Photocatalytic oxidation of aromatic aldehydes with Co(II)tetra-(benzoyloxyphenyl)porphyrin and molecular oxygen

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Abstract

Illuminated with 450 W high pressure mercury lamp (HPML), the oxidation of aromatic aldehydes was investigated with molecular oxygen in the presence of Co(II)[meso-tetra(benzoyloxy-phenyl) porphyrin] (CoTBCOPP). The oxygen uptake was measured during the reaction process. Under the mild condition (30°C, 1 atm O_2), the oxidation reactions occurred without consumption of reducing agent. It was observed that CoTBCOPP could catalyze the oxidation of aromatic aldehydes by reversibly binding molecular oxygen. The effects of the concentrations of catalyst and substrate in the oxidation reaction system were studied, meanwhile the factor of solvents was discussed in detail. The induction period was greatly shortened by raising the temperature of oxidation system or adding hydrogen dioxide. However, low dioxygen absorbed and the long induction period were obtained when imidazole was added as the fifth ligand. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalytic oxidation; Cobalt(II)porphyrin; Aromatic aldehydes; Molecular oxygen

1. Introduction

Metal complexes of porphyrin, especially cobalt porphyrins were often used as catalysts for selective oxidation of organic substrate under the mild condition owing to their function of molecule oxygen-activating [1–3]. Yasukazu et al. [4,5] reported that CoTPP could catalyze the oxidation of aldehydes. They also noticed that CoTPP could be recovered quantitatively, and recycled after the reaction. But some of the studies (Wang et al. [6–8]) found that the metalloporphyrins were nominal catalysts. According to their observation, the oxidation reaction occurred from the interaction between metalloporphyrin and percarboxylic acid which was accumulated with the destruction of porphyrin ring during the course of the reaction. In this paper, it is the first time that high pressure mercury lamp (HPLM) was used to radiate and initiate the oxidation in order to investigate the effect of light on the oxidation of aromatic aldehydes in presence of Co(II)porphyrin which was used as photocatalyst. Illuminated with 450 W HPML, the porphyrin ring was destroyed completely after 22 min, meanwhile large amounts of oxygen were absorbed, but the porphyrin ring could not be broken down within 6 days without any direct light. It indicated that light could initiate

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the destruction of porphyrin ring, which could form some catalytically active species.

2. Experimental

2.1. Material

Co(II)tetraphenylporphyrin (CoTPP) was prepared as in early publication methods [9]. The M-meso-tetra(benzoyloxyphenyl) porphyrin (MTBCOPP, M = Co(II), Fe(III), Cu(II)) and Co(II)-meso-tetra(benzenesulfonyoxy-phenyl) porphyrin characterized according to the methods described in the literature [10,11] respectively. *p*-Chorobenzaldehyde was chromatographic grade reagent and used immediately after being obtained from Fluka. Benzaldehyde was carefully distilled under nitrogen atmosphere to ensure the complete removal of oxidized material. *p*-Hydroxybenzaldehyde and *p*-nitrobenzaldehyde used were chemical grade reagents, and all the solvents were analytical grade materials. The pure dioxygen was used from the steel bottle without any further treatment.

2.2. 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. Adding a certain amount of CoTBCOPP into a reactor containing 10 ml 0.6 mol/l solution of substrates, then sealed and stirred with magnetic stirrer prior to illumination with various luminous sources. The amounts of oxygen absorbed during the course of reaction were pursued by means of a gas burette which was connected to the reactor.

3. Results and discussion

During the course of aromatic aldehyde oxidation, it could be observed that a great deal of white solid appeared with the change of solution color from brownish red to brownish black, then to light yellowish. (The colour was light greenish when the metalloporphyrin's concentration was high.) Some researchers [6,8,12] believed that the transformation of solution color can be attributed to the destruction of porphyrin ring. Some literatures [4,6] have also confirmed that the porphyrin ring was completely destroyed during the course of reaction with accumulation of percarboxylic acid which was formed as intermediate species. The experiment gained the same trend of a decrease in absorbance of Soret band which could characterize with porphyrin as the former literature indicated [6]. Therefore, the oxidation was dramatically accelerated with accumulation of percarboxylic acid.

3.1. The effect of substrates

In the presence of CoTBCOPP, the photocatalytic oxidation of *p*-chlorobenzaldehyde appeared much faster than benzaldehyde, while in some derivatives of benzaldehyde which have electron donor or attractor, such as *p*-hydroxybenzaldehyde and *p*-nitrobenzaldehyde, the change of solution color could not be observed and obvious absorption of dioxygen at 30°C occurred after 12 h. ([catalyst]:[substrate] = 1:1000). As mentioned above, it was found in our experiment that the effect of substrate on the oxidation reaction had very complicated processes which are shown in Fig. 1. It seemed 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 which was on the *para*-position could inhibit the formation of active species by its hyper-conjugate effect.

3.2. The effect of para-substituted phenyl ester groups of porphyrin

The oxidation of *p*-chlorobenzaldehyde in benzene with dioxygen was investigated using *para*-substituent phenyl ester metalloporphyrin
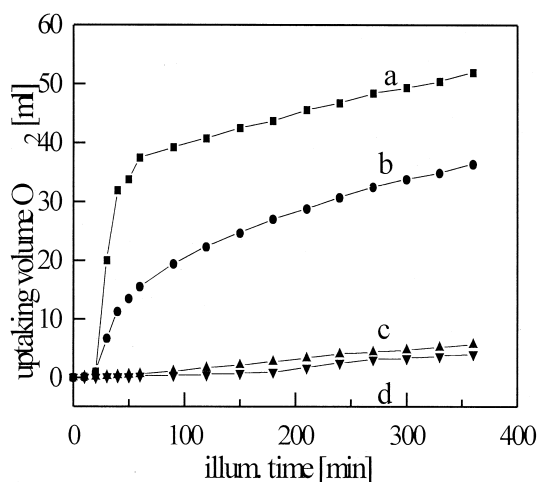
Fig. 1. Effect of substrate.

as photocatalyst at 30°C. The results are shown in Fig. 2 and the active order of photocatalyst is shown as follows: CoTPP > CoTBCOPP > CoTBSOPP. In presence of CoTPP [4], aromatic aldehydes could be autooxidized without any direct light, while it was found that the light was essential to initiate the oxidation in presence of CoTBCOPP or CoTBSOPP. According to electron-donating effect of *para*-substituent group, the following conclusion can be drawn: Electron-donating substituent group could enhance photocatalytic activity 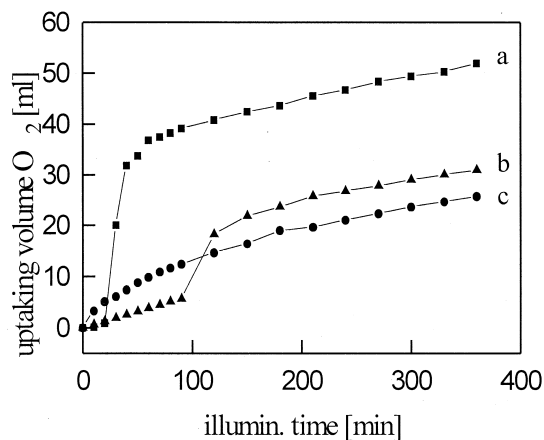of metalloporphyrin, in contrast to electron-withdrawing group, it could weaken catalytic activity of the photocatalyst. This might be explained that the dioxygen combined with metal center Co(II) by an unpaired electron residing essentially in a dioxygen π^* orbital and could be considered to be a dioxygen present in the form of $Co^{III}(O2-)$ [13]. The electron-attracting substituent attached to the phenyl groups of the porphyrin ring weakened electron cloud density of the porphyrin ring resulting in a decrease in electron cloud density of the metal center, in other words, this unfacilitated the formation of active dioxygen, and reduced the activity of the catalyst. In this work, it has been confirmed that illumination offers a favorable condition to initiate the oxidation of aldehydes.

3.3. The effect of central metal

Illuminated with HPML, the kinetic curves of absorbed oxygen during the oxidation of *p*-chlorobenzaldehyde were investigated in the presence of CoTBCOPP, CuTBCOPP and FeTBCOPP. The observation results are shown in Fig. 3. Under illumination with HPML, a long induction period was required in the presence of CuTBCOPP though the same oxygen was absorbed as CoTBCOPP, also a low absorption of oxygen and a long induction period were ob-

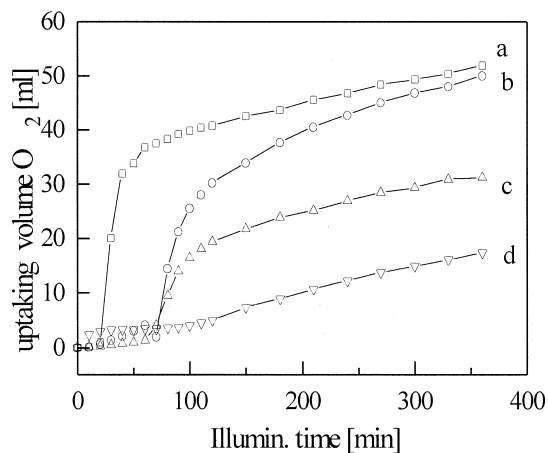Fig. 2. Effect of substituted group.

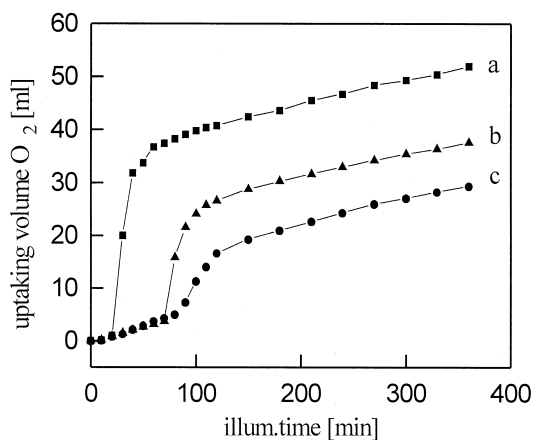

Fig. 3. Effect of various catalyst.

Fig. 4. The effect of luminous flux.

tained when FeTBCOPP was used as catalyst. However, in the presence of CoTBCOPP, the absorption of oxygen and the change of solution colour could not be observed within 150 h with lack of any direct light. While illuminated with 450 W HPML, the oxidation was greatly accelerated after 22 min induction period, while large amounts of oxygen were absorbed. It was well interpreted that the light could accelerate the oxidation of aldehyde and stimulate the chain reaction.

3.4. The effect of luminous flux

It is well know that HPML has a characteristic spectra of ultra-violet and visible light, while Iodine Tungster Lamp (ITL) is characterized with visible light. In order to investigate light flux effect, the oxygen absorbed curve was measured by substitution of the illuminant with 125 W HPML or 300 W ITL. (Fig. 4) As for HPML, it was obtained that absorbed dioxygen increased with light flux of illuminant. The results proved that the higher the power of lamp was, in general, the more dioxygen was absorbed, and the shorter the induction period. As compared with 125 W HPML, longer induction period and lower absorption of oxygen were obtained under illumination with 300 W ITL. It would be emphasized the ultra-violet light of HPML played a key role in the initiation of

oxidation, while the visible light of ITL did little effect on the oxidation.

3.5. The effect of metalloporphyrin's concentration on oxidation

In the presence of CoTBCOPP, the oxidation process of aromatic aldehydes included two stages: Prior to destruction of porphyrin ring, metalloporphyrin inhibited the oxidation and showed as an induction period. After the destruction of porphyrin ring, the obvious absorption of oxygen occurred due to photocatalytic effect of active species which formed during the reaction. Oxygen absorption curves of the oxidation in benzene for *p*-chlorobenzaldehyde were tested in different concentrations of metalloporphyrin. When the ratios between CoTBCOPP and substrate were equal to 1:5000; 1:3500; 1:1000; 1:750 and 1:500, the induction period of reaction were measured as 3.0, 3.5, 22.0, 28.0, 32.0 min, respectively. The induction period increased with the quantity of the added metalloporphyrin. That is, when there was more metalloporphyrin, it had a stronger inhibitive effect, and the longer the induction period. It was obvious that the amount of oxygen uptake varied considerably depending on concentration of CoTBCOPP. (as shown in Fig. 5). The highest oxygen uptake was obtained
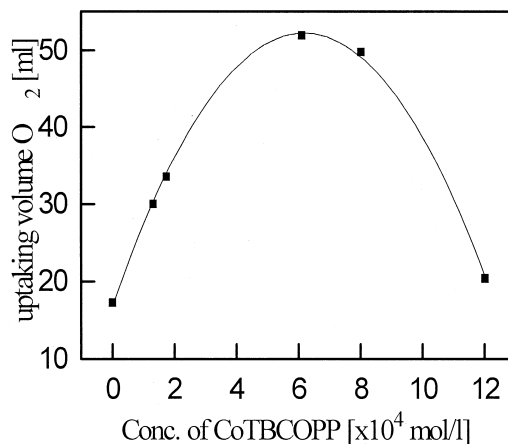

Fig. 5. Effect of CoTBCOPP conc. on absorbed O_2.

when [cat.]:[sub.] was used as 1:1000. This might be interpreted that metalloporphyrin would be dimerized when its concentration was high, thus reduced the valid concentration of metalloporphyrin which could be used as catalyst, as a result, the catalytic capacity was reduced.

3.6. The effect of the temperature of oxidation system

The kinetic curves of oxygen were investigated in benzene at 20, 30, 40°C respectively in presence of CoTBCOPP. It indicated that the induction period of reaction shortened with the increase of temperature of the oxidation system, the order is shown as follows: 24 min (20°C) > 22 min (30°C) > 16 min (40°C). This may well explain that high temperature might facilitate to destroy the porphyrin ring resulting in formation of active species. Thus, induction period could be saved by raising the temperature. But, the highest oxygen was absorbed at 30°C. So the optimize oxidation temperature was chosen at 30°C.

3.7. 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 [12,14] in the catalytic system. In the presence of CoTBCOPP, the rate of oxygen absorption varied considerably depending on the amounts of imidazole added. The effect of addition of imidazole as fifth ligand on the catalytic action of photocatalyst was studied in the range from 0.5 to 5 mg. It is evident that addition of the fifth ligand could extend the induction period, also a negative effect on the amount of absorbed oxygen appeared, that is, the more amount of imidazole added, the greater effect was made. It is obvious that the oxygen absorbed was in reverse proportional to the amounts of added imidazole in the range from 0.5 to 5 mg. The

relations are shown in Fig. 6, and the regression equation was calculated as follows:

$$V = 51.2704 - 6.4686\chi$$
$$(R = -0.9958; N = 5)$$

where V denotes the volume of oxygen absorbed; χ denotes the amount of added imidazole.

With respected to the fifth ligand, Elvidge and Lever [15] found that manganese phthalocyanine carried an oxygen molecule reversibly in pyridine solution. Calvin et al. explained this oxygen-carrying by means of a spectrophotometric method and pointed out the activation of oxygen by coordination of pyridine at *trans*-position. Zhang et al. [16] also found Fe-phthalocyanine in which iron had d^6 orbital, could donate an electron and stayed a state of half-full when a fifth ligand was added. The catalytic activity of photocatalyst would be greatly improved with enhancement of the active effect of catalysts.

Cobalt which has a d^7 orbital could not behave as above. In this paper, the less oxygen was absorbed when some organic bases such as imidazole or DMF were added as the fifth ligand. The reason was that the fifth ligand was competed with molecule oxygen to coordinate with central ion, then the compound of CoTB-
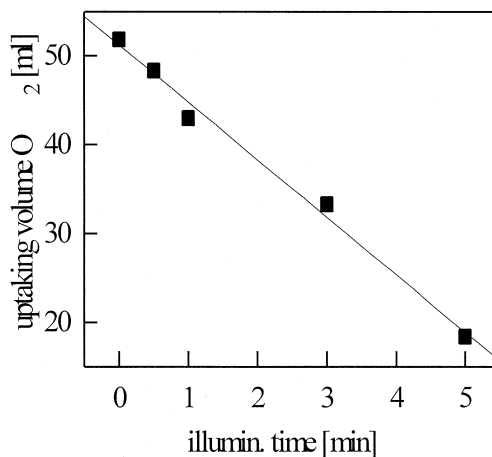

Fig. 6. Effect of amount of added imidazole.

COPP... O^2 was greatly reduced, which can represent active oxygen, finally the oxidation of aldehyde was reduced and the less oxygen was absorbed.

3.8. The effect of solvent

Under illumination with HPML, the dioxygen absorption kinetic of p-chlorobenzaldehyde in various solvent such as ethyl acetate, carbon tetrachloride, etc. were investigated at 30°C in detail (Fig. 7). The oxidation rate in the presence of metalloporphyrin was considerably dependent on polarity of solvent. The induction period of reaction in different solvents are shown as follows: Acetic acid > Acetone > Ethyl acetate > carbon tetrachloride > benzene. The order basically accorded with the decrease order of dielectric constant ($\varepsilon 25$) which can be used to estimate approximately the polarity of solvent: Acetone(20.7) > Acetic acid(6.15) > Ethyl acetate(6.02) > benzene(2.274) > carbon tetrachloride(2.228). It indicates that the induction period increased with the strength of polarity, that is, the induction period of oxidation reaction of aldehyde in inert solvent is much shorter than that in strong polar solvent. The induction period of reaction was 22 min in benzene, while
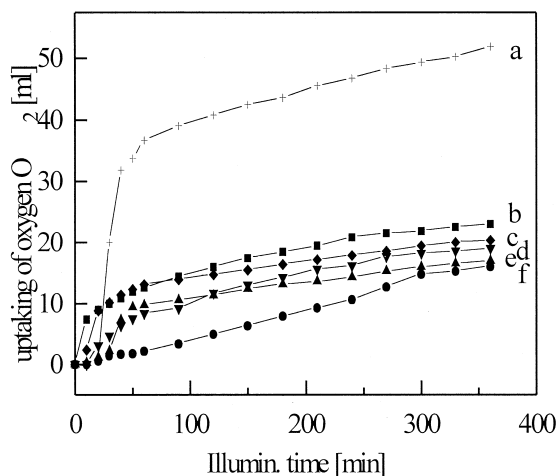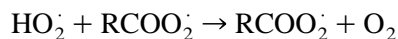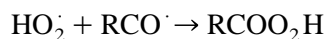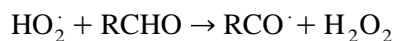

Fig. 7. The effect of solvent.

in some strong polar solvents such as N,N-dimethylformamide (DMF), the induction period of reaction was longer than 6 h. This can be explained that DMF, which acts as both solvent and the fifth ligand, very easily coordinates in axial direction with CoTBCOPP, thus this may reduce coordination of Co^{2+} with molecule O_2, then the rate of oxidation was decreased dramatically. So the following conclusion was drawn that the stronger the polar solvent, the easier axially coordination of solvents was induced, the fewer the active species were, which formed by coordinating with molecule oxygen, then the longer induction period was required.

3.9. Hydrogen peroxide effect

It is well known that $HO_2^{\cdot}$ radical and $HO^{\cdot}$ radical which played an important role to initiate the chain reaction was easy to generate from hydrogen peroxide under illumination. In the catalytic system of aldehydes, Meguru et al. [4] believed that the hydroperoxy radical could abstract a hydrogen atom from aldehyde to initiate the oxidation by forming hydrogen peroxide.

$$HO_2^{\cdot} + RCHO \rightarrow RCO^{\cdot} + H_2O_2$$
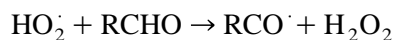
hydroperoxy radical may also react with other free radicals and form inert compound

$$HO_2^{\cdot} + RCHO \rightarrow RCO^{\cdot} + H_2O_2$$

$$HO_2^{\cdot} + RCO^{\cdot} \rightarrow RCOO_2H$$

$$HO_2^{\cdot} + RCOO_2^{\cdot} \rightarrow RCOO_2^{\cdot} + O_2$$

The photocatalytic oxidation of p-chlorobenzaldehyde and benzaldehyde was investigated in the presence of H_2O_2 over 3 h. Thus, addition of 0.1 mol/l H_2O_2 could greatly accelerate oxidation. This is due to the participation of H_2O_2 in the oxidation of aromatic aldehydes, then the oxygen was formed in the reaction. Therefore, the induction periods were significantly shortened, and dioxygen absorbed was greatly reduced. The relevant results are shown in Table 1.
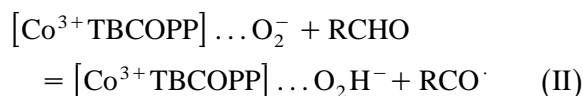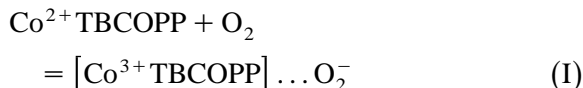
Table 1
Induction period and absorbed oxygen in absence or in presence of hydrogen peroxide

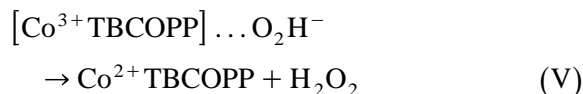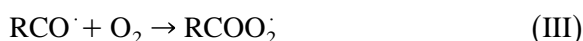| | In presence of hydrogen peroxide | | In absence of hydrogen peroxide | |
Substrate	p-chlorobenzaldehyde	Benzaldehyde	p-chlorobenzaldehyde	Benzaldehyde
Induction period(min)	5	20	22	32
Amount of oxygen (ml)	18.5	21.5	43.6	27.0

[a]The concentration of hydrogen peroxide was 0.1 mol/l.

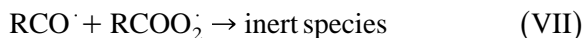### 3.10. The mechanism of photocatalytic oxidation

As described above, the center ion and oxygen were combined with π^* orbital by sharing an unpaired electron from the oxygen. It was widely accepted that a molecule oxygen activated through the electron transfer from a cobalt ion abstracted the hydrogen atom of aldehyde, thus induced chain reaction by producing radical. The oxidation of aldehyde is widely accepted to proceed through the following steps:Initiation:

$$Co^{2+}TBCOPP + O_2$$
$$= [Co^{3+}TBCOPP] \ldots O_2^- \qquad (I)$$
$$[Co^{3+}TBCOPP] \ldots O_2^- + RCHO$$
$$= [Co^{3+}TBCOPP] \ldots O_2H^- + RCO^\cdot \qquad (II)$$

Propagation:

$$RCO^\cdot + O_2 \rightarrow RCOO_2^\cdot \qquad (III)$$
$$RCOO_2^\cdot + RCHO \rightarrow RCOO_2H + RCO^\cdot \qquad (IV)$$
$$[Co^{3+}TBCOPP] \ldots O_2H^-$$
$$\rightarrow Co^{2+}TBCOPP + H_2O_2 \qquad (V)$$

Termination:

$$Co^{2+}TBCOPP + RCOO_2^\cdot \rightarrow inert\,species \qquad (VI)$$
$$RCO^\cdot + RCOO_2^\cdot \rightarrow inert\,species \qquad (VII)$$
$$2RCOO_2^\cdot \rightarrow inert\,species \qquad (VIII)$$

According to mechanism, it is understood that the catalyst activates a molecule oxygen to superoxidation which abstracts the labile hydrogen from aldehyde to initiate oxidation. The light can initiate the oxidation and shorten inhibition period, facilitate to produce the radical RCO$^\cdot$ and induce chain reaction, consequently accelerate the oxidation of aldehydes.

4. Conclusion

(1) CoTBCOPP could catalyze the oxidation of aromatic aldehydes under illuminated HPML, and the optimum oxidation condition was carried out in benzene at 30°C when the ratio between catalyst and substrate was used as 1:1000.

(2) The induction periods was greatly shortened by raising the temperature of oxidation system or adding hydrogen dioxide.

(3) The long induction period and low absorbed oxygen was obtained with adding the fifth ligand and the amounts of absorbed oxygen was in reverse proportional to added imidazole in the range from 0.5 to 5 mg.

Acknowledgements

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