J)=INFIN
1160 IF YMIN>TY(J) THEN YMIN=TY(J)
1170 IF TY(J)>YMAX THEN YMAX=TY(J)
1180 NEXT J
1190 COL=3:J2=1:J1=I:GOSUB 3210
1200 FOR J=1 TO I:FY(J)=TY(J):NEXT J
1210 COL=1:J2=1:J1=I:GOSUB 3280
1220 LOCATE 25,1:PRINT "Press D when done viewing";
1230 A$=INKEY$:IF A$="" GOTO 1230
1240 IF A$="d" GOTO 1270
1250 IF A$="D" GOTO 1270
1260 GOTO 1230
1270 COLOR 7,0:CLS:SCREEN 2:SCREEN 0:LOCATE 10,10:INPUT "Do you
want to view the percentage differences";Y$
1280 IF Y$="Y" GOTO 1340
1290 IF Y$="y" GOTO 1340
1300 IF Y$="n" GOTO 1590
1310 IF Y$="N" GOTO 1590
1320 LOCATE 20,10:COLOR 4,7:PRINT "INCORRECT RESPONSE, PLEASE TRY
AGAIN";
1330 LOCATE 10,10:COLOR 0,0:PRINT SP$;:COLOR 7,0:GOTO 1270
1340 J9=1
1350 IF Y(1)=0 THEN J9=2:FY(1)=0
1360 YMIN=(Y(J9)-TY(J9))*100/Y(J9):YMAX=YMIN:FY(J9)=YMIN:J9=J9+1
1370 FOR J=J9 TO I
1380 IF Y(J)=0 THEN FY(J)=0:GOTO 1420
1390 FY(J)=(Y(J)-TY(J))*100/Y(J)
1400 IF FY(J)>YMAX THEN YMAX=FY(J):GOTO 1420
1410 IF YMIN>FY(J) THEN YMIN=FY(J)
1420 NEXT J
1430 COL=1:J2=1:J1=I:GOSUB 3210:YINCRE=(YMAX-YMIN)/4
1440 TEST=INSTR(1,STR$(YMIN),"E"):IF TEST=0 THEN TEST1$="" ELSE
TEST1$=RIGHT$(STR$(YMIN),LEN(STR$(YMIN))-TEST+1)
```

```
1450 V$=LEFT$(STR$(YMIN),2)+TEST1$:LOCATE 20,1:PRINT V$;
1460 V1=YMIN+YINCRE:TEST=INSTR(1,STR$(V1),"E"):IF TEST=0 THEN
    TEST1$="" ELSE TEST1$=RIGHT$(STR$(V1),LEN(STR$(V1))-TEST+1)
1470 V$=LEFT$(STR$(V1),2)+TEST1$:LOCATE 15,1:PRINT V$;
1480 V1=YMIN+YINCRE*2:TEST=INSTR(1,STR$(V1),"E"):IF TEST=0 THEN
    TEST1$="" ELSE TEST1$=RIGHT$(STR$(V1),LEN(STR$(V1))-TEST+1)
1490 V$=LEFT$(STR$(V1),2)+TEST1$:LOCATE 10,1:PRINT V$;
1500 V1=YMIN+YINCRE*3:TEST=INSTR(1,STR$(V1),"E"):IF TEST=0 THEN
    TEST1$="" ELSE TEST1$=RIGHT$(STR$(V1),LEN(STR$(V1))-TEST+1)
1510 V$=LEFT$(STR$(V1),3)+TEST1$:LOCATE 5,1:PRINT V$;
1520 V1=YMAX:TEST=INSTR(1,STR$(V1),"E"):IF TEST=0 THEN TEST1$=""
    ELSE TEST1$=RIGHT$(STR$(V1),LEN(STR$(V1))-TEST+1)
1530 V$=LEFT$(STR$(YMAX),2)+TEST1$:LOCATE 1,1:PRINT V$;:LOCATE
    25,1:PRINT "Press D when done viewing";
1540 A$=INKEY$:IF A$="" GOTO 1540
1550 IF A$="d" GOTO 1580
1560 IF A$="D" GOTO 1580
1570 GOTO 1540
1580 COLOR 7,0:CLS:SCREEN 2:SCREEN 0
1590 CLS:LOCATE 10,10:INPUT "Do you want a hard copy";Y$
1600 IF Y$="y" GOTO 1660
1610 IF Y$="Y" GOTO 1660
1620 IF Y$="n" GOTO 1820
1630 IF Y$="N" GOTO 1820
1640 COLOR 4,7:LOCATE 20,10:PRINT "INCORRECT RESPONSE, PLEASE TRY
    AGAIN";
1650 GOTO 1590
1660 FOR J8=1 TO 3:LPRINT "" :NEXT J8
1670 LPRINT ,,"Data File Name : ";FILES$
1680 LPRINT ""
1690 LPRINT ,,"Starting Data Point = ";N
1700 LPRINT ,,"Final Data Point = ";N1
1710 LPRINT ,,"Number of Data Point Fitted = ";W
1720 LPRINT ,,"Initial Y-value = ";Y(1)
1730 LPRINT ,,"Y-value at infinity = ";INFIN
1740 LPRINT ""
1750 LPRINT ""
1760 LPRINT ,,"Slope = ";SLOPE
1770 LPRINT ,,"y-intercept = ";INTERCEPT
1780 LPRINT ,,"r^2 coefficient = ";R2
1790 LPRINT ,,"chi-square = ";CHI
1800 LPRINT ,,"% of data fit = ";PERCENT
1810 FOR J8=18 TO 66:LPRINT "" :NEXT J8
1820 INPUT "Do you want to analyze another part of this data
    set";Y$
1830 IF Y$="y" GOTO 3355
1840 IF Y$="Y" GOTO 3355
1850 IF Y$="n" GOTO 1880
```

```
1860 IF Y$="N" GOTO 1880
1870 PRINT " ":GOTO 1820
1880 INPUT "Do you want to analyze another set of data";Y$
1890 IF Y$="y" GOTO 40
1900 IF Y$="Y" GOTO 40
1910 IF Y$="n" GOTO 4000
1920 IF Y$="N" GOTO 4000
1930 PRINT "" :GOTO 1880
1940 N=YINDEX(1):N1=YINDEX(2)
1950 FOR J=N TO N1:TY(J)=LOG((Y(1)-INFIN)/(Y(J)-INFIN)):
    TX(J)=X(J):NEXT J
1960 GOSUB 2980
1970 IF FLAG$="N" GOTO 1820
1980 YMIN=YMIN:XMIN=XMIN:YMAX=YMAX:XMAX=XMAX
1990 PRINT "" :LOCATE 24,10:INPUT "Do you want to view the linear
    ln correlation";Y$
2000 IF Y$="y" GOTO 2060
2010 IF Y$="Y" GOTO 2060
2020 IF Y$="n" GOTO 1590
2030 IF Y$="N" GOTO 1590
2040 COLOR 4,7:LOCATE 20,10:PRINT "INCORRECT RESPONSE, PLEASE TRY
    AGAIN";
2050 LOCATE 10,10 :PRINT SP$;:GOTO 1990
2060 XMIN=TX(N):XMAX=TX(N):YMIN=TY(N):YMAX=TY(N)
2070 FOR J=N TO N1:IF TX(J)>XMAX THEN XMAX=TX(J):GOTO 2090
2080 IF XMIN>TX(J) THEN XMIN=TX(J)
2090 IF TY(J)>YMAX THEN YMAX=TY(J):GOTO 2110
2100 IF YMIN>TY(J) THEN YMIN=TY(J)
2110 FX(J)=TX(J):FY(J)=TY(J):NEXT J
2120 FOR J=N TO N1:TY(J)=SLOPE*TX(J)+INTERCEPT
2130 IF TY(J)>YMAX THEN YMAX=TY(J):GOTO 2150
2140 IF YMIN>TY(J) THEN YMIN=TY(J)
2150 NEXT J
2160 J1=N1:J2=N:COL=3:GOSUB 3210
2170 FOR J=N TO N1:FY(J)=TY(J):NEXT J
2180 COL=1:J1=N1:J2=N:GOSUB 3280
2190 LOCATE 25,1:PRINT "Press D when done viewing";
2200 A$=INKEY$:IF A$="" GOTO 2200
2210 IF A$="D" THEN 2240
2220 IF A$="d" THEN 2240
2230 GOTO 2200
2240 COLOR 7,0:CLS:SCREEN 2:SCREEN 0
2250 LOCATE 10,10:INPUT "Do you want to see the exponential
    fit";Y$
2260 IF Y$="Y" GOTO 2320
2270 IF Y$="y" GOTO 2320
2280 IF Y$="n" GOTO 1590
2290 IF Y$="N" GOTO 1590
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2300 LOCATE 20,10:PRINT "INCORRECT RESPONSE, PLEASE TRY AGAIN";
2310 COLOR 0,0:LOCATE 10,10:PRINT SPC$;:COLOR 7,0 :GOTO 2250
2320 FOR J=1 TO I:FX(J)=X(J):FY(J)=Y(J):NEXT J
2330 XMIN=XMIN1:XMAX=XMAX1:YMIN=YMIN1:YMAX=YMAX1
2340 FOR J=1 TO I:TY(J)=(Y(1)-INFIN)*EXP(-SLOPE*X(J))+INFIN
2350 IF TY(J)>YMAX THEN YMAX=TY(J):GOTO 2370
2360 IF YMIN>TY(J) THEN YMIN=TY(J)
2370 NEXT J
2380 COL=3:J2=1:J1=I:GOSUB 3210
2390 FOR J=1 TO I:FY(J)=TY(J):NEXT J
2400 COL=1:GOSUB 3280
2410 LOCATE 25,1:PRINT "Press D when done viewing";
2420 A$=INKEY$:IF A$="" GOTO 2420
2430 IF A$="d" GOTO 1270
2440 IF A$="D" GOTO 1270
2450 GOTO 2420
2460 N=YINDEX(1):N1=YINDEX(2)
2470 FOR J=N TO N1:TY(J)=1/(Y(J)-INFIN):TX(J)=X(J):NEXT J
2480 GOSUB 2980
2490 IF FLAG$="N" GOTO 1820
2500 YMIN1=YMIN:XMIN1=XMIN:YMAX1=YMAX:XMAX1=XMAX
2510 PRINT ""':LOCATE 24,10:INPUT "Do you want to view the 1/Y vs
X correlation";Y$
2520 IF Y$="y" GOTO 2580
2530 IF Y$="Y" GOTO 2580
2540 IF Y$="n" GOTO 1590
2550 IF Y$="N" GOTO 1590
2560 COLOR 4,7:LOCATE 20,10:PRINT "INCORRECT RESPONSE, PLEASE TRY
AGAIN";
2570 LOCATE 10,10 :PRINT SP$;:GOTO 2510
2580 XMIN=TX(N):XMAX=TX(N):YMIN=TY(N):YMAX=TY(N)
2590 FOR J=N TO N1:IF TX(J)>XMAX THEN XMAX=TX(J):GOTO 2610
2600 IF XMIN>TX(J) THEN XMIN=TX(J)
2610 IF TY(J)>YMAX THEN YMAX=TY(J):GOTO 2630
2620 IF YMIN>TY(J) THEN YMIN=TY(J)
2630 FX(J)=TX(J):FY(J)=TY(J):NEXT J
2640 FOR J=N TO N1:TY(J)=SLOPE*TX(N)+INTERCEPT
2650 IF TY(J)>YMAX THEN YMAX=TY(J):GOTO 2670
2660 IF YMIN>TY(J) THEN YMIN=TY(J)
2670 NEXT J
2680 J1=N1:J2=N:COL=3:GOSUB 3210
2690 FOR J=N TO N1:FY(J)=TY(J):NEXT J
2700 COL=1:J1=N1:J2=N:GOSUB 3280
2710 LOCATE 25,1:PRINT "Press D when done viewing";
2720 A$=INKEY$:IF A$="" GOTO 2720
2730 IF A$="D" THEN 2760
2740 IF A$="d" THEN 2760
2750 GOTO 2720
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2760 COLOR 7,0:CLS:SCREEN 2:SCREEN 0
2770 LOCATE 10,10:INPUT "Do you want to see the X-Y fit";Y$
2780 IF Y$="Y" GOTO 2840
2790 IF Y$="y" GOTO 2840
2800 IF Y$="n" GOTO 1590
2810 IF Y$="N" GOTO 1590
2820 LOCATE 20,10:PRINT "INCORRECT RESPONSE, PLEASE TRY AGAIN";
2830 COLOR 0,0:LOCATE 10,10:PRINT SPC$;:COLOR 7,0 :GOTO 2770
2840 FOR J=1 TO I:FX(J)=X(J):FY(J)=Y(J):NEXT J
2850 XMIN=XMIN1:XMAX=XMAX1:YMIN=YMIN1:YMAX=YMAX1
2860 FOR J=1 TO I
2865 TY(J)=(Y(1)-INFIN)/((Y(1)-INFIN)*SLOPE*X(J)+1)+INFIN
2870 IF TY(J)>YMAX THEN YMAX=TY(J):GOTO 2890
2880 IF YMIN>TY(J) THEN YMIN=TY(J)
2890 NEXT J
2900 COL=3:J2=1:J1=I:GOSUB 3210
2910 FOR J=1 TO I:FY(J)=TY(J):NEXT J
2920 COL=1:GOSUB 3280
2930 LOCATE 25,1:PRINT "Press D when done viewing";
2940 A$=INKEY$:IF A$="" GOTO 2940
2950 IF A$="d" GOTO 1270
2960 IF A$="D" GOTO 1270
2970 GOTO 2940
2980 A1=0:A2=0:A3=0:A4=0:A5=0:A6=0:A7=0:FLAG$="":SLOPE=0:CHI=0:
R2=0:INTERCEPT=0:PERCENT=0
2990 FOR J=N TO N1
3000 A1=A1+TX(J)*TY(J):A2=A2+TX(J):A3=A3+TY(J):A6=A6+TX(J)^2:
A7=A7+TY(J)^2
3010 NEXT J
3020 A4=A2^2:A5=A3^2
3030 W=N1-N+1
3040 SLOPE=(A1-A2*A3/W)/(A6-A4/W):INTERCEPT=A3/W-SLOPE*A2/W
3050 R2=(A1-A2*A3/W)^2/((A6-A4/W)*(A7-A5/W))
3060 PRINT "":PRINT ""
3070 PRINT "Slope = ";SLOPE,"y-intercept = ";INTERCEPT,"St.# =
";N,"Fit # = ";W
3080 PRINT "Coefficient of Determination : r^2 = ";R2
3090 IF R2<R THEN N1=N1-DE:GOTO 3110
3100 GOTO 3130
3110 IF N1<1 THEN PRINT "There is no group of analysis with r^2>
";R:flag$="N":go to 2830
3120 GOTO 2980
3130 FOR J=N TO N1:IF TY(J)=0 GOTO 3150
3140 TEMP=SLOPE*TX(J)+INTERCEPT:CHI=((TY(J)-TEMP)^2)/TY(J))+CHI
3150 NEXT J
3160 Y18=ABS(Y(N)-INFIN):Y19=ABS(Y(N1)-INFIN):IF Y18>Y19 THEN
3180
3170 Y18=Y(N1)-Y(N):GOTO 3190
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3180 Y18=Y(N)-Y(N1)
3190 PERCENT=(Y18)*100/(Y20):PERCENT=ABS(PERCENT)
3200 RETURN
3210 CLS:SCREEN 1,0:COLOR 0,1:LINE (20,5)-(300,5):LINE (300,5)-
      (300,160):LINE (300,160)-(20,160):LINE (20,160)-(20,5)
3220 YMIN=YMIN-.1*ABS(YMIN):YMAX=YMAX+.06*ABS(YMAX)
3230 FOR J=J2 TO J1
3240 YINC=155/(YMAX-YMIN):XINC=280/(XMAX-XMIN)
3250 PY=160-(FY(J)-YMIN)*YINC:PX=20+(FX(J)-XMIN)*XINC
3260 PX=INT(PX):PY=INT(PY):PSET (PX,PY),COL:NEXT J
3270 RETURN
3280 FOR J=J2 TO J1-1
3290 PY=160-(FY(J)-YMIN)*YINC:PX=20+(FX(J)-XMIN)*XINC
3300 PY1=160-(FY(J+1)-YMIN)*YINC:PX1=20+(FX(J+1)-XMIN)*XINC
3310 LINE (PX,PY)-(PX1,PY1),COL
3320 NEXT J
3330 LOCATE 2,5:PRINT "SLOPE = ";SLOPE;:LOCATE 3,5:PRINT
      "Y-INTER. = ";INTERCEPT;:LOCATE 4,5:PRINT "R^2 COEFF. =
      ";R2;
3340 LOCATE 5,5:PRINT "% of data fit = ";PERCENT;:LOCATE
      6,5:PRINT "CHI^2 = ";CHI;
3350 RETURN
3355 CLS
3356 LOCATE 10,5:INPUT "Do you want to change the absorbance at
      infinity";Y$
3360 IF Y$="y" GOTO 140
3365 IF Y$="Y" GOTO 140
3370 IF Y$="n" GOTO 410
3380 IF Y$="N" GOTO 410
3390 LOCATE 20,5:PRINT "INCORRECT RESPONSE, PLEASE TRY
      AGAIN":GOTO 3356
4000 CLS:END
```