

# The catalytic and photocatalytic autoxidation of $S_x^{2-}$ to $SO_4^{2-}$ by water-soluble cobalt porphyrin

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## Abstract

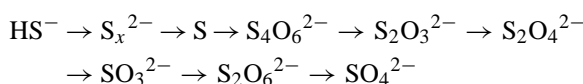
The catalytic and photocatalytic transformation of  $S_4^{2-}$ ,  $S_3^{2-}$ ,  $S_2^{2-}$  and  $S^{2-}$  to  $SO_4^{2-}$  by water-soluble cobalt tetrakis (*N*-methyl-4-pyridyl) porphyrin (Co(4-TMPyP)) was performed by a two-step process. The catalytic autoxidation of  $S_x^{2-}$  ( $x = 2, 3$  and 4) to  $S_2O_3^{2-}$  by Co(4-TMPyP) in the presence of oxygen was followed by the photocatalytic oxidation of  $S_2O_3^{2-}$  by Co(4-TMPyP) under illumination in presence of oxygen at a strong basic solution. The direct transformation of  $S_x^{2-}$  to  $SO_4^{2-}$  was also performed. The catalytic activity of Co(4-TMPyP) was compared to Fe(2-TMPyP) and Mn(4-TMPyP). All three catalysts have activity towards autoxidation of  $S_4^{2-}$  to  $S_2O_3^{2-}$ . The trend in photocatalytic oxidation activity of the porphyrin complexes is Co(4-TMPyP) > Fe(2-TMPyP) > Mn(4-TMPyP). The electrocatalytic reactions of  $S_x^{2-}$  by Co(4-TMPyP) were also observed. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Photocatalytic autoxidation; Polysulfide ions; Electrocatalytic reduction

## 1. Introduction

Sulfur transformation constitutes a significant part of the global sulfur cycle. Polysulfide ions ( $S_x^{2-}$ ,  $x > 1$ ) may cause from the incomplete oxidation of sulfide ( $HS^-$ ,  $H_2S$ ) in the catalyst Fe(III) presence [1,2], the transformation of polysulfide ions is in the bacterial processes and water in a redox boundary [1–3]. In general,  $HS^-$  is oxidized to elemental sulfur, but elemental sulfur can also react with  $HS^-$  to form polysulfide. The transformation of sulfur oxoanions ( $S_2O_3^{2-}$ ,  $S_4O_6^{2-}$ ,  $SO_3^{2-}$ ) and sulfide ( $HS^-$ ,  $S^{2-}$ ) is interesting to workers in chemistry and biology, and concerns the sulfur cycle [4–8]. The oxidation state of sulfur, polysulfides and sulfur oxoanions in order

of oxidation state from lower to higher is as follows:



Lower oxidation state sulfur compounds such as  $S_2O_3^{2-}$  and  $HS^-$  are oxidized to  $SO_4^{2-}$  by *Thiobacilli* and many enzymes [4–5].

We have reported in previous papers, the electrocatalytic reduction of –S–S– compounds (tetrathionate ( $(O_3SSSSO_3)^{2-}$ ), oxidized form of glutathione (GSSG), and L-cystine (CySSCy)) through  $Co^I$  and  $Fe^I$  species [9–14]. The cleavage of –S–S– bond to –S (thiosulfate ( $SSO_3^{2-}$ ), reduced form of glutathione (GSH), L-cysteine (CySH)) were catalyzed by cobalt porphyrins and iron porphyrins through Co(II/III)P, and Fe(III/IV)P redox couples. Some electrocatalytic

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oxidation concerning these redox couples were also reported [9–10,13–17].

Porphyrin complexes resemble phthalocyanines [18] as active parts in visible light-driven processes. These complexes exhibit many photochemical applications [19–21]. The photocatalytic reaction of porphyrin complexes [22,23] were previously reported.

Decomposition or photocatalytic oxidation of sulfite and sulfur oxoanions, and polysulfides ions have potential utility in solving the environmental pollution problem [24]. Some reports concerning  $\text{SO}_3^{2-}$  and  $\text{S}^{2-}$  photooxidation [25–26] and the photocatalytic autoxidation [18,27–28] have been studied.

In this paper, we discuss the catalytic autoxidation of  $\text{S}_x^{2-}$  ( $x = 1-4$ ) to  $\text{S}_2\text{O}_3^{2-}$  and  $\text{SO}_4^{2-}$  by Co(4-TMPyP) and the photocatalytic autoxidation of  $\text{S}_2\text{O}_3^{2-}$  to  $\text{SO}_4^{2-}$  under illumination with 419 nm light by the same catalyst in oxygen-saturated strong basic aqueous solution at room temperature. In the second part, we discuss the photocatalytic oxidation of  $\text{S}_x^{2-}$  by Co(4-TMPyP) directly in a strong basic solution. The catalytic properties of Co(4-TMPyP) are compared to those of Fe(2-TMPyP) and Mn(4-TMPyP). The electrocatalytic reactions of  $\text{S}_x^{2-}$  by Co(4-TMPyP) were also observed.

## 2. Experimental

Co(4-TMPyP) was prepared by refluxing  $\text{H}_2$ (4-TMPyP) with  $\text{CoCl}_2$  in distilled water for 10 h.  $[\text{Co}^{\text{III}}(4\text{-TMPyP})]^{5+}$  was precipitated by drops of saturated  $\text{NaClO}_4$  solution and recrystallized with water. The products were identified by their UV–VIS, IR and NMR spectra.

All of the chemicals were of analytical grade. Aqueous solutions were prepared with doubly-distilled deionized water. Solutions were deoxygenated by purging with pre-purified nitrogen gas. Buffer solutions were prepared from  $\text{H}_2\text{SO}_4$ , KHP, acetate, phosphate, borate, carbonate and KOH for the pH range 0–14.  $\text{Na}_2\text{S}_x$  was used for preparing solution of  $\text{S}_x^{2-}$ . The pH values were measured with a HANNA Model 8418 pH meter.

Electrochemical analyses were performed with a Bioanalytical system (West Lafayette, IN) Model CV-50W potentiostat and a BAS X-Y recorder. Cyclic voltammetry was conducted with the use of

a three-electrode cell in which a BAS glassy carbon electrode (area  $0.07\text{ cm}^2$ ) was used as the working electrode. The glassy carbon electrode was polished with  $0.05\text{ }\mu\text{m}$  alumina on Buehler felt pads, and ultrasonicated for 1 min. The auxiliary compartment contained a platinum wire which was separated by a medium-sized glass frit. All cell potentials were taken with the use of a Ag/AgCl/KCl (saturated KCl solution) reference electrode.

UV–VIS spectra were measured with a HITACHI Model U-3300 spectrophotometer.

Irradiation was carried out on 15 ml quartz sample tube containing  $\text{S}_x^{2-}$  and catalyst in buffer solution. The irradiation light was 419 nm 8 lamps (RPR-4190 A, 112 W) equipped with a Rayonet photochemical chamber reactor model RPR-100.

The ion chromatograph used in the experiments was a Dionex Instruments Ion chromatography DX-100 consisting of a pump, conductivity detector, an electrochemical detector and a syringe loading system with  $25\text{ }\mu\text{l}$  sample loop. The IC chromatograms were recorded using a Spectra-Physics DataJet computing intergrator. The columns used throughout were an IonPac AG4A guard column, an IonPac AS4A analytical column and a self-regenerating suppressor column. Typical LC operational parameters were as follows: mobile phase was a  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  buffer solution, mobile phase flow rate was  $2\text{ ml/min}$ ; the column temperature was at room temperature. These parameters were used analyzing sulfate, sulfite and thiosulfate.

Thiosulfate and  $\text{S}_2\text{O}_6^{2-}$  were analyzed by an MPIC-NG1 guard column, an MPIC-NS1 analytical column and a suppressor column.  $\text{S}^{2-}$  were analyzed by a PA1 guard column, a PA1 analytical column and an electrochemical detector. An ion selective electrode was also used in the experiments for measuring the concentration of  $\text{S}^{2-}$  in the solutions.

## 3. Results and discussion

### 3.1. The photocatalytic oxidation of $\text{S}_2\text{O}_3^{2-}$ to $\text{SO}_4^{2-}$ by Co(4-TMPyP)

The photocatalytic autoxidation of  $\text{S}_2\text{O}_3^{2-}$  to  $\text{SO}_4^{2-}$  by Co(4-TMPyP) was carried out under oxygen at pH 13.0. Fig. 1 shows the oxidation of  $\text{S}_2\text{O}_3^{2-}$  to

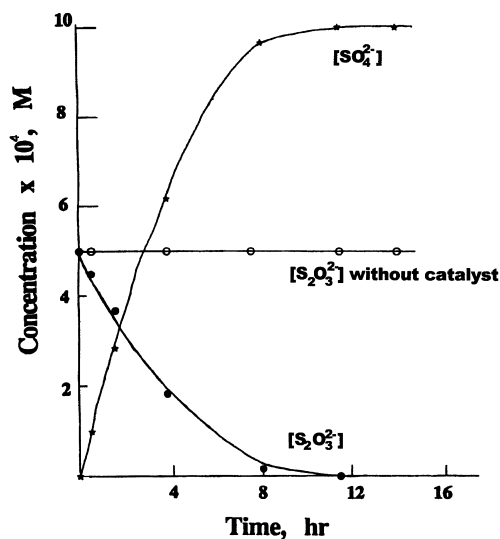


Fig. 1. Concentration of sulfur oxoanions vs. time under oxygen at pH 13.0 KOH solution using  $3 \times 10^{-5}$  M of Co(4-TMPyP) with initial  $[S_2O_3^{2-}] = 5 \times 10^{-4}$  M under illumination with 419 nm light: (●)  $[S_2O_3^{2-}]$ ; (★)  $[SO_4^{2-}]$ ; (○)  $[S_2O_3^{2-}]$  without catalyst.

$SO_4^{2-}$  in the presence and absence of Co(4-TMPyP) under illumination with a 419 nm monochromatic light. The half-life of the disappearance of  $S_2O_3^{2-}$  is about 3 h. This is the same as the  $t_{1/2}$  of  $SO_4^{2-}$  production. When  $S_2O_3^{2-}$  is illuminated in the absence of Co(4-TMPyP) with saturated oxygen, disappearance of  $S_2O_3^{2-}$  is very slow (○). When Co(4-TMPyP) ( $3 \times 10^{-5}$  M) is present, the initial rates of  $S_2O_3^{2-}$  disappearance and  $SO_4^{2-}$  production are  $2 \times 10^{-6}$  and  $4 \times 10^{-6}$  M/min, respectively.

The results show almost all  $S_2O_3^{2-}$  is transferred to  $SO_4^{2-}$  when in the presence of Co(4-TMPyP) with saturated oxygen for 12 h.

### 3.2. The catalytic autoxidation of $S_4^{2-}$ by Co(4-TMPyP) at different pH

The catalytic autoxidation of  $S_4^{2-}$  to  $S_2O_3^{2-}/SO_4^{2-}$  by Co(4-TMPyP) was performed under oxygen at different pH.  $Na_2S_4$  was used for making up solutions of  $S_4^{2-}$ . The buffer solutions used for pH 11.5, 12.2 and 13.0 were carbonate, carbonate + KOH and KOH, respectively. Fig. 2 shows that the catalytic autoxidation of  $S_4^{2-}$  to  $S_2O_3^{2-}$  (major product) and  $SO_4^{2-}$  (minor product) in the presence and

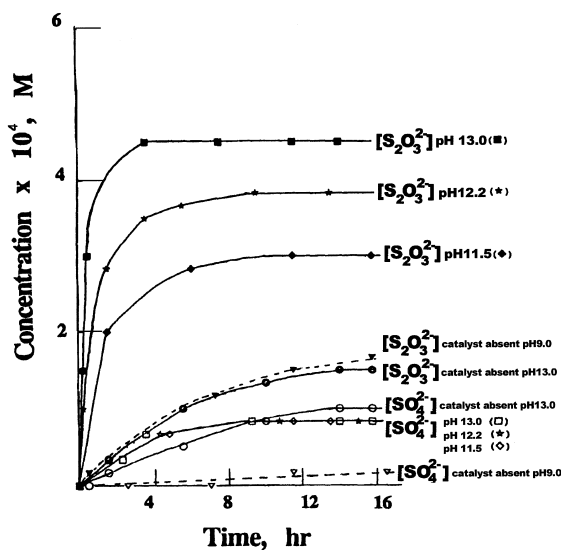


Fig. 2. Concentration of sulfur oxoanions vs. time under oxygen in various pH buffered solution using  $3 \times 10^{-5}$  M of Co(4-TMPyP) with initial  $[S_4^{2-}] = 2.5 \times 10^{-4}$  M without illumination. pH 9 (borate buffer); pH 11.5 (carbonate buffer); pH 12.2 (carbonate + KOH); pH 13.0 (KOH solution). (A) Co(4-TMPyP) present:  $[S_2O_3^{2-}]$  at pH 13.0 (■), pH 12.2 (★), pH 11.5 (◆);  $[SO_4^{2-}]$  at pH 13.0 (□), pH 12.2 (☆), pH 11.5 (◇). (B) Co(4-TMPyP) absent:  $[S_2O_3^{2-}]$  at pH 13.0 (□), pH 9.0 (▽);  $[SO_4^{2-}]$  at pH 13.0 (○), pH 9.0 (▽).

absence of Co(4-TMPyP) have a pronounced pH-dependence.

After 16 h, the percentage of  $S_4^{2-}$  transformed to  $S_2O_3^{2-}$  by Co(4-TMPyP) were 60, 78 and 90% at pH 11.5, 12.2 and 13.0, respectively.  $SO_4^{2-}$  is the minor product of  $S_4^{2-}$  autoxidation, and the percentage yield were all about 10% at pH 11.5, 12.2 and 13.0, respectively.

All  $S_4^{2-}$  is converted to  $S_2O_3^{2-}$  or  $SO_4^{2-}$  at pH 13, but the overall yield is significantly lower at lower pH. The remaining  $S_4^{2-}$  is oxidized to elemental sulfur ( $S_x$ ) at lower pH. The autoxidation of  $S_4^{2-}$  to  $S_2O_3^{2-}$  in the absence of Co(4-TMPyP) has lower percentage yield between pH 9 and 13.

### 3.3. The direct photocatalytic autoxidation of $S_4^{2-}$ by Co(4-TMPyP)

From the results of Figs. 1 and 2, we can combine the catalytic autoxidation of  $S_4^{2-}$  to  $S_2O_3^{2-}$  and the

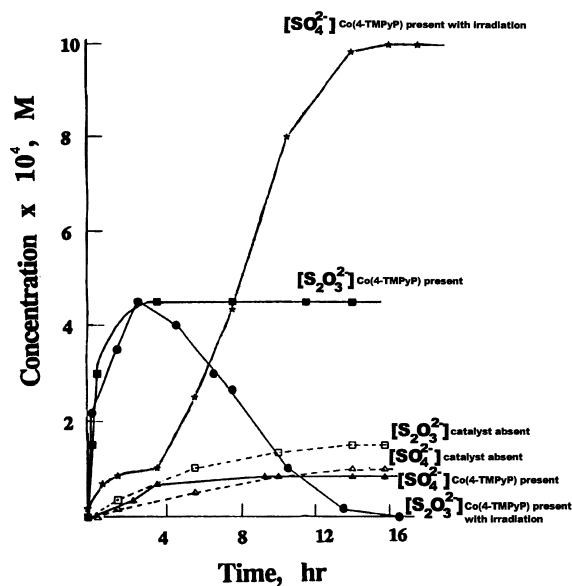


Fig. 3. Concentration of sulfur oxoanions vs. time under oxygen at pH 13.0 KOH solution using  $3 \times 10^{-5}$  M of Co(4-TMPyP).  $[S_4^{2-}] = 2.5 \times 10^{-4}$  M under illumination with 419 nm. (A) Co(4-TMPyP) present with illumination:  $[S_2O_3^{2-}]$  (●);  $[SO_4^{2-}]$  (★). (B) Co(4-TMPyP) present without illumination:  $[S_2O_3^{2-}]$  (■);  $[SO_4^{2-}]$  (▲). (C) Co(4-TMPyP) absent but with illumination:  $[S_2O_3^{2-}]$  (□);  $[SO_4^{2-}]$  (△).

photocatalytic autoxidation of  $S_2O_3^{2-}$  to  $SO_4^{2-}$  by the same catalyst Co(4-TMPyP).

The direct photocatalytic autoxidation of  $S_4^{2-}$  to  $SO_4^{2-}$  by Co(4-TMPyP) under illumination with 419 nm light was performed under oxygen at pH 13.0. Fig. 3 shows the photocatalytic autoxidation of  $S_4^{2-}$  to  $S_2O_3^{2-}$  (intermediate) and  $SO_4^{2-}$  (product) in the presence of Co(4-TMPyP).

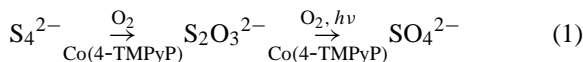
After 18 h, the results indicate that 90% of  $S_4^{2-}$  was transformed to  $S_2O_3^{2-}$  (■) and the rest to  $SO_4^{2-}$  (▲). When Co(4-TMPyP) catalyst is absent, only about 25% of  $S_4^{2-}$  was transformed to  $S_2O_3^{2-}$  (□).

After performing the experiment for 2 h, the concentration of  $S_2O_3^{2-}$  seems sufficient to allow for photocatalytic formation of  $SO_4^{2-}$ , but the concentration of  $SO_4^{2-}$  only begins to rise obviously after 4 h, when almost all of the  $S_4^{2-}$  has been converted. This is due to competition of  $S_4^{2-}$  for the catalyst. At lower pH, we would expect  $S_4^{2-}$  to be less competitive than  $S_2O_3^{2-}$  for the catalyst, because of the smaller rate

and yield of catalytic autoxidation of  $S_4^{2-}$  to  $S_2O_3^{2-}$  at lower pH.

After 16 h, almost all  $S_2O_3^{2-}$  (produced from  $S_4^{2-}$ ) were transformed to  $SO_4^{2-}$ .

The reaction processes can be expressed as follows:



### 3.4. The two-step catalytic and photocatalytic autoxidation of $S_x^{2-}$ ( $x = 2, 3, 4$ ) by Co(4-TMPyP) at pH 13.0

Fig. 4 shows the catalytic autoxidation of  $S_x^{2-}$  ( $x = 2, 3, 4$ ) by Co(4-TMPyP) without illumination performed for 8 h and followed by the photocatalytic autoxidation with illumination for 12 h under oxygen at pH 13.0.  $Na_2S_x$  was used for making solutions of  $S_x^{2-}$ . Although, the ionic strength was different for  $S_2^{2-}$ ,  $S_3^{2-}$  and  $S_4^{2-}$ , it does not have a significant effect on the catalytic autoxidation of  $S_2O_3^{2-}$ . The

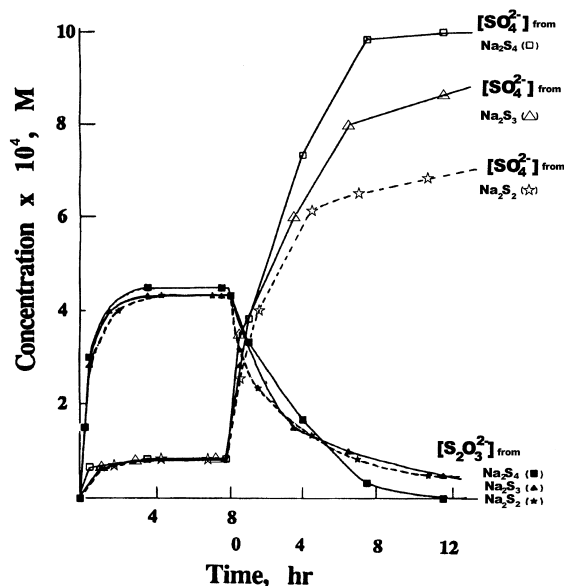


Fig. 4. Concentration of sulfur oxoanions vs. time under oxygen at pH 13.0 KOH solution using  $3 \times 10^{-5}$  M of Co(4-TMPyP) with various  $S_x^{2-}$  without illumination for 8 h, then with illumination for 12 h. (A)  $[S_4^{2-}] = 2.5 \times 10^{-4}$  M:  $[S_2O_3^{2-}]$  (■);  $[SO_4^{2-}]$  (□). (B)  $[S_3^{2-}] = 3.3 \times 10^{-4}$  M:  $[S_2O_3^{2-}]$  (▲);  $[SO_4^{2-}]$  (△). (C)  $[S_2^{2-}] = 5.0 \times 10^{-4}$  M:  $[S_2O_3^{2-}]$  (★);  $[SO_4^{2-}]$  (☆).

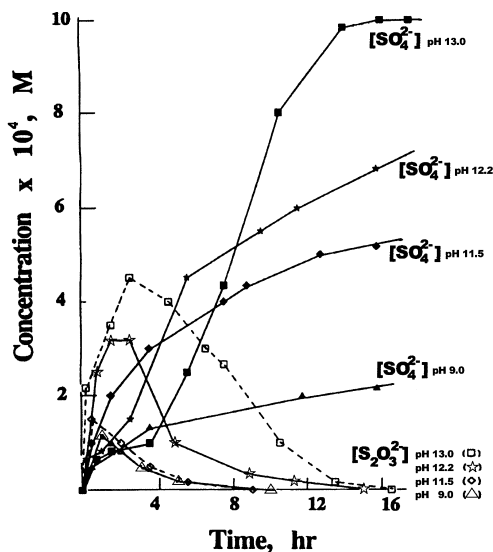


Fig. 5. Concentration of sulfur oxoanions vs. time under oxygen in various pH buffered solution using  $3 \times 10^{-5}$  M of Co(4-TMPyP) with initial  $[S_4^{2-}] = 2.5 \times 10^{-4}$  M with illumination.  $[S_2O_3^{2-}]$  at pH 13.0 ( $\square$ ); pH 12.2 ( $\star$ ); pH 11.5 ( $\diamond$ ); pH 9.0 ( $\triangle$ ).  $[SO_4^{2-}]$  at pH 13.0 ( $\blacksquare$ ); pH 12.2 ( $\blackstar$ ); pH 11.5 ( $\blacklozenge$ ); pH 9.0 ( $\blacktriangle$ ). pH 9 (borate buffer); pH 11.5 (carbonate buffer); pH 12.2 (carbonate + KOH); pH 13.0 (KOH solution).

results show that almost 80–90% of  $S_x^{2-}$  changed to  $S_2O_3^{2-}$  in the first stage, and minor product is  $SO_4^{2-}$ .

The second step involves the photocatalytic autoxidation of  $S_2O_3^{2-}$  to  $SO_4^{2-}$  by Co(4-TMPyP). The data indicate that the percentage of  $S_x^{2-}$  transformed to  $SO_4^{2-}$  in two steps were 70, 85 and 98% from  $S_2^{2-}$ ,  $S_3^{2-}$  and  $S_4^{2-}$ , respectively, after illuminated for 12 h.

### 3.5. The direct photocatalytic autoxidation of $S_x^{2-}$ by Co(4-TMPyP) at different pH

The direct photocatalytic autoxidation of  $S_4^{2-}$  to  $SO_4^{2-}$  by Co(4-TMPyP) was performed under oxygen at different pH. Fig. 5 shows the direct photocatalytic autoxidation of  $S_4^{2-}$  to  $SO_4^{2-}$  in the presence and absence of Co(4-TMPyP) under illumination.

After 18 h, the percentage of  $S_4^{2-}$  transformed to  $SO_4^{2-}$  were 20, 55, 70 and 100% at pH 9.0 ( $\blacktriangle$ ), 11.5 ( $\blacklozenge$ ), 12.2 ( $\blackstar$ ), 13.0 ( $\blacksquare$ ), respectively.  $S_2^{2-}$  and  $S_3^{2-}$  also show a similar trend.

A higher percentage yield of  $SO_4^{2-}$  is observed at higher pH of aqueous solution.

### 3.6. The two-step catalytic and photocatalytic autoxidation of $S_x^{2-}$ ( $x = 2, 3, 4$ ) by different catalysts at pH 13.0

Fig. 6 shows the catalytic autoxidation of  $S_x^{2-}$  by Fe(2-TMPyP), Mn(4-TMPyP) and Co(4-TMPyP) performed without illumination for 8 h followed by photocatalytic autoxidation with illumination for 12 h in the presence of oxygen at pH 13.0 under a 419 nm light.

The results show that Fe(2-TMPyP), Mn(4-TMPyP) and Co(4-TMPyP) catalyzes the reaction of  $S_4^{2-}$  with different rates. The results also show a similar percentage transformation of  $S_x^{2-}$  to  $SO_4^{2-}$  in the first 8 h, and the decrease of  $S_2O_3^{2-}$  and the rise of  $SO_4^{2-}$  concentration after 8 h.

Some intermediates may exist in the reaction process as deduced from the species concentration calculation. The final yield of  $SO_4^{2-}$  does not equal the

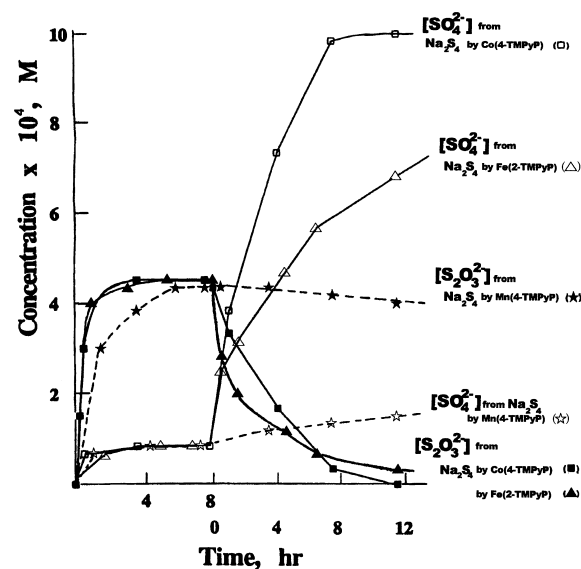


Fig. 6. Concentration of sulfur oxoanions vs. time under oxygen at pH 13.0 KOH solution using  $3 \times 10^{-5}$  M of various catalysts  $[S_4^{2-}] = 2.5 \times 10^{-4}$  M without illumination for 8 h, then with illumination for 12 h. (A) Co(4-TMPyP) present: ( $\blacksquare$ )  $[S_2O_3^{2-}]$ ; ( $\square$ )  $[SO_4^{2-}]$ . (B) Fe(2-TMPyP) present: ( $\blacktriangle$ )  $[S_2O_3^{2-}]$ ; ( $\triangle$ )  $[SO_4^{2-}]$ . (C) Mn(4-TMPyP) present: ( $\blackstar$ )  $[S_2O_3^{2-}]$ ; ( $\star$ )  $[SO_4^{2-}]$ .

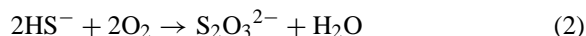
quantitative summation of  $[\text{SO}_4^{2-}] + 2[\text{S}_2\text{O}_3^{2-}]$  in the photocatalytic autoxidation process. So other intermediates may be present in the photocatalytic processes. This is valid for all the three catalysts.

The trend in photocatalytic oxidation activity of the porphyrin complexes is  $\text{Co}(4\text{-TMPyP}) > \text{Fe}(2\text{-TMPyP}) > \text{Mn}(4\text{-TMPyP})$ . After 12 h illumination, the percentage of  $\text{SO}_4^{2-}$  yield from  $\text{S}_4^{2-}$  is 100, 75 and 15% by  $\text{Co}(4\text{-TMPyP})$ ,  $\text{Fe}(2\text{-TMPyP})$  and  $\text{Mn}(4\text{-TMPyP})$ , respectively.

### 3.7. The two-step autoxidation and photocatalytic autoxidation of $\text{HS}^-$

Table 1 summarizes that the two-step autoxidation and photocatalytic autoxidation of  $\text{HS}^-$  to  $\text{SO}_4^{2-}$ . The first step involves autoxidation in the presence of oxygen without illumination and catalyst, and the second step involves the photocatalytic autoxidation in the presence of oxygen and  $\text{Co}(4\text{-TMPyP})$  catalyst.

The autoxidation of  $\text{HS}^-$  to  $\text{S}_2\text{O}_3^{2-}$  was performed for 30 min.  $\text{HS}^-$  is oxidized to  $\text{S}_2\text{O}_3^{2-}$  according the following equation:



Following the autoxidation of  $\text{HS}^-$ , the photocatalytic autoxidation was performed for 12 h. Almost all  $\text{S}_2\text{O}_3^{2-}$  is oxidized to  $\text{SO}_4^{2-}$  (Table 1).

Table 1

The transformation of  $\text{HS}^-$  to  $\text{SO}_4^{2-}$  by a two-step process at pH 13.0

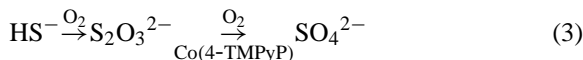
Time (min)	$\text{S}_2\text{O}_3^{2-}$ (M) <sup>a</sup>	$\text{SO}_4^{2-}$ (M)
Non-catalytic oxidation <sup>b</sup>		
0	0	0
30	$3.8 \times 10^{-4}$	0
Photocatalytic oxidation by $\text{Co}(4\text{-TMPyP})$ <sup>c</sup>		
0	$3.8 \times 10^{-4}$	$4 \times 10^{-5}$
30	$3.4 \times 10^{-4}$	$1.1 \times 10^{-4}$
120	$2.1 \times 10^{-4}$	$3.8 \times 10^{-4}$
240	$1.3 \times 10^{-4}$	$5.3 \times 10^{-4}$
480	$2 \times 10^{-5}$	$7.5 \times 10^{-4}$
720	0	$8.0 \times 10^{-4}$

<sup>a</sup> More than 75% of  $\text{HS}^-$  is transformed to  $\text{S}_2\text{O}_3^{2-}$ .

<sup>b</sup>  $[\text{HS}^-] = 10^{-3}$  M, pH 13.0.

<sup>c</sup>  $[\text{HS}^-] = 10^{-3}$  M, pH 13.0, but adding  $[\text{Co}(4\text{-TMPyP})] = 3 \times 10^{-5}$  M, and then irradiation by 419 nm light.

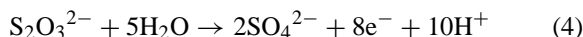
$\text{HS}^-$  is transformed to  $\text{SO}_4^{2-}$  by a two-step process of autoxidation and photocatalytic autoxidation.



### 3.8. The electrocatalytic properties of $\text{S}_x^{2-}$ by $\text{Co}(4\text{-TMPyP})$

The absorption spectra of  $\text{Co}(4\text{-TMPyP})$  between pH 6 and 14 are shown in Fig. 7.  $\text{Co}(4\text{-TMPyP})$  shows absorbance at 419 nm between pH 6 and 14. The Soret band of  $\text{Co}(4\text{-TMPyP})$  is at 435 and 443 nm in pH 6.5 and 13.5, respectively.

If the photocatalytic autoxidation of  $\text{S}_2\text{O}_3^{2-}$  is through an electron transfer process, an increase in pH will favor the reaction  $\text{S}_2\text{O}_3^{2-}$  to  $\text{SO}_4^{2-}$ .



The absorption spectrum of  $\text{Co}(4\text{-TMPyP})$  in various pH aqueous solutions are shown in Fig. 7. The Soret band of  $\text{Co}(4\text{-TMPyP})$  is 443 and 435 nm, at pH 13.5 and 6.5, respectively. It shows that the molar absorption of  $\text{Co}(4\text{-TMPyP})$  at 419 nm increases as the pH values of the aqueous solution decreases. But the rate of the photocatalytic autoxidation increases as the pH values of the aqueous solution increases. The photocatalytic autoxidation reaction rate behaves abnormally, because the effect of pH

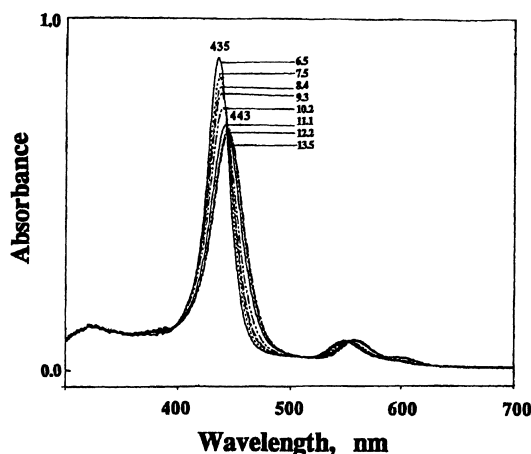


Fig. 7. Absorption spectra of  $4.5 \times 10^{-6}$  M  $\text{Co}^{\text{III}}(4\text{-TMPyP})$  at various pH aqueous solutions. Path length = 1.0 cm.

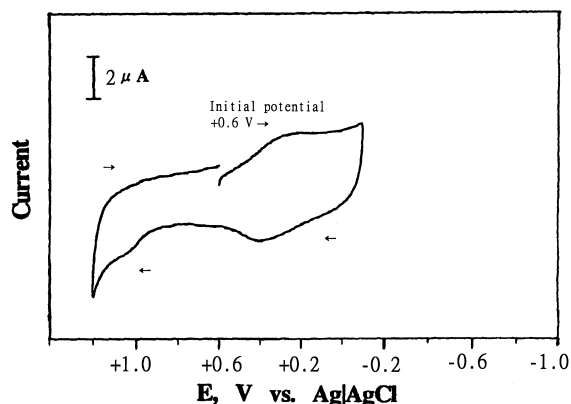


Fig. 8. Cyclic voltammograms of  $3 \times 10^{-4}$  M Co(4-TMPyP) in a pH 1.5 buffered solution. Scan rate 0.1 V/s.

is greater than the effect of shift in the molar absorption of Co(4-TMPyP). The effect of pH is more significant on the oxidation of  $S_2O_3^{2-}$  to  $SO_4^{2-}$  by Co(4-TMPyP) in the presence of oxygen due to the reaction involving proton transfer. Both the catalysts Fe(2-TMPyP) and Mn(4-TMPyP) have similar trend.

Fig. 8 shows the cyclic voltammograms of Co(4-TMPyP) at a pH 1.5 buffered solution. The cyclic voltammogram of Co(4-TMPyP) is similar to FeTSPP (a reversible redox couple of M(III/II) at pH 1.5) at the same pH buffer solution [12]. There is a reversible reduction wave of the Co(III/II)(4-TMPyP) (with a  $E^{0'}$  at about +0.3 V) (versus Ag|AgCl). The spectroelectrochemistry for the reduction of Co(III)(4-TMPyP) was performed at pH 1.5 (Fig. 9). Absorption spectra of Co<sup>III</sup>(4-TMPyP) at pH 1.5 aqueous solution in various potentials (versus Ag|AgCl). Fig. 9A shows the absorption spectra change for  $E_{\text{appl}}$  from -0.1 to +0.6 V. The Soret band at 436 nm shifts to 429 nm. Some isosbestic points are present.

The potential from +0.6 to +1.15 V show decreasing absorbance. There are no new Soret band and isosbestic points. Interesting absorption spectra can be observed for applied potential from +1.2 to +0.6 V (Fig. 9B). This is the porphyrin ring oxidation of the  $[\text{Co(III)(4-TMPyP)}]/[\text{Co(III)(4-TMPyP)}^+]$  redox couple.

Fig. 10 shows the cyclic voltammograms of Co(4-TMPyP) at a pH 13 buffer solution. The cyclic voltammogram of Co(4-TMPyP) is similar to FeTSPP, a reversible redox couple of M(II/I), an irreversible

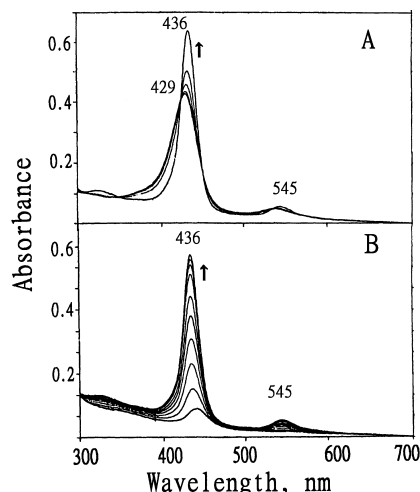


Fig. 9. Absorption spectra of  $3 \times 10^{-5}$  M Co<sup>III</sup>(4-TMPyP) at pH 1.5 aqueous solution with various applied potentials (vs. Ag|AgCl).  $E_{\text{appl}}$ : (A) -0.1 to +0.6 V; (B) +1.15 to +0.6 V. Path length = 0.1 cm.

reduction wave and an irreversible oxidation wave of M(III/II) at the same pH buffer solution [12]. There is an irreversible reduction wave of Co(III)(4-TMPyP) (with a  $E_{\text{pc}}$  at about -0.45 V) (versus Ag|AgCl).

The spectroelectrochemistry for the reduction of Co(III)(4-TMPyP) was performed at pH 13.0 (Fig. 11). Absorption spectra of Co<sup>III</sup>(4-TMPyP) at pH 13.0 aqueous solution at various potentials (ver-

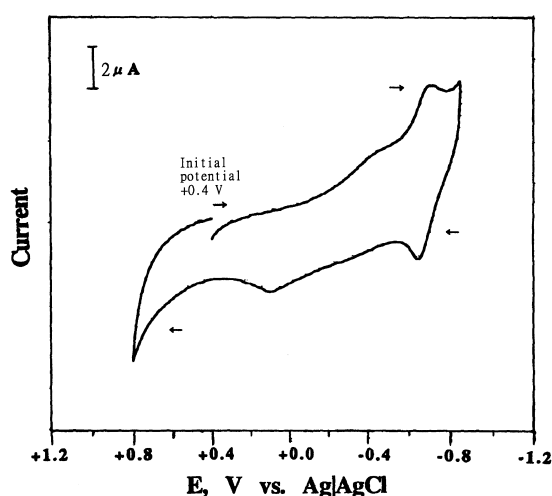


Fig. 10. Cyclic voltammograms of  $3 \times 10^{-4}$  M Co(4-TMPyP) at pH 13.0 buffered solution. Scan rate 0.1 V/s.

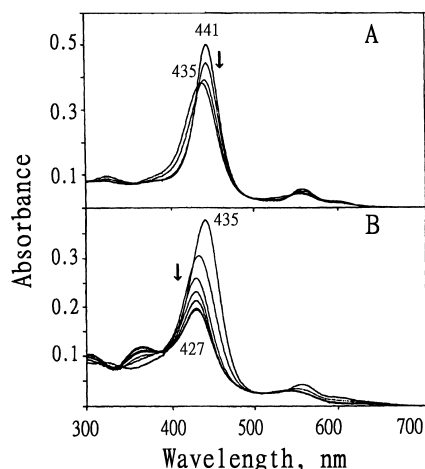


Fig. 11. Absorption spectra of  $3 \times 10^{-5}$  M  $\text{Co}^{\text{III}}(4\text{-TMPyP})$  at pH 13.0 aqueous solution with various applied potentials (vs.  $\text{Ag}|\text{AgCl}$ ).  $E_{\text{appl}}$ : (A) +0.4 to  $-0.55$  V; (B)  $-0.55$  to  $-0.8$  V. Path length = 0.1 cm.

vs.  $\text{Ag}|\text{AgCl}$ ) was observed. Fig. 11A shows the absorption spectra for  $E_{\text{appl}}$  from +0.4 to  $-0.55$  V. The Soret band at 441 nm shifts to 435 nm, and some isosbestic points are present. When we applied the potential from  $-0.55$  to  $-0.80$  V, the absorption spectra also show isosbestic points and new absorption peaks (Fig. 11B) (Table 2).

Fig. 10 shows that the  $\text{Co}^{\text{II/I}}(4\text{-TMPyP})$  redox couple [9] has a formal potential  $E^{0'} = -0.65$  V (versus  $\text{Ag}|\text{AgCl}$ ), and the reduction peak of the  $\text{Co}^{\text{III/II}}$  has a peak potential  $E_{\text{Pc}} = -0.45$  V and  $E_{\text{Pa}} = +0.1$  V (versus  $\text{Ag}|\text{AgCl}$ ), respectively.

Fig. 12A–C show the cyclic voltammograms of  $\text{Co}(4\text{-TMPyP})$  in a pH 13.0 buffered solution using samples of  $\text{S}_2^{2-}$ ,  $\text{S}_3^{2-}$  and  $\text{S}_4^{2-}$  in various concentrations, respectively. The cathodic peak current of the  $\text{Co}^{\text{II/I}}(4\text{-TMPyP})$  redox couple develop a peak before this redox couple ( $\text{Co}^{\text{III}}$ ) reduction wave) increases noticeably.

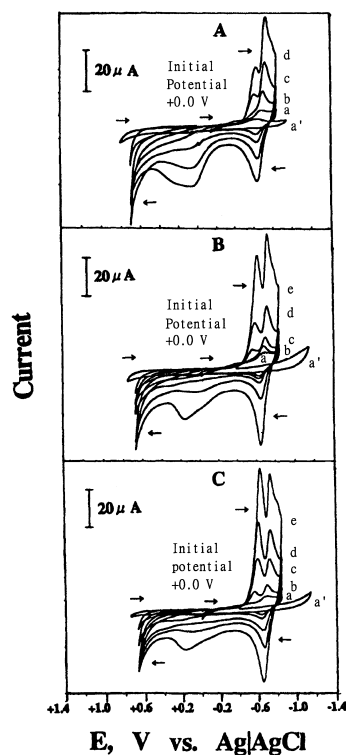


Fig. 12. Cyclic voltammograms of  $3 \times 10^{-4}$  M  $\text{Co}^{\text{III}}(4\text{-TMPyP})$  at pH 13.0 in the presence of different  $\text{S}_x^{2-}$  concentrations. (A)  $[\text{S}_4^{2-}]$ : (a) 0.0 M; (b)  $4 \times 10^{-4}$  M; (c)  $8 \times 10^{-4}$  M; (d)  $1.2 \times 10^{-3}$  M; (a') only  $1.2 \times 10^{-3}$  M  $\text{S}_4^{2-}$ ; scan rate = 0.1 V/s. (B)  $[\text{S}_3^{2-}]$ : (a) 0.0 M; (b)  $4 \times 10^{-4}$  M; (c)  $8 \times 10^{-4}$  M; (d)  $1.2 \times 10^{-3}$  M; (e)  $1.6 \times 10^{-3}$  M; (a') only  $1.6 \times 10^{-3}$  M  $\text{S}_3^{2-}$ ; scan rate = 0.1 V/s. (C)  $[\text{S}_2^{2-}]$ : (a) 0.0 M; (b)  $4 \times 10^{-4}$  M; (c)  $8 \times 10^{-4}$  M; (d)  $1.2 \times 10^{-3}$  M; (e)  $1.6 \times 10^{-3}$  M; (a') only  $1.6 \times 10^{-3}$  M  $\text{S}_2^{2-}$ ; scan rate = 0.1 V/s.

When the electrocatalytic reduction of  $\text{S}_4^{2-}$  (or  $\text{S}_3^{2-}$ ,  $\text{S}_2^{2-}$ ) through  $\text{Co}^{\text{I}}(4\text{-TMPyP})$  is performed, polysulfide or disulfide are reduced [9]. There are two continuous reduction wave appearance and  $\text{S}_2^{2-}$  (or  $\text{S}^{2-}$ ,  $\text{S}_3^{2-}$ ) are produced, and the electrocatalytic oxidation current increases. It is interesting that both the second reduction cathodic current and the anodic

Table 2

The cyclic voltammogram data of  $\text{Co}(4\text{-TMPyP})$  and  $\text{FeTSPP}$  at pH 13

Porphyrin	$E_{\text{Pc}}$ [M(III/II)P] (V)	$E^{0'}$ [M(II/I)P] (V)	$E_{\text{Pa}}$ [M(II/III)P] (V)
FeTSPP	$-0.95^{\text{a}}$	$-1.15$	$-0.5$
$\text{Co}(4\text{-TMPyP})$	$-0.45$	$-0.65$	$+0.1$

<sup>a</sup> The  $\mu$ -oxo-dimer reduction wave.



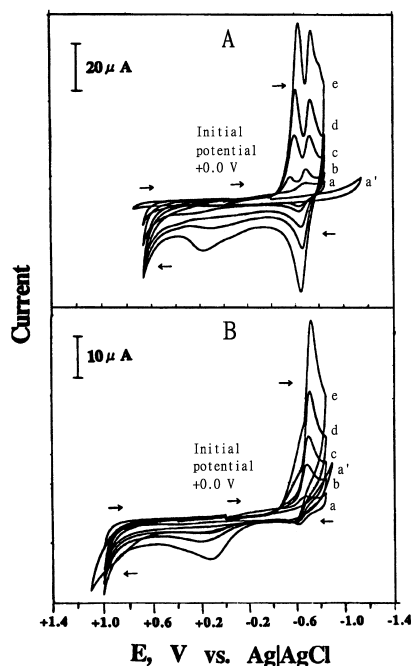
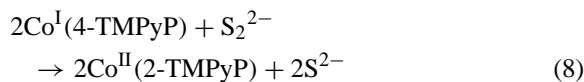
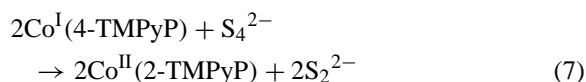
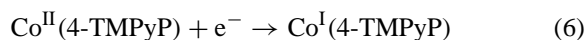
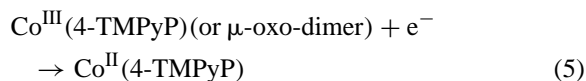


Fig. 13. Cyclic voltammograms of  $3 \times 10^{-4}$  M  $\text{Co}^{\text{III}}(4\text{-TMPyP})$  in various pH buffer in the presence of different  $\text{S}_4^{2-}$  concentrations. (A) pH 13.0: (a) 0.0 M; (b)  $2.0 \times 10^{-4}$  M; (c)  $9 \times 10^{-4}$  M; (d)  $1.4 \times 10^{-3}$  M; (e)  $1.8 \times 10^{-3}$  M; (f)  $2.2 \times 10^{-3}$  M; (a') only  $2.2 \times 10^{-3}$  M  $\text{S}_4^{2-}$ ; scan rate = 0.1 V/s. (B) pH 9.0: (a) 0.0 M; (b)  $4.5 \times 10^{-4}$  M; (c)  $9 \times 10^{-4}$  M; (d)  $1.4 \times 10^{-3}$  M; (e)  $1.8 \times 10^{-3}$  M; (f)  $2.2 \times 10^{-3}$  M; (a') only  $2.2 \times 10^{-3}$  M  $\text{S}_4^{2-}$ ; scan rate = 0.1 V/s.

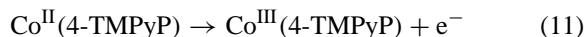
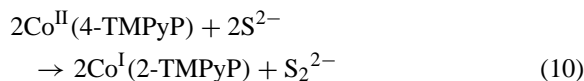
current are increasing. The phenomena may be due to the fact that the reduction product is easily reoxidized in the close potential and also electrocatalytic oxidation through  $\text{Co}^{\text{I}}(4\text{-TMPyP})$  species (Fig. 12), but this phenomena is not obvious in lower basic aqueous solution (Fig. 13). The first electrocatalytic reduction is not obvious in the lower basic aqueous solution.

According to the experimental results, the electrocatalytic reduction process of  $\text{S}_4^{2-}$  through a  $\text{Co}^{\text{I}}(2\text{-TMPyP})$  species is proposed as follows:

(A) negative scan



(B) positive scan after negative scan



The electrocatalytic oxidation of polysulfide ions were also active with  $E_{\text{Pa}}$  close +0.2 V (versus  $\text{Ag}|\text{AgCl}$ ).

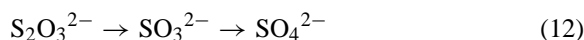
### 3.9. Discussion of the photocatalytic autoxidation processes

Product analysis by ion chromatography identified  $\text{S}_2\text{O}_3^{2-}$  and  $\text{SO}_4^{2-}$  as the products of catalytic autoxidation of  $\text{S}_x^{2-}$  by  $\text{Co}(4\text{-TMPyP})$  and the other catalysts.  $\text{SO}_4^{2-}$  was also identified as the product of the combined reactions of photocatalytic autoxidation and catalytic autoxidation of  $\text{S}_x^{2-}$ .

We have reported in previous papers, the electrocatalytic reduction of tetrathionate ( $(\text{O}_3\text{SSSSO}_3)^{2-}$ ), oxidized form of glutathione (GSSG) and L-cysteine (CySSCy) through  $\text{Co}^{\text{I}}$  and  $\text{Fe}^{\text{I}}$  species [9–14]. The electrocatalytic reduction involves cleavage of the  $-\text{S}-\text{S}-$  bond, and reduced it to  $-\text{S}$  (to form thiosulfate ( $\text{SSO}_3^{2-}$ ), reduced form of glutathione (GSH) and L-cysteine (CySH)).

The oxidation of  $\text{S}_x^{2-}$  to  $\text{S}_2\text{O}_3^{2-}$  may include cleavage of  $-\text{S}-\text{S}-$  bond of  $\text{S}_4^{2-}$  in a strong basic aqueous solution with oxygen.

The photocatalytic autoxidation proceeds through three steps.



We have recently shown that the electrocatalytic oxidation of  $\text{S}_2\text{O}_3^{2-}$  and  $\text{S}_4\text{O}_6^{2-}$  by cobalt porphyrin [9] is through the  $\text{Co}^{\text{III}}\text{P}$  species with obvious activity. The electrocatalytic oxidation of  $\text{S}_2\text{O}_3^{2-}$  is not very active by  $\text{Fe}(2\text{-TMPyP})$  and  $\text{Mn}(4\text{-TMPyP})$  in the cyclic voltammetry time scale. The electrocatalytic reaction results are also consistent with the photocatalytic decomposition rate of  $\text{S}_2\text{O}_3^{2-}$ .

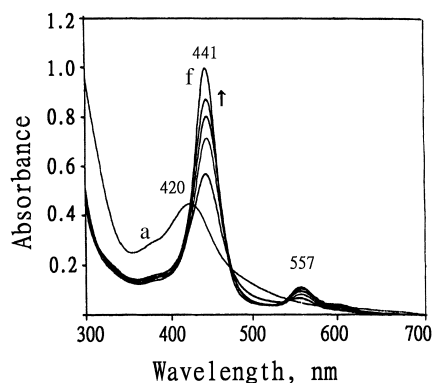


Fig. 14. Absorption spectra of  $5 \times 10^{-5}$  M  $\text{Co}^{\text{III}}(4\text{-TMPyP})$  at pH 13.0 aqueous solution (a) after  $1.0 \times 10^{-4}$  M  $\text{Na}_2\text{S}_4$  is added in the absence of oxygen, and then (b)–(f) exposed to air. Path length = 0.1 cm. The sample was exposed to air for 3 min interval before each spectrum was taken.

When  $\text{S}_2\text{O}_3^{2-}$  is transferred to  $\text{SO}_3^{2-}$ , then catalytic autoxidation of  $\text{SO}_3^{2-}$  by porphyrin complexes is easy in the presence of oxygen [10,29].

About 70% of  $\text{Co}(4\text{-TMPyP})$  survived after 8 h of catalytic autoxidation and 12 h of photocatalytic autoxidation in the presence oxygen and illumination with 419 nm light.

Fig. 14 shows the absorption spectra for the catalytic autoxidation by  $\text{Co}(4\text{-TMPyP})$  without illumination after  $1 \times 10^{-4}$  M  $\text{Na}_2\text{S}_4$  is added in the absence of oxygen (Fig. 14(a)) and then exposed to air (oxygen) for 3 h. The results show that  $\text{Co}(\text{III})(4\text{-TMPyP})$  is reduced by  $\text{Na}_2\text{S}_4$ , then reoxidized and returned to  $\text{Co}(\text{III})(4\text{-TMPyP})$  with higher percentage remaining when exposed to oxygen.

#### 4. Conclusion

The results presented in this study have shown that  $\text{S}_x^{2-}$  ( $x = 1\text{--}4$ ) can be transformed to  $\text{SO}_4^{2-}$  by the catalyst  $\text{Co}(4\text{-TMPyP})$  in a strong basic aqueous solution.

The transformation of  $\text{S}_2\text{O}_3^{2-}$  to  $\text{SO}_4^{2-}$  by  $\text{Co}(4\text{-TMPyP})$  can be achieved by photocatalytic autoxidation in a basic aqueous solution.

$\text{S}_x^{2-}$  was transformed to  $\text{SO}_4^{2-}$  following a two-step process. The first step involves the catalytic autoxidation of  $\text{S}_x^{2-}$  to  $\text{S}_2\text{O}_3^{2-}$ , and the second step

involves the photocatalytic oxidation of  $\text{S}_2\text{O}_3^{2-}$  to  $\text{SO}_4^{2-}$ .

$\text{HS}^-$  can be transformed to  $\text{SO}_4^{2-}$  in two steps, including a chemical process employing  $\text{O}_2$  in the solution and followed by the photocatalytic autoxidation of  $\text{S}_2\text{O}_3^{2-}$  to  $\text{SO}_4^{2-}$ .

The percentage yield of  $\text{SO}_4^{2-}$  is dependent on the amount of  $\text{S}_x^{2-}$  changed to  $\text{S}_2\text{O}_3^{2-}$  at different pH and in the presence of different catalysts.

#### Acknowledgements

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#### References

- [1] R.J. Huxtable, W.M. Lafranconi, *Biochemistry of Sulfur*, Plenum press, New York, 1986.
- [2] J. Boulegue, C.J. Lord III, T.M. Church, *Geochim. Cosmochim. Acta* 46 (1982) 453.
- [3] G.W. Luther III, T.M. Church, J.R. Scudlark, M. Cosman, *Science* 232 (1986) 746.
- [4] C.N. Alpers, D.W. Blowes, *Environmental Geochemistry of Sulfide Oxidation*, American Chemical Society, Washington, DC, 1994.
- [5] C. Plas, H. Harant, H. Danner, E. Jelinek, K. Wimmer, P. Holubar, R. Braun, *Appl. Microbiol. Biotechnol.* 36 (1992) 817.
- [6] R. Banerjee, R. Das, A.K. Chakraborty, *J. Chem. Soc., Dalton Trans.* (1991) 987.
- [7] P.A. Siskos, N.C. Peterson, R.E. Huil, *Inorg. Chem.* 23 (1984) 1134.
- [8] N.M. Moscardo-Levelut, V. Lichon, *J. Electrochem. Soc.* 131 (1984) 1545.
- [9] S.-M. Chen, *J. Electroanal. Chem.* 432 (1997) 101.
- [10] S.-M. Chen, *J. Electroanal. Chem.* 407 (1996) 123.
- [11] S.-M. Chen, *Inorg. Chim. Acta* 244 (1996) 155.
- [12] S.-M. Chen, *Electrochim. Acta* 42 (1997) 1663.
- [13] S.-M. Chen, P.-J. Sun, Y. Oliver Su, *J. Electroanal. Chem.* 294 (1990) 151.
- [14] S.-M. Chen, *J. TIT (Taiwan, ROC)* (1991) 431.
- [15] S.-M. Chen, Y. Oliver Su, *J. Chem. Soc., Chem. Commun.* (1990) 491.
- [16] K.R. Rodgers, R.A. Reed, Y. Oliver Su, T.G. Spiro, *Inorg. Chem.* 31 (1992) 2688.
- [17] R.A. Reed, K.R. Rodgers, K. Kushmeider, Y. Oliver Su, T.G. Spiro, *Inorg. Chem.* 29 (1990) 2881.
- [18] W. Spiller, D. Wohrle, G. Schulz-Ekloff, W.T. Ford, G. Schneider, J. Stark, *J. Photochem. Photobiol. A: Chem.* 95 (1996) 161.

- [19] B.W. Henderson, T.J. Dougherty, *Photochem. Photobiol.* 55 (1992) 145.
- [20] G. Jori, *J. Photochem. Photobiol. A: Chem.* 62 (1992) 371.
- [21] C.E. Hoyle, D.E. Hutchens, S.F. Thames, *Macromol. Chem.* 22 (1989) 3913.
- [22] D. Schlettwein, M. Kaneko, A. Yamada, D. Wöhrle, N.I. Jaeger, *J. Phys. Chem.* 95 (1991) 1748.
- [23] J.R. Darwent, P. Douglas, A. Harriman, G. Porter, M.-C. Richoux, *Coord. Chem. Rev.* 44 (1982) 83.
- [24] C. Brandt, R. van Eldik, *Chem. Rev.* 95 (1995) 119.
- [25] M. Fischer, P. Warneck, *J. Phys. Chem.* 100 (1996) 15111.
- [26] U. Deister, P. Warneck, *J. Phys. Chem.* 94 (1990) 2191.
- [27] I.B. Rufus, B. Viswanathan, V. Ramakrishnan, J.C. Kuriacose, *J. Photochem. Photobiol. A: Chem.* 91 (1995) 63.
- [28] G. Schneider, D. Wöhrle, W. Spiller, J. Stark, G. Schulz-Ekloff, *Photochem. Photobiol.* 60 (1994) 333.
- [29] S.-M. Chen, *J. Mol. Catal. A: Chem.* 112 (1996) 277.