

Photocatalytic activity study of Co(II)tetra(chloromethyl-phenyl) porphyrin in oxidation reaction of aromatic aldehydes[†]

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In the presence of Co(II)[meso-tetra(chloromethyl-phenyl) porphyrin] (CoTCMPP), the oxidation of aromatic aldehydes has been investigated with molecular oxygen under illumination with 450W high pressure mercury lamp (HPML). The oxygen uptake is measured during the reaction process. It is observed that CoTCMPP can catalyze the oxidation of aromatic aldehydes under the mild condition (30°C, 1 atm O₂). The major products are aromatic acids. The effects of some factors, such as catalyst, substrate, solvent and additive in the oxidation reaction system are discussed in detail.

As early as 1970s, Yasukazu and Meguru *et al.*^{1,2} reported that CoTPP could catalyze the oxidation of aldehydes without direct light. They also noticed that CoTPP could be recovered quantitatively, and recycled after the reaction. But, some of the studies (X.Y. Wang *et al.*³ and J.Q. Wang^{4,5}) revealed that metalloporphyrins seemed to be the nominal catalysts. They also indicated that the oxidation reactions occurred in the interaction between metalloporphyrins and per-carboxylic acid which was accumulated with the destruction of porphyrin ring during the reactions. Metalloporphyrins, especially the complexes of transition metals, were often used as photocatalysts for selective oxidation of organic substrate under the mild conditions due to their super photosensitivity.^{6,7} There are only a few reports⁸ involving in the photocatalytic oxidations of aromatic aldehydes. In this paper, the CoTCMPP was used as photocatalyst to initiate the oxidation of aromatic aldehydes. Irradiated with 450 W HPML, the porphyrin ring was decomposed completely after 26 min. In the time, large quantity of oxygen was absorbed, but the porphyrin ring could not be broken down until 6 days under the condition of taking any direct light. It indicated that light was important to initiate the destruction of porphyrin ring. As a result, some catalytically active species were formed.

Experimental Section

Materials: The meso-tetra(chloro-methyl phenyl)

porphyrin was purchased from Tokyo Chemical Industry Co. Ltd. The preparation of CoTCMPP: 1.05 g (*ca.* 3.6 mmole) cobalt acetate was added to 40.0 mL DMF in which 0.3723 g (*ca.* 0.45 mmole) H₂TCMPP was dissolved. After refluxing and stirring for 2 hr, the mixture was poured into equal volume of cold distilled water. The precipitate was filtered and washed with distilled water twice, then dried after standing for 12 hr. The crude product was purified by chromatography over 200-300 mesh neutral aluminium oxide column using chloroform as eluant. The product was dried *in vacuo* for 4 hr at 80°C before being characterized by UV and IR-spectrum.

p-Chlorobenzaldehyde used was a chromatographic grade reagent. Benzaldehyde was carefully distilled under nitrogen atmosphere to ensure the complete removal of oxidized materials. Both *p*-hydroxybenzaldehyde and *p*-nitrobenzaldehyde used were chemical grade reagents, and all the solvents were analytical grade materials. The pure dioxygen used was stored in a steel bottle without any further treatment.

Procedures of photocatalytic oxidation

Using benzene as the solvent, the photocatalytic oxidation of aldehyde was carried out in a two-layered quartz reactor with a thermostatant, and stirred at 30°C for more than 6 hr. Added a certain amount of CoTCMPP into the reactor containing 10 mL 0.6 mole/L solution of substrates, then sealed and stirred with a magnetic stirrer prior to illumination by using various luminous sources.

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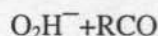
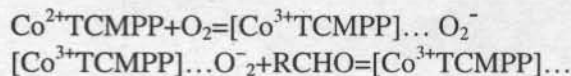
Analysis

The quantity of oxygen absorbed in the processes of the reactions were pursued by means of a gas burette which was connected with the reactor. The powder product resulted from the reaction was filtered, washed with benzene, recrystallized from ethanol, dried and characterized by IR-spectrum and GC-MS spectrum.

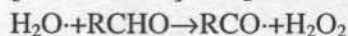
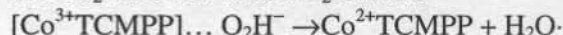
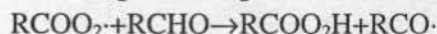
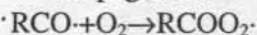
Results and Discussion

During the course of aromatic aldehyde oxidation, it could be observed that a great deal of white solid appeared following the change of solution colour from brownish red to brownish black, then to light yellowish. (The colour was light greenish when the metalloporphyrin's concentration was high). The white solid was characterized by IR spectrum and GC-MS spectrum, the spectrum completely matched with the standard spectrum of *p*-chlorobenzoic acid^{9,10}. Some researchers^{3,5} pointed out that the change of solution colour could attribute to the destruction of porphyrin ring, and some^{1,3} have confirmed that porphyrin ring was completely destroyed, with accumulation of percarboxylic acid which was formed as intermediate species and therefore the oxidation was dramatically accelerated. It was widely accepted that molecule oxygen could be activated through the electron transformation from cobalt(II) ion abstracted the hydrogen atom of aldehyde, thus chain reaction was induced by produced radical. The mechanism may be considered as follows:

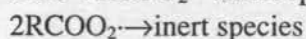
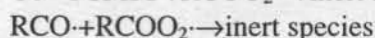
Initiation:



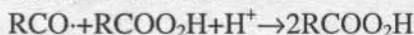
Propagation:



Termination:



Percarboxylic acid finally transformed into *p*-chlorobenzoic acid.



The light could initiate the oxidation and shorten inhibition period, facilitate production of radical $\text{RCO}\cdot$ and induce chain reaction, consequently accelerated the oxidation of aldehydes.

The effect of central metal

Under illumination with HPML, a very low absorption of oxygen and a long induction period were occurred when H_2TCMPP was used as catalyst. The absorption of oxygen and the change of solution colour could not be observed in presence of CoTCMPP until 150 hr lacking of any direct light. However illuminated with 450W HPML, the oxidation was greatly accelerated only after 26 min induction period, meanwhile a large amount of oxygen was absorbed. The observation results are shown in **Figure 1**. It was well-interpreted that the central metals with variable valences could accelerate the oxidation of aldehydes. A noteworthy implication is that the light could also stimulate the chain reaction and accelerate the oxidation of aldehyde.

The effect of substrates

The effects of substrate on the oxidation reactions found in the experiments are shown in **Figure 2**. It could be seen that the photocatalytic oxidation of *p*-chlorobenzaldehyde appeared much faster than benzaldehyde in the presence of CoTCMPP . However, the changes of solution colour and obvious absorption of dioxygen had not observed at 30°C after 6 hr when some derivatives of benzaldehyde which had electron donor or attractor, such as *p*-hydroxybenzaldehyde and *p*-nitrobenzaldehyde, were used as substrate.

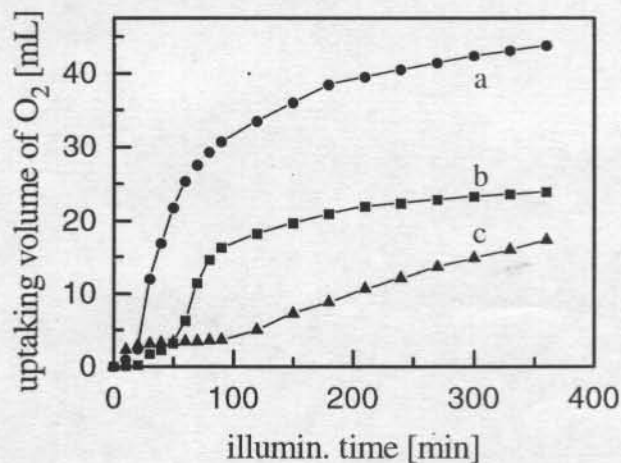


Figure 1—Effect of various catalyst: solvent: benzene; temp.: 30°C; illum.: 450 W HPML; [Catal.]= 6×10^{-4} mol/L; [*p*-chlorobenzaldehyde]=0.6 mol/L. a, CoTCMPP ; b, H_2TCMPP ; c, No catalyst.

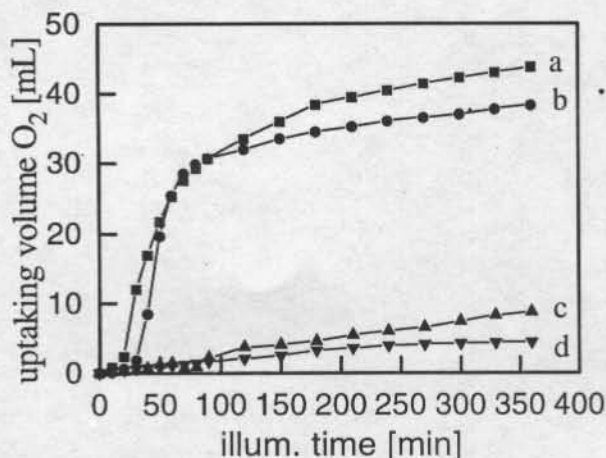


Figure 2—Effect of substrate: solvent : benzene; temp.: 30°C; illum.: 450 W HPML; [Catal.] (CoTCMPP)= 6×10^{-4} mol/L; [sub]=0.6 mol/L. a, *p*-chlorobenzaldehyde; b, benzaldehyde; c, *p*-nitrobenzaldehyde; d, *p*-hydroxybenzaldehyde.

([catalyst]:[substrate]=1:1000). 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 conjugative electron donating effect^{4,5}.

The effect of luminous flux

It is well-known that HPML has a characteristic spectrum of ultra-violet and visible light while Iodine Tungster Lamp (ITL) is characterized by visible light. In the experiments, in order to investigate the effect of light, the illuminant was replaced with 125 W HPML or 300 W ITL (Figure 3). As to HPML, it was obtained that absorbed dioxygen increased with light flux of illuminant. As compared with 125 W HPML, longer induction period and lower absorption of oxygen were observed under illumination with 300 W ITL. It would be emphasized the UV light of HPML played a role in the initiation of oxidation, however the visible light of ITL did little effect on the oxidation.

The effect of metalloporphyrin's concentration on the oxidation

In presence of CoTCMPP, the oxidation process of aromatic aldehydes could be considered as two stages: Prior to destruction of porphyrin ring, metalloporphyrin inhibited the oxidation and was shown as an induction period; then, the obvious absorption of

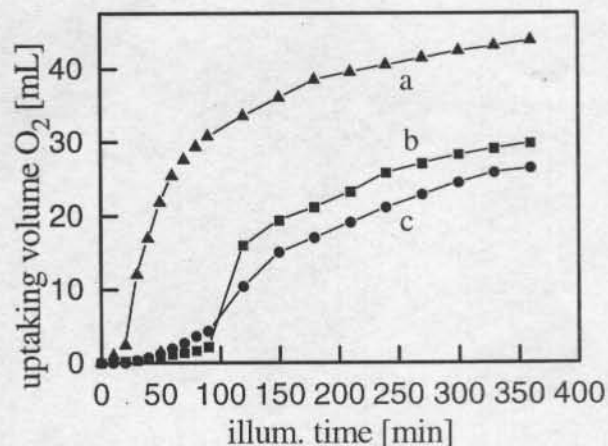


Figure 3—The effect of luminous flux: solvent : benzene; temp.: 30°C; [substrate]=0.6 mol/L; [cat.]= 6×10^{-4} mol/L. a, 450 W HPML; b, 125 W HPML; c, 300 W ITL.

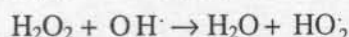
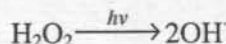
Table I—Absorbed oxygen and induction period at the various ratio of substrate and catalyst

Ratio of [cat.]:[sub.]	1:5000	1:2500	1:1000	1:750	1:500
[catalyst] $\times 10^4$ [mol/L]	1.2	2.4	6.0	8.0	12.0
absorbed oxygen [mL]	28.7	27.4	43.8	36.9	33.1
induction period [min]	6	13	26	46	104

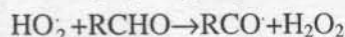
oxygen occurred due to photocatalytic effect of active species which formed during the reaction after the destruction of porphyrin ring. Oxygen absorption quantity of the oxidation for *p*-chlorobenzaldehyde were measured in different concentrations of metalloporphyrin. When the ratios between CoTCMPP and substrate were changed, the absorption and induction period varied considerably, and the relevant results are shown in Table I. The highest oxygen uptake was obtained when [cat.] : [sub.] was as 1:1000, this might be interpreted that metalloporphyrin was to be dimerized at the higher concentration. As a result, the valid concentration of metalloporphyrin which could be used as catalyst, and its catalytic capacity were reduced. The induction period increased with the quantity of the added metalloporphyrin.

The effect of hydrogen peroxide

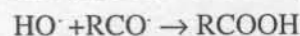
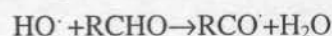
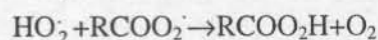
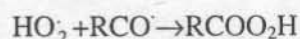
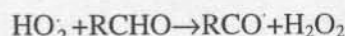
It is well-known that HO_2 and HO radicals which play an important role to initiate the chain reaction are easy to generate from hydrogen peroxide under illumination.^{11,12}



In the catalytic system of aldehydes, Meguru¹ believed that the hydroperoxy radical could abstract a hydrogen atom from aldehyde to initiate the oxidation by forming hydrogen peroxide.



Hydroperoxy radical and $\text{HO} \cdot$ may also react with other free radical and form inert compound



The photocatalytic oxidation of *p*-chlorobenzaldehyde and benzaldehyde was investigated in presence of H_2O_2 over 3 hr. Thus, addition of 0.1 mole/l H_2O_2 could greatly accelerate oxidation. Due to the participation of H_2O_2 in the oxidation of aromatic aldehydes, the active oxygen was formed in the reaction. Therefore, the induction periods were significantly shortened, and the external oxygen absorbed was greatly reduced. The relevant results were shown in **Table II**.

Table II—Induction period and absorbed oxygen in absence or in presence of hydrogen peroxide

Substrate	In presence of hydrogen peroxide		In absence of hydrogen peroxide	
	<i>p</i> -Chloro-benzaldehyde	Benzaldehyde	<i>p</i> -Chloro-benzaldehyde	Benzaldehyde
Induction period (min)	10	24	22	32
Amount of oxygen (ml)	24.3	17.6	43.6	27.0

* The concentration of hydrogen peroxide was 0.1 mole/L

The effect of 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 **Figure 4**. The oxidation rate in the presence of metalloporphyrin was considerably dependent on polarity of solvent. The induction periods of reaction in different solvents were consequanted as: DMF (>4 h)>acetone (35 min)

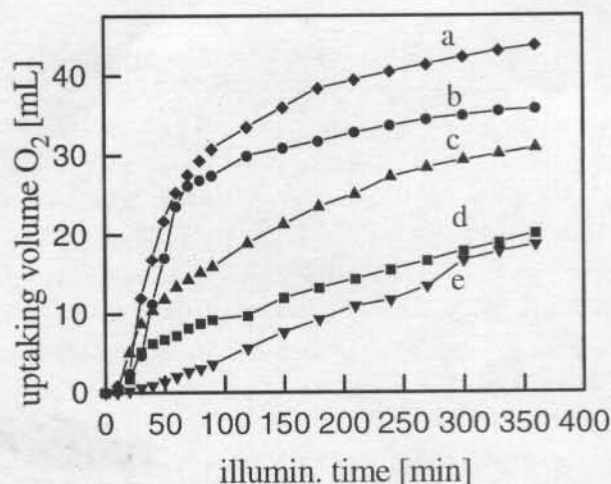


Figure 4—The effect of solvent: temp.: 30°C; illum.: 450 W HPML; [Catal.]= 6×10^{-4} mol/L; [*p*-chlorobenzaldehyde]=0.6 mole/L. a, benzene; b, acetic acid; c, ethyl acetate; d, acetone; e, dimethylformamine.

>acetic acid (32 min)>benzene (26 min)>ethyl acetate (20 min). The consequence basically related with the decrease order of the dielectric constant values (-25°C) which could be used to estimate approximately the polarity of solvent: Acetone(20.7)>acetic acid (6.15)>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 reaction was 26 min in benzene. However, with some strong polar solvents such as, *N,N*-dimethylformamide (DMF), the induction period of reaction was longer than 4 hr. This could be explained that DMF acted both as solvent and the fifth ligand, was very easy to coordinate with CoTCMPP in axial direction, therefore, reduced coordination of Co^{2+} with molecule O_2 , as a result, the rate of oxidation was decreased dramatically.

The effect of the fifth ligand on oxidation

The effect of addition of Imidazole as the fifth ligand on the catalytic action of photocatalyst was studied. It was evident that addition of the fifth ligand could extend the induction period, and it appeared a negative effect on the amount of absorbed oxygen. Under this condition, the absorbed oxygen only was 32.0 mL, meanwhile the induction period was 67 min.

With respect to the fifth ligand, Elvidge and Lever found that manganese phthalocyanine carried off an oxygen molecule reversibly in pyridine solution¹³. 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. W D Zhang¹⁴ also found Fe-phthalocyanine in which iron had d^6 orbital, could donate an electron and retained a half-full state after the fifth ligand was added. The catalytic activity of photocatalyst would be greatly improved with enhancement of the active effect of catalysts.

Behaviour of Cobalt with the d^7 orbital was different from above. It is thus concluded that 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 competed with molecular oxygen to coordinate with central ion, then the compound of CoTBCOPP..O² was greatly reduced, which affected activity of oxygen. Finally, the oxidation of aldehyde was reduced and the less oxygen was absorbed.

Conclusion

(i) CoTCMPP could catalyze the oxidation of aromatic aldehydes at the illumination condition with HPML, and the optimum oxidation condition was determined in benzene at 30°C when the ratio between catalyst and substrate was used as 1:1000.

(ii) The induction periods was greatly shortened by adding hydrogen peroxide while the long induction

period and low absorbed oxygen was obtained with adding the fifth ligand.

(iii) The major product of oxidation was measured as aromatic acid.

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