BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 692—696 (1968)

Organic Catalysts. V.[1] Specific Catalytic Properties of Copper-Iron-Polyphthalocyanine in the Oxidation of Aldehydes

Hiroo INOUE, Yasuji KIDA and Eiji IMOTO

Department of Applied Chemistry, College of Engineering, The University of Osaka Prefecture, Sakai, Osaka

(Received September 22, 1967)

Copper-iron-polyphthalocyanine showed a specific catalysis for the oxidations of the substituted benzaldehydes and the saturated aldehydes with oxygen. The catalytic activity of copper-iron-polyphthalocyanine was solvent-dependent: tetrahydrofuran, ethanol, acetonitrile, ethyl acetate and anisole inhibited the oxidation of benzaldehyde by copper-iron-polyphthalocyanine and oxygen, while benzene and acetone resulted in catalytic oxidation. Benzaldehyde and the saturated aliphatic aldehydes in benzene were oxidized catalytically with copper-iron-polyphthalocyanine and oxygen to afford the corresponding peroxy acids and acids in quantitative yields. Furthermore, oxygen was absorbed with no induction period; the rate of oxygen absorption was in the range of 8—13 m*l*/min. On the other hand, the unsaturated aliphatic aldehydes, cinnamaldehyde and acrolein, were oxidized with a very slow rate of oxygen absorption in spite of the existence of copper-iron-polyphthalocyanine in the reaction system. *p*-Methylbenzaldehyde and *p*-chlorobenzaldehyde were oxidized by copper-iron-polyphthalocyanine and oxygen in induction periods of about 8 and 15 min respectively, thus affording the corresponding peroxy acids and acids. However, no oxidations of *p*-nitrobenzaldehyde, *p*-hydroxycarbonylbenzaldehyde, *p*- and *m*-hydroxybenzaldehyde, *p*- and *m*-methoxybenzaldehyde and *p*-dimethylaminobenzaldehyde with copper-iron-polyphthalocyanine and oxygen were observed.

The autoxidations of aldehydes to carboxylic acids have been shown by a large number of investigators to be catalyzed by metal ions and peroxy acids.[2] It is the purpose of this paper to describe the specific catalytic activities of copper-iron-polyphthalocyanine in the oxidations of a series of aliphatic and aromatic aldehydes. The series of aldehydes chosen for investigation includes benzaldehyde, monosubstituted benzaldehydes (*p*-substituents: $-NO_2$, $-Cl$, $-CH_3$, $-OH$, $-OCH_3$ and $-N(CH_3)_2$, and *m*-substituents: $-OH$ and $-OCH_3$), and saturated and unsaturated aliphatic aldehydes.

Experimental

Materials. All of the aldehydes used here were of a commercial grade and had been purified by recrystallization or by distillation before use. It was confirmed by gas chromatography that aldehydes contain no impurity after purification. The absence of peroxide was confirmed by an iodine-starch test. Copper-polyphthalocyanine (Cu-poly PC), iron-polyphthalocyanine (Fe-poly PC), and copper-iron-polyphthalocyanine (Cu-Fe-poly PC), which were used as the catalysts for the oxidations of aldehydes, were prepared by the method (A)[3] or by the method used to prepare Fe-poly PC (No. 1)[1] in previous papers.

Oxidation. In most of the experiments, the oxidations of aldehydes were carried out by the same apparatus and procedure as have been described in the previous paper.[3] For the measurement of the rate of oxygen absorption, 5 m*l* of a solution of aldehyde at 6×10^{-1} M in an organic solvent, such as benzene, was oxidized at the atmospheric pressure of oxygen at 30°C. The oxidation products were determined after the oxygen absorption had been completed. The time-course investigation of the amounts of the oxidation products was carried out by using 450 m*l* of a solution of benzaldehyde at 6×10^{-1} M in benzene. 5-m*l* portions of the reaction mixture were pipetted out at appropriate time intervals, and the oxidation products were determined.

Analyses. The peroxy acids and acids formed in the oxidation process were identified by means of the iodine-starch test, the infrared absorption spectrum, and gas chromatography. The peroxy acid was determined by iodometric titration, the unreacted aldehyde by 2, 4-dinitrophenylhydrazone method. The formed acid was calculated by subtracting the sum of the amounts of peroxy acid and the unreacted aldehyde from the initial amount of the aldehyde.

Results and Discussion

Oxidation of Benzaldehyde. *The Catalytic Properties of Cu-, Fe- and Cu-Fe-Poly PC.* Fe-, Cu- and Cu-Fe-poly PC showed catalytic activity in the oxidation of benzaldehyde with oxygen. As

---

[1] Part IV of this series: H. Inoue, Y. Kida and E. Imoto, This Bulletin, **41**, 684 (1968).

[2] J. P. Mcnesby and C. A. Heller, *Chem. Revs.*, **54**, 325 (1954).

[3] H. Inoue, Y. Kida and E. Imoto, This Bulletin, **40**, 184 (1967).

Fig. 1 and Table 1 show, a remarkable difference in the catalytic activity for Fe-, Cu-, and Cu-Fe-poly PC was observed. The oxidation of benzaldehyde in the presence of Cu-poly PC as a catalyst proceeded very slowly, with a rate of oxygen absorption of 0.7 m*l*/min in the stationary state after an induction period of about 10 min; the oxidation percentage of benzaldehyde at the reaction time of 107 min was about 60%.

In the case of Fe-poly PC, the oxygen absorption was started after an induction period of about 2 min and reached to completion after a reaction time of 25—30 min, with a rate of oxygen absorption of 8.1 m*l*/min in the stationary state.

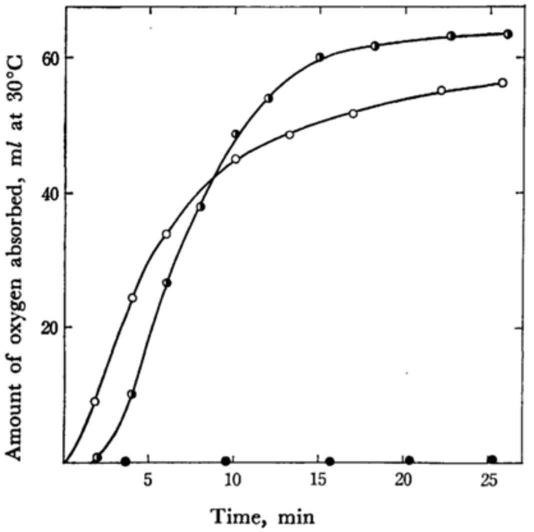


Fig. 1. The oxidation of benzaldehyde in the presence of Cu-, Fe- or Cu-Fe-poly PC: Catalyst; 50 mg.
○ Cu-Fe-poly PC, ◑ Fe-poly PC,
● Cu-poly PC.

The catalytic action of Cu-Fe-poly PC differed from those of Cu- and Fe-poly PC in the initial state of the oxygen absorption. As shown in Fig. 1, the oxygen absorption started as soon as Cu-Fe-poly PC and benzaldehyde are mixed in benzene. There was, however, no significant difference in the rate of oxygen absorption in the stationary state between the cases of Fe- and Cu-Fe-poly PC. Thus, the action of Cu-Fe-poly PC seems to be characteristic of the activation of oxygen in the initial state of the oxidation process.

As shown in Table 1, peroxybenzoic acid and benzoic acid were obtained as the oxidation products. In all cases of Fe-, Cu-, and Cu-Fe-poly PC, the amount of the oxidized benzaldehyde was identical with the sum of the amounts of benzoic acid and peroxybenzoic acid produced. The catalytic efficiency (the reaction percentage of benzaldehyde per unit of weight of the catalyst until the oxygen absorption becomes constant) of each catalyst for the oxidation of benzaldehyde was higher than that of acetaldehyde ethylene acetal described previously.1) No significant difference in the molar ratio of peroxybenzoic acid to benzoic acid, however, was observed in the cases of Cu-, Fe-, and Cu-Fe-poly PC.

Variations in the Amounts of Products in the Reactiou Course. The amounts of the products, peroxybenzoic acid and benzoic acid, were determined by taking out portions of the reaction mixture at appropriate times during the oxidation of benzaldehyde. These results are shown in Fig. 2.

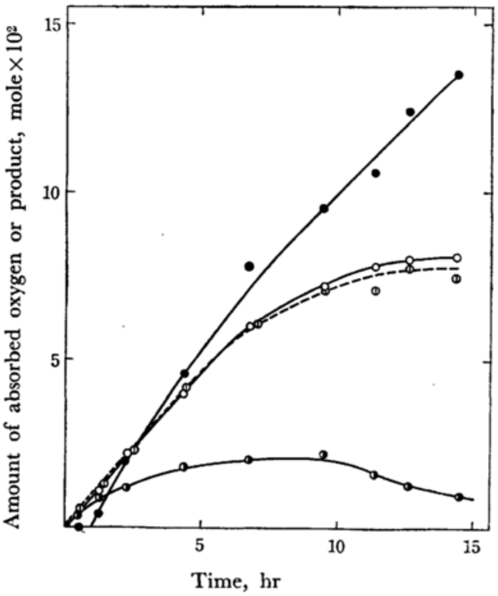


Fig. 2. The amounts of oxygen absorbed and the oxidation products in the oxidation course of benzaldehyde: Cu-Fe-Poly PC; 0.3 g. Benzaldehyde solution; 450 m*l* (6×10^{-1} M in benzene).
○ Absorbed oxygen, ◑ C_6H_5COOOH,
● C_6H_5COOH,
⦶ $C_6H_5COOOH + \frac{1}{2}C_6H_5COOH$.

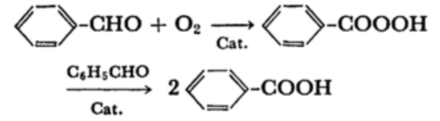
The absorption of oxygen was observed as soon as benzaldehyde and Cu-Fe-poly PC were mixed in benzene at an atmospheric pressure of oxygen at 30°C, and it increased linearly with the reaction time. After a reaction time of 7 hr, the rate of oxygen absorption decreased, however, until the absorption of oxygen stopped after a reaction time of about 15 hr.

The amount of peroxybenzoic acid produced increased with an increase in the amount of oxygen absorbed, and reached a constant after a reaction time of 3 hr. After staying almost constant for several hours, it started to decrease when the rate of oxygen absorption decreased.

On the other hand, another product, benzoic acid, was not produced even after a reaction time of 2 hr after the absorption of oxygen started.

After 2 hr, the amount of the benzoic acid started to increase with the reaction time. Even after the absorption of oxygen had become almost constant, the production of benzoic acid was observed. In the reaction mixture, no water or other compounds were produced. Furthermore, during the course of the oxidation, the amount of oxygen absorbed was identical with the sum of the amount of peroxybenzoic acid produced and half the amount of benzoic acid produced.

These facts show that the catalytic oxidation of benzaldehyde by Cu-Fe-poly PC with oxygen proceeds *via* the reaction steps represented by the following equation:



The catalyst contributes to the activation of oxygen, giving perbenzoic acid through the reaction of the activated oxygen and benzaldehyde, and to the decomposition of perbenzoic acid, thus giving benzoic acid quantitatively by the reaction of peroxybenzoic acid and benzaldehyde. Furthermore, the catalytic oxidation processes seem to indicate the character of Cu-Fe-poly PC as an oxidation catalyst.

The Effects of Solvents on the Oxidation of Benzaldehyde. The Fe(II) ion of Cu-Fe-poly PC acts as an active site for the activation of oxygen and for the decomposition of peroxide in the oxidation process. The catalytic activity of Cu-Fe-poly PC may be affected by the kind of solvent, since the Fe(II) ion may be solvated or coordinated by the solvent. The influence of solvents in the catalytic oxidation of benzaldehyde by Cu-Fe-poly PC with oxygen were investigated. As the solvents, benzene, acetone, ethyl acetate, tetrahydrofuran, acetonitrile, ethanol, and anisole were chosen. These results are shown in Fig. 3 and Table 1. Benzaldehyde in benzene or acetone containing Cu-Fe-poly PC was oxidized with oxygen to peroxybenzoic acid and benzoic acid, but no oxidation of benzaldehyde with oxygen was observed in tetrahydrofuran, ethanol, acetonitrile, ethyl acetate, or anisole, despite the presence of Cu-Fe-poly PC. The disappearance of the catalytic activity of Cu-Fe-poly PC when the latter solvents were used may be caused by the solvation or the coordination of the solvent to the Fe(II) ion as an active site, or by solvation to the Fe(II)$\cdots$O$_2$ intermediate. Furthermore, these phenomena must be related to the inhibition of pyridine and 2-phenylimidazole for the catalytic action of Cu-Fe-poly PC in the oxidation of acetaldehyde ethylene acetal, an inhibition described previously.[1]

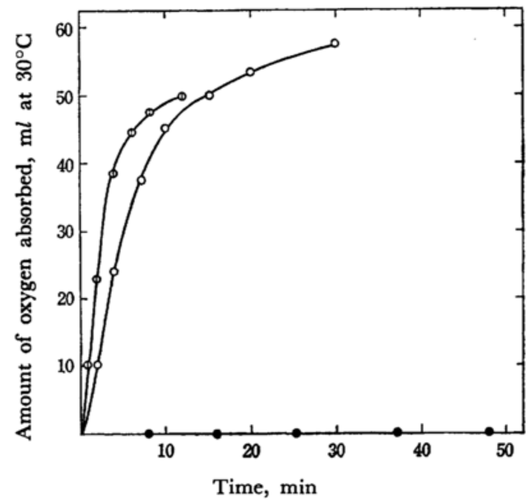


Fig. 3. Influence of solvent in the oxidation of benzaldehyde: Cu-Fe-Poly PC; 50mg,

⦶ acetone, ○ benzene and ● tetrahydrofuran, acetonitrile, ethyl acetate, ethanol and anisole.

The Oxidations of Monosubstituted Benzaldehydes. The oxidations of *p*-substituted benzaldehydes by peroxybenzoic acids are affected by the electron-donating or electron-withdrawing power of the substituent, although the rate of oxidation is independent of the Hammett substituent

TABLE 1. THE CATALYTIC ACTION OF Cu-, Fe- AND Cu-Fe-poly PC IN THE OXIDATION OF BENZALDEHYDE

Catalyst	Rate of oxygen[a] absorption, ml/min	Yield, %[b]	
		C_6H_5COOOH	C_6H_5COOH
Cu-poly PC	0.7[c]	34	26
Fe-Poly PC	8.1[c]	58	42
Cu-Fe-poly PC	8.1[c]	61	39
	11.0[d]	14	86
	0.0[e]	0	0

a) This is the rate of the oxygen absorption at the stationary state at 30°C.
b) The yield is the value for the initial amount of benzaldehyde.
c) The solvent : benzene.
d) The solvent : acetone.
e) The solvent : tetrahydrofuran, acetonitrile, ethanol and ethyl acetate, respectively.

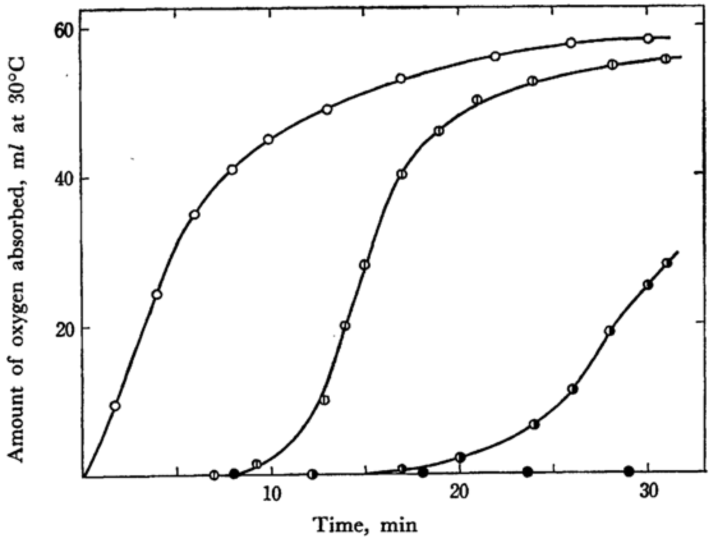


Fig. 4. The oxidation of monosubstituted benzaldehydes in the presence of Cu-Fe-poly PC : Cu-Fe-poly PC; 50mg.

○ Benzaldehyde, ⦶ *p*-CH_3-, ◑ *p*-Cl- (5×10^{-1} M, Cu-Fe-poly PC 20 mg), ● *p*-$(CH_3)_2N$-, *p*-HO-, *p*-CH_3O-, *p*-O_2N-, *p*-HOOC-, *m*-HO-, *m*-CH_3O- and *o*-HO-benzaldehyde.

constant.[4] The substituent effects on the catalytic oxidations of monosubstituted benzaldehydes by Cu-Fe-poly PC were also investigated. The oxidations of the monosubstituted benzaldehydes (*p*-substituents: $-NO_2$, $-Cl$, $-CH_3$, $-OH$, $-OCH_3$ and $-N(CH_3)_2$, and *m*-substituents: $-OH$ and $-OCH_3$) with oxygen in the presence of Cu-Fe-poly PC were carried out under the same conditions as in the case of benzaldehyde. These results are shown in Fig. 4. *p*-Methylbenzaldehyde and *p*-chlorobenzaldehyde were oxidized catalytically by Cu-Fe-poly PC and oxygen to give the corresponding peroxy acids and acids, with induction periods of 8 min or 15 min respectively, while no oxidations of the other monosubstituted benzaldehydes were observed. That is, the catalytic effect of Cu-Fe-poly PC on the oxidation of monosubstituted benzaldehyde with oxygen was independent of the electron-donating or electron-withdrawing power of the substituent, and monosubstituted benzaldehydes, the substituents of which may coordinate to the Fe(II) ion, seem not to be oxidized by Cu-Fe-poly PC and oxygen. This is probably caused by the inhibition of the activation of oxygen in the oxidation processes; these facts seem to be related to the findings regarding the solvent effects on the catalytic action of Cu-Fe-poly PC.

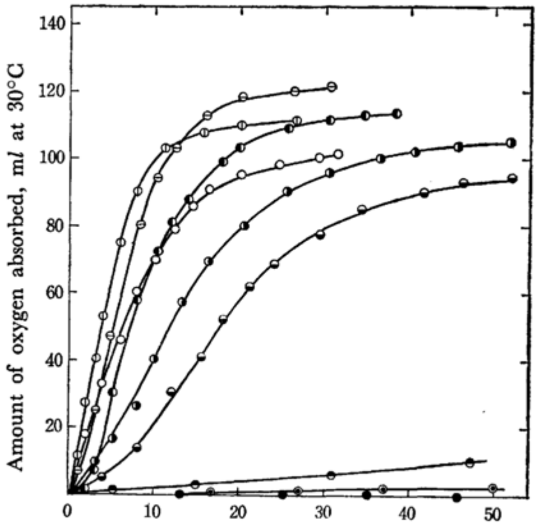


Fig. 5. The oxidation of aliphatic aldehydes in the presence of Cu-Fe-poly PC: Cu-Fe-poly PC; 30mg.

○ Propionaldehyde, ⦶ *n*-butyraldehyde, ◑ caprylaldehyde, ⊖ 2-ethylcaproaldehyde, ◒ crotonaldehyde, ◓ cinnamaldehyde, ⊙ acrolein, ◐ benzaldehyde.

The Oxidations of Aliphatic Aldehydes. Investigation was extended to the oxidations of aliphatic aldehydes, propionaldehyde, *n*-butyraldehyde, caprylaldehyde, 2-ethylcaproaldehyde, crotonaldehyde, cinnamaldehyde, and acrolein with Cu-Fe-poly PC and oxygen. The relation between the amount of oxygen absorbed and the

---

[4] W. Cooper, *J. Chem. Soc.*, **1952**, 2408; C. G. Swain, W. H. Stockmeyer and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5426 (1950).

TABLE 2. THE OXIDATION OF ALIPHATIC ALDEHYDES IN THE PRESENCE OF Cu-Fe-poly PC[a]

Aldehyde	Rate of oxygen[b] absorption, ml/min	Yield, %[c]	
		Peroxy acid	Acid
Propionaldehyde	7.7	29	55
n-Butyraldehyde	13.0	44	52
Caprylaldehyde	4.8	47	48
2-Ethylcaproaldehyde	12.0	52	45
Acrolein	0.1	1[d]	1
Crotonaldehyde	3.7	38[d]	40
Cinnamaldehyde	0.5	5[d]	3

a) Aldehyde; 10 m*l* (6×10^{-1} M in benzene) and Cu-Fe-poly PC; 30 mg.
b) This is the rate of the oxygen absorption at the stationary state at 30°C.
c) The yield is the value for the initial amount of benzaldehyde.
e) The reaction time; 1 hr.

reaction time in the oxidation of each of the aliphatic aldehydes is shown in Fig. 5. Cu-Fe-poly PC showed a remarkable catalytic action in the oxidations of the saturated aliphatic aldehydes; the oxidations gave the corresponding peroxy acids and acids as the oxidation products in nearly quantitative yields (Table 2). On the other hand, the unsaturated aliphatic aldehydes, cinnamaldehyde and acrolein, were oxidized very slowly in spite of the presence of Cu-Fe-poly PC in the reaction system. Crotonaldehyde was oxidized, however, more easily than acrolein and cinnamaldehyde. These facts were similar to those of the case of metal-salt-catalyzed oxidation of unsaturated aldehydes in acetic acid.[5]

---

[5] W. F. Brill and F. Lister, *J. Org. Chem.*, **26**, 565 (1961).