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Organic Catalysts. IV.[1] The Role of the Iron as an Oxidation Catalyst in Copper-Iron-Polyphthalocyanine

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The role of the iron in copper-iron-polyphthalocyanine in the catalytic action in the oxidation of acetaldehyde ethylene acetal and cyclohexene was investigated on the basis of the inhibition of the reaction by the treatment of copper-iron-polyphthalocyanine with iron-binding agents and oxidizing agents. The catalytic action of copper-iron-polyphthalocyanine decreased or disappeared upon the addition of 2-phenylimidazole and pyridine to the reaction system, and upon the treatment with bromine or concentrated hydrochloric acid in the presence of air. However, the reduction of the oxidized copper-iron-polyphthalocyanine with ascorbic acid or sodium thiosulfate recovered the catalytic activity. Furthermore, the catalytic activities of iron-metal-polyphthalocyanines (metal; V, Cr, Mn, Co, Ni, Cu and Zn) and copper-metal-polyphthalocyanines (metal; V, Cr, Co, Ni and Zn) in the oxidation of acetaldehyde ethylene acetal were investigated. The former groups showed the catalytic actions, but no catalytic actions were observed in the latter groups. The catalytic activities of iron-metal-polyphthalocyanines increased with a decrease in the activation energy of the electrical conductivity of the polymer. From these results, it was presumed that the Fe(II) ions located in the conjugated system act as active sites for the activation of oxygen and for the decomposition of peroxide.

Copper-iron-polyphthalocyanine, which has a unit structure similar to the structure of an iron or copper porphyrin in biological oxygenases, shows a remarkable acceleration in the oxidation of acetaldehyde ethylene acetal with oxygen.[1]

The copper-iron-polyphthalocyanine has a sensitive catalytic activity related to its electronic and stereochemical structure. Furthermore, the action of the iron ion in the activation of oxygen and in the decomposition of peroxide may be interpreted in terms of the electronic character of the iron ion with the assistance of coordination chemistry.

In this paper, we will describe the role of the iron ion in polyphthalocyanine in the catalytic action. Our conclusions are based on the following results: 1) the inhibition of the reaction by iron-binding agents, such as pyridine and 2-phenylimidazole; 2) the disappearance of the catalytic activity upon treatment with an oxidizing agent, such as bromine or hydrochloric acid in the presence of oxygen; 3) the requirement of a reducing agent, such as ascorbic acid, for the catalytic activity, and 4) the effect on the catalytic activity of the coexistence of vanadium, chromium, manganese, cobalt and zinc instead of copper with the iron in the polyphthalocyanine structure.

Experimental

Preparation of Metal Polyphthalocyanine. *Iron- and Copper-Iron-Polyphthalocyanine (Fe-poly PC and Cu-Fe-poly PC).* Cu-Fe-poly PC was prepared according to the method described in a previous paper,[1] except that the reaction temperature was 175°C instead of 190°C. Fe-poly PC was prepared under various conditions: at different temperatures, with different solvents, and with different amounts of anhydrous ferric chloride. The results are shown in Table 1. The results of the elementary analyses of the Fe-poly PC and Cu-Fe-poly PC obtained are shown in Table 2.

Iron- and Copper-Metal-Polyphthalocyanine (Fe-M-poly PC and Cu-M-poly PC). Fe-M- and Cu-M-poly PC were prepared according to a method, A, described in the previous paper.[1] However, the reaction temperatures for the preparation of the metal polyphthalocyanines in this paper were changed according to the kinds of metal ions coexisting with the iron ion. The reaction mixture turned green. For all the experiments, the product, 1.2—1.4 g of an infusible bluish or greenish-black powder, was obtained from the starting materials of 4.26×10^{-4} mol of anhydrous ferric chloride, 4.22×10^{-4} mol of metal salt, and 4.21×10^{-3} mol of 1, 2, 4, 5-tetracyanobenzene.

The properties and the conditions for the preparation of all the polymers obtained here are summarized in Tables 5 and 6.

Treatment of Metal Polyphthalocyanines (Cu-Fe-Poly PC and Fe-Poly PC (No. 1)). *By Bromine.* Into a solution of 5 g of potassium bromide and 10 m*l* of bromine in 100 m*l* of distilled water, 0.5 g of metal polyphthalocyanine was added; the mixture was then stirred at room temperature for 9 hr. After filtering off, the precipitate was washed sequentially with distilled water, methanol, and ether, and was dried over calcium chloride under a reduced pressure of 10 mmHg,

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[1] Part III of this series: H. Inoue, Y. Kida and E. Imoto, This Bulletin, **40**, 184 (1967).

TABLE 1. THE CONDITIONS OF THE PREPARATIONS OF Cu-, Fe- AND Cu-Fe-POLY PC

Polymer	Material, g			Solvent[a]	Reaction temperature, °C
	T. C. B.[b]	$CuCl_2$	$FeCl_3$		
Cu-Poly PC	1.5	0.67	0.00	E. G.	175
Cu-Fe-poly PC	1.5	0.11	0.14	E. G.	175
Fe-poly PC (No. 1)	1.5	0.00	0.67	E. G.	175
Fe-poly PC (No. 2)	1.5	0.00	0.67	E. G.	190
Fe-poly PC (No. 3)	1.5	0.00	0.48	E. G.	175
Fe-Poly PC (No. 4)	1.5	0.00	0.67	D. E. P.	190

a) The amount of the solvent is 16 g.
E. G. and D. E. P. mean ethylene glycol and diethyl phthalate, respectively.
b) T. C.B. means 1, 2, 4, 5-tetracyanobenzene.

TABLE 2. THE ELEMENTARY ANALYSES OF Cu-, Fe- AND Cu-Fe-POLY PC

Polymer	Elementary analysis, %				
	C	H	N	Cu	Fe
Cu-poly PC	50.7	2.13	18.3	11.6	0.0
Cu-Fe-poly PC	54.5	2.22	21.6	3.8	2.8
Fe-poly PC (No. 1)	46.7	2.76	14.2	0.0	12.6
Fe-poly PC (No. 2)	54.6	2.70	16.9	0.0	—
Fe-poly PC (No. 3)	50.8	2.80	18.0	0.0	—
Fe-poly PC (No. 4)	55.5	2.11	20.5	0.0	—

thus yielding 0.5 g of the powder.

By Ascorbic Acid. A solution of 2 g of ascorbic acid in 40 m*l* of distilled water was adjusted to pH 4 with sodium acetate; then into the solution there was added 0.5 g of the polymer treated by bromine, and the mixture was stirred under a nitrogen atmosphere for 2 hr at room temperature. After filtering off, the precipitate was washed and dried as has been described above.

By Sodium Thiosulfate. Into 100 m*l* of a 0.5 N sodium thiosulfate solution there was added 0.2 g of the polymer treated by bromine, and then the mixture was stirred at room temperature for one day. After filtering off, the precipitate (about 0.2 g) was washed and dried as has been described above.

By Concentrated Hydrochloric Acid. A solution of 0.4 g of the polymer in 300 m*l* of concentrated hydrochloric acid was heated while being stirred at 90°C for 1.5 hr according to Linstead's method, in which Fe(II) phthalocyanine is oxidized by air to Fe(III) phthalocyanine.[2] After the reaction, the precipitate was washed and dried by the method described above.

Oxidation of Acetaldehyde Ethylene Acetal and Cyclohexene with Oxygen. *Materials.* Acetaldehyde ethylene acetal and cyclohexene were prepared according to the methods described in the literature[3,4] and were purified before use by distilling them repeatedly through a Vigreux column over sodium under a nitrogen atmosphere. Acetaldehyde ethylene acetal; n_D^{25} 1.3960, bp 85°C, and cyclohexene; n_D^{25} 1.4465, bp 83°C. The absence of peroxide was confirmed by an iodine-starch test.

Apparatus and Procedure. The oxidation of acetaldehyde ethylene acetal or cyclohexene was carried out by stirring a suspension of 30 mg of the polymer in 5 m*l* of acetaldehyde ethylene acetal or cyclohexene at the atmospheric pressure of oxygen at 30°C using the same apparatus and procedure as have been described in a previous paper.[1]

Analyses of the Oxidation Products. The oxidation products, ethylene glycol monoacetate, 2-cyclohexenol, and 2-cyclohexenone, were analyzed with a gas chromatograph, Yanagimoto GCG-5DH, in which polyethylene glycol-6000 was used as an adsorbent and helium gas as a carrier gas. The results were similar to those described previously.[1]

The Measurement of the D. C. Resistivity. The d. c. resistivity of the polymer was measured in an applied electric field of 100—200 V/cm under a pressure of 1000 kg/cm² *in vacuo* according to a method described in a previous paper.[5] The electrical resistivity (ρ) at an ascending temperature (T) was identical with that at a descending temperature, and a linear relationship between log ρ and $1/T$ was observed. The resistivities of the polymers, as typical organic semiconductors, fit the following equation;

$$\rho = \rho_0 \exp(\Delta\varepsilon/2\boldsymbol{k}T)$$

where $\Delta\varepsilon$ is the energy gap and $\boldsymbol{k}$, the Boltzmann constant.

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[2] P. A. Barrett, D. A. Frye and R. P. Linstead *J. Chem. Soc.*, **1938**, 1157.

[3] H. Hibbert and J. A. Timm, *J. Am. Chem. Soc.*, **46**, 1283 (1924).

[4] A. Lapworth and J. A. MacRae, *J. Chem. Soc.*, **1922**, 1699.

[5] H. Inoue, S. Hayashi and E. Imoto, This Bulletin, **37**, 336 (1964).

Results and Discussion

Properties of the Polymers. *Cu-, Fe-, and Cu-Fe-Poly PC.* Cu-, Fe-, and Cu-Fe-poly PC are insoluble in any organic solvents, but are soluble in concentrated sulfuric acid, giving a green color. The elementary analyses, the ratio of carbon to nitrogen (C/N ratio), the ratio of copper to iron (Cu/Fe ratio), and the electrical conductivities of Cu-, Fe- and Cu-Fe-poly PC are summerized in Tables 2 and 3. These results and, furthermore, the visible absorption spectra of the polymers are identical with those of the phthalocyanine polymer of Type A described previously.1) The infrared absorption spectra of the polymers differed from those of the previously-prepared polymers1) only in the absorption of the –CN group, 2200 cm^{-1}. Therefore, the structure of the polymers obtained here must be of a phthalocyanine type, with end groups of –CN and –CONHCO–. Furthermore, the degree of the polymerization of the phthalocyanine unit of Cu-Fe-poly PC is presumed to be larger than that of Cu- and Fe-poly PC on the basis of the C/N ratios and the electrical conductivities, which are shown in Table 3.

The electron spin resonance spectra of the polymers were measured in the air at room temperature. The results are shown in Fig. 1. The electron spin resonance spectra of Fe-poly PC (No. 1—4) have no absorption. These facts indicate that the central iron ion of Fe-poly PC has an oxidation state of +2 and a coordination number of 6.6) On the other hand, the electron spin resonance spectra of Cu- and Cu-Fe-poly PC have absorptions at the g values of 2.072 and 2.055 respectively. Therefore, the central iron and copper ions of Cu- and Cu-Fe-poly PC must have oxidation states of +2 and coordination numbers of 6 and 4 respectively. Furthermore, in the case of Cu-Fe-poly PC only, one more absorption was observed, as shown in Fig. 1. This must be based on the free electron in the conjugated system of the polymer. This fact may mean that Cu-Fe-poly PC has a larger degree of polymerization of the phthalocyanine unit than that of Fe- or Cu-poly PC.

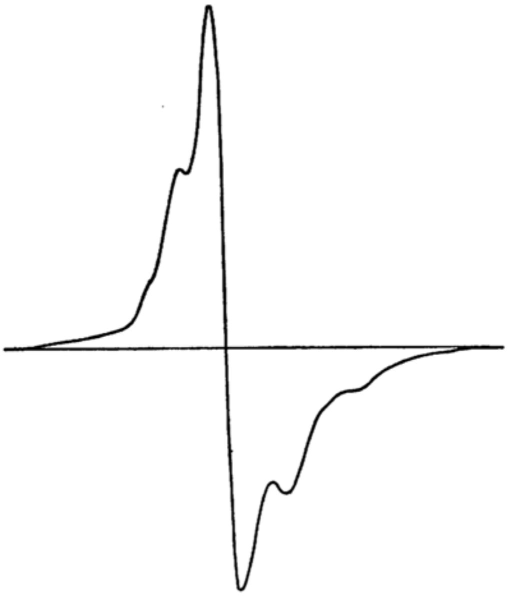

Fig. 1. ESR spectrum of Cu-Fe-poly PC (g: 2.055).

Fe- and Cu-Fe-Poly PC Treated with Bromine, Ascorbic Acid, and Sodium Thiosulfate. The treatment of Cu-Fe-poly PC and Fe-poly PC with bromine resulted in an increase in the halogen content from 0.85 to 4.07%; the halogen content was then recovered almost quantitatively to 0.78% by treatment with ascorbic acid or sodium thiosulfate, as shown in Table 4. By treatment with bromine and then with ascorbic acid, no significant differences in the C/N ratios, the infrared absorption spectra, the visible absorption spectra, and the electron spin resonance spectra of the polymers were observed from those of the untreated polymers, although some variations in the electrical conductivities were observed. This means that the phthalocyanine structure of the polymers, and

TABLE 3. THE VALUES OF C/N RATIO, Cu/Fe RATIO, $\Delta\varepsilon$ AND ρ_{20} OF Cu-, Fe- and Cu-Fe-POLY PC

Polymer	C/N ratio a)	Cu/Fe ratio a)	Electrical properties	
			$\Delta\varepsilon$, eV	ρ_{20}, Ω-cm
Cu-poly PC	3.24	—	1.00	1.6×10^8
Cu-Fe-poly PC	2.95	1.18	0.35	5.0×10^5
Fe-poly PC (No. 1)	3.84	—	0.58	1.6×10^6
Fe-poly PC (No. 2)	3.78	—	0.55	2.2×10^6
Fe-poly PC (No. 3)	3.28	—	0.62	1.3×10^6
Fe-poly PC (No. 4)	3.16	—	—	—

a) $\text{C/N ratio} = \dfrac{14\times \text{C}\%}{12\times \text{N}\%}$, $\text{Cu/Fe ratio} = \dfrac{55.6\times \text{Cu}\%}{63.5\times \text{Fe}\%}$

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6) A. B. P. Lever, *J. Chem. Soc.*, **1965**, 1821.

TABLE 4. THE VALUES OF THE HALOGEN CONTENT, C/N RATIO, $\Delta\varepsilon$ AND ρ_{20} OF Fe- AND Cu-Fe-POLY PC TREATED WITH BROMINE, ASCORBIC ACID OR CONCENTRATED HYDROCHLORIC ACID PLUS AIR

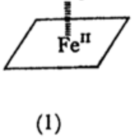
Treatment	Halogen, %	C/N ratio	Electrical properties	
			$\Delta\varepsilon$, eV	ρ_{20}, Ω-cm
Cu-Fe-poly PC				
Untreated	0.85	2.95	0.35	5.0×10^5
Bromine	4.07[a)]	2.89	0.72	2.1×10^6
Ascorbic acid	0.78	2.90	0.53	1.2×10^6
Fe-poly PC (No. 3)				
Untreated	—	3.28	0.62	1.3×10^7
Conc. HCl plus air	—	3.66	0.89	3.5×10^7

a) This is the chlorine plus bromine contents.

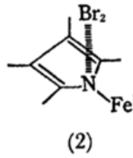
TABLE 5. THE CONDITIONS OF THE PREPARATIONS AND THE ELEMENTARY ANALYSES OF Fe-M- AND Cu-M-POLY PC

Polymer	Metal salt	Reaction temp. °C	Elementary analysis, %			
			C	H	N	Ash
Fe-V-poly PC	V_2O_5	180	53.7	2.18	21.6	—
Fe-Cr-poly PC	$CrCl_3\cdot6H_2O$	175	51.2	1.80	19.5	—
Fe-Mn-poly PC	$MnCl_2\cdot xH_2O$	185	50.9	2.30	19.6	—
Fe-Co-poly PC	$CoCl_2$	180	54.1	2.51	20.6	—
Fe-Ni-poly PC	$NiCl_2$	175	52.4	2.13	20.7	—
Fe-Zn-poly PC	$ZnCl_2$	175	53.5	2.60	20.5	—
Fe-Pd-poly PC	$PdCl_2$	175	49.7	2.30	19.7	—
Fe-Sn-poly PC	$SnCl_2\cdot2H_2O$	180	49.8	2.49	20.8	—
Fe-Cd-poly PC	$CdCl_2$	210	50.6	2.26	18.1	—
Cu-V-poly PC	V_2O_5	180	56.5	2.03	22.3	9.9
Cu-Cr-poly PC	$CrCl_3\cdot6H_2O$	180	53.8	2.63	20.9	6.9
Cu-Mn-poly PC	$MnCl_2\cdot xH_2O$	180	54.9	2.36	22.7	6.5
Cu-Co-poly PC	$CoCl_2$	180	57.5	2.22	22.7	10.0
Cu-Ni-poly PC	$NiCl_2$	180	57.0	2.15	23.8	11.0
Cu-Zn-poly PC	$ZnCl_2$	180	55.7	2.36	22.0	—
Mn-poly PC	$MnCl_2\cdot xH_2O$	180	54.6	2.34	19.8	11.0

both the oxidation states and the coordination numbers of the central metal ions do not change with the treatment with bromine and ascorbic acid. Moreover, the bromine treatment may form a complex between bromine and the central iron ion (1), or between bromine and the nitrogen atom of the pyrrole of the phthalocyanine structure (2).



(1)



(2)

Fe- and Cu-Fe-Poly PC Treated by Air in Concentrated Hydrochloric Acid. The oxidation of the central iron ions of Fe- and Cu-Fe-poly PC by air was carried out in concentrated hydrochloric acid as has been described before. The polymer obtained from Fe-poly PC showed properties similar to those of the untreated Fe-poly PC in respect to the C/N ratios, the electrical conductivities, and the infrared absorption spectra (Table 4). However, the infrared absorption spectrum of the polymer obtained from Cu-Fe-poly PC showed an increase in the absorption of the –CONHCO– group with a decrease in that of the –CN group. This means that some of the –CN groups were changed to –CONHCO– groups in the process of the treatment with concentrated hydrochloric acid. In the case of both Fe- and Cu-Fe-poly PC, the electron spin resonance spectra showed absorption at the *g* value of 2.051 in the existence of the Fe(III) ion.

Fe-M- and Cu-M-Poly PC. The polyphthalocyanines containing various metals (M) with iron or copper (Fe-M- or Cu-M-poly PC) were bluish or greenish-black powders; those powders were insoluble in any organic solvents, but were soluble in concentrated sulfuric acid. The results of the elementary analyses (Table 5), the C/N ratios (Table 6), and the infrared absorption spectra of Fe-M- and Cu-M-poly PC were similar to those of Cu-Fe-poly PC. On the other hand, the visible absorption spectra of Fe-M-poly PC, observed by the use of a KBr disk method, showed differences from those of Cu-M-poly PC, which have two absorption maxima, at about 720—740 mμ and 880—900 mμ. Most of the Fe-M-poly PC's showed an absorption maximum at 570—580 mμ besides those at 720—740 mμ and 880—900 mμ. Among the Fe-M-poly PC's, the absorption maxima of Fe-Zn-poly PC and Fe-Mn-poly PC at 750 mμ, and of Mn-poly PC at 770 mμ and 935 mμ, were shifted toward the longer wavelength side by 10—30, 50, and 55 mμ respectively as compared with those of the other Fe-M-poly PC's. The values of ρ_{20} and $\Delta\varepsilon$ of the electrical conductivity were in the range of 10^4—10^8 ohm-cm and 0.4—1.3 eV respectively (Table 6). The values of the electrical resistivities of Cu-M-poly PC and Mn-poly PC were lower than those of Fe-M-poly PC. Mn-poly PC showed the highest electrical conductivity, ρ_{20}-3.4×10^3 ohm-cm.

TABLE 6. THE VALUES OF C/N RATIO, $\Delta\varepsilon$ AND ρ_{20} OF Fe-M- AND Cu-M-poly PC

Polymer	C/N ratio	Electrical properties	
		$\Delta\varepsilon$, eV	ρ_{20}, Ω-cm
Fe-V-poly PC	2.90	1.20	2.2×10^8
Fe-Cr-poly PC	3.06	1.30	1.1×10^9
Fe-Mn-poly PC	3.02	0.87	7.0×10^5
Fe-Co-poly PC	3.06	0.83	2.3×10^6
Fe-Ni-poly PC	2.95	0.87	4.1×10^6
Fe-Zn-poly PC	3.05	0.66	1.1×10^7
Fe-Pd-poly PC	2.95	0.42	5.0×10^5
Fe-Sn-poly PC	2.79	1.20	5.5×10^8
Fe-Cd-poly PC	3.26	1.30	2.1×10^8
Cu-V-poly PC	2.83	0.61	1.3×10^4
Cu-Cr-poly PC	3.00	0.65	3.5×10^5
Cu-Mn-poly PC	2.82	0.59	1.1×10^4
Cu-Co-poly PC	2.96	0.70	1.7×10^5
Cu-Ni-poly PC	2.80	0.83	2.5×10^5
Cu-Zn-poly PC	2.96	0.64	1.4×10^7
Mn-poly PC	3.22	0.53	3.4×10^3

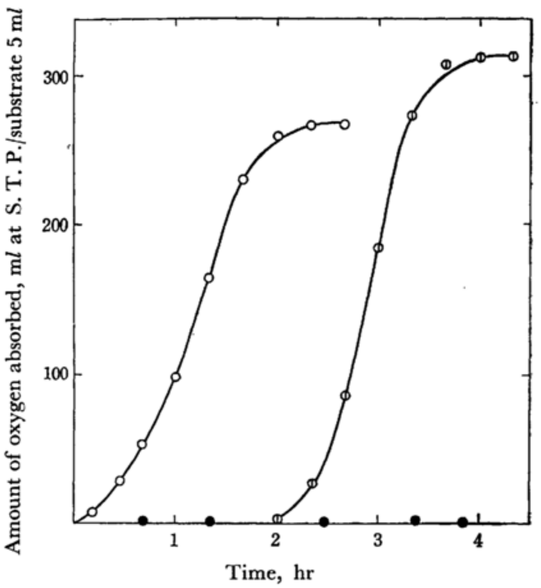


Fig. 2. The catalytic activity of Fe-poly PC prepared under the different conditions: Fe-poly PC; 30 mg.
○ No. 1 ⦶ No. 3 ● No. 2 and 4

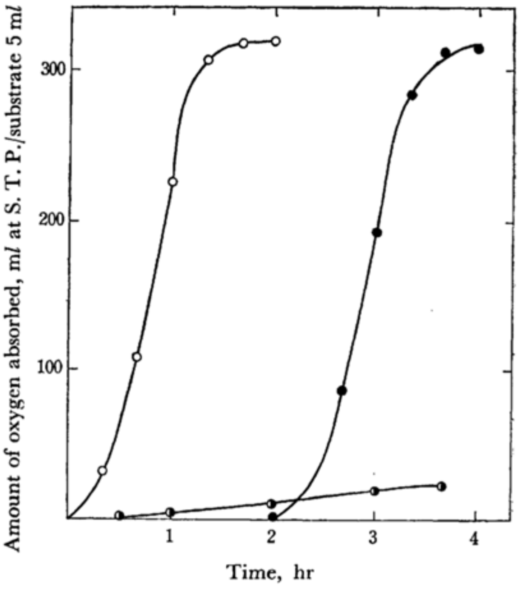


Fig. 3. The effect of t-butylhydroperoxide on the oxidation of acetaldehyde ethylene acetal in the presence of Fe-poly PC at 30°C: Fe-poly PC; 30 mg.
○ t-BuOOH (0.5 ml) plus Fe-poly PC
● Fe-poly PC alone
◑ t-BuOOH alone (0.5 ml)

Oxidations of Acetaldehyde Ethylene Acetal and Cyclohexene. *Catalytic Actions of Fe-Poly PC and Cu-Fe-Poly PC.* The oxidations of acetaldehyde ethylene acetal and cyclohexene by Fe-poly PC and Cu-Fe-poly PC with oxygenat 30°C were carried out as has been described previously.[1] The catalytic ability of Fe-poly PC depends on the synthetic conditions, that is, on the reaction temperature and on the ratio of anhydrous ferric chloride to 1, 2, 4, 5-tetracyanobenzene, as shown in Fig. 2. There were some difficulties in preparing the catalytically active Fe-poly PC as compared with the case of Cu-Fe-poly PC. Although the (No. 1 and 3) Fe-poly

PC's showed catalytic activity in the oxidation of acetaldehyde ethylene acetal, the (No. 2 and 4) Fe-poly PC's did not show any activity. The (No. 3) Fe-poly PC showed a long induction period in the oxidation of acetaldehyde ethylene acetal, but the induction period disappeared upon the addition of *t*-butyl hydroperoxide to the reaction system (Fig. 3). Thus, the catalytic action of the (No. 3) Fe-poly PC is not effective in the activation of oxygen, but it is effective in the decomposition of the peroxide formed in the oxidation process. Remarkable differences in catalytic activity between Fe-poly PC and Cu-Fe-poly PC were observed in the case of the oxidation of cyclohexene. As shown in Fig. 4, even Fe-poly PC (No. 1), which showed a significant catalytic action in the oxidation of acetaldehyde ethylene acetal, showed a longer induction period for the oxygen absorption than that of Cu-Fe-poly PC. These facts must mean that the catalytic action of Cu-Fe-poly PC in the oxidation of acetaldehyde ethylene acetal and cyclohexene is more effective than that of Fe-poly PC.

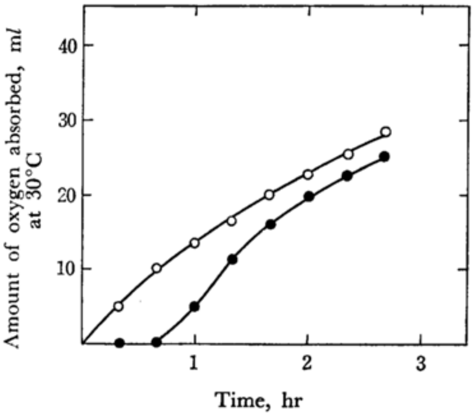


Fig. 4. The oxidation of cyclohexene in the presence of Fe- and Cu-Fe-poly PC: Catalyst; 30 mg.
○ Cu-Fe-poly PC ● Fe-poly PC (No. 1)

Effects of Various Treatments on the Catalytic Activities of Fe- and Cu-Fe-Poly PC. Cu-Fe-poly PC and Fe-poly PC treated with bromine showed no catalytic action in the oxidation of acetaldehyde ethylene acetal. However, the catalytic action was recovered to some extent by the reduction of bromine in Fe- and Cu-Fe-poly PC by ascorbic acid or sodium thiosulfate. The rate and the total amount of oxygen absorption into the system are shown in Fig. 5. Thus, bromine acts as an inhibitor of the catalytic action of Fe- and Cu-Fe-poly PC in the oxidation of acetaldehyde ethylene acetal. Probably this inhibition is caused by the formation of a complex between bromine and the polymer, as has been assumed previously.

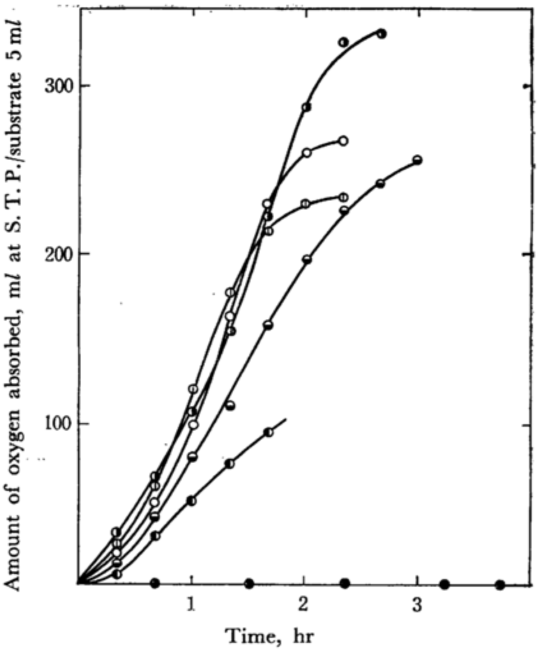


Fig. 5. The changes of the catalytic activities of Fe- and Cu-Fe-poly PC by the treatments of bromine and ascorbic acid: Catalyst; 30 mg.
◑ Cu-Fe-poly PC ○ Fe-poly PC
● Fe- and Cu-Fe-poly PC treated with Br_2
◒ Cu-Fe-poly PC treated with Br_2 and followed by ascorbic acid
◐ Cu-Fe-poly PC treated Br_2 and followed by sodium thiosulfate
⦶ Fe-poly PC treated with Br_2 and followed by ascorbic acid

The oxidation of acetaldehyde ethylene acetal by Fe- and Cu-Fe-poly PC treated with concentrated hydrochloric acid and air showed the induction period of the oxygen absorption of 4 or 5 hr, as shown in Fig. 6. This indicates that the change of the Fe(II) to the Fe(III) ion in Fe- or Cu-Fe-poly PC upon treatment of concentrated hydrochloric acid and air results in a lowering of the catalytic activity in the activation of oxygen in the oxidation process. That is, the Fe(II) ion should be involved in Fe- and Cu-Fe-poly PC in order to contribute effectively to the acceleration of the oxygen absorption in the oxidation of acetaldehyde ethylene acetal. Furthermore, the addition of 2-phenylimidazole or pyridine to the reaction system containing Fe- or Cu-Fe-poly PC resulted in an increase in the induction period for oxygen absorption or a decrease in the rate of oxygen absorption. The effect of the inhibition by 2-phenylimidazole was greater than that by pyridine (Figs. 7 and 8). This may be caused by the stronger ligand field of 2-phenylimidazole as compared with that of pyridine. In the case of Fe-poly PC, the induction period increased proportionally with an increase in the amount of 2-phenylimidazole added, as shown in Fig. 9. The

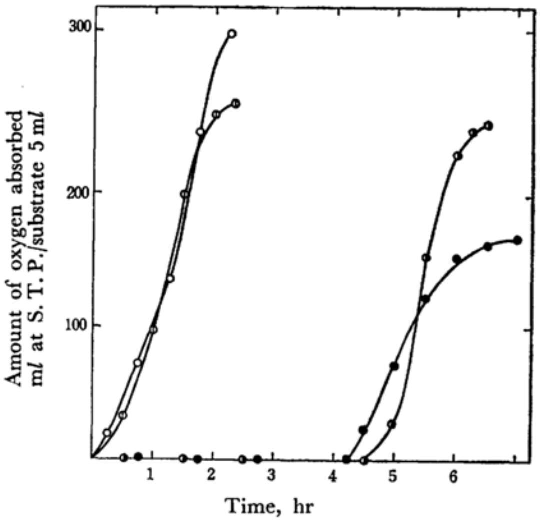


Fig. 6. The changes of the catalytic activities of Fe- and Cu-Fe-poly PC by the treatment of concentrated hydrochloric acid plus air: Catalyst; 30 mg.
○ Cu-Fe-Poly PC ⦶ Fe-poly PC
● Cu-Fe-poly PC treated with conc. HCl plus air
◑ Fe-poly PC treated with conc. HCl plus air

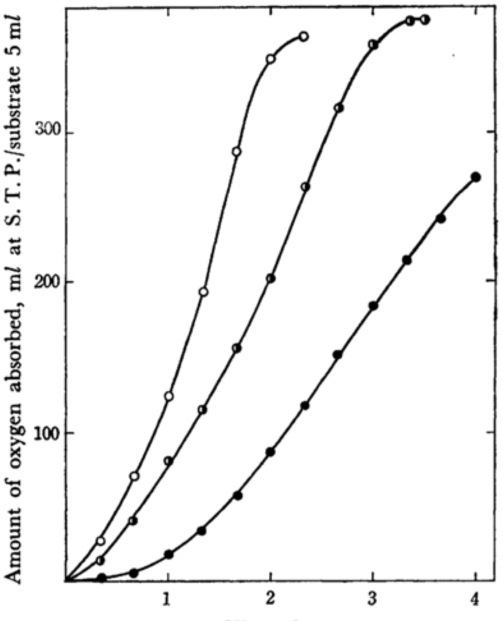


Fig. 7. The effect of pyridine on the oxidation of acetaldehyde ethylene acetal in the presence of Cu-Fe-poly PC: Catalyst; 30 mg.
The amount of the added pyridine: ○ none, ◑ 0.1 ml and ● 1.0 ml

decrease in the catalytic activity of Fe-poly PC with 2-phenylimidazole was larger than in the case of Cu-Fe-poly PC (Fig. 9). This may represent the difference between the properties of Fe- and Cu-

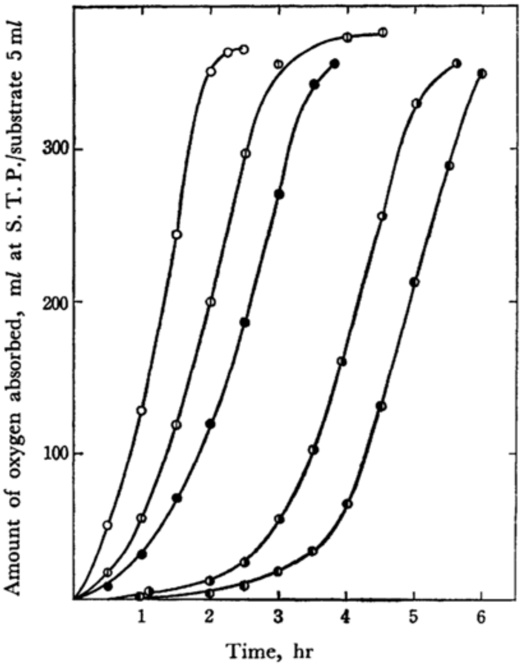


Fig. 8. The effect of 2-phenylimidazole on the oxidation of acetaldehyde ethylene acetal in the presence of Cu-Fe-poly PC: Catalyst; 30 mg.
The amount of the added 2-phenylimidazole: ○ none, ⦶ 4.29 mg, ● 5.90 mg, ◑ 8.16 mg and ◐ 10.14 mg

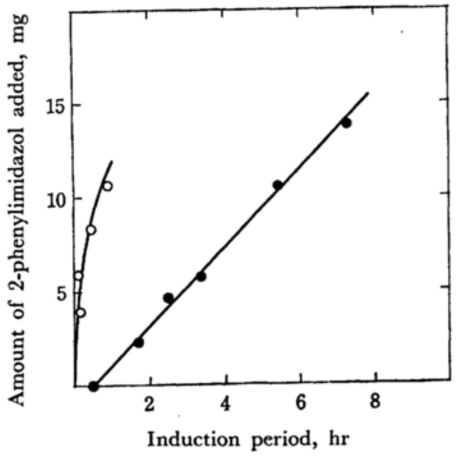


Fig. 9. Relationship between the amount of 2-phenylimidazole added and the induction period: Catalyst; 30 mg.
Acetaldehyde ethylene acetal: 5 ml
○ Cu-Fe-poly PC ● Fe-poly PC (No. 1)

Fe-poly PC as a catalyst, that is, the difference in the electronic properties of the Fe(II) ions located in the conjugated system. Thus, the electronic property of the Fe(II) ion conjugated with the π electron of the ligand seems to be important in making it an active site for the activation of oxygen.

Oxidation of Acetaldehyde Ethylene Acetal in the Presence of Fe-M-Poly PC or Cu-M-Poly PC. As shown in Fig. 10, Fe-M-poly PC (M; Cr, V, Co, Ni and Zn), Cu-Mn-poly PC, and Mn-poly PC all showed catalytic activity in the oxidation of acetaldehyde ethylene acetal with oxygen, while Cu-M-poly PC did not. Therefore, the iron and manganese ions contained in the polyphthalocyanine polymer must play important roles in the catalytic action, probably as active sites. Furthermore, in the case of Fe-M-poly PC (M; Cr, V, Mn, Co, Ni and Cu), there was a linear relationship between the catalytic activity (the rate of oxygen absorption) and the activation energy ($\Delta\varepsilon$) of the electrical conductivity of Fe-M-poly PC, as shown in Fig. 11. That is, the catalytic activity of Fe-M-poly PC increases with a decrease in the $\Delta\varepsilon$ value of Fe-M-poly PC, namely, with an increase in the conjugated system of the π electron. Thus, the electronic property of an iron or manganese ion, which is modified by the conjugation of the π electron of ligand and the electronic property of the other metal ion coexisting with the iron or manganese ion, seems to contribute effectively to the catalytic action of Fe-M-poly PC.

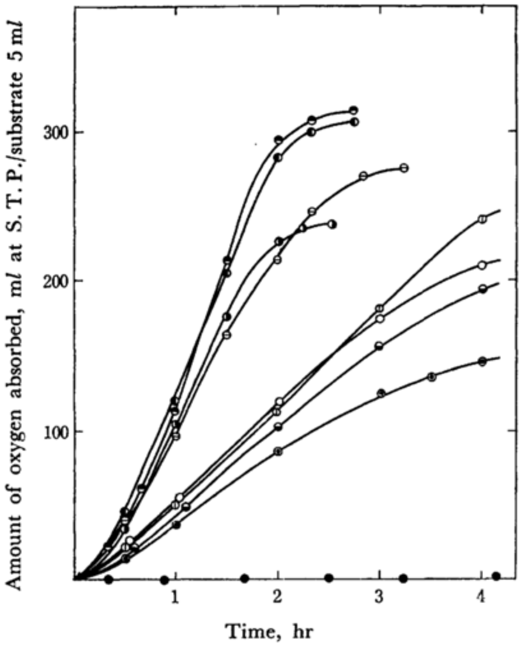


Fig. 10. The oxidation of acetaldehyde ethylene acetal in the presence of Fe-M- and Cu-M-poly PC: Catalyst; 30 mg.

○ Fe-V- ⦶ Fe-Cr- ⊖ Fe-Mn-
◑ Fe-Co- ◐ Fe-Ni- ◓ Fe-Cu-
◒ Cu-Mn- ⊙ Mn-
● Cu- and Cu-M-poly PC (M: V, Cr, Co, Ni and Zn)

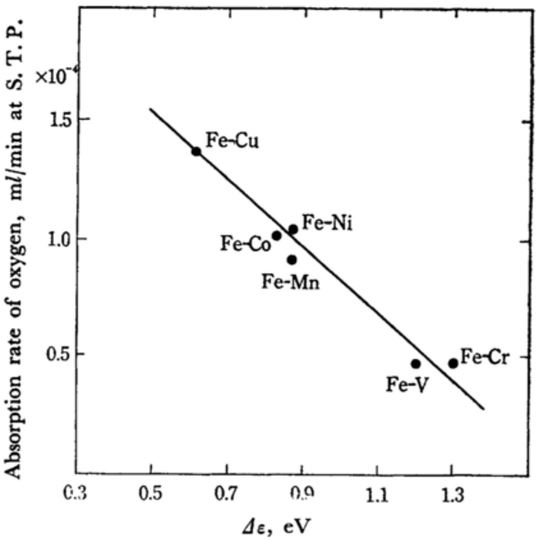


Fig. 11. Relationship between the absorption rate of oxygen in the oxidation of acetaldehyde ethylene acetal in the presence of Fe-M-poly PC and the value of $\Delta\varepsilon$ of Fe-M-poly PC: Fe-M-poly PC; 30 mg.
Acetaldehyde ethylene acetal; 5 ml