

# Heterogeneous catalysis of the air oxidation of thiols by the cobalt porphyrin intercalated into a phosphatoantimonic acid host

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## Abstract

Cobalt porphyrin (TPPCo) has been prepared in situ as a guest molecule in the layered host material phosphatoantimonic acid,  $\text{HSb}(\text{PO}_4)_2$ , here denoted SbP. The powder X-ray diffraction of the purified sample, the SbP-intercalated cobalt porphyrin (SbPTPPCo), showed the expanded interlamellar distance of SbP upon the intercalation. The electronic absorption and electron paramagnetic resonance spectra revealed the retention of cobalt porphyrin in the layered host material. The catalytic behaviour of the novel catalyst SbPTPPCo for the thiol autoxidation was investigated in quantitative detail. In our experimental conditions, the catalytic autoxidation proceeded without induction period for oxygen consumption. The intercalated cobalt porphyrin appears to be a promising catalyst owing to its good catalytic capability. No loss in activity was observed for SbPTPPCo after eight reaction cycles and a total of more than 5390 turnovers. The proposed reaction scheme for the autoxidation catalyzed by SbPTPPCo involves the formation of catalytic center of mononuclear complex by which the electron of  $\text{RS}^-$  is transferred to bound and activated dioxygen. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Intercalation; Cobalt porphyrin; Phosphatoantimonic acid; Autoxidation; Thiols

## 1. Introduction

There is much current interest to design and synthesize an inorganic mimic of the enzyme, cytochrome P450 [1]. The approach has been to develop effective and stable oxidation catalysts for partial oxidation of organic substrates under mild conditions.

The capability of zeolite-encapsulated metal complexes for catalytic oxidation was reported [2,3]. The site isolation of active center (complex) created by bonding to the supercage of zeolite was thought to prevent the formation of less reactive dimers. However, the main short-coming of a zeolite-encapsulated metal complex is due to the fact that only those molecules small enough to diffuse quickly through the channels filled with large chelate complexes can be converted catalytically by this system at a reasonable rate. When iodosobenzene is used as an oxygen atom donor, pore blockage leads to shut-down of the reactivity after only a few catalytic cycles.

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Corma [4] reported the catalytic air oxidation of thiols mediated at a Mo(VI)O<sub>2</sub> complex center intercalated into an anion exchanger, layered double hydroxide. Our research work [5–7] demonstrated that the intercalation of metal phthalocyanines and porphyrins into layered host materials improved the catalytic behaviour for the decomposition of hydrogen peroxide and the epoxidation of cyclohexene. In this paper, we present the intercalation of TPPCo in situ into layered host material SbP and its catalytic behaviour for the autoxidation of thiols. The layered host material SbP [8] differs from the well-known phosphatozirconic acid, ZrP. In SbP, the metal, antimony, is in the 5<sup>+</sup> oxidation state rather than the 4<sup>+</sup> state. Thus, the charge density of SbP is half that of ZrP, which would result in the layers of SbP being more able to separate than those of ZrP. The advantage of layered pillared structure over fixed zeolite structure lies in its better spacing access for reactant and resulting species to diffuse into active centers and meantime the prevention against the formation of inactive-dimers of cobalt porphyrin in the autoxidation of thiols.

## 2. Experimental

### 2.1. Preparation

Layered phosphatoantimonic acid, SbP, was prepared by previously described methods [8]. TPPCo was formed in situ as a guest molecule in layered host material SbP. At first, SbP was ion-exchanged with cobalt cations by slurring the material in a solution of the appropriate amount of cobalt cations in water at room temperature. The filtered, washed and dried material was then ready for in situ synthesis of porphyrin. Freshly distilled pyrrol (1.8 ml) and benzaldehyde (2.7 ml) were added to a suspension of 8% cobalt-exchanged SbP in propionic acid. The mixture was then refluxed for 2 h. The resulting mixture was allowed to cool for 12 h to room temperature. Filtration, washing and drying were carried out to give a purple free-running powder.

The electronic absorption spectra of the product were recorded with a DV-7(HS) spectrophotometer. The XRD data and EPR spectra were recorded on a XD-3A X-ray diffractometer and a F1ESG1 spectrometer, respectively.

### 2.2. Catalytic activity experiment

Each catalytic experiment was conducted under a constant oxygen pressure in the range 98.0–101 kPa. Dioxygen depletion was monitored with a gas buret. Reactions proceeded under alkaline conditions. An amount of catalyst SbPTPPCo in stirred suspension was allowed to equilibrate for 1 h under an oxygen atmosphere prior to the injection of required amount of 1-decanethiol in 10 ml cyclohexane. The thiol concentrations of the organic phase were determined by potentiometric titration.

## 3. Results and discussion

### 3.1. Intercalation of cobalt porphyrin

We intercalated TPPCo into the interlayer of SbP by the reflux of the cobalt-exchanged SbP with freshly distilled pyrrol and benzaldehyde in freshly distilled propionic acid. In the in-situ intercalation,

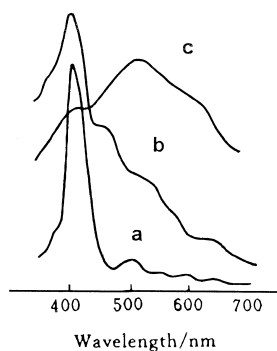


Fig. 1. UV-Vis spectra of porphyrins; (a) *meso*-tetraphenylporphyrin, (b) desorption extract and (c) Nujol mull spectrum of the purple product.

we used the organic acid as the solvent instead of water which Cady and Pinnavaia [9] did for the intercalation of porphyrins into mica-type silicates. The acidity of the solvent and the higher refluxing temperature speeded up the in-situ intercalation of the cobalt porphyrin to a great extent. The proper ratio of the molar amount of pre-exchanged cobalt ion, pyrrole and benzaldehyde is 1:1.5:1.5. We observed that the white color of SbP became dark purple after a reaction time of 20 min owing to the formation of the porphyrin.

The partial desorption of the purified purple product with chloroform containing  $(C_2H_5)_4N^+$  exhibited the electronic absorption spectra of the porphyrin, shown in Fig. 1. The band at 415 nm in the spectrum of the desorption extract is assigned to the desorbed porphyrin. The shoulder at 450–485 nm should be assigned to porphyrin dication and porphyrin intermediate [9]. The Nujol mull spectrum of the purple product exhibits an intense and extensive absorption of porphyrin at 510 nm or so with a shift similar to the silicate-intercalated porphyrin. The EPS spectra for the product (SbPTPPCo) and cobalt-exchanged SbP (SbPCo) are given in Fig. 2. The EPS spectra were recorded under the conditions: field  $335.7 \pm 10$  mT, frequency 100 K, amplitude  $3.2 \times 10^2$ , sweep time 4 min. Under the EPR condition, the signal of  $Co^{2+}$  in SbPCo did not exit, but the signal typical of TPPCo appeared in the spectrum of the product. The results of the electronic absorption and the electron paramagnetic resonance revealed the retention of cobalt porphyrin in the dark purple product. The elemental analysis of the purified solid product showed that it contained 16.8% (w/w) of cobalt porphyrin.

It was found that the XRD  $d_{002}$  spacing of SbP was increased with the formation of the porphyrin. The observed  $d_{002}$  spacing of purified and dried porphyrin-intercalated product, as shown in Fig. 3, was 1.28 nm, indicative of a gallery height 0.50 nm, a value near the van der Waals' thickness of

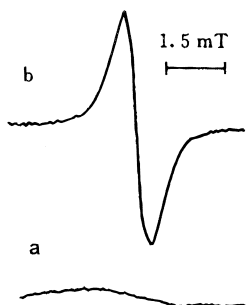


Fig. 2. EPR spectra of (a) SbPCo and (b) SbPTPPCo.

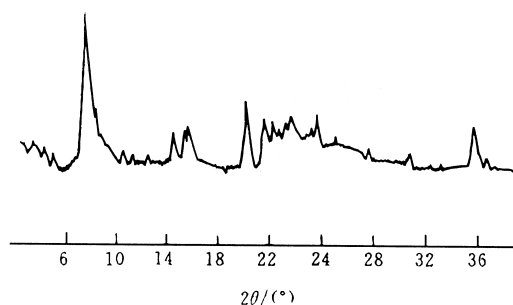
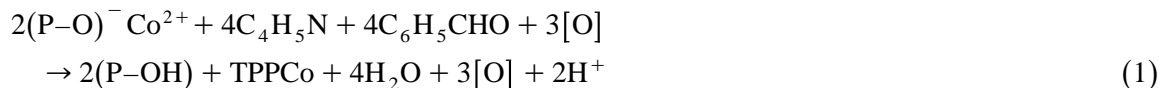


Fig. 3. X-ray diffraction pattern of SbPTPPCo.

porphyrin. It indicated that the TPPCo molecule did not stand up between layers of SbP very much in the dried state of the product. In addition, in the same preparation condition as above, the preparation for the SbP-intercalated iron(II) porphyrin failed. We did not observe the formation of iron(II) porphyrin and the increase of the interlamellar distance in the layered host material SbP.

The synthesis of the intercalated porphyrin involves a complex series of reactions that may be represented by the overall equation:



In Eq. (1), [O] represents an oxidizing equivalent of any suitable oxidant and might be identified with either benzaldehyde or  $\frac{1}{2}\text{O}_2$ ; P–O refers to the P–O bond in SbP. The synthesis of the SbP-intercalated porphyrin involved the reaction of cobalt-exchanged SbP with pyrrol and benzaldehyde. To do this, the pyrrol and benzaldehyde needed to be intercalated into the host SbP and then diffuse to the cobalt ion. However, it was also possible that the porphyrin was at first formed in propionic acid and then intercalated into the cobalt ion in the interlayer of SbP to form the cobalt porphyrin. Clearly, the reaction proceeds under the acidic catalysis within or outside the host.

### 3.2. Autoxidation of thiols

The catalytic activity of SbPTPPCo for the thiol autoxidation under different heterogeneous reaction conditions was studied in quantitative detail. The results are summarized in Table 1 and Figs. 4 and 5, which showed the good effectiveness of the intercalated cobalt porphyrin as a catalyst. The initial rate,  $v_0$ , was determined with the gas buret and was expressed in either ml of consumed dioxygen/min or mol of thiols/l/s in the early stage of the catalytic reaction.

Table 1  
Activity of SbPTPPCo for autoxidation of 1-decanethiol in various reaction conditions

| [RSH] ( $\text{mol} \cdot \text{l}^{-1}$ ) | $[\text{OH}^{-1}]$ ( $\text{mol} \cdot \text{l}^{-1}$ ) | SbPTPPCo (g) | Initial rate, $v_0$ ( $\text{ml O}_2 \cdot \text{min}^{-1}$ ) |
|--|---|--------------|---|
| 0.385                                      | 2.0   | 0.050        | 3.1   |
| 0.770                                      | 2.0   | 0.050        | 4.4   |
| 1.54                                       | 2.0   | 0.050        | 5.8   |
| 0.770                                      | 0.40  | 0.050        | 0.57  |
| 0.770                                      | 1.0   | 0.050        | 1.8   |
| 0.770                                      | 2.0   | 0.025        | 2.6   |
| 0.770                                      | 2.0   | 0.10         | 5.5   |

All experiments were carried out at 303 K.

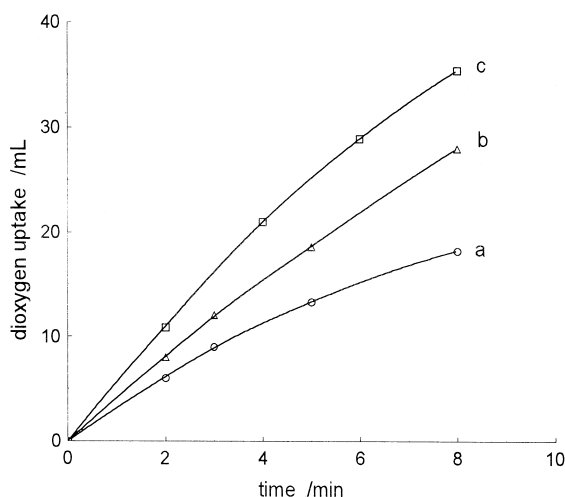


Fig. 4. The variation in oxygen uptake versus time and the concentration of 1-decanethiol, (a)  $0.385 \text{ mol}\cdot\text{l}^{-1}$ , (b)  $0.770 \text{ mol}\cdot\text{l}^{-1}$  and (c)  $1.54 \text{ mol}\cdot\text{l}^{-1}$ , SbPTPPCo  $0.050 \text{ g}$ ,  $[\text{OH}^-] = 2.0 \text{ mol}\cdot\text{l}^{-1}$ ,  $T = 303 \text{ K}$ .

The dioxygen uptake of the autoxidation on the amount of 1-decanethiol is present at the start of the reaction, no induction period is exhibited in our experimental conditions. Fig. 4 shows the variation in the oxygen uptake versus time and the increase of dioxygen uptake with the concentration of decanethiol. A reaction time of 15 min leads to a nearly full conversion ( $> 99\%$ ) of  $3.85 \text{ mmol}$  1-decanethiol in  $10 \text{ ml}$  cyclohexane. The autoxidation is accelerated by reaction temperature; the initial rate of the autoxidation at  $323 \text{ K}$  is  $40\%$  or so more than that at  $303 \text{ K}$ .

SbPTPPCo as a catalyst results in the increase of the rate of autoxidation of thiols. The kinetic feature is shown in Table 1 when the amount of catalyst is varied. Besides, the catalytic autoxidation of 1-decanethiol is intensely influenced by the alkaline concentration in the reaction system, as shown in Fig. 5. The research work of organic polymer-bound phthalocyanine [10–12] showed that the rate of catalytic autoxidation of thiols increased with the pH of reaction medium; however, in the high pH

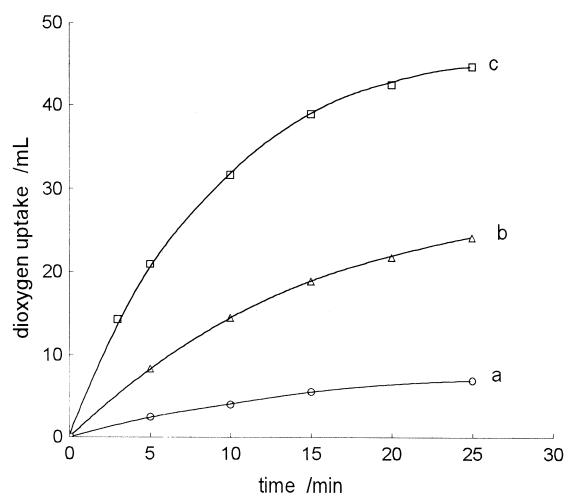


Fig. 5. The variation in oxygen uptake versus time and the concentration of  $[\text{OH}^-]$ , (a)  $0.40 \text{ mol}\cdot\text{l}^{-1}$ , (b)  $1.0 \text{ mol}\cdot\text{l}^{-1}$  and (c)  $2.0 \text{ mol}\cdot\text{l}^{-1}$ , SbPTPPCo  $0.050 \text{ g}$ ,  $[\text{RSH}] = 0.77 \text{ mol}\cdot\text{l}^{-1}$ ,  $T = 303 \text{ K}$ .

of reaction medium, above pH 8.6, the catalytic effect diminished a lot and the latexes were less colloiddally stable at higher pH. As for SbPTPPCo, it is not only stable even in high alkaline concentration, but also very effective on the catalytic autoxidation of thiols.

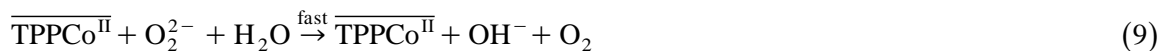
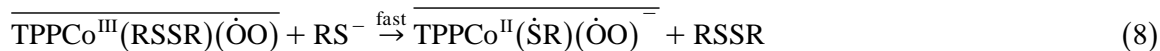
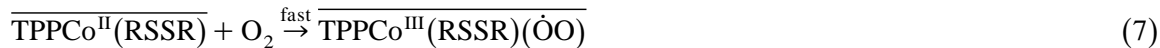
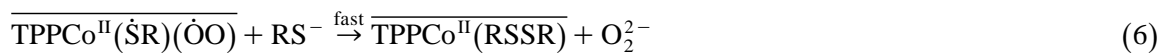
In all the experiment conditions of Table 1, no decomposition and deactivation of the intercalated cobalt porphyrin in SbPTPPCo were found at the end of the catalytic cycle. Seven additional catalytic cycles for a total of 5390 turnovers were carried out in the same reaction vessel without a detectable loss of activity. During the repeated run under the same reaction conditions as SbPTPPCo, the secondly reused catalyst TPPCo was 0.93 times as active as the fresh TPPCo, losing a little catalytic activity; however, much differently, the thirdly reused TPPCo was only 0.47 times as active as the fresh catalyst. At high pH, a large amount of hydroxyl ions induce the formation of the inactive  $\mu$ -oxo dimers and thus lower the efficiency of Co-complexes [13]. However, the intercalated cobalt porphyrin, SbPTPPCo, possesses good effectiveness and stability for the thiol autoxidation even at very high pH. This may show us the fact that the layered pillared structure of SbPTPPCo can much better prevent against the formation of inactive  $\mu$ -oxo dimers in the thiol autoxidation than some organic polymer-supported complexes. The intercalation of metal porphyrins in the layered host material appears to be a promising method to improve the longevity of certain types of biomimetic metallo macrocyclic complexes in the oxidation catalysis.

The rate of consumption of 1-decanethiol is limited by the mass transfer of either dioxygen from the gas phase or 1-decanethiol from the insoluble droplets to the active sites on the SbP-intercalated porphyrin particles. The good catalytic capability of the SbP-intercalated cobalt porphyrin may be attributed to some factors: the better distribution of the intercalated cobalt porphyrin than the aggregated form of porphyrin in organic solution; the prevention of inactive  $\mu$ -oxo dimers owing to the intercalation of porphyrin; the higher concentration of 1-decanethiol absorbed on intercalated porphyrin particles and so on.

The autoxidation of thiols is accelerated in the presence of complexes in which the metal center has access to more than one stable oxidation state. Leung [14] proposed the mechanism that the autoxidation of thiols proceeds via a dimeric catalytic center that is bridged by the  $RS^-$  anion, electron transfer from the Co(II) metal center to bound dioxygen was considered to be the rate-determining step. The existence of  $H_2O_2$  was detected in the reaction mixture of the catalytic autoxidation of thiols [12,15]. Shirai and Tsuike [16] demonstrated the existence of a  $(O_2^-)$  with the help of the EPR spectra for Co(II)-oapc and Fe(III)-oapc aqueous solution at 77 K which revealed the sharp signal at  $g = 2.003$  of the superoxide anion radical. It was found that only one side-reaction occurs, viz. the formation of  $H_2O_2$  [17,18].

In our case, we intercalate the porphyrin into the layered host material and so propose that the autoxidation involves the formation of catalytic center of mononuclear complex. The electron of  $RS^-$  is transferred by the intercalated cobalt porphyrin to bound dioxygen. With the knowledge of  $H_2O_2$  obtained previously, the catalytic behaviour of the intercalated porphyrin is thought to proceed as the following scheme:





where the bars identify surface or intercalated species.

The kinetic data in Fig. 5 show that the rate of autoxidation of 1-decanethiol increases with the alkaline concentration, and thus the thiolate anion is likely to be the reactive species. At the higher pH of the reaction medium, there is a higher concentration of thiolate. It is favourable to the binding of the thiolate into the intercalated cobalt porphyrin and the proceeding of the direct reaction in the elementary steps of Eq. (3). At neutral pH, we detected the formation and accumulation of hydrogen peroxide in the reaction mixture, which was analyzed by iodometric titration. However, at high pH, we found that the formed hydrogen peroxide was rapidly decomposed to release dioxygen according to Eq. (9) in addition to its reaction with the thiol compound. The large amount of hydroxyl anion at high pH induces the dissociation of hydrogen peroxide into peroxide ion, which is readily decomposed by the catalysis of porphyrins [7]. The product analysis of the catalytic reaction mixture showed that disulphide was the major product, only a very small amount of sulphur-containing oxyacids were formed in the autoxidation.

Sulphur ligands are generally good  $\pi$ -donors and, therefore, they should enhance the rate of oxygenation and strengthen the Co-oxygen bond. The rate constants for dioxygen binding by a variety of Co-complexes have been reported to be large. Both oxygen binding and substrate complexation should be rapid ligand substitutions [14]. The elementary step of Eq. (5) involving the electron

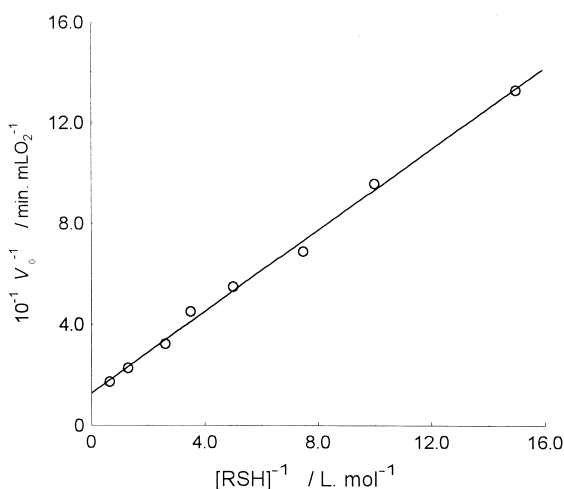


Fig. 6. Kinetic plot of reciprocal reaction rate versus reciprocal substrate concentration for the oxidation of 1-decanethiol by SbPTPPCo, SbPTPPCo 0.050 g,  $[\text{OH}^-] = 2.0 \text{ mol} \cdot \text{l}^{-1}$ ,  $T = 303 \text{ K}$ .

transfer is considered to be the rate-determining step. According to the reported method [16,19], the rate law can be written as:

$$v_0 = -\frac{d[\text{TPPCoSR}^- \text{O}_2]}{dt}$$

$$= \frac{k_4[\text{RS}^-][\text{O}_2][\text{TPPCo}]_t}{[\text{RS}^-][\text{O}_2] + ((k_{-3} + k_4)/k_3)[\text{RS}^-] + (k_4/k_2)[\text{O}_2] + ((k_{-2}k_{-3} + k_{-1}k_4)/k_2k_3)}$$

when  $[\text{O}_2] \gg [\text{RS}^-]$ ,  $[\text{RS}^-] \rightarrow \infty$ , then  $v \rightarrow v_{\max}$ ,

$$v_0 = -\frac{d[\text{TPPCoSR}^- \text{O}_2]}{dt} = \frac{v_{\max}[\text{RS}^-]_0}{K_A + [\text{RS}^-]_0}$$

$$\frac{1}{v_0} = \frac{1}{v_{\max}} + \frac{K_B}{v_{\max}[\text{RSH}]_0}$$

where  $v_{\max} = k_4[\text{TPPCo}]_0$ ,  $K_A = k_4/k_2$ ,  $K_B = K_A k_{-1}^{\text{H}}[\text{H}^+]/k_1^{\text{H}}$ .

These type of equations were originally suggested by the Lineweaver–Burk equation. Fig. 6 shows a plot of  $v_0^{-1}$  against  $[\text{RSH}]_0^{-1}$  at constant  $[\text{O}_2]$  under the same conditions. The linear nature of this plot (correlation coefficient  $> 0.99$ ) leads support to the proposed scheme, which exhibits enzyme-like kinetic behaviour.

#### 4. Conclusions

To our knowledge, this study constitutes the first report of the catalyst, SbPTPPCo, its preparation and catalytic behaviour for the thiol oxidation by molecular oxygen. The intercalation of cobalt porphyrin into the layered host material SbP can proceed in situ more effectively in an organic acid solvent than in water. The acidity of the solvent and higher refluxing temperature accelerate the preparation reaction to a great extent. The autoxidation of thiols catalyzed by SbPTPPCo involves the formation of catalytic center of mononuclear complex. The SbP-intercalated cobalt porphyrin transfers the electron of  $\text{RS}^-$  to bound dioxygen. SbPTPPCo demonstrates very good efficiency and stability for the catalytic thiol autoxidation even at very high pH. Our results show the potentialities of the intercalation of cobalt porphyrin into the layered structure of SbP to prevent the formation of inactive  $\mu$ -oxo dimers and the degradation of cobalt porphyrin in the oxidation reaction. Therefore, it occurred to us that the intercalation into SbP provides a good way to improve the catalytic capability of some neutral or cationic biomimetic metallo macrocyclic complexes.

#### Acknowledgements

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