

## Kinetic and mechanism of the aqueous selective oxidation of sulfides to sulfoxides: insight into the cytochrome P450-like oxidative metabolic process

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**ABSTRACT:** The selective oxidation of sulfides with hydrogen peroxide to give sulfoxides was carried out in aqueous solution by water-soluble manganese porphyrin as mimics of cytochrome P450-like catalyst. Different factors that influencing the selective oxidation of sulfides, for example, catalyst, amount of catalyst, solvent and reaction temperature were investigated. MnTE4PyP (*meso*-tetrakis(*N*-ethylpyridinium-4-yl) manganese porphyrin) was efficient and selective catalyst for oxidation of various sulfides. The reaction showed first-order dependence in both [sulfide] and [H<sub>2</sub>O<sub>2</sub>], and a fractional order respect to catalyst. Oxygen atom transfer mechanism involves high-valence intermediate was proposed, which was supported by kinetic orders and spectrophotometric evidences.

**KEYWORDS:** metalloporphyrins, oxidation, sulfide, sulfoxide, kinetic.

## **INTRODUCTION**

The selective oxidation of organic sulfides to sulfoxides without any over-oxidation to sulfones is a challenging research interest in synthetic organic chemistry, partly because of the importance of sulfoxides as intermediates in biologically active compounds [1]. Among all methods described so far, the oxidation of sulfides by various metal catalysts is one of the most attractive routes. To this end, copper, iron oxide nanoparticles, polyoxometalate, silicavanadia and Mo(VI) have been used as the catalysts [2].

As models of hemes or cytochrome P450, metalloporphyrins are effective catalysts for the selective oxidation of hydrocarbon and other organic compounds under mild conditions [3]. The sulfoxidation of sulfides catalyzed by metalloporphyrins is a subject of current interest as a direct route for selectively producing sulfoxides or sulfones [4], in which various oxidants, for example, NaOCl [5], NaIO<sub>4</sub> [6] and Oxone [7] were used. Although hydrogen peroxide is widely accepted as a "green" and effective oxidant in organic oxidations, the sulfoxidation pertaining to the use of metalloporphyrins in combination with hydrogen peroxide is limited [8]. Baciocchi's group reported series works on the efficient oxidation of sulfides with hydrogen peroxide in  $C_2H_5OH$ , in which the pentafluoro-substituted iron porphyrins were used as catalyst [9]. Most recently, Simonneaux and co-authors reported the first example on the asymmetric oxidation of sulfides catalyzed by chiral iron porphyrin using hydrogen peroxide as oxidant in methanol and water. Sulfonate groups were introduced into iron porphyrins with the aim of water-solubility of catalyst [8c].

Another kind of water-soluble metalloporphyrins could be prepared by introducing pyridinium group on the phenyl rings. This kind of cationic metalloporphyrins could be immobilized on supports and used commonly as heterogeneous catalyst in oxidations [10]. Cationic metalloporphyrins could also be used directly in homogeneous oxidation in aqueous solution. We developed efficient procedures for the oxidation of alcohols, oximes, and oxidative coupling reaction of amines catalyzed by pyridinium group substituted water soluble metalloporphyrins [11]. To our knowledge, direct selective oxidation of sulfides to sulfoxides catalyzed by cationic manganese porphyrins is still unknown.

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The aim of this work was to develop an efficient procedure for preparing sulfoxides catalyzed by cationic metalloporphyrins in aqueous solution with hydrogen peroxide as oxidant. Particular attention was devoted to identify the role of oxo-metal species in the oxidation process. The study is also intended to gain insight into the effects of reactants on the reaction rate and present a reasonable mechanism of the sulfoxidation. Besides achieving the mimicking oxidation of sulfides to sulfoxides procedures, the study could also provide the understanding on the cytochrome P450 to promote oxidative metabolism kinetic process in living organisms.

### **RESULTS AND DISCUSSION**

#### Catalysis of various catalysts for the aqueous oxidation of sulfides

For the initial studies on the catalytic activity of different water-soluble metalloporphyrins catalysts in the oxidation of sulfides in aqueous solution, thioanisole was selected as model substrate to assess their catalytic properties. The results are summarized in Table 1.

The reaction was examined at 60 °C. As shown in Table 1, in the presence of water-soluble metalloporphyrins catalyst, all the reactions proceeded with high conversions (entries 1-9). Compared with cobalt and iron porphyrin catalysts, manganese porphyrins presented

Table 1. Oxidation of thioanisole catalyzed by various catalysts in aqueous solution<sup>4</sup>

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S.	C H <sub>2</sub> O <sub>2</sub> , Solvent (H <sub>2</sub> O/C	atalyst H <sub>3</sub> CN=1/1, <i>v/v</i> ), 60°C	O S +	o o S
Entry	Catalyst	Conv., %	Selectivity, %	
			sulfoxide	sulfone
1	MnTM4PyP	95	99	1
2	MnTE4PyP	98	99	1
3	MnTPPS	96	15	85
4	FeTM4PyP	86	95	5
5	FeTE4PyP	89	96	4
6	FeTPPS	97	5	95
7	CoTM4PyP	89	93	7
8	CoTE4PyP	96	99	1
9	CoTPPS	92	8	92

<sup>a</sup>Thioanisole (1 mmol),  $H_2O_2$  (30 wt%, 2 mmol), catalyst (1 × 10<sup>-3</sup> mmol), solvent (10 mL,  $H_2O/CH_3CN = 1/1$ , v/v), 60 min, 60 °C.

**Table 2.** Oxidation of thioanisole with  $H_2O_2$  in various solvents<sup>a</sup> Selectivity, % Solvent Entry Conv., % sulfoxide sulfone 1 10 Cyclohexane 12 90 2 Ethyl acetate 28 92 8 3 **EtOH** 33 46 54 35 4 MeOH 38 62 39 5 CH<sub>3</sub>CN 35 65 6 H<sub>2</sub>O 95 2 98 7<sup>b</sup> H<sub>2</sub>O/CH<sub>3</sub>CN 78 99 1 8° H<sub>2</sub>O/CH<sub>3</sub>CN 98 99 1

<sup>a</sup>Thioanisole (1 mmol), H<sub>2</sub>O<sub>2</sub> (30 wt%, 2 mmol), MnTE4PyP (1×10<sup>-3</sup> mmol), solvent (10 mL), 60 min, 60 °C.  ${}^{b}H_{2}O/CH_{3}CN = 4/1$ , v/v.  ${}^{c}H_{2}O/CH_{3}CN =$ 1/1, v/v.

> slight higher activity no matter cationic or anionic group on the phenyl rings. For the catalysts with same central ion, it also could be known that the metalloporphyrins with ethyl pyridine group on the outside ring showed higher activity than methyl pyridine and sulfonatophenyl (such as entries 1-3).

> It is interesting to note that the cationic metalloporphyrins show much higher selectivity toward sulfoxide, while sulfone is the main product when the reaction catalyzed by anionic metalloporphyrins (entries 1-2 and entry 3 as example). It is likely due to the presence of stronger electron withdrawing substituents on the porphyrin ligand, which results in the increment of the redox potential of catalyst. For catalyst with

> > higher redox potential, high valent metal-oxo intermediate is more easily reduced to initial valence. Therefore, the reaction could be wellcontrolled in the stage of sulfoxide based on the low probability that the over-oxidation of sulfoxide by metal-oxo intermediate. Therefore, manganese porphyrin (MnTE4PyP), the most selective among the studied catalysts, was chosen for further investigations.

#### Effect of solvents on the aqueous oxidation of sulfides

Table 2 shows the effect of solvents on oxidation of thioanisole with H<sub>2</sub>O<sub>2</sub> over watersoluble manganese porphyrin (MnTE4PyP).

Nonpolar solvent, cyclohexane is unfavorable for the oxidation, in which only 12% thioanisole was converted (entry 1). It could be explained by the poor solubility of catalyst in nonpolar solvent. As shown in Table 2, the conversion of thioanisole increased with the increasing polarity of solvent (entries 2-6). It is interesting that the selectivity toward sulfone was higher than that of sulfoxide in strong polarity solvent, especially in water (entry 6). The interpretation for this phenomenon may be related to the nature of solvation effect of solvent. The electronic cloud density of sulfur atom in sulfoxide is increased in water, which the sulfoxide tends to be further oxidized by the metal-oxo intermediate. However, when little amount of acetonitrile was added in the water solution, the selectivity toward sulfoxide was remarkably enhanced (entry 7). Increasing the amount of acetonitrile continually  $(H_2O)$  $CH_3CN = 1/1, v/v$ , thioanisole could be converted to sulfoxide in stoichiometry (entry 8). It indicates that the mixed medium is efficient for the oxidation of sulfide with hydrogen peroxide and water-soluble manganese porphyrin. One hand, the mass transfer is significantly accelerated by the excellent solubility of catalyst in water. And on the other side, sulfoxide could be preserved against from the over-oxidation in the presence of acetonitrile.

## Effect of catalyst amount on the aqueous oxidation of sulfides

The influence of MnTM4PyP catalyst amount on the aqueous oxidation of thioanisole in the presence of hydrogen peroxide is summarized in Fig. 1.

As shown in Fig. 1, with increases in the amount of catalyst, the conversion of thioanisole and the selectivity toward sulfoxide increased greatly. As the amount of catalyst was increased continually, the selectivity toward sulfoxide declined apparently though the conversion could be up to over 98%. It indicates that the excess catalyst promote the over-oxidation of sulfoxide with metal-oxo intermediate. Therefore, the optimal amount of catalyst for the aqueous oxidation of thioanisole was 0.1% (based on substrate).



**Fig. 1.** Effect of the amounts of catalyst on the selective oxidation of thioanisole



Fig. 2. Effect of temperature on the selective oxidation of thioanisole

## Effect of temperature on the aqueous oxidation of sulfides

The effect of reaction temperature on the conversion of thioanisole, and the selectivity toward sulfoxide for the MnTM4PyP-catalyzed system were studied, and the results are presented in Fig. 2.

As shown in Fig. 2, the conversion of thioanisole increased greatly with the rising temperature from 30 to 60 °C, then kept unchanged at temperature over 60 °C. When the oxidation was conducted under 60 °C, an excellent selectivity toward sulfoxide was obtained. The selectivity toward sulfoxide decreased while the temperature was over 60 °C. Evidently, sulfoxide could be further oxidized to sulfone at higher temperature. The optimal reaction temperature for the selective oxidation of sulfide was 60 °C.

# Aqueous oxidation of various sulfides catalyzed by MnTM4PyP

To evaluate the scope of the catalytic system, various sulfides were subjected to the reaction system using 0.1%.mol (based on substrate) of water-soluble manganese porphyrins (Table 3). As shown in Table 3, most substrates could be smoothly converted to corresponding sulfoxides with high conversion rate and excellent selectivity.

It can be observed that the efficiency of the oxidation in this catalytic system is related with the electronic property of substrates. Compared with the electron-donating groups at *p*-position, the electron-withdrawing groups seemed more unfavorable to the formation of sulfoxides. It indicated the electron-withdrawing effect retarded the combination of substrate with metal-oxo intermediate (entries 1–5). The influence of steric effects could further be observed from the oxidation of diphenyl sulfide, in which the conversion was 82% after much longer reaction time (entry 6). Comparing with thioanisole, methyl benzyl sulfides could be converted under the same conditions with longer reaction

Entry	Substrate	Time, min	Conv., %	Selectivity, %	
	Substrate			sulfoxide	sulfone
1	S_	60	98	99	1
2	S	90	99	97	3
3	H <sub>3</sub> CO	90	97	98	2
4	CI	90	89	98	2
5	O <sub>2</sub> N S	120	25	96	4
6	S	120	82	98	2
7	S	120	96	96	4
8	∽~s∽∽	60	>99	99	1
9	S O	60	99	99	1
10	С З ОН	120	62	99	1

Table 3. Selective oxidation of various sulfides catalyzed by MnTE4PyP in aqueous solution<sup>a</sup>

<sup>a</sup> Sulfide (1 mmol),  $H_2O_2$  (30 wt%, 2 mmol), catalyst (1 × 10<sup>-3</sup> mmol), solvent (10 mL,  $H_2O/CH_3CN = 1/1$ ,  $\nu/\nu$ ), 60 °C.

time (entry 7). Sulfoxidation of the linear chain di-n-butyl sulfide smoothly proceeded with high conversion and selectivity (entry 8). Cyclic sulfide, that is, 1,4-thioxane, could also be efficiently sulfoxidated to the corresponding sulfioxide stoichiometrically. In addition, the catalytic system exhibited specific selective oxidation performance towards the sulfide contains hydroxyl group, and no products from hydroxyl group oxidation were detected (entry 10).

#### Mechanistic and kinetic studies

To explore the kinetic behavior over the aqueous oxidation of sulfide (using thioanisole as model compound), factors influencing the rate of oxidation such as effects of (i) [sulfide], (ii) [ $Mn^{II}$ ], and (iii) [ $H_2O_2$ ] effect have been studied. Rate and activation parameters were

evaluated. The rate constant obtained for the variations of sulfide, catalyst and  $H_2O_2$  are tabulated in Table 4.

(1) Effect of [sulfide]. The kinetics of oxidation of sulfide has been investigated under pseudo first order conditions, keeping the concentrations of  $H_2O_2$  always in large excess (nearly 10-folds) over that of [sulfide]. The oxidation followed first-order kinetics with respect to [sulfide], as evidenced by the linear plot of log[sulfide]<sub>t</sub> vs. time up to 80% conversion of [sulfide]<sub>0</sub> (Fig. 3) (r > 0.9988). Further, effect of varying ( $2.0 \times 10^{-3} - 6 \times 10^{-3}$  M) on the rate of oxidation has been studied at a constant [Mn<sup>II</sup>] ( $0.5 \times 10^{-5}$  M), [H<sub>2</sub>O<sub>2</sub>] ( $5.0 \times 10^{-2}$  M). The pseudo first order rate constant  $k_{obs}$  were found to be independent of [sulfide]<sub>0</sub>, indicating that the rate of the oxidation was first order in sulfide (Table 4).

(2) Effect of  $[H_2O_2]$ . At a constant [sulfide] (4.0 × 10<sup>-3</sup> M) and [Mn<sup>II</sup>] (0.5 × 10<sup>-5</sup> M), the kinetic runs were carried out with various initial concentrations of

Table 4. Effect of the concentration of sulfide, manganese porphyrin catalyst and  $H_2O_2$  on the reaction rate at 323 K

[Sulfide] $\times$ 10 <sup>3</sup> , M	$[\mathrm{Mn^{II}}] \times 10^5, \mathrm{M}$	$[H_2O_2] \times 10^2$ , M	$k_{\rm obs}  imes 10^3$ min <sup>-1</sup>
[Sulfide] variation			
2.0	0.5	5.0	5.38
3.0	0.5	5.0	5.40
4.0	0.5	5.0	5.45
5.0	0.5	5.0	5.58
6.0	0.5	5.0	5.43
[H <sub>2</sub> O <sub>2</sub> ] variation			
4.0	0.5	1.0	1.13
4.0	0.5	3.0	3.29
4.0	0.5	5.0	5.45
4.0	0.5	7.0	7.48
4.0	0.5	9.0	9.87
[Mn <sup>II</sup> ] variation			
4.0	0.2	5.0	3.03
4.0	0.4	5.0	4.83
4.0	0.6	5.0	6.08
4.0	0.8	5.0	7.82
4.0	1.0	5.0	9.53



**Fig. 3.** Plot of log [sulfide]<sub>t</sub> vs. time at 323 K

hydrogen peroxide, which yielded rate constants whose values depended on  $[H_2O_2]$ . The pseudo first order rate constants  $k_{obs}$  (min<sup>-1</sup>) thus obtained were found to increase with  $[H_2O_2]$  (Table 4) over a range of  $[H_2O_2]$  used  $(1.0 \times 10^{-3} \sim 5.0 \times 10^{-3} \text{ M})$ . This shows the reaction obeys first order with respect to  $[H_2O_2]$ . This was confirmed by the linear plots of  $k_{obs}$  (min<sup>-1</sup>) vs.  $[H_2O_2]$  which yielded a straight line passing through the origin (Fig. 4).

(3) Effect of  $[Mn^{II}]$ . The reaction rates were measured at constant [sulfide]  $(4.0 \times 10^{-3} \text{ M})$ ,  $[\text{H}_2\text{O}_2]$   $(5.0 \times 10^{-2} \text{ M})$ but various  $[\text{Mn}^{II}]$   $(0.2 \times 10^{-5} \sim 1.0 \times 10^{-5} \text{ M})$ . Under similar experimental conditions, an increase in  $[Mn^{II}]_0$ increased the  $k_{obs}$  values (Table 4). A plot of rate constant  $k_{obs}$  (min<sup>-1</sup>) against  $[Mn^{II}]$  yields a straight line with a non-zero intercept (Fig. 5). Observed reaction order of  $[Mn^{II}]$  can be obtained from linear regression of log  $k_{obs}$  vs. log  $[Mn^{II}]$  (order ~0.698) at 323 K. This indicates that the reaction is of fractional order with respect to  $[Mn^{II}]$ . The fractional order in the rate with the catalyst concentration should be result from formation of manganese hydroperoxo intermediate. Then an oxo species in a high valence oxidation state was generated *via* heterolytic cleavage of oxygen-oxygen bond of the hydroperoxo intermediate.

(4) Effect of temperature. The present oxidation study was carried out in the range (313–333 K) and the results are shown in Table 5. The  $k_{obs}$  values increased with an increase in the temperature. The plot of log  $k_{obs}$  vs. 1/T was a straight line (Fig. 6). From Arrhenius plot, the value of energy of activation ( $E_a$ ) was calculated. The calculated activation energy from the slope was 56.1 kJ/mol.



Fig. 4. The linear plot of  $k_{obs}$  vs.  $[H_2O_2]$  confirms the first order reaction with respect to  $[H_2O_2]$ 



**Fig. 5.** The linear plot of rate constant  $k_{obs}$  (min<sup>-1</sup>) vs. [Mn<sup>II</sup>] with nonzero intercept confirms that the reaction is fractional order with respect to [Mn<sup>II</sup>]

**Table 5.** Effect of temperature variation on pseudo first order rate constant  $k_{obs}^{a}$ 

Entry	<i>Т</i> , К	$k_{\rm obs} \times 10^4$ , min <sup>-1</sup>
1	313	2.98
2	318	3.71
3	323	5.45
4	328	7.78
5	333	10.39

<sup>a</sup>[Sulfide] =  $4.0 \times 10^{-3}$  M, [Mn<sup>II</sup>] =  $0.5 \times 10^{-5}$  M, [H<sub>2</sub>O<sub>2</sub>] =  $5.0 \times 10^{-2}$  M



Fig. 6. Arrhenius plot of the rate constants for the oxidation of sulfide



Fig. 7. In situ UV-vis spectra of MnTE4PyP in the aqueous oxidation of thioanisole

In addition, the results from the controlled experiments as shown in Table 5 have demonstrated that manganese porphyrin is crucial for the selective oxidation of sulfides. Generally for the metalloporphyrins-catalyzed oxidations, high valence intermediate is accepted as the active species [12]. High valence manganese porphyrin in the catalytic system was verified from the *in situ* UV-vis spectroscopy as shown in Fig. 7.



**Fig. 8.** Profile of oxidation of thioanisole catalyzed by MnTE4PyP in the presence of hydrogen peroxide

The initial characteristic absorption peaks of MnTE4PyP were at 463 and 493 nm. By adding hydrogen peroxide and substrate into the solution, *in situ* UV-vis measurement revealed a new absorption peak at 558 nm, while the characteristic absorption peak of MnTE4PyP was weakened gradually. These evidence suggested the generation of high-valent oxidant active species oxo-Mn(IV) in the aqueous solution [13].

With hydrogen peroxide as oxidant, profile for the oxidation of thioanisole catalyzed by MnTE4PyP in aqueous solution was shown in Fig. 8.

As shown in Fig. 8, the conversion of thioanisole increased sharply within the first 20 min, and almost all of the substrate was oxidized in one hour in this catalytic system. The salient feature of the present oxidation is its high selectivity toward sulfoxide during the whole catalytic process. It indicated that the generation of sulfoxide was *via* the reaction of oxo-Mn(IV) and sulfide. After that, oxo-Mn(IV) was reduced initial valence and no chance to generate sulfone by the reaction of sulfoxide and oxo-Mn(IV).

On the basis of the previous observations and results, a mechanism for the aqueous oxidation of sulfides with MnTE4PyP as catalyst was proposed:

$$\mathbf{Mn}^{\mathrm{II}} + \mathbf{H}_2 \mathbf{O}_2 \xleftarrow{K_1} \mathbf{Mn}^{\mathrm{III}} \mathbf{O} \cdot \mathbf{O} \cdot \mathbf{H} + \mathbf{H}^+$$
(1)

$$\mathbf{Mn}^{\text{III}} - \mathbf{O} - \mathbf{O} - \mathbf{H} \xrightarrow{K_2} \mathbf{Mn}^{\text{IV}} = \mathbf{O} + \mathbf{OH}^{\bullet}$$
(2)

$$Mn^{IV} = O + R_1 \xrightarrow{S} R_2 \xrightarrow{k_3} \prod_{R_1} \xrightarrow{O} R_2 + Mn^{II} \qquad (3)$$

An oxo species in a high valence oxidation state was generated *via* heterolytic cleavage of oxygen-oxygen bond of the hydroperoxo intermediate. The formation of sulfoxide was *via* an oxygen atom transfer process between oxo-Mn(IV) and sulfide (direct oxygen atom transfer). However, Baciocchi ever proposed the ET mechanism (eletctron transfer) towards the oxidation of a number of aromatic sulfides by  $H_2O_2$  in aqueous acidic medium (pH = 3) [8a].

The mechanism for the oxidation of thioanisole by manganese porphyrin is as follows:

$$-\frac{d[Sulfide]}{dt} = k_3[O = Mn^{\text{IV}}][Sulfide]$$

Substituting the concentration of above terms in the rate equation, the rate expression may thus be represented by Equation 4.

$$Rate = K_1 K_2 k_3 [Mn^{II}] [Sulfide] [H_2 O_2]$$
(4)

That is,

$$Rate = K[Mn^{II}][Sulfide][H_2O_2]$$
(5)

where,  $K = K_1 K_2 k_3$ .

The rate expression is quite consistent with kinetic results.

#### **EXPERIMENTAL**

All materials are commercial reagent grade and were purchased from Alfa Aesar or Aldrich without further purification unless indicated. Pyrrole was redistilled before use. Other solvents were all of analytical grade.

UV-vis spectrum was recorded on a Shimadzu UV-2450 spectrophotometer. Mass spectra were obtained on a Shimadzu LCMS-2010A. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> with a Varian Mercury-Plus 300 spectrometer. GC analyses were performed on a Shimadzu GC-2010 plus chromatography equipped with Rtx-5 capillary column (30 m × 0.25 mm × 0.25 µm). GC-MS analyses were recorded on a Shimadzu GCMS-QP2010 equipped with Rxi-5ms capillary column (30 m × 0.25 mm × 0.25 µm).

#### Procedures of preparing catalysts

The selected water-soluble metalloporphyrins for this study are shown in Scheme 1, including cationic and anionic metalloporphyrins. The procedures of synthesizing catalysts are described as follows.



M = Mn, Fe, Co

**Scheme 1.** The structures of water-soluble metalloporphyrins used as catalyst

#### **Synthesis**

Synthesis of meso-tetrakis(1-methyl-4-pyridyl)metalloporphyrin. Pyrrole (20 mL) and 4-pyridinecarbaldehyde (20 mL) were refluxed in propionic acid (200 mL) for 60 min to produce meso-tetrakis(4pyridyl) porphyrin (T4PyP) with the yield of 24%. Next, T4PyP (0.25 g) and manganese acetate (1 g) were refluxed in dimethylformamide (35 mL) for 6 h under nitrogen atmosphere to form meso-tetrakis(4pyridyl) manganese porphyrin (MnT4PyP) with the yield of 88%. In the following step, MnT4PyP (0.2 g) and methyl p-toluenesulfonate (12 g) were added to 100 mL dimethylformamide solution. The mixture was stirred for 12 h at 90 °C, and the solution was cooled to room temperature. Ethyl ether (20 mL) was added in the mixture and was kept overnight. After filtration, the filter cake was washed thoroughly with ethyl ether and was purified by recrystallization with water/acetone (1:2) to obtain meso-tetrakis(1-methyl-4-pyridyl) manganese porphyrin (MnTM4PyP) with 80% yield. The other metallopophyrins could be synthesized with similar procedures by replacing other metal ions. The spectral and analysis data of metalloporphyrins catalysts were listed as following. [MnTM4PyP]<sup>4+</sup>. EI-MS: m/z 731. UV-vis (H<sub>2</sub>O):  $\lambda_{max}$ , nm (log  $\varepsilon$ ) 464 (2.48), 559 (1.25). IR (KBr): v, cm<sup>-1</sup> 1640, 1009. Anal. calcd. for  $C_{44}H_{36}N_8Mn$ : C, 72.22; H, 4.96; N, 15.31. Found C, 71.79; H, 4.92; N, 15.16. [CoTM4PyP]<sup>4+</sup>. EI-MS: *m/z* 735. UV-vis (H<sub>2</sub>O):  $\lambda_{max}$ , nm (log  $\epsilon$ ) 418 (2.47), 539 (0.93). IR (KBr): v, cm<sup>-1</sup> 1640, 1005. Anal. calcd. for C<sub>44</sub>H<sub>36</sub>N<sub>8</sub>Co: C, 71.83; H, 4.93; N, 15.23. Found C, 71.43; H, 4.72; N, 14.96. **[FeTM4PyP]**<sup>4+</sup>. EI-MS: *m/z* 732. UV-vis (H<sub>2</sub>O): λ<sub>max</sub>, nm (log ε) 415 (2.84), 543 (1.23). IR (KBr): ν, cm<sup>-1</sup> 1638, 1002. Anal. calcd. for C<sub>44</sub>H<sub>36</sub>N<sub>8</sub>Fe: C, 72.13; H, 4.95; N, 15.29. Found C, 72.32; H, 4.95; N, 15.31.

Synthesis of meso-tetrakis(N-ethylpyridinium-4-yl)metalloporphyrin. MnTPyP (0.15 g, 0.221 mmol) and fresh distilled iodoethane (0.62 mg, 4 mmol) were added to 20 mL dimethyl formamide solution. The mixture was stirred for 4 h at 45 °C, and the solution was cooled to room temperature. Next, 20 mL ethyl ether was added, and the mixture was kept overnight. After filtration, the filter cake was washed thoroughly with ethyl ether and recrystallized with water/acetone (1:2) to obtain 0.189 g (MnTE4PyP) (71.4%). The other metallopophyrins could be synthesized with similar procedures by replacing other metal ions. The spectral and analysis data of metalloporphyrins catalysts were listed as following. [MnTE4PyP]4+. EI-MS: m/z 787. UV-vis (H<sub>2</sub>O):  $\lambda_{max}$ , nm (log  $\epsilon$ ) 463 (2.48), 493 (1.25), 675 (0.87), 769 (0.54). IR (KBr): v, cm<sup>-1</sup> 1623, 1001. Anal. calcd. for C<sub>48</sub>H<sub>44</sub>N<sub>8</sub>Mn: C, 73.18; H, 5.64; N, 14.22. Found C, 74.67; H, 5.51; N, 13.99. [CoTE4PyP]4+. EI-MS: m/z 791. UV-vis (H<sub>2</sub>O):  $\lambda_{max}$ , nm (log  $\varepsilon$ ) 437 (2.56), 545 (0.87), 615 (0.34). IR (KBr): v, cm<sup>-1</sup> 1640, 1002. Anal. calcd. for C48H44N8Co: C, 72.81; H, 5.60; N, 14.15. Found C, 71.67; H, 5.72; N, 15.56.

[FeTE4PyP]<sup>4+</sup>. EI-MS: m/z 788. UV-vis (H<sub>2</sub>O):  $\lambda_{max}$ , nm (log ε) 417 (3.04), 545 (1.59). IR (KBr): v, cm<sup>-1</sup> 1625, 1001. Anal. calcd. for C<sub>48</sub>H<sub>44</sub>N<sub>8</sub>Fe: C, 73.09; H, 5.62; N, 14.21. Found C, 72.52; H, 5.95; N, 15.12.

Synthesis of (meso-tetrakis(p-sulfonatophenyl)metalloporphyrin. Tetra sodium meso-tetra(sulfonatophenyl)porphyrin (TPPS) was synthesized according to reported procedures [14]. TPPS (0.2 g, 0.18 mmol) and MnSO<sub>4</sub>H<sub>2</sub>O (0.3 g, 1.8 mmol) were added and stirred in 20 mL deionized water. The reaction was monitored by UV-vis (the soret band of the porphyrin was shifted from 414 nm to 467 nm). So as to wipe off the excess manganese ion, the reaction solution was passed through an Amberlite IR-120 column after it was finished. Then the solution was neutralized by 0.1 moL/L NaOH. Removal of water under vacuum afforded the crude MnTPPS, which was dissolved by methanol to eliminate the salts for three times to give 0.15 g (75.6%) MnTPPS. The reaction conditions for the synthesis of other MTPPS are the same as those for MnTPPS. MnTPPS. EI-MS: *m/z* 982. UV-vis (H<sub>2</sub>O):  $\lambda_{max}$ , nm (log  $\epsilon$ ) 467 (2.78), 563 (1.43). IR (KBr): v, cm<sup>-1</sup> 1654, 1008. Anal. calcd. for C<sub>44</sub>H<sub>24</sub>N<sub>4</sub>O<sub>12</sub>S<sub>4</sub>Mn: C, 53.71; H, 2.46; N, 5.69. Found C, 55.01; H, 2.51; N, 5.92. CoTPPS. EI-MS: m/z 985. UV-vis (H<sub>2</sub>O):  $\lambda_{max}$ , nm (log  $\varepsilon$ ) 419 (3.14), 542 (1.23). IR (KBr): v, cm<sup>-1</sup> 1654, 1006. Anal. calcd. for  $C_{44}H_{24}N_4O_{12}S_4Co$ : C, 53.50; H, 2.45; N, 5.67. Found C, 54.23; H, 2.72; N, 5.96. **FeTPPS.** EI-MS: m/z 984. UV-vis (H<sub>2</sub>O):  $\lambda_{max}$ , nm (log ε) 413 (2.94), 556 (1.43). IR (KBr): ν, cm<sup>-1</sup> 1656, 1005. Anal. calcd. for  $C_{44}H_{24}N_4O_{12}S_4Fe: C, 53.66; H,$ 2.46; N, 5.69. Found C, 52.92; H, 2.95; N, 5.31.

#### General procedure for oxidation of sulfides

Thioanisole (1 mmol), catalyst ( $1 \times 10^{-3}$  mmol) and  $H_2O_2$  (2 mmol) were added in 10 mL solvent ( $H_2O/$  CH<sub>3</sub>CN = 1/1,  $\nu/\nu$ ), the mixture was stirred at 60 °C for 60 min. After the reaction was finished, the aqueous solution was extracted with ethyl acetate ( $3 \times 5$  mL) and dried over anhydrous MgSO<sub>4</sub>. Naphthalene (0.05 g) was added as internal standard for the oxidation of sulfide. The consumption of sulfide and formation of sulfoxide were monitored by GC (Shimadzu GC-2010 plus) and GC-MS (Shimadzu GCMS-QP2010 plus).

#### **Kinetic measurements**

Kinetic studies were carried out in aqueous medium under pseudo first order conditions with a large excess of hydrogen peroxide over sulfide. The rate of the reaction was determined from the concentration of the unreacted sulfide at different time intervals. From the concentration values, plots of log [sulfide] *vs*. time were made and from the slope of such plots, the pseudo first order rate constants  $k_{obs}$  were obtained. To evaluate  $k_{obs}$ , generally 5–8 values at least up to 80% completion of the reaction were used. The observed rate constants were reproducible within the experimental error ±5%.

### CONCLUSION

In conclusion, an environmental-friendly protocol has been developed for selective oxidation of sulfides to sulfoxides with hydrogen peroxide in aqueous solution. Compared with anionic metalloporphyrins, the cationic metalloporphyrins showed high selectivity for sulfoxide. The MnTE4PyP-based catalytic system has proved to be effective in the oxidation of various sulfides with hydrogen peroxide as terminal oxidant. The kinetic parameters were determined, and the reaction scheme was also presented. The proposed mechanism, involving high-valence manganese porphyrins formed as a result of heterolytic cleavage of oxygen–oxygen bond of the hydroperoxo intermediate was supported by kinetic orders and spectrophotometric evidences.

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