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Organic Catalysts. III.[1] The Catalytic Action of Copper-Iron-Polyphthalocyanine on the Oxidation of Acetaldehyde Ethylene Acetal[*1]

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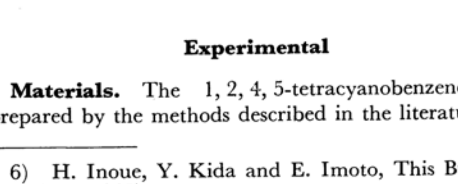
Copper-iron-polyphthalocyanine shows catalytic activity on the oxidation of acetaldehyde ethylene acetal with oxygen at 30°C; this catalytic activity is remarkably dependent on the atomic ratio of copper to iron ions involved and on the activation energy of the electrical conductivity of copper-iron-polyphthalocyanine. The catalytic oxidation of acetaldehyde ethylene acetal with oxygen in the presence of copper-iron-polyphthalocyanine gives, selectively, ethylene glycol monoacetate as the main reaction product, together with small amounts of ethylene glycol diacetate, ethylene glycol, acetaldehyde, and acetic acid. This catalyst is also effective in the selective oxidation of cumene and benzaldehyde ethylene acetal.

Recently, there have been several studies of the catalytic action of copper-polyphthalocyanine on the decomposition of hydrogen peroxide,[2] the exchange reaction between hydrogen and deuterium,[3] and the oxidation of such hydrocarbons as cumene and cyclohexene.[4] The catalytic effects on them increase with an increase in the degree of the conjugation of the phthalocyanine polymer in these cases. On the other hand, the catalytic action of cytochrome in oxidation-reduction in a biological system has been explained by the synergetic actions of copper (II) and iron-(II) ions contained in heme protein.[5] Also, a number of binary metals or metal oxides have been used as effective catalysts for various reactions. Therefore, a conjugated polymer containing two kinds of metal ions may have a characteristic action as a catalyst on oxidation-reduction because of some interactions between two kinds of metal ions through the conjugated system. In this paper, we will investigate the catalytic action of copper-iron-polyphthalocyanine on the oxidation of acetaldehyde ethylene acetal with oxygen at 30°C. The acetal was selected as a model compound because it may be oxidized easily according to the following equation:



(1)

Some of the results of this investigation have already been reported in a previous communication.[6]

Experimental

Materials. The 1, 2, 4, 5-tetracyanobenzene was prepared by the methods described in the literature[7,8];

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[1] Part II of this series: H. Inoue, Y. Kida and E. Imoto, This Bulletin, **39**, 551 (1966).

[*1] Presented at the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, March, 1966.

[2] S. Z. Roginskii, A. A. Berlin, O. A. Golovina, E. S. Dokukina, M. M. Sakharov and L. G. Cherkashina, *Kinetika i Kataliz,* **4**, 431 (1963).

[3] G. J. K. Acres and D. D. Eley, *Trans. Faraday Soc.,* **60**, 1157 (1964).

[4] S. Z. Roginskii, A. A. Berlin, L. N. Kutseva, R. M. Aseeva, L. G. Cherkashina, A. I. Sherle and N. G. Matveeva, *Dokl. Akad. Nauk S. S. S. R.,* **148**, 118 (1963).

[5] K. Okunuki, I. Sekuzu, T. Yonetani and S. Takemori, *J. Biochem.,* **45**, 847 (1958); S. Takemori, I. Sekuzu and K. Okunuki, *Biochim. et Biophys. Acta,* **38**, 158 (1960).

[6] H. Inoue, Y. Kida and E. Imoto, This Bulletin, **38**, 2214 (1965).

[7] A. S. Bailey, B. R. Henn and J. M. Langdon, *Tetrahedron,* **19**, 161 (1963).

[8] A. Epstein and B. S. Wildi, *J. Chem. Phys.,* **32**, 324 (1960).

mp 260—263°C. The anhydrous ferric chloride, anhydrous cupric chloride, and ethylene glycol were of a commercial grade.

The Preparation of Copper-Iron-Polyphthalocyanines (Cu-Fe-Poly PC). The procedures reported by Epstein and Wildi,[8] and Assour, Goldmacher and Harrison[9] were modified to prepare Cu-Fe-poly PC in various atomic ratios of copper to iron ions. The procedures for the preparations of the polymers of No. 8 (method A) and No. 12 (method B) will here be described as examples.

Method A. A suspension of 1.5 g of 1, 2, 4, 5-tetracyanobenzene, 0.14 g of anhydrous ferric chloride, and 0.11 g of anhydrous cupric chloride in 16 g of ethylene glycol was stirred at 180—200°C for 5 hr. After the reaction mixture had then been cooled, 50 m*l* of water was added to it. The precipitate was collected by centrifugation, washed by decantation with three 100-m*l* portions of water, and then filtered off. Furthermore, the precipitate was refluxed twice with 30 m*l* of methanol for 30 min, subsequently washed with ether, and dried over calcium chloride under a reduced pressure of 10 mmHg to give Cu-Fe-poly PC as an insoluble greenish black powder (0.9 g). The polymers of Nos. 1—9 in Table 1 were prepared according to this method.

Method B. A mixture of 1.5 g of 1, 2, 3, 5-tetracyanobenzene, 0.12 g of cuprous chloride, 0.30 g of ferric chloride, and 0.50 g of urea was heated at 300°C under a nitrogen atmosphere in a sealed tube for 18 hr. The temperature was raised to 350°C during the next 2 hr. The solidified mixture was then pulverized to powder in a mortar and purified by the method described above. About 1.2 g of a greenish-black powder was obtained. The polymers of No. 10—12 were prepared according to this method.

The properties and the conditions for the preparations of all the polymers obtained here are summarized in Tables 1 and 2.

TABLE 1. THE CONDITIONS FOR THE PREPARATION OF Cu-Fe-poly PC

Exp. No.	Starting material, g			Preparation method	Yield g
	TCB*	$CuCl_2$	$FeCl_3$		
1	0.9	0.40	0.00	A	1.0
2	0.9	0.00	0.40	A	0.8
3	0.9	0.20	0.25	A	0.9
4	1.5	0.22	0.45	A	1.1
5	0.9	0.10	0.40	A	0.9
6	1.5	0.10	0.40	A	1.0
7	1.5	0.08	0.72	A	0.6
8	1.5	0.11	0.14	A	0.9
9	1.5	0.34	0.96	A	0.6
	TCB	CuCl	$FeCl_3$		
10	1.2	0.40	0.00	B	1.2
11	1.2	0.00	0.30	B	1.1
12	1.5	0.12	0.30	B	1.2

* TCB means 1,2,4,5-tetracyanobenzene.

TABLE 2. THE ELEMENTARY ANALYSIS OF Cu-Fe-poly PC

Exp. No.	Elementary analysis, %				
	C	H	N	Cu	Fe
1	46.01	2.39	14.00	15.37	0.00
2	54.73	4.25	12.24	0.00	7.20
3	47.09	2.73	12.95	6.52	5.14
4	45.21	1.97	15.00	6.03	2.60
5	37.52	2.21	10.74	3.59	5.75
6	52.32	2.22	16.87	4.68	2.26
7	51.71	2.42	14.82	5.18	3.48
8	48.00	2.16	18.31	5.10	4.06
9	50.44	2.74	13.79	7.48	3.64
10	46.18	2.53	28.76	19.47	0.00
11	38.57	1.95	26.36	0.00	10.40
12	45.08	2.34	26.97	5.40	6.61

Analyses of Copper and Iron Ions. A weighed amount of Cu-Fe-poly PC was decomposed by heating at 300°C in 1 m*l* of fuming nitric acid in a sealed tube. The solution was diluted with distilled water, adjusted to pH 2 with 1 N sodium hydroxide solution, and titrated with 0.1 N EDTA solution by a photometric method.

Oxidation. *Material.* Acetaldehyde ethylene acetal was prepared according to the method described in the literature[10] and purified before use by distilling it repeatedly through a Vigreux column over sodium under a nitrogen atmosphere, n_D^{25} 1.3960; bp 85°C. It was confirmed by gas chromatography that the acetal contains no impurity. The absence of peroxide was confirmed by an iodo-starch test.

Apparatus and Procedure. The oxidation of acetaldehyde ethylene acetal was carried out by using the apparatus shown in Fig. 1. The temperature of the gas

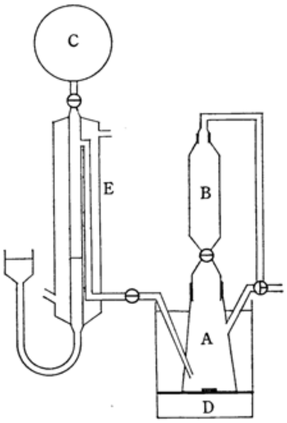

Fig. 1. Apparatus.

A: Reaction vessel
B: Dropping funnel
C: Storage of oxygen
D: Magnetic stirrer
E: Gas buret

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[9] J. M. Assour, J. Goldmacher and S. E. Harrison, *J. Chem. Phys.*, **43**, 159 (1965).

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

buret was kept constant at 30°C by circulating water from the thermostat to the outside of the gas buret.

In each experiment, 50 mg of the catalyst was placed into a reaction vessel (A) (capacity, 70 m*l*), which had previously been placed in a thermostat (F) at 30°C. Then, the air space of the entire apparatus was filled with oxygen. In the dropping funnel (B) there was placed 5 m*l* of the acetal; this was then dropped into the reaction vessel and stirred vigorously by a magnetic stirrer (D). The amount of oxygen absorbed at each interval of the reaction time was measured by the gas buret at atmospheric pressure.

Analyses of the Reaction Products. The ethylene glycol monoacetate, ethylene glycol diacetate, acetaldehyde, acetic acid, ethylene glycol, and water formed in the reaction 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 Measurement of the D. C. Resistivity. The d. c. resistivity of the polymers was measured at an applied electric field of 100—200 V/cm under a pressure of 1000 kg/cm² *in vacuo* according to the method described in a previous paper.[11] The electrical resistivity (ρ) at an ascending temperature was identical with that at a descending temperature, and a linear relationship between log ρ and $1/T$ was observed. The resistivity of the polymers fit the following equation, as does a typical organic semiconductor:

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

Results and Discussion

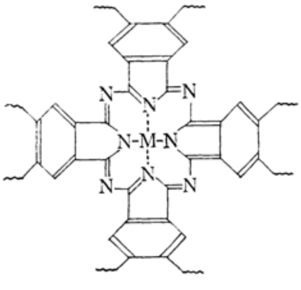
The Properties of Cu-Fe-Poly PC. All of the polymers obtained here were infusible, greenish-black powder. They may be classified into two groups, one group (Nos. 1—9) prepared by method A (type A), and another group (Nos. 10—12) prepared by method B (type B).

The Phthalocyanine Polymers of Type A. Cu-, Fe- and Cu-Fe-poly PC were insoluble in any organic solvent, but were soluble in concentrated sulfuric acid to give a green color. The infrared absorption spectra of Cu-Fe-poly PC were similar to those of copper- and iron-polyphthalocyanine (Cu- and Fe-poly PC); they showed absorption bands at 1130—1137, 1100, 1065, 910, 780—800 and 739—742 cm^{-1}, bands which corresponded to those of copper phthalocyanine (Cu-PC) at 1163, 1090, 1065, 899, 770 and 753 cm^{-1}. In addition to these, the absorption bands of the –CONHCO– group at 3200—3400, 1760 and 1710 cm^{-1} were observed. However, the absorption band of the –CN group at 2200 cm^{-1} was not observed in any of the phthalocyanine polymers of type A. Therefore, the –CN groups of 1, 2, 4, 5-tetracyanobenzene seem to have been converted to the structure of a phthalocyanine or imide type such as I or II.

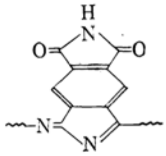
The contents of copper and iron ions in Cu-Fe-poly PC varied with the amounts of ferric chloride and cupric chloride used as the starting materials, as is shown in Table 2. The molecular weight (M) of the structure unit per metal ion in Cu-, Fe- and Cu-Fe-poly PC was calculated by the following equation, where X and Y are Cu%/63.5 and Fe %/55.6 respectively:

$$M = \frac{100}{X + Y}$$

The values of M for Cu-, Fe- and Cu-Fe-poly PC were about 414, 775, and 513—877 respectively, as Table III shows. The ratios of carbon to nitrogen (the C/N ratio) of Cu-, Fe- and Cu-Fe-poly PC had values of 3.8, 5.2 and 3.1—4.3 respectively. The values of M and of the C/N ratio seem to show the degree of polymerization of the phthalocyanine unit. If the structure of the phthalocyanine polymer consists completely of that of I, the values of M and of the C/N ratio must be 420 and 2.5 for Cu-poly PC. Therefore, when the values of M and of the C/N ratio of the phthalocyanine polymer are larger than 420 and 2.5 respectively, the phthalocyanine polymer may contain the imide structure (II) as a part of a structure such as I.



(I)



(II)

The Phthalocyanine Polymers of Type B. Cu-, Fe- and Cu-Fe-poly PC were almost insoluble even in concentrated sulfuric acid. The infrared absorption spectra of Cu-, Fe- and Cu-Fe-poly PC of type B were broader than those of Cu-Fe-poly PC of type A, and they had not the absorption bands of the –CN and –CONHCO– groups, though the other absorption bands were similar to those of type A. The values of M and of the C/N ratio were about 326—538 and 1.7—2.0 respectively. Thus, Cu-, Fe- and Cu-Fe-poly PC of type B seem to have a higher degree of the polymerization of 1, 2, 4, 5-tetracyanobenzene in comparison with the phthalocyanine polymers of type A, and the structure of Cu-, Fe- and Cu-Fe-poly PC of type B seems to be similar to that of I.

The Visible Absorption Spectra of Cu-, Fe- and Cu-Fe-Poly PC of Types A and B. As is shown in Fig. 2, the visible absorption spectrum of Cu-PC

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

or Fe-PC as observed by the use of a KBr disk showed two main absorption maxima, at 620 and 700 mμ, or at 677 and 868 mμ. On the other hand, that of Cu- or Fe-poly PC of type A shows the main absorption at 720 or 725 mμ and a very weak absorption at 880 or 830 mμ respectively. Thus, the main absorption at 720 or 725 mμ shifts toward the longer wave side by 100 and 48 mμ respectively as compared with that of Cu- or Fe-PC.

The visible absorption spectra of Cu - Fe - poly PC of type A showed two absorption maxima, at about 715—725 and 880—892 mμ, and became broader with the decrease in the C/N ratio of the polymers, though the positions of the absorption peaks did not differ apparently from polymer to polymer. Moreover, the peak at 880—892 mμ became more intense in comparison with that of Cu- and Fe-poly PC. This may mean that Cu-Fe-poly PC is not a simple mixture of Cu- and Fe-poly PC. The visible absorption spectra of Cu-Fe-poly PC of type B showed two absorption maxima, at 760 and 910 mμ; these became broader than those of type A, as is shown in Fig. 2. This may mean that the degree of the conjugation of π electrons of type B is larger than that in the case of type A.

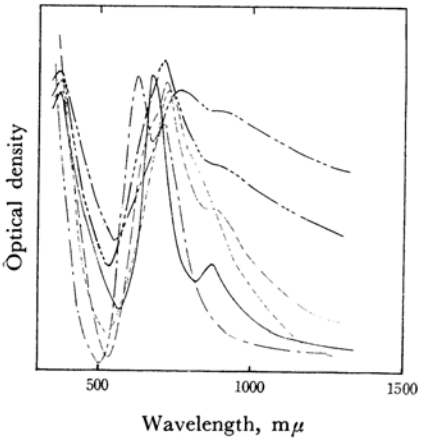


Fig. 2. The visible absorption spectra of Cu- and Fe-PC and Cu-, Fe- and Cu-Fe-poly PC of type A and B:
—-— Cu-PC, —— Fe-PC, — — Cu-poly PC, ---- Fe-poly PC, —----— Cu-Fe-poly PC of type A (No. 8), and —---— Cu-Fe-poly PC of type B (No. 12).

The Activation Energy of the Electrical Conductivity. The activation energy ($\Delta\varepsilon$) of the dark-conductivity of the polymers was determined from the dependency of the d. c. resistivity on the temperature. As is shown in Table 3, the values of $\Delta\varepsilon$ were in the range of about 0.34—1.03 eV. The values of $\Delta\varepsilon$ of Cu-Fe-poly PC of type B became smaller than those of type A. Furthermore, the values of $\Delta\varepsilon$ of Cu-Fe-poly PC of the types A and B decreased almost linearly with a decrease in the C/N ratio, though they showed no tendency in relation to the copper and iron ion contents, as is shown in Fig. 3. This means that the value of $\Delta\varepsilon$ depends on the structure of the polymers rather than on the properties of the metal ions.

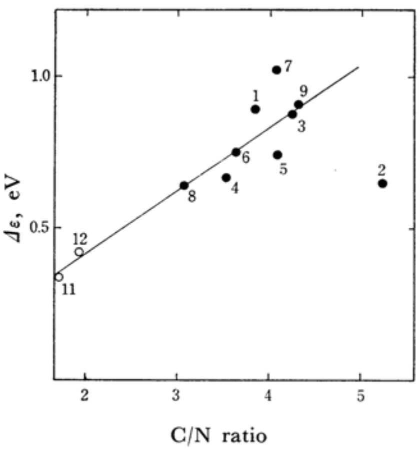


Fig. 3. Relationship between the activation energy and the C/N ratio.

The Catalytic Actions of Cu-Fe-Poly PC. *The Effects of Cu-, Fe- and Cu-Fe-poly PC on the Rate of Oxygen Absorption.* As has been described in a previous communication,⁶⁾ Cu-Fe-poly PC showed a catalytic action on the oxidation of acetaldehyde ethylene acetal with oxygen, though Cu-poly PC, Fe-poly PC, Cu- and Fe-PC appeared not to have

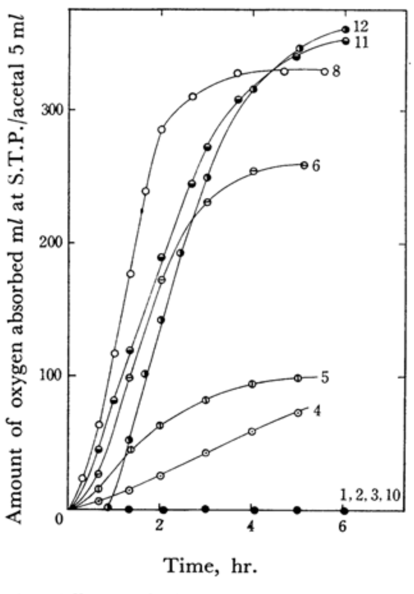


Fig. 4. Effects of Cu-, Fe- and Cu-Fe-poly PC on the absorption rates of oxygen.

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

Exp. No.	M	C/N ratio	Cu/Fe ratio	Electrical properties $\Delta\varepsilon$ (eV)	 ρ_{20} (Ω-cm)
1	414	3.8	—	0.89	2.2×10^9
2	775	5.2	0.0	0.65	8.5×10^6
3	513	4.2	1.1	0.88	2.4×10^7
4	704	3.5	2.0	0.67	4.5×10^6
5	626	4.1	0.6	0.74	5.1×10^6
6	877	3.6	1.8	0.75	1.0×10^7
7	694	4.1	1.3	1.03	6.4×10^8
8	654	3.1	1.1	0.64	6.3×10^5
9	547	4.3	1.8	0.91	3.7×10^7
10	326	1.9	—	—	—
11	538	1.7	0.0	0.34	2.9×10^2
12	491	2.0	0.7	0.43	9.7×10^2

TABLE 4. THE ABSORPTION RATES AND THE TOTAL AMOUNT OF OXYGEN ABSORBED AND THE YIELD OF ETHYLENE GLYCOL MONOACETATE

Exp. No.	Rate, m*l*/min at S.T.P.	Reaction time, hr	Total amount m*l* at S.T.P.	Yield, %	Conversion%[*3] from Acetal	 Oxygen
1	0.0	5.5[*1]	0	0	0	0
2	0.0	7.3[*1]	0	0	0	0
3	0.0	3.8[*1]	0	0	0	0
4	0.3	8.3[*2]	102	11	61	70
5	0.6	5.1[*2]	98	11	62	70
6	1.7	4.8[*2]	260	26	77	60
7	0.2	8.5[*1]	38	8	60	—
8	2.9	4.0[*2]	337	32	71	60
9	0.2	7.8[*2]	65	7	42	70
10	0.0	7.7[*1]	0	0	0	0
11	1.8	5.3[*2]	350	50	100	88
12	1.9	5.3[*2]	364	37	79	64

[*1] Reaction time until the reaction is stopped.

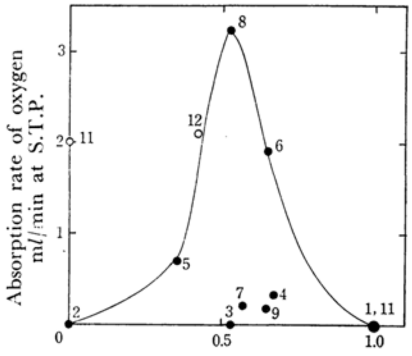
[*2] Reaction time until the catalytic ability disappeares.

[*3] The conversion efficiency was calculated by the following equation:

$$\text{Acetal\%} = \frac{\text{Amount (mol) of ethylene glycol monoacetate produced}}{\text{Amount (mol) of acetal reacted}} \times 100$$

$$\text{Oxygen\%} = \frac{\text{Amount (mol) of ethylene glycol monoacetate produced}}{2 \times \text{Amount (mol) of oxygen absorbed}} \times 100$$

the catalytic ability within the reaction time examined. The amount of oxygen absorbed increased linearly with the reaction time after a short induction period, as is shown in Fig. 4. However, the catalytic activity disappeared after a certain reaction time. The absorption rates, the induction periods, and the total amounts of oxygen absorbed differed from polymer to polymer. The shorter the induction period became, the more the absorption rate tended to increase. Furthermore, the total amount of oxygen absorbed until the catalytic ability disappeared increased with an increase in the absorption rate. In the case of No. 8, it reached 337 m*l*, which was the largest value among Cu-Fe-poly PC's of type A. The absorption rates were related to the $\Delta\varepsilon$ values of the phthalocyanine polymers and the atomic ratios of the copper to the iron ions present in the phthalocyanine polymers. When the $\Delta\varepsilon$ value was above 0.9 eV, oxygen absorption was scarcely observed at all. However, in the case of the phthalocyanine polymers with $\Delta\varepsilon$ values of about 0.6—0.7 eV, oxygen absorptions were observed, the catalytic activity tends to depend on the atomic ratio of copper to iron ions, as is shown in Fig. 5. The absorption rates reach a maximum at the copper to iron ratio of 0.52. However, when the value of $\Delta\varepsilon$ became too small (No. 11 and No. 12), the remarkable effect by copper and iron ions was not observed, and consequently even Fe-poly PC came to show catalytic activity. Thus, the properties of copper and iron ions as active sites



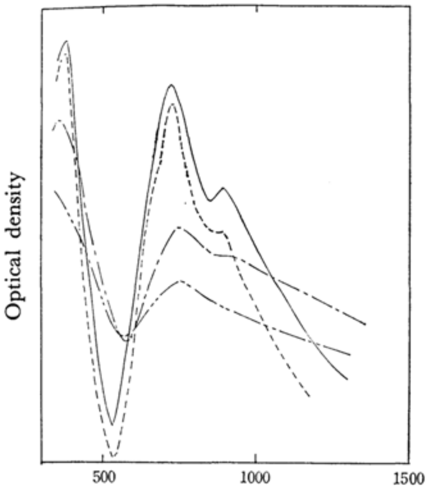
Cu/Cu+Fe ratio

Fig. 5. Relationship between the absorption rate of oxgen and Cu/Cu+Fe ratio:
● type A and ○ type B.

seem to be influenced by the degree of the conjugation of π electrons in the phthalocyanine polymer.

The Reaction Products. The catalytic oxidation of acetaldehyde ethylene acetal with oxygen gave ethylene glycol monoacetate as the main product, and ethylene glycol diacetate, acetic acid, acetaldehyde, ethylene glycol and water as by-products. No other products were obtained. The yield of ethylene glycol monoacetate differed from polymer to polymer; it was proportional simply to the total amount of oxygen absorbed, as Table 4 shows. In the case of No. 12, a 37% yield of ethylene glycol monoacetate was obtained; it was the best among the Cu-Fe-poly PC's of types A and B. Furthermore, the selectivity of the conversion of an absorbed oxygen or a reacted acetaldehyde ethylene acetal to ethylene glycol monoacetate by the reaction 1 was 64 or 79% respectively, as is shown in Table 4. Here, 21% of the acetaldehyde ethylene acetal was consumed to produce ethylene glycol diacetate, acetic acid, acetaldehyde, ethylene glycol and water. The selectivity of the conversion of oxygen or acetaldehyde ethylene acetal to ethylene glycol monoacetate did not vary remarkably from polymer to polymer in the case of Cu-Fe-poly PC's of types A and B. Thus, the catalysts obtained here seem to have some selectivity and an accelerating action on the formation of ethylene glycol monoacetate.

The Properties of Cu-Fe-Poly PC after the Reaction After the oxidation of acetaldehyde ethylene acetal with oxygen in the presence of Cu-Fe-poly PC of No. 5 or 12 had been carried out at 30°C, the reaction mixture was filtered off; the recovered polymer was washed successively with water, methanol and ether, and then dried over calcium chloride under the reduced pressure of 10 mmHg. No remarkable differences in the color of the polymers between before and after the reaction were observed in either case. The infrared spectra of the recovered polymers of Nos. 5 and 12 were similar to those before the reaction. The visible absorption spectrum of the recovered polymer that the absorptions in the longer-wavelength region tend to of No. 5 observed by the use of a KBr disk showed that the absorptions in the longer-wavelength region tend to decrease, although no remarkable variation in the absorption curve was observed, as is shown in Fig. 6. This may show that the degree of the conjugation of π electrons in the recovered polymer becomes smaller than that of the polymer before the reaction. On the other hand, the spectral variation in No. 12 was qulitatively investigated, since the polymer of No. 12 was not mixed uniformly with KBr. The oxidation of acetaldehyde ethylene acetal with oxygen in the presence of the recovered polymer of No. 5 or 12 was carried out again under the same conditions as the initial oxidation. In the case of No. 12, the oxygen absorption was observed after a long induction period. The rate of the oxygen absorption was nearly equal to that in the case of the initial oxidation. However, in the case of No. 5 the absorption of oxygen was not observed even after the reaction time of 4 hr. This may suggest that the degree of the conjugation of π electrons in the polymer plays an important role in the catalytic action.



Wavelength, mμ

Fig. 6. The visible absorption spectra of the recovered polymer of Nos. 5 and 12:
Before the reaction; —— No. 5 and – – – – No. 12, and after the reaction; ······ No. 5 and — — — No. 12.

The Oxidations of the Other Acetals and Cumene. The catalytic action of Cu-Fe-poly PC of No. 8 on the oxidation of benzaldehyde ethylene acetal, acetaldehyde dimethyl acetal, acetaldehyde diethyl acetal, and cumene with oxygen respectively was investigated under the same conditions

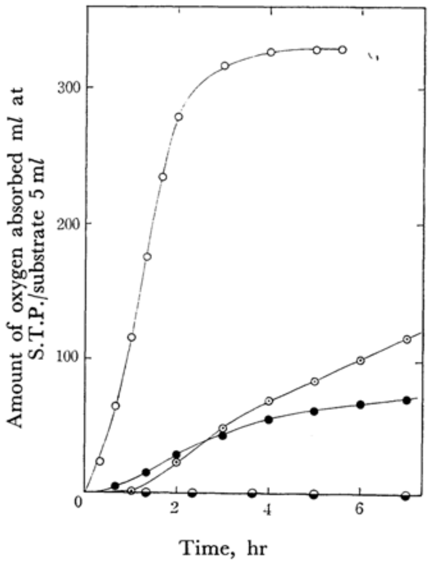


Fig. 7. The amounts of oxygen absorbed to the reaction time for the acetals and cumene: Catalyst; No. 8, —○— acetaldehyde ethylene acetal, —●— benzaldehyde ethylene acetal, —⊙— cumene, —◒— acetaldehyde dimethyl acetal and —◒— acetaldehyde diethyl acetal.

as in the case of acetaldehyde ethylene acetal. In the case of acetaldehyde dimethyl acetal and acetaldehyde diethyl acetal, oxygen was not absorbed even after the reaction time of 7 hr. However, in the case of benzaldehyde ethylene acetal and cumene, the oxygen absorption was observed, although the absorption rates were slower than that in the case of acetaldehyde ethylene acetal, as Fig. 7 shows. Furthermore, the oxidation of cumene with oxygen gave dimethylphenylcarbinol and α-methylstylene as the main reaction products, while that of benzaldehyde ethylene acetal gave mainly ethylene glycol monobenzoate. Thus, the catalytic action of Cu-Fe-poly PC was small for substrates, such as cumene or benzaldehyde ethylene acetal, which have bulky groups on the tertiary carbon. Therefore, the catalytic ability of Cu-Fe-poly PC may be controlled by the necessity of a precise fit between the substrate and an active site on the surface of Cu-Fe-poly PC. Furthermore, the fact that acetaldehyde dimethyl acetal and acetaldehyde diethyl acetal were not oxidized may be explained by the lack of a strained ring structure.