

Synthesis and photocatalytic oxidation properties of Co(II)-tetra-[4-(*p*-toluene-sulfonyloxy) phenyl] porphyrin

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Abstract

A meso-tetra-[4-(*p*-toluene-sulfonyloxy) phenyl] porphyrin (H₂TTSOPP) was synthesized under the condition of phase-transfer catalyst. The complexes of cobalt(II) and manganese(II) were also synthesized. All of the synthesized products were characterized by elemental analysis, electronic absorption spectrum, IR spectrum and proton magnetic resonance spectrum. The oxidation of aromatic aldehydes with O₂ was likewise investigated in the presence of porphyrin complexes, which were used as photocatalysts under illuminated with 450 W high-pressure mercury lamp (HPML). The oxygen uptaking volume was measured during the reaction process. It was observed that the complex could catalyze the oxidation of aromatic aldehydes. The photocatalytic oxidation kinetics of *p*-chlorobenzaldehyde was also investigated. It was found that apart from the first sampling time — which was included in the induction period — the disappearance of *p*-chlorobenzaldehyde thoroughly conformed with first-order kinetics, and the kinetics decay constant was 0.00561 min⁻¹, while the lifetime was 134.3 min. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Benzaldehyde is an important industrial material in making commodity chemicals such as lauraldehyde, lauric acid, benzybenzoate, phenylacetadehyde, etc. However, aromatic aldehydes have proven to be toxic pollutants in the environment. Thus, both their oxidation and toxicity elimination are important for environmental protection. In the presence of complexes of porphyrins, the catalytic oxidation of organic substrate with molecular oxygen is getting im-

portant consideration under mild conditions owing to their function of molecular oxygen-activation [1–4]. Meguro et al. [5], Yasukazu et al. [6], X.Y. Wang et al. [7], Wang and Ni [8] and J.Q. Wang et al. [9] reported that cobalt porphyrins could catalyze the oxidation of aldehydes without any direct light. According to their observation, they considered that the oxidation reaction occurred from the interaction between metalloporphyrin and percarboxylic acid, which was produced and accumulated with the decomposition of porphyrin ring. Recently, in our laboratory, a series of metalloporphyrins were synthesized and used as photocatalysts for the oxidation of aromatic aldehydes [10–12]. In

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this paper, a new meso-tetra-[4-(*p*-toluene-sulfonyloxy) phenyl] porphyrin ($H_2TTSOPP$) and its complexes of cobalt(II) and manganese(II) were synthesized and characterized. High-pressure mercury lamp (HPML) was also used to radiate and initiate the oxidation in order to investigate the effect of light on the oxidation of aromatic aldehydes in the presence of complexes of porphyrin, which was used as photocatalyst. The porphyrin ring could not be broken down until 6 days without any direct light. Illuminated with 450 W HPML, however, the porphyrin ring was destroyed completely after 28 min. Meanwhile, large amounts of oxygen were absorbed. It is believed that the light could initiate the destruction of porphyrin ring, which could form some active catalysis species — such as percarboxylic acid, which in turn, could accelerate the oxidation reaction.

2. Experimental

2.1. Material

The H_2THPP was prepared and characterized according to methods published earlier [13].

2.1.1. Synthesis of $H_2TTSOPP$

We dissolved 1.356 g of H_2THPP (ca. 2 mmol) and 15 mg phase-transfer catalyst (hexadecyltrimethylammonium bromide) in 50 ml of aqueous 5% sodium hydroxide by stirring. The whole mixture was stirred for 15 min, and the color changed from green to deep gray. Then, 25 ml solution of *p*-toluene-sulfonyloxy chloride (ca. 20 mmol) in dry chloroform was added dropwisely with vigorous stirring. The solution color gradually transformed from deep-gray into brownish red, and was stirred for another 20 min in order to complete the reaction. Water (50 ml) was poured in and the chloroform phase was separated; then the water phase was extracted with 10 ml chloroform twice. The crude product was obtained after the removal of solvent, and also was separated twice

with neutral alumina oxide (200–300 mesh) column chromatography, was eluted with chloroform. Then the eluent of first violet band was collected, concentrated and the violet crystal was obtained. The yield was 68.6%. Anal. found (Calculated for $C_{72}H_{54}O_{12}N_4S_4 \cdot 4H_2O$): C: 62.49% (62.36%); H: 4.64% (4.36%); N: 4.44% (4.80%).

2.1.2. Preparation of Co(II) meso-tetra-[4-(*p*-toluene-sulfonyloxy) phenyl] porphyrin (CoTT-SOPP)

Cobalt acetate, at 0.367 g (ca.1.3 mmol), was added into 40.0 ml *N,N*-dimethylformamide (DMF) of dissolved 0.2 g (ca. 0.15 mmol) H_2TCMPP . After refluxing and stirring for 2 h, the mixture was poured into equal volumes of cold, distilled water. The precipitation was filtered and washed with distilled water twice, then dried after being left for 12 h. The crude product was purified by chromatography. The product was dried under vacuum for 4 h at 80°C after removing the solution. Anal. found (Calculated for $CoC_{72}H_{52}O_{12}N_4S_4 \cdot 2H_2O$): C: 61.60% (61.19%); H: 4.02% (4.04%); N: 4.31% (4.02%).

The Mn(II) H_2THPP was prepared according to the above synthesis method of CoTT-SOPP. Anal. found (Calculated for $MnC_{72}H_{52}O_{12}N_4S_4$): C: 64.44% (64.13%); H: 3.78% (3.89%); N: 4.31% (4.15%).

The Co(II)-meso-tetra(benzoyloxyphenyl) porphyrin (CoTBCOPP) and Co(II)-meso-tetra(benzene-sulfonyoxy-phenyl) porphyrin were synthesized and characterized, respectively, according to the methods described in literature [14,15]. *p*-Chlorobenzaldehyde was a chromatographic-grade reagent. Benzaldehyde was carefully distilled under nitrogen atmosphere to ensure the complete removal of oxidized material. *p*-Hydroxybenzaldehyde was a chemical grade reagent, and all the solvents were analytical grade. The pure dioxygen was used from the steel bottle without any further treatment.

2.2. Apparatus

The electronic absorption spectra were recorded on a HITACHI U-3400 spectrophotometer. The IR spectra were measured by Alpha Centauri FT-IR. The proton magnetic resonance spectroscopy was detected with Bruker AC-400 FT-NMR. The content of C, H, and N was determined with Vario EL1106 elemental analyzer (Ger.). The reaction was monitored through GC-15/16A gas chromatography with FI detector, and the powdered product was analyzed by GC-MS 9A Gas chromatography-Mass spectrophotometer.

2.3. Oxygen absorption kinetics procedure of photocatalytic oxidation

The photocatalytic oxidation of aldehydes was carried out in benzene at 30°C using a thermostatic, stirred, two-layered quartz reactor over the reaction period of 6 h. A certain amount of CoTTSOPP, containing 10 ml 0.6 mol/l solution of substrates, was added into the reactor. The reactor was sealed and stirred with magnetic stirrer prior to illumination with various luminous source. The amount of oxygen absorbed during the course of reaction was pursued by means of a gas burette connected with the reactor.

2.4. Analysis

2.4.1. Gas chromatography condition

Analytical gas chromatography were performed using a flame ionization detector with GC-15A/16A gas chromatography set at 220°C, and a chromatographic column used was OV-17 column (3 m × 3 mm). Operating condition: column temperature was controlled by programmed procedure at the range of 80–180°C, and temperature increase rate was 15°C/min; injection port, 200°C; nitrogen carrier gas flow rate, 50 ml/min; A C-R3A chromatopac integrator was used to integrate peak areas; Sampling volume, 2 μl. During the oxidation of

p-chlorobenzaldehyde, the disappearing kinetics of *p*-chlorobenzaldehyde was measured with programmed temperature gas chromatography. First, the samples were prepared according to the procedure mentioned above, then mixed homogeneously in 1 ml sampled reaction mixture and 1 ml ethylbenzene, which was used as inner standard. Finally, 2 μl sample was set aside to inject into the injection port.

A calibration curve was obtained for *p*-chlorobenzaldehyde and was found to be linear in the range of 0.03–0.36 mol/l (Fig. 1). The concentrations of *p*-chlorobenzaldehyde and the peak area ratios between *p*-chlorobenzaldehyde and inner standard were well correlated with the regression equation as follows:

$$A_p/A_i = 0.00049 + 0.25816C \text{ (mol/l)}$$

$$(R = 0.99935)$$

A_p is the peak area of *p*-chlorobenzaldehyde; A_i is the peak area of inner standard; C is the molar concentration of *p*-chlorobenzaldehyde and R is the coefficient for the straight line.

2.4.2. Product analysis

The powdered product, which was accumulated during the reaction process, was filtered, washed with benzene twice, recrystallized from ethanol, dried over and characterized by IR-spectrum and GC-MS spectrum.

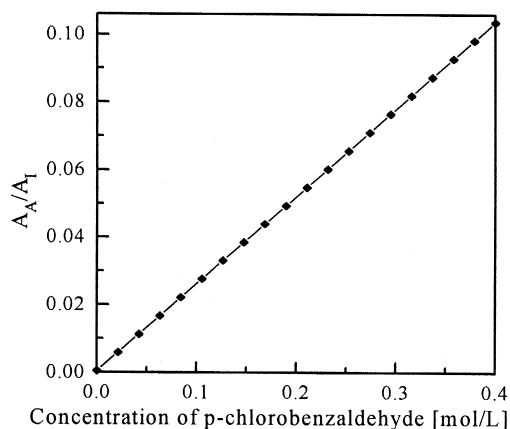


Fig. 1. The calibration curve.

3. Result and discussion

3.1. Synthesis section

3.1.1. UV spectra

The H₂TTSOPP and complexes of cobalt (CoTTSOPP) and manganese (MnTTSOPP) were recorded in DMF by electronic absorption spectrum. The porphyrin ligand exhibited a strong Soret band at 417.4 nm, Q_x(0–0) band at 645.3 nm, Q_x(1–0) band 589.6 nm, Q_y(0–0) band in 548.0 nm, and Q_y(1–0) band at 514.1 nm. It is a typical UV–Vis spectrum of porphyrin ligand. But in the solution of metalloporphyrin, the number of the Q bands decreased, and the Soret band also had a slight shift. CoTTSOPP exhibited Soret band at 415.5 nm, and Q_y(1–0) at 529.8 nm, and MnTTSOPP also exhibited Soret band 465.8 nm, Q_x(0–0) at 680.6 nm, Q_x(1–0) at 600.2 nm, and Q_y(0–0) at 566.6 nm.

3.1.2. IR spectra

The vibration spectrums were recorded in KBr. The IR spectroscopic data proved that some functional groups exist. Take H₂TTSOPP, for example — the absorption band of ligand at 1011.6 cm⁻¹ (in planarity) and 739.7 cm⁻¹ (out of planarity) were assignable to the N–H bond, the ν N–N weak absorption band was about 3319.3 cm⁻¹, and S=O vibration band occurred at 1198.7cm⁻¹. But in the complexes, all of the three bonds disappeared and a strong absorption band appeared at almost 1000 cm⁻¹.

3.1.3. Proton magnetic resonance spectrum

As for H₂TTSOPP, porphyrinato hydrogen at the center of ligand shifts greatly to high field and shows the peak at -2.92 δ ppm. However, the peak disappeared after the complexing of porphyrin with metal. The ¹H NMR data of H₂TTSOPP, CoTTSOPP and MnTTSOPP are shown in Table 1.

3.2. Photocatalytic oxidation of aromatic aldehydes

It is well known that aromatic aldehydes could be autooxidized in the presence of air, and the light could catalyze the reaction. However, illuminated with 450-W HPML, in the reaction during over 360 min only 17.2 ml dioxygen was absorbed. When the metalloporphyrin were used to catalyze the oxidation of aromatic aldehydes with molecular oxygen illuminated with 450 W HPML, the absorbed volume of oxygen was greatly increased and reached 36.3 ml. So we may obtain a conclusion that the light could initiate the destruction of porphyrin ring, which could result in the change of solution color from brownish red to brownish black, then to light yellowish. A great deal of white powder was obtained during the reaction. The white solid was also characterized by the IR and GC-MS spectra — the spectrum completely matched with the standard spectrum of *p*-chlorobenzoic acid [16,17]. Some researchers [7–9] believe that the change of solution color could be at-

Table 1
¹HMR spectra data of H₂TTSOPP and CoTTSOPP

Compounds	Pyrrole H	Phenyl H		-CH ₃	-NH
		External	Internal		
H ₂ TTSOPP	8.75 (8H)	8.09–8.12 (8H) 7.47–7.49 (8H)	7.97–7.99 (8H) 7.40–7.42 (8H)	2.53 (12H)	-2.94
CoTTSOPP	8.65 (8H)	7.94 (8H) 7.39–7.42(8H)	8.12 (8H) 7.46 (8H)	2.52 (12H)	-

tributed to the destruction of porphyrin ring, and some studies [5,7,9–12] have also stated that the porphyrin ring was completely destroyed during the reaction with the accumulation of percarboxylic acid, which was formed as an intermediate species. The experiment yielded the same trend of a decrease in the absorbency of Soret band, which could characterize with porphyrin as earlier studies have reported [7–12].

3.2.1. The oxidation mechanism of an aldehyde

The mechanism was discussed in detail in our earlier works [10–12]. As we have observed, the light may be considered to initiate the oxidation of aldehydes, shorten the inhabitation period, facilitate to produce the radical RCO, and induce chain reaction — thus, consequently accelerating the oxidation of aldehydes.

3.2.2. Reaction kinetic analysis

Illuminated with 450 W HPML, the oxidation kinetics of *p*-chlorobenzaldehyde in benzene with dioxygen was investigated using CoTTSOPP as photocatalyst at 30°C. It is easy to see that after a short induction period, *p*-chlorobenzaldehyde disappeared dramatically while being illuminated with HPML. It could also be inferred that apart from the first sampling time — which was included in the induction period — the disappearance of *p*-chlorobenzaldehyde completely conformed with

first-order kinetics (Fig. 2), and the kinetics regression equation were shown as the following:

$$\ln C_t = -0.8448 - 0.00561t \quad (R = -0.9979),$$

when life time $t_{1/2} = 134.3 \text{ min}^{-1}$ (HPML).

3.2.3. The effect of para-substituted phenyl ester group of porphyrin

Various para-substituent phenyl ester metalloporphyrins were used as photocatalyst to catalyze the oxidation of *p*-chlorobenzaldehyde in benzene with dioxygen at 30°C. The active order of photocatalyst was shown as follows: CoTPP > CoTBCOPP > CoTTSOPP > CoTBSOPP. In the presence of CoTPP [5], aromatic aldehydes could be autooxidized without any direct light, while it was found that light was essential to initiate oxidation in the presence of CoTBCOPP, CoTBSOPP and CoTTSOPP. Based on the electron-donating effect of the para-substituent group, the following conclusion could be drawn: electron-donating substituent group could enhance the photocatalytic activity of metalloporphyrin, while in contrast, the electron-withdrawing group could weaken the catalytic activity of the photocatalyst. It might be explained that dioxygen combined with center metal Co(II) by an unpaired electron residing essentially in a dioxygen π^* orbital in the form of $\text{Co}^{\text{III}}(\text{O}_2^-)$ [18]. The electron-attracting substituent group attached to the phenyl groups of porphyrin ring weakened the electron cloud density of porphyrin ring resulting in a decrease in electron cloud density of metal center — in other words, this unfacilitated to form active dioxygen, and hampered the activity of the catalyst. Various para-substituted ester groups attached to the porphyrin's phenyl have the following electron-attracting sequence: benzene-sulfonyoxy > 4-(*p*-toluene-sulfonyoxy) > benzoyloxyphenyl, and the induction period has the same sequence: 58, 28, and 26 min. In this work, it is confirmed that illumination offers a favorable condition that would initiate the oxidation of aldehydes.

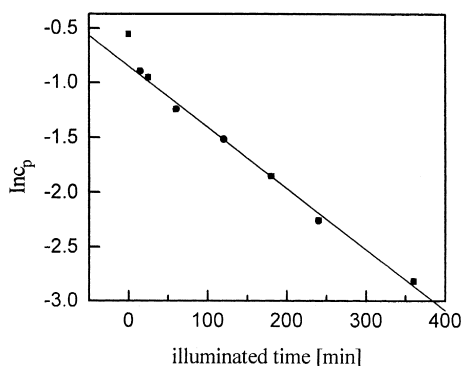


Fig. 2. The kinetics curve of *p*-chlorobenzaldehyde.

3.2.4. The effect of central metal

In the presence of two metalloporphyrins, the kinetic curves of absorbed dioxygen during the oxidation of *p*-chlorobenzaldehyde were investigated under illumination from 450 W HPML (Fig. 3). It shows that MnTTSOPP has the same effect as CoTTSOPP on the oxidation reaction. However, a long induction period is required in the presence of MnTTSOPP. In the presence of CoTTSOPP, the absorption of oxygen and the change of solution color could not be observed within 6 days if there is a lack of any direct light. While under illumination by 450 W HPML, the oxidation was greatly accelerated after the 28-min induction period, and large amounts of oxygen were absorbed.

3.2.5. The effect of substrates

In order to investigate the photocatalytic effect of CoTTSOPP on various substrates, the oxidation kinetics of three substrates, such as *p*-chlorobenzaldehyde, benzaldehyde and *p*-hydroxybenzaldehyde were studied, respectively. In the presence of CoTTSOPP, the photocatalytic oxidation of *p*-chlorobenzaldehyde appeared much faster than benzaldehyde. The change could not be observed for some derivatives of benzaldehyde, which have electron donor or attractor functions — such as *p*-hydroxybenzaldehyde and *p*-nitrobenzaldehyde. As described in early papers [7–12], it was also

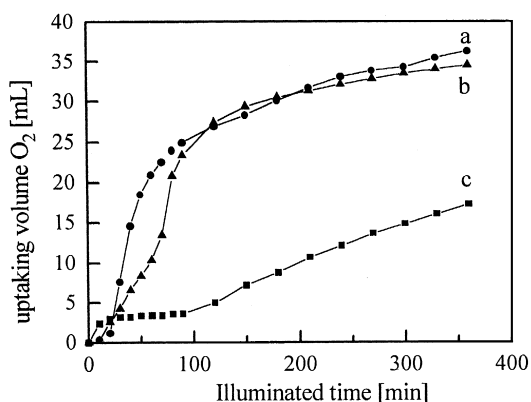


Fig. 3. The effect of central metal. (a) CoTTSOPP; (b) MnTTSOPP; (c) no catalyst.

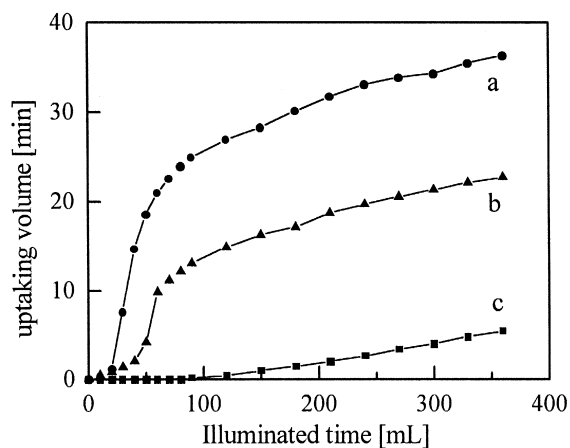


Fig. 4. The effect of substrates. (a) *p*-Chlorobenzaldehyde; (b) benzaldehyde; (c) *p*-hydroxybenzaldehyde.

found in this experiment that the effect of substrate on oxidation reaction involved a very complicated processes, which are shown in Fig. 4. It is interpreted that para-substituted chlorine atom could strengthen the stability of active species, which formed in the reaction by its inductive effect, while hydroxyl or methoxyl could inhibit the formation of active species through its conjugative electron-donating effect [8,9].

3.2.6. The effect of concentration of photocatalyst on the oxidation

The oxidation kinetics of aldehydes were studied with various concentrations of porphyrin when the ratios between CoTTSOPP and substrate were 1:2000, 1:1500, 1:1000, 1:500, and the induction period of reaction were measured as 11, 18, 28, 62 min, respectively. It seems that the induction period increased with the quantity of the added metalloporphyrin — that is, when the quantity of metalloporphyrin was increased, the strength of the inhibitive effect was correspondingly greater and the induction period longer. It was also obvious that the amounts of oxygen uptake varied considerably depending on the concentration of CoTTSOPP (as shown in Fig. 5). The highest oxygen uptake was obtained when the catalyst/substrate ratio was

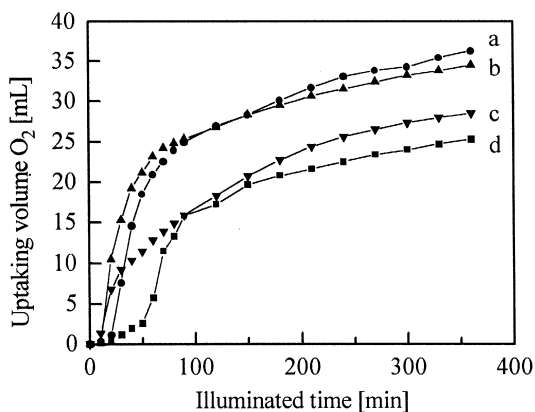


Fig. 5. The effect of concentration of photocatalyst. (a) 1000:1; (b) 1500:1; (c) 2000:1; (d) 500:1.

1:1000. The same trend was obtained according to the literature [10–12]. It might be interpreted that metalloporphyrin would be dimerized when its concentration was high, thus when the valid concentration of metalloporphyrin — which could be used as catalyst — was reduced, the catalytic capacity was likewise reduced.

3.2.7. The effect of luminous flux

In order to investigate the effect of light, the illuminant was replaced with 125 W HPML or 300 W Iodine Tungster Lamp (ITL). It is easy to see from Table 2 that absorbed dioxygen increased with light flux of illuminant when various flux of HPML were used to radiate the oxidation. As compared with 125 W HPML, longer induction period and lower absorption of oxygen were obtained under illumination with 300 W ITL. It should be emphasized that HPML played a role in the initiation of oxidation, while ITL had little effect on oxidation. It is because

Table 2
Induction period and absorbed oxygen under various illuminants
The substrate was *p*-chlorobenzaldehydes.

Illuminant	450 W HPML	125 W HPML	300 W ITL
Induction period (min)	28	70	74
Amount of oxygen (ml)	36.3	23.3	20.3

HPML has a characteristic spectra of UV and visible light, while ITL is characterized by visible light alone — that is, the UV light of HPML has a greater effect than the visible light of ITL on the oxidation of aldehydes.

3.2.8. The effect of various solvent

Under illumination with HPML, The dioxygen absorption kinetic of *p*-chlorobenzaldehyde in various solvents, such as ethyl acetate and DMF, etc., were investigated at 30°C and is shown in Fig. 6. The oxidation rate in the presence of metalloporphyrin was considerably dependent on the polarity of solvent. The induction periods of reaction in different solvents were sequenced as: DMF (> 6 h) > acetone (30 min) > ethyl acetate (28 min) = benzene (28 min). The sequence is basically related with the decreasing order of the dielectric constant values (ϵ 25°C), which could be used to approximately estimate the polarity of solvent: acetone (20.7) > ethyl acetate (6.02) > benzene (2.274). It proved that the induction period increased with the polarity strength of solvents, for instance, the induction period of the reaction was 28 min in benzene. However, with some strong polar solvents such as DMF, the induction period of reaction was longer than 6 h. This could be explained by the fact that DMF acted as a solvent and the fifth ligand was very easy to coordinate with CoTTSOPP in the axial direc-

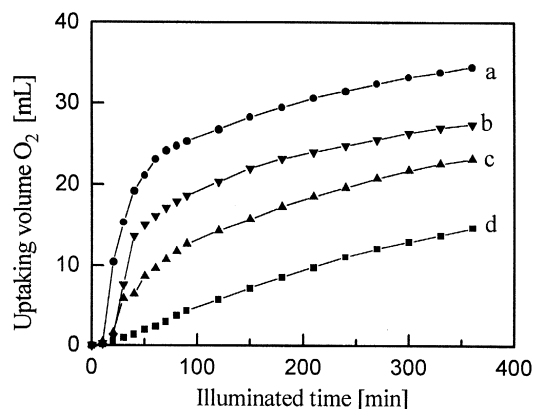


Fig. 6. The effect of various solvents. (a) Benzene; (b) ethyl acetate; (c) acetone; (d) dimethylformamine.

Table 3

Induction period and absorbed oxygen in the absence or presence of hydrogen peroxide
The concentration of hydrogen peroxide was 0.1 mol/l.

Substrate	Presence of hydrogen peroxide		Absence of hydrogen peroxide	
	<i>p</i> -Chlorobenzaldehyde	Benzaldehyde	<i>p</i> -Chlorobenzaldehyde	Benzaldehyde
Induction period (min)	8	15	28	55
Amount of oxygen (ml)	16.4	12.5	36.3	22.7

tion, consequently reducing the coordination of Co^{2+} with molecule oxygen and as a result, the rate of oxidation was decreased dramatically.

3.2.9. The effect of hydrogen peroxide

The photocatalytic oxidation of *p*-chlorobenzaldehyde and benzaldehyde was investigated in presence of H_2O_2 over 3 h. It is well known that $\text{HO}_2\cdot$ and $\text{HO}\cdot$ radicals, which play an important role in initiating the chain reaction, are easy to generate from hydrogen peroxide under illumination [19,20].

The addition of 0.1 mol/l H_2O_2 could greatly accelerate oxidation. The active oxygen was formed in the reaction due to the participation of H_2O_2 in the oxidation of aromatic aldehydes. Therefore, the induction periods were significantly shortened and the external oxygen absorbed was greatly reduced. The relevant results were shown in Table 3.

In the catalytic system of aldehydes, Meguru et al. [5] believed that the hydroperoxy radical could abstract a hydrogen atom from the aldehyde to initiate oxidation by forming hydrogen peroxide. Hydroperoxy radical and $\text{HO}\cdot$ may also react with other free radicals and form inert compounds.

3.2.10. The effect of the fifth ligand on oxidation

When metalloporphyrins or metallophthalocyanines were used as catalysts, the effect of addition to axial ligand was an interesting issue [21,22] in the catalytic system. In our experiment, the effect of adding 5 mg imidzole as fifth ligand on the photocatalytic oxidation was studied over the reaction of 3 h. Compared with 30.1 ml, without addition of imidzole, only 15.6 ml oxygen were absorbed. It is evident that the

addition of fifth ligand could extend the induction period and also appeared to have a negative effect on the amount of absorbed oxygen.

4. Conclusions

1. CoTTSOPP and MnTTSOPP could catalyze the oxidation of aromatic aldehydes under illumination from HPML, and the higher absorption oxygen and shorter induction period was obtained when CoTTSOPP was used as photocatalyst. In the presence of CoTTSOPP, the optimum oxidation condition was carried out in benzene at 30°C when the catalyst/substrate ratio used was 1:1000.

2. The long induction period and low amount of absorbed oxygen was obtained the fifth ligand was added. However, the induction period was greatly shortened by the addition of hydrogen dioxide.

3. The major product of oxidation was measured as aromatic acid.

Acknowledgements

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