The Liquid-phase Oxidation of Acetaldehyde with Metal Polyphthalocyanines. Solvent Effect

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(Received October 1, 1975)

Acetaldehyde was oxidized using metal polyphthalocyanines as catalysts. Metal polyphthalocyanines, especially Fe,Cu-polyphthalocyanine, were found to be useful oxidation catalysts for the selective formation of peracetic acid from acetaldehyde. The rate of oxidation was much affected by the nature of the solvents. The solvent is considered to take part in the initiation oxidation reaction in two ways: one is based on the prevention of the oxygen molecule from coordination with a metal polyphthalocyanine and subsequent activation, and the other is due to the solvation with the activated oxygen molecules on the catalyst. Preferable solvents were ethyl acetate, bromobenzene, benzene, and acetone.

Since metal phthalocyanines were discovered to carry oxygen molecules, they have been used as catalysts in the autoxidation of many organic compounds, the mechanism of their action on the oxidation reaction has also been investigated.[1–4] Kropf *et al.* reported that an active species, an oxygen complex derived from a metal pathalocyanine and molecular oxygen in the presence of a base such as pyridine, could abstract the hydrogen atom from a substrate to generate free radicals, resulting in the initiation of autoxidation.[5–7] Other investigators[8,9] proposed another mechanism for the action of metal phthalocyanines, especially the ability to decompose hydroperoxide homolytically to initiate autoxidation. Contrary to the oxidations using metal phthalocyanines, there are only a few papers available concerning the metal polyphthalocyanine-catalyzed autoxidation.[10–13] But studies of the metal polyphthalocyanine in comparison with its monomeric analogue are expected to throw some light on the elucidation to the chemical behavior of metal polyphthalocyanine as one of the macromolecular catalysts complexed with metal ions, the structure of which possesses a close similarity to hemoglobin. In our papers, various metal polyphthalocyanines were synthesized and shown to be effective catalysts for the autoxidation of cumene[11] and acrolein.[12,13]

In this paper, the liquid-phase oxidation of acetaldehyde was tried using various metal polyphthalocyanines as catalyst. The action of the catalyst and the effect of solvents on the oxidation are discussed in detail.

Experimental

Materials: Metal polyphthalocyanines were synthesized and purified according to the method descrided in an earlier paper.[13] The metal contents in Fe,Cu-polyphthalocyanine were analyzed by a spectrophotometric method; the ratio of iron to copper ions was 1.52. The metal polyphthalocyanine was sufficiently pulverized with a mortar before use. The oxidation rate with micro-crystals of metal polyphthalocyanine was, however, found to be essentially the same as that with the pulverized metal. Acetaldehyde was carefully distilled under nitrogen atmosphere to insure the complete removal of the oxidized materisls; solvents were used after conventional purification with careful drying.

Procedure and Analysis: The oxidation apparatus and oxidation process were described in the literature.[14]
Peroxide products were analyzed by an iodometric titration method determining individual concentrations of hydrogen peroxide, peracetic acid, and other peroxides such as acetoyl peroxide.[15] Other oxidation products were quantitatively determined by gas liquid chromatography.

Results and Discussion

Outline of Autoxidation: Purified samples of metal polyphthalocyanines have been shown to lack the ability to decompose a hydroperoxide, though they catalyzed the liquid-phase oxidation of organic compounds such as cumene and acrolein. The oxidation of acetaldehyde with a metal polyphthalocyanine also gave peracetic acid quantitatively in such solvents as benzene, ethyl acetate, and acetone (Table 1). This fact may be emphasized as one of the characteristic actions of metal polyphthalocyanines, because metal phthalocyanines and other catalysts such as metal acetylacetonates and naphthenates are known to decompose peracetic acid formed during the oxidation of acetaldehyde through a homogeneous mechanism.[16,17] The selectivity of peracetic acid in benzene and ethyl acetate as solvents was inclined to decrease with the reaction time. This may be ascribed to the formation of acetaldehyde monoperacetate in these solvents, followed by its heterogeneous decomposition. In acetone, the rate of oxidation was slower than in ethyl acetate, but the selectivity remained about 93% even after three hours. This suggests that metal polyphthalocyanines can be made use of as catalysts for the selective formation of peracetic acid, and shows that they have no ability to decompose peracetic acid, resulting in the initiation of autoxidation.

The rate of oxygen absorption, as shown in Table 2, was much affected by the nature of the solvent. The dielectric constants of the solvents are also listed in Table 2. The oxidation reaction seems to proceed much faster in a solvent which has an adequate polarity, such as ethyl acetate. There is, however, no linear relationship between the rate and the dielectric constant.

The role of solvents in an autoxidation reaction catalyzed by an organometallic complex can be considered in general in terms of the following two ways. First, the solvent may take part in the chain-propagating step to interrupt autoxidation:

$$CH_3COOO\cdot + RH \longrightarrow CH_3COOOH + R\cdot \quad (A)$$

in which RH denotes a solvent. Secondly, it may

Table 1. The oxidation products in the oxidation of acetaldehyde catalyzed by metal polyphthalocyanines

		Catalyst (solvent)		
		Fe, Cu (Benzene)	Fe, Cu (Ethyl acetate)	Fe (Acetone)
Acetaldehyde charged ($\times 10^3$M)		45.0	45.2	46.3
Peracetic acid formed ($\times 10^3$M)	a*	12.8	23.4	19.7
	b*	20.3	28.0	27.6
	c*	21.1	26.6	28.6
Peroxide formed ($\times 10^3$M)	a	0.57	0.39	0.49
	b	1.34	0.95	0.59
	c	1.29	1.10	0.82
$\frac{\text{Peracetic acid formed}}{\text{Acetaldehyde charged}}$ (%)	a	28.4	51.7	42.5
	b	45.4	61.9	59.6
	c	47.0	58.8	61.4
$\frac{\text{Oxygen absorbed}}{\text{Acetaldehyde charged}}$ (%)	a	29.5	57.4	44.2
	b	58.3	73.1	59.7
	c	60.5	79.5	66.1
$\frac{\text{Peracetic acid formed}}{\text{Oxygen absorbed}}$ (%)	a	96.4	90.2	102
	b	77.8	84.7	99.9
	c	77.2	73.7	92.8

Reaction conditions: (catalyst), 4.82×10^{-3}M; temperature, 10 °C.

*a, b, and c represent one, two, and three hours of reaction time, respectively.

Table 2. The rate of oxygen absorption in the oxidation of acetaldehyde by two metal polyphthalocyanines in various solvents

Me–poly-Pc	Solvent	Dielectric constant	$-\mathrm{d}(O_2)/\mathrm{d}t$ $\times 10^5$M s^{-1}
Fe, Cu	*p*-Xylene	2.27	0.0
	Benzene	2.28	8.51
	Bromobenzene	5.40	10.6
	Ethyl acetate	6.02	13.7
	Acetone	20.7	8.44
	Benzonitrile	25.2	0.22
	Methanol	32.7	0.0
Fe	Chlorobenzene	5.62	7.64
	Acetone	20.7	7.62
	Nitrobenzene	34.8	0.61

Reaction conditions: (CH_3CHO), 4.52×10^{-1}M; (catalyst), 4.8×10^{-3}M; temperature, 10 °C.

Table 3. The rate of oxygen absorption with and without catalyst in carboxylate solvents

Solvent	$-\mathrm{d}(O_2)/\mathrm{d}t, \times 10^5$ M s^{-1}		Ratio of (b) to (a)
	(a) Uncatalyzed	(b) Catalyzed	
Ethyl acetate	0.89	13.7	15.4
Isopropyl acetate	0.89	5.84	6.6
Ethyl chloroacetate	0.1	2.45	28.0

Reaction conditions: temperature, 10 °C; catalyst, Fe,Cu–poly-Pc, 4.81×10^{-3}M; acetaldehyde, 4.52×10^{-1}M.

interact with the complexes as a catalyst to change their activity. Imamura found that the oxidation rate of acetaldehyde catalyzed by cobalt naphthenate depended substantially on the kind of solvents and concluded that the oxidation was probably governed by a reaction according to Eq. A in the case of the presence of a hydrocarbon solvent.[17]

If the solvent effect is observed only on the propagation and termination steps of a general autoxidation mechanism as discussed below, though ester solvents were mostly used in this paper, the relative rates of the oxidation in the presence of the catalyst to that in the absence of the catalyst must be same regardless of the kind of solvents. The ratio in Table 3 does not show any solvent effect on such chain steps. This fact also proposes that the solvent effect is operative in the initiation step rather than the chain steps in the present oxidation reaction using a metal polyphthalocyanine as catalyst.

Solvent Effect: The effect of solvents on the rate of oxidation was investigated in detail using various esters, such as acetates (CH_3COOR) and ethyl carboxylates ($R'COOC_2H_5$), as solvents. The oxidation rate in the presence of a metal polyphthalocyanine was considerably dependent on the kind of substituent groups R and R′ (Table 4). It was found that there was a certain relation between the oxidation rates and the electronic properties of the substituents (R and R′) in terms of their polar substituent constants σ^* for Taft's equation.

In the case of acetates (Fig. 1), the logarithm of the rates increased linearly with increase of σ^* of R in the range of $\sigma^* < -0.10$. The constants ρ^* can be calculated as 6.7 and -0.3 over the ranges of σ^* below and above -0.10, respectively, except for methyl acetate, which is very difficult to purify and constains a small amount of methanol which makes the metal polyphthalocyanine inactive (Table 2). A similar result was also obtained for the ethyl carboxylates, as illustrated in Fig. 1b;

TABLE 4. SOLVENT EFFECT OF VARIOUS ACETATES AND ETHYL CARBOXYLATES ON THE OXIDATION RATES

Solvent	Substituents R-	R'-	$-d(O_2)/dt$ $\times 10^5$ M s^{-1}
Acetates			
methyl acetate	CH_3-		2.33
butyl acetate	$CH_3(CH_2)_3$-		17.2
isopropyl acetate	$(CH_3)_2CH$-		5.84
benzyl acetate	$(C_6H_5)CH_2$-		2.58
ethyl acetate	C_2H_5-	CH_3-	13.7
Ethyl carboxylates			
ethyl propionate		C_2H_5-	6.10
ethyl chloroacetate		CH_2Cl-	2.45
ethyl isobutyrate		$(CH_3)_2CH$-	3.14
ethyl dichloroacetate		$CHCl_2$-	0.18

Reaction conditions: (acetaldehyde), 4.52×10^{-1}M; (Fe,Cu-poly-Pc), 4.8×10^{-3}M; temperature, 10 °C.

values of ρ^* were calculated as 4.4 and -1.0 for the straight lines of the left and right sides of ethyl acetate, respectively. For simplicity, a series of solvents having positive ρ^* value are hereafter called M, while the series having negative ρ^* are called N. Considering the absolute values of ρ^* for solvent series M and N, the values for the series M are much larger than those for series N. The ρ^*'s also have different signs for the two series of solvents. These facts imply that the mechanisms of solvent effects are different in these series. The rather large values of ρ^* for series M may suggest that such solvents take part as more polarized species in the initiation reaction.

TABLE 5. THE CONSTANT k_1K_1 OF THE INITIATION REACTION OF ACETALDEHYDE BY VARIOUS METAL POLYPHTHALOCYANINES

Metals	$-d(O_2)/dt$ $\times 10^5$ M s	k_1K_1 $\times 10^2$ M^{-2} s^{-1}
Fe,Cu	21.6	7.2
Fe,Mo	12.1	2.0
Fe	8.6	1.1
Fe,Co	8.5	1.1
Cu,Co	1.1	0.0017

Reaction conditions: (CH_3CHO), 0.45M; (catalyst), 4.82×10^{-3}M; solvent, ethyl acetate; temperature, 10 °C.

A Possible Reaction Mechanism: In order to explain the results mentioned above and to explain the oxidation mechanism, especially the initiation reaction, in more detail, the oxidation reaction was investigated kinetically under reaction conditions including those shown in Figs. 1(a) and 1(b). The reactions were confirmed not to proceed under diffusion control of oxygen in the reaction system. The dependence of the rates of oxygen absorption on concentrations of acetaldehyde and the catalyst and on oxygen pressure was determined in three kinds of solvents, isopropyl acetate belonging to series M and ethyl acetate and ethyl monochloroacetate belonging to series N (Figs. 2a, 2b, and 2c).

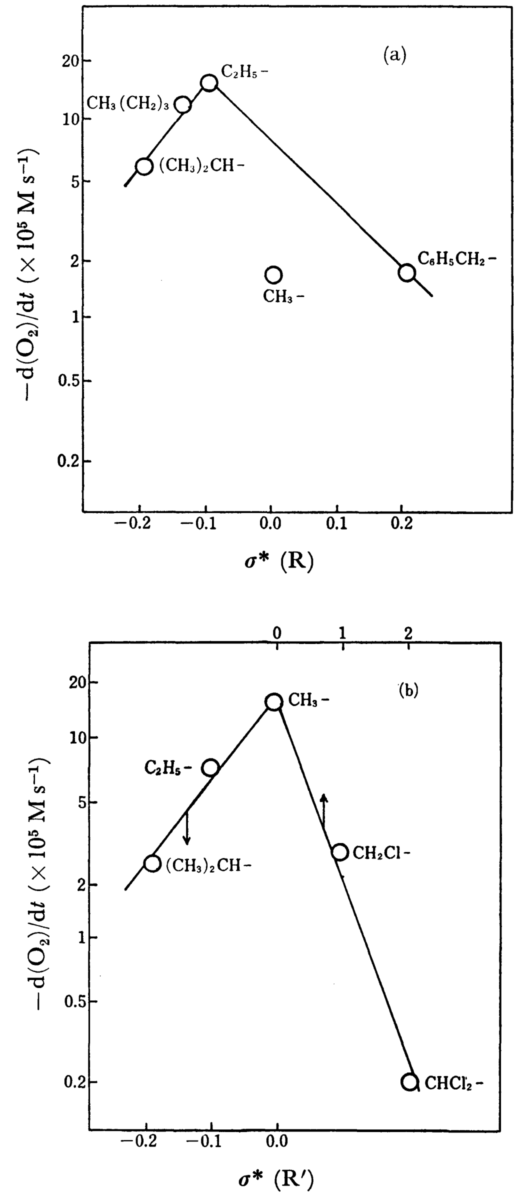


Fig. 1. The effects of the substituents R and R' of esters (R'COOR) as solvents on the rate of oxidation.

The rate equations, except for that obtained with a lower pressure of oxygen in isopropyl acetate, were equal and could be written as Eq. I:

$$-\frac{d(O_2)}{dt}=k(CH_3CHO)^{3/2}(\text{catalyst})^{1/2}(O_2)^{1/2} \quad (I)$$

in which k means a rate constant. This equation can be compared with the rate equation (II)

$$-\frac{d(O_2)}{dt}=k_p/(2k_t)^{1/2}(CH_3CHO)\cdot R_i^{1/2} \quad (II)$$

derived from the general elementary steps of autoxidation under no diffusion control of oxygen as follows;

initiation: $CH_3CHO \longrightarrow CH_3\dot{C}O \ : R_i$ (1)

chain propagation:

$$CH_3\dot{C}O + O_2 \longrightarrow CH_3COOO\cdot \quad (2)$$

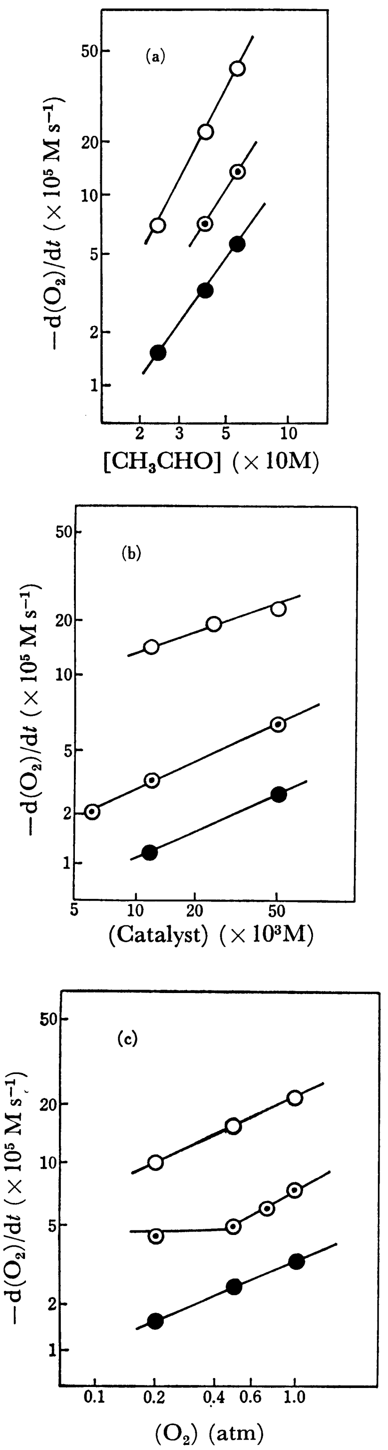


Fig. 2. Effects of concentrations of acetaldehyde, Fe, Cu–polyphthalocyanine, and oxygen on the oxidation rates.

Reaction conditions: (CH_3CHO), 0.45 M; (Fe,Cu-poly-Pc), 4.82×10^{-3} M; and O_2 pressure, 1 atm were used as standard. Temperature was 10°C.

○: Ethyl acetate, ⊙: isopropyl acetate, ●: ethyl chloroacetate.

$$CH_3COOO\cdot + CH_3CHO \xrightarrow{k_p} CH_3COOOH + CH_3\dot{C}O \quad (3)$$

$$\text{termination: } 2CH_3COOO\cdot \xrightarrow{k_t} \text{non-radical} \quad (4)$$

in which R_i represents the rate of initiation, and k_p and k_t represent the rate constants of Steps 3 and 4. Consequently the rate of initiation is obtained as

$$R_i = \{k/k_p/(2k_t)^{1/2}\}^2(CH_3CHO)(\text{catalyst})(O_2) \quad (III)$$

It is possible, therefore, to discuss the initiation mechanism as follows:

$$\text{Me-polyPc} + O_2 \rightleftarrows \text{Me}^+\text{-polyPc-}O_2^- \quad (1\text{-a})$$

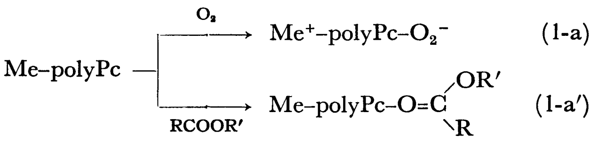
$$\text{Me}^+\text{-polyPc-}O_2^- + CH_3CHO \longrightarrow (\text{Me-polyPc-}O_2H) + CH_3\dot{C}O \quad (1\text{-b})$$

When the equilibrium constant of Scheme 1-a and the rate constant of Scheme 1-b are assumed to be K_1 and k_1 respectively, the rate equation of initiation is

$$R_i = k_1K_1(CH_3CHO)(\text{catalyst})(O_2) \quad (IV)$$

at the stationary state. This equation is equal to Eq. III.

It is well known that such substrates as acetic acid and methanol are easily coordinated with a metal ion in the conjugated system of a metal phthalocyanine through the electron pair on the oxygen atom. In the above initiation mechanism, the solvents in series M are considered to have considerably stronger electron-donating substituents corresponding to the lower values of σ^*, resulting in the stronger coordination through their carbonyl oxygen. In other words, the degree of the electron density on the oxygen atom of the carbonyl group increases with the increase of the electron-donating ability of the substituents R and R′. The reaction 1-a is, therefore, considered to be competitive with the reaction between a metal polyphthalocyanine and a solvent as follows:



$$\text{Me-polyPc} \begin{cases} \xrightarrow{O_2} \text{Me}^+\text{-polyPc-}O_2^- & (1\text{-a}) \\ \xrightarrow[\text{RCOOR}']{} \text{Me-polyPc-O=C}\begin{matrix}\diagup OR' \\ \diagdown R\end{matrix} & (1\text{-a}') \end{cases}$$

As the σ^* values of the solvents become smaller, the equilibrium 1-a′ is much more shifted to the right side. The stronger interaction of a solvent with a metal ion will leave fewer chances for the O_2 molecule to be activated by coordination. This interaction can be explained by the higher values (6.7 and 4.4) of ρ^* in series M, which are considered to be based on the interaction of solvents with the polarized species as mentioned before.

Negative values of the reaction constant ρ^* were obtained in the solvents of series N. As the absolute values of ρ^* are smaller compared with those in series M, these solvents are considered to have a weaker interaction with the initiation reaction. According to the explanation with respect to solvents of series M, the larger value of σ^* has to facilitate the activation of the molecular oxygen by a metal ion. But in the case of the electron-attracting ability of the substituent becoming too large, the electron density on the oxygen atom decreases to a certain extent, and consequently the metal polyphthalocyanine–O_2 complex is not apt to react with acetaldehyde, because these kinds of solvents may solvate with such an activated oxygen complex, resulting in the prevention of the hydrogen-abstracting reaction from acetaldehyde (1-b). No evidence to support this explanation is yet available, but this will be discussed in detail in our next paper.[18] A possible reaction mechanism is

$$\text{Me}^+\text{-polyPc-O}_2^- \begin{cases} \xrightarrow{\text{CH}_3\text{CHO}} \text{Me}^+\text{-polyPc-O}_2^-\text{-CH}_3\text{CHO} & \text{(1-b)} \\ \xrightarrow[\text{solvent}]{} \text{Me}^+\text{-polyPc-O}_2^-\text{-solvent} & \text{(1-b}'\text{)} \end{cases}$$

In this case, the lower absolute value of ρ^* may be explained by the above-mentioned Schemes 1-b and 1-b′.

It is concluded, as the sum of these two effects of solvents on the initiation mechanism, that such a solvent as ethyl acetate or ethyl propionate is an optimum one whose substituent shows an adequate degree of the electron-donating and -attracting abilities for the carbonyl group.

In the oxidation of acetaldehyde in isopropyl acetate, the partial pressure of oxygen had no influence on the rate of oxygen absorption in the range of the oxygen pressure below 400 Torr. This means that the activation of oxygen does not occur because of low concentration of oxygen dissolved and/or the more preferable conditions for the reaction 1-a′ than 1-a, and suggests that Fe,Cu–polyphthalocyanine directly abstracts the hydrogen atom from aldehyde, as is well known.[19]

The constants k_1K_1 of Eq. IV are compared for various metal polyphthalocyanines. The rate equation can be written as when the R_i of Eq. IV is put into Eq. II.

$$-\frac{d(O_2)}{dt} = (k_1K_1)^{1/2}k_p/(2k_t)^{1/2}(CH_3CHO)^{3/2} \times (\text{catalyst})^{1/2}(O_2)^{1/2} \qquad \text{(V)}$$

The rate constant k_p at 0 °C is reported to be 2.7×10^3 M^{-1} s^{-1} and the activation energy of k_p is assumed to be 4.2 kcal/mol, which is determined in the oxidation of decanal.[20] Then the approximate value of k_p at 10 °C is calculated to be 3.6×10^3 M^{-1} s^{-1}. On the other hand, the rate constant $2k_t$ at 0 °C is reported to be 1.04×10^8 M^{-1} s^{-1}. As $2k_t$ is considered not to be so influenced by the temperature, $k_p/(2k_t)^{1/2}$ can be obtained as 3.6×10^{-1} $M^{-1/2}$ $s^{-1/2}$ at 10 °C. The concentration of oxygen dissolved in ethyl acetate at 10 °C is reported to be 1.15×10^{-2} M.[21] Table 5 summarizes the calculated k_1K_1 values. The metal polyphthalocyanines are effective to activate the oxygen molecule in the order of Fe,Cu–≫Fe,Mo–>Fe–>Fe,Co–≫Cu, Co–polyphthalocyanines. Iron seems to be essential to such activation.

The authors would like to express their thanks to Prof. Teiji Tsuruta for giving fruitful advice on finishing this work.

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