March 1977]   BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (3), 701—705 (1977)   701

The Liquid-phase Oxidation of Aldehydes with Fe, Cu-Polyphthalocyanine and Cobalt Tetra-*p*-tolylporphyrin

Yasukazu Ohkatsu, Osamu Sekiguchi, and Tetsuo Osa

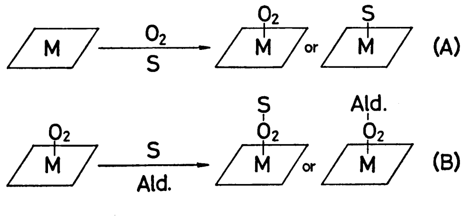
Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

(Received October 1, 1975)

The effect of chemical species in a reaction system on the oxidation reaction of aldehydes was studied using Fe,Cu-polyphthalocyanine and cobalt tetra-*p*-tolylporphyrin as catalysts. Both catalysts activated the oxygen molecule on their central metals and then abstracted the hydrogen atom from aldehydes to initiate autoxidation. In this initiation step, every chemical species present in the reaction system, such as the solvent, the aldehyde, the oxygen molecule and the catalyst, is found to have an effect, one after another, either to accelerate or to retard the rate of initiation. The correlation of the nature of chemical species with such mutual interaction was discussed in detail.

There are only a few papers[1,2] about liquid-phase oxidations using metal polyphthalocyanines and porphyrins as catalysts. Imoto *et al.*[3] utilized polyphthalocyanines containing two kinds of transition metals in the oxidation of acetaldehyde ethylene acetal. Such polyphthalocyanines have been reported to show no activities except for polyphthalocyanines including both iron and manganese, or both manganese and another metal. The oxidation rates has a good correlation with the activated energies (ΔE) calculated from the dependence of the electroconductivity of the catalyst on the temperature. In other words, the oxidation activity of a polyphthalocyanine increased with the decrease in ΔE, namely, the enlargement of the π-electron conjugated system. They concluded that the central metal of a polyphthalocyanine was the active site, which contributed to the activation of oxygen and the decomposition of a hydroperoxide. We also investigated the effects of the kinds of transition metals on the oxidation rate, and found that iron was one of the essential metals and that Fe,Cu-polyphthalocyanine was most effective in the oxidation of acetaldehyde.[4]

In the oxidations of cumene,[5] acrylaldehyde,[6,7] and acetaldehyde,[4] the activity of a metal polyphthalocyanine was also found to be much affected by the nature of the solvents with respect to the activation of oxygen and the catalytic performance. The effect of solvents in the liquid-phase oxidation of acetaldehyde with a metal polyphthalocyanine complex was elucidated in terms of the interaction between the central metal ion of the complex and a solvent, or the interaction of the aldehyde and/or the solvent with the oxygen molecule activated on the complex:



In the above schemes, M means the transition metals, S means the solvent, and Ald. means acetaldehyde. This paper will described some of the evidence for the vaguuness of the proposed schemes, especially Scheme B, using several kinds of aldehydes. Cobalt tetra-*p*-tolylporphyrin was utilized as a catalyst in comparison with Fe,Cu-polyphthalocyanine.

Experimental

Materials. The Fe,Cu-polyphthalocyanine used as a catalyst was synthesized and purified according to the conventional method.[8] Cobalt tetra-*p*-tolylporphyrin was prepared by the use of pyrrole, *p*-tolualdehyde, and cobalt(II) acetate.[9] Solvents such as ethyl carboxylates and aldehydes, such as acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, acryldehyde, cinnamaldehyde, and benzaldehyde, were purified by conventinal methods. The aldehydes were carefully purified just before use in order to remove the pre-oxidation products.

Procedure. The liquid-phase oxidation of aldehydes was carried out using an atmosphere-tight and oxygen-circulating reaction apparatus reported before.[10] The reaction was started by the first charge of a solvent and the purge of the system with oxygen, subsequently we added a catalyst and an aldehyde.

In some cases, oxygen was bubbled and circulated into a reaction solution containing a solvent and a catalyst thirty minutes before the start of oxidation, so that the oxygen complex was formed previously, and then an aldehyde was added.

The amount of oxygen absorbed was followed by means of a gas burett, sometimes a portion of the reaction solution was sampled out to detemined its content of a percarboxylic acid by an iodine method.[11]

Results and Discussion

The oxidation of an aldehyde is widely accepted to proceed through the following steps:

$$\mathrm{RCHO} \longrightarrow \mathrm{R\dot{C}O}\ \text{(initiation rate, } R_\mathrm{i}\text{)} \tag{1}$$

$$\mathrm{R\dot{C}O} + \mathrm{O_2} \xrightarrow{k_2} \mathrm{RCOO_2\cdot} \tag{2}$$

$$\mathrm{RCOO_2\cdot} + \mathrm{RCHO} \xrightarrow{k_p} \mathrm{RCOO_2H} + \mathrm{R\dot{C}O} \tag{3}$$

$$\left.\begin{array}{ll} 2\mathrm{R\dot{C}O} \xrightarrow{k_4} & (4) \\ \mathrm{R\dot{C}O} + \mathrm{RCOO_2\cdot} \xrightarrow{k_5} & (5) \\ 2\mathrm{RCOO_2\cdot} \xrightarrow{k_t} & (6) \end{array}\right\}\ \text{inert products}$$

In the autoxidation of saturated aldehydes and benzaldehyde using Fe,Cu-polyphthalocyanine or cobalt tetra-*p*-tolylporphyrin as a catalyst, the rate of oxidation was obtained as follows (see, Tables 1 and 2):

TABLE 1. OXIDATION OF ISOBUTYRALDEHYDE USING Fe,Cu-POLYPHTHALOCYANINE IN ETHYL ACETATE

Isobutyraldehyde (M)	Fe,Cu-polyphthalocyanine $\times 10^4$(M)	Oxygen pressure (Torr)	$-\mathrm{d(O_2)/d}t$ $\times 10^4$(M s^{-1})	$\dfrac{-\mathrm{d(O_2)/d}t}{(\mathrm{RCHO})^{3/2}(\mathrm{cat})^{1/2}(\mathrm{O_2})^{1/2}}$ $\times 10^3$(M^{-1} s^{-1} Torr$^{-1/2}$)
0.5	1.0	760	0.93	0.95
0.5	5.0	760	2.24	1.0
0.5	10	760	3.39	1.1
0.5	20	760	4.32	0.99
0.5	5.0	500	1.73	0.98
0.5	5.0	400	1.42	0.90
0.5	5.0	160	0.80	0.80
0.1	5.0	760	0.10	0.98
0.3	5.0	760	1.03	1.0
0.7	5.0	760	3.39	1.1
1.0	5.0	760	7.39	1.2

Reaction condition: temperature, 10 °C.

TABLE 2. OXIDATION OF BENZALDEHYDE USING COBALT TETRA-*p*-TOLYLPORPHYRIN IN ETHYL ISOBUTYRATE

Benzaldehyde (M)	Cobalt tetra-*p*-tolylporphyrin $\times 10^4$(M)	Oxygen pressure (Torr)	$-\mathrm{d(O_2)/d}t$ $\times 10^4$(M s^{-1})	$\dfrac{-\mathrm{d(O_2)/d}t}{(\mathrm{RCHO})^{3/2}(\mathrm{cat})^{1/2}(\mathrm{O_2})^{1/2}}$ $\times 10^3$(M^{-1} s^{-1} Torr$^{-1/2}$)
0.5	2.0	760	1.15	0.83
0.5	3.0	760	1.61	0.95
0.5	5.0	760	2.16	0.99
0.5	8.0	760	2.70	0.98
0.5	5.0	500	1.56	0.88
0.5	5.0	400	1.34	0.85
0.1	5.0	760	0.16	0.83
0.3	5.0	760	0.97	0.96
0.8	5.0	760	4.41	1.0
1.0	5.0	760	6.47	1.1

Reaction condition: temperature, 10 °C.

$$-\frac{\mathrm{d(O_2)}}{\mathrm{d}t} = k(\mathrm{RCHO})^{3/2}(\mathrm{catalyst})^{1/2}(\mathrm{O_2})^{1/2} \qquad \text{(I)}$$

It was ascertained that enough oxygen was present in a reaction system for Step 2 by other experiments using azobisisobutylonitrile under the radiation of UV as initiator.

These results give the rate of initiation:

$$R_\mathrm{i} = K(\mathrm{RCHO})(\mathrm{catalyst})(\mathrm{O_2}) \qquad \text{(II)}$$

in which $K = \left\{\dfrac{k(2k_\mathrm{t})^{1/22}}{k_\mathrm{p}}\right\}$

by the same treatment as that described in a previous paper.[4] This establishes that the initiation reaction consists of a reaction among an aldehyde, a catalyst, and oxygen.

Seven kinds of aldehydes were oxidized. Table 3 shows the rates of the oxidation of the aldehydes in combination with esters as solvents. Zaikov *et al.*[12] studied the oxidation of acetaldehyde, heptanal, octanal, pivaldehyde, and benzaldehyde in chlorobenzene at 0 °C. They concluded that the reason why these aldehydes were oxidized at similar rates under similar conditions was due to compensating changes in the rate constants for chain propagation (k_p) and chain termination ($2k_\mathrm{t}$), that is to say, the values of $k_\mathrm{p}/(2k_\mathrm{t})^{1/2}$ were almost constant, regardless of the kind of aldehydes.

The oxidation rates in Table 3, therefore, are estimated to parallel the initiation rates using Fe,Cu-polyphthalocyanine and tetra-*p*-polyporphyrin. The oxidation rates of some aldehydes are plotted in logarithm against Taft's σ^* values of alkyl groups of ethyl carboxylate (Fig. 1). Every aldehyde shows a similar type of figure; their slopes are calculated to be as is shown in Table 4.

The aldehyde with a conjugated double bond to the formyl group, such as acrylaldehyde and cinnamaldehyde, showed higher ρ^* values on the left-hand side of graph. This may be ascribed to the fact that the oxidation-rate equation cannot be written as Eq. I. In the autoxidation of acrylaldehyde,[13] for example, the equation is obtained as:

$$-\frac{\mathrm{d(O_2)}}{\mathrm{d}t} = \frac{R_\mathrm{i}^{1/2}k_2k_\mathrm{p}(\text{acrylaldehyde})(\mathrm{O_2})}{k_\mathrm{p}(2k_4)^{1/2}(\text{acrylaldehyde}) + k_2(2k_\mathrm{t})^{1/2}(\mathrm{O_2})} \qquad \text{(IV)}$$

in which $k_\mathrm{p}(2k_\mathrm{t})^{-1/2} = 5.5\times10^{-2}$ M$^{-1/2}$ s$^{-1/2}$, and $k_2(2k_4)^{-1/2} = 3.7\times10$ M$^{-1/2}$ s$^{-1/2}$ at 40 °C. This suggests that the reaction of the acyl radical of acrylaldehyde with oxygen is one of the rate-determining steps because of the stabilization of the acyl radical *via* the conjugated double bond:

Table 3. Rates of oxidation of aldehydes

Aldehydes	Rate of oxidation ($\times 10^5$ M s^{-1}) in solvent of						
	Ethyl isobutyrate	Ethyl butyrate	Ethyl propionate	Ethyl acetate	Ethyl acetyl-acetate	Ethyl chloro-acetate	Ethyl dichloro-acetate
Isobutyradehyde	20.1	26.5	25.5	22.4		11.3	
Butyraldehyde	15.3	20.0	23.2	21.2		8.50	5.95
Propionaldehyde	3.40	4.92	6.73	14.6		5.42	2.87
Acetaldehyde	3.14	4.58	6.10	13.7	4.75	2.45	6.79
Acrylaldehyde	0.38	1.57	2.07			1.50	0.015
Cinnamaldehyde	0.77	1.80	2.45			0.089	
Benzaldehyde	5.55	6.80 7.24	9.21 9.55	24.5		3.60	1.56
Acetaldehyde[a)]	14.1		12.3	11.8	3.05		
Benzaldehyde[a)]	21.6			15.4		7.03	

Reaction conditions: Fe,Cu-polyphthalocyanine, 5×10^{-4} M; aldehyde, 0.5 M; and 10 °C.
a) An equimolecular amount of cobalt tetra(*p*-methylphenyl)porphyrin was used in place of the polyphthalocyanine.

Table 4. Reaction constants, ρ^*, for solvents in the oxidation of aldehydes[a)]

Aldehydes	Left side		Right side	
	ρ^*	Relative value	ρ^*	Relative value
Isobutyraldehyde	3.23	0.74	−0.30	0.39
Butyraldehyde	3.01	0.69	−0.35	0.45
Propionaldehyde	3.70	0.85	−0.41	0.53
Acetaldehyde[b)]	4.35	1.00	−0.77	1.00
Acrylaldehyde	6.67		−1.10	
Cinnamaldehyde	5.50		−1.16	
Benzaldehyde[b)]	3.85		−0.66	

a) Reaction conditions: Fe,Cu-polyphthalocyanine, 5×10^{-4}M; aldehyde, 0.5M, and temperature, 10°C.
b) An equimolecular amount of cobalt tetra-*p*-tolylporphyrin was also used in place of the polyphthalocyanine. ρ^* values obtained: −0.77 for acetaldehyde and −1.11 for benzaldehyde.

$$CH_2{=}CH{-}\dot{C}{=}O \longleftrightarrow \dot{C}H_2{-}CH{=}C{=}O$$

Therefore, these aldehydes do not belong to the substrates, to which the correspondence of the oxidation rates to the initiation rates mentioned above can be applied.[13,14)]

According to the explanation presented in a previous paper,[4)] the reaction constant, ρ^*, of oxidation in ester solvents (R′COOR) with substituents (R and R′) of lower σ^* values are most likely to be independent of the kind of aldehydes (see Scheme A). In such solvents as the reported as "left-side" in Table 4, almost constant values of ρ^* were obtained for all aldehydes except for acrylaldehyde and cinnamaldehyde, compared with those of the oxidation in solvents referred to as "right-side." This supports Scheme A, though it cannot positively be said to be true because of the incomplete constancy of ρ^* values: the small difference in the ρ^* values will be discussed hereafter.

On the other hand, a considerable difference among values of ρ^* was observed in solvents with higher σ^* values. This means some participation of solvent in the initiation reaction and suggests the effect of such solvents on the interaction with activated oxygen molecules on catalysts (Scheme B).

Table 5. Rates of oxygen absorbed in the oxidation of benzaldehyde with or without the pre-bubbling of oxygen

Solvents	Rates of oxygen absorbed $\times 10^5$ M s^{-1}	
	With pre-bubbling	Without pre-bubbling
Ethyl isobutyrate	7.66	5.55
Ethyl butyrate	10.3	7.24
Ethyl chloroacetate	3.83	3.60

Reaction conditions: Fe,Cu-polyphthalocyanine, 5×10^{4}M; benzaldehyde, 0.5 M, and temperature, 10 °C.

Other experimental data are shown in Table 5. In ethyl isobutyrate and ethyl butyrate, the oxidation rate corresponding to the initiation rate was higher when oxygen was bubbled into the reaction solution thirty minutes before the start of oxidation by the addition of an aldehyde, than when all of the reactants were charged at once to commence oxidation. This fact means not only that there occurs the competitive coordination of a solvent and an oxygen molecule with the complex, but also that an aldehyde has some interaction with such a coordination reaction. Ethyl chloroacetate belonging to a solvent as the "right side" did not show enough difference in the oxidation rate to be discussed. This supports the explanation mentioned above that the solvent is not considered to participate in the activation of the oxygen molecule, but to interact with the activated oxygen according to Scheme B. The coordination of carbonyl compounds such as an aldehyde and an ester with a metal complex is explained by the fact well known in the chemistry of the reaction of an alkyl metal complex with a carbonyl compound: an aldehyde is more reactive with the complex than an ester.[15)] The coordination of acrylaldehyde with cobaltous acetylacetonate through its carbonyl group has also been reported.[16)] It is not surprizing, therefore, that the formation of the oxygen complex is accelerated by the absence of the aldehyde, which will behave competitively as a ligand like an ester solvent. This pheno-

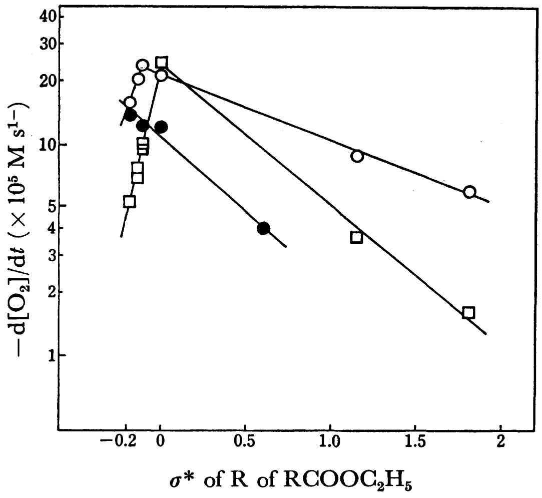


Fig. 1. Arrangement of rate of oxidation against σ^* value of R of $RCOOC_2H_5$ solvents.
Reaction consitions: aldehyde, 0.5 M; catalyst, 5×10^{-4} M; and temperature, 10°C.
○: Fe,Cu-polyphthalocyanine, butyraldenyde,
□: Fe,Cu-polyphthalocyanine, benzaldehyde,
●: cobalt tetra-*p*-tolylporphyrin, acetaldehyde.

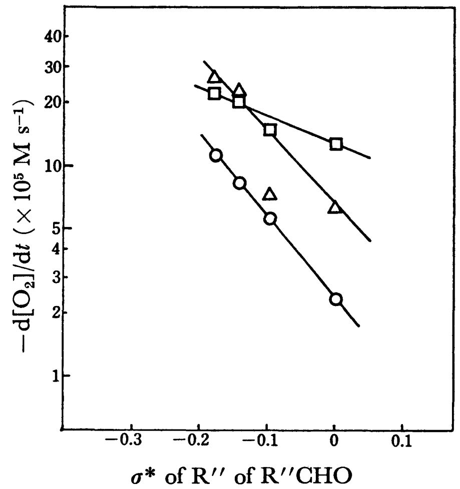


Fig. 2. Arrangement of rate of oxidation against σ^* value of R″ of R″CHO.
Reaction conditions: aldehyde, 0.5 M; Fe,Cu-polyphthalocyanine, 5×10^{-4} M; and temperature, 10°C.
□: Ethyl acetate, △: ethyl propionate, ○: ethyl chloroacetate.

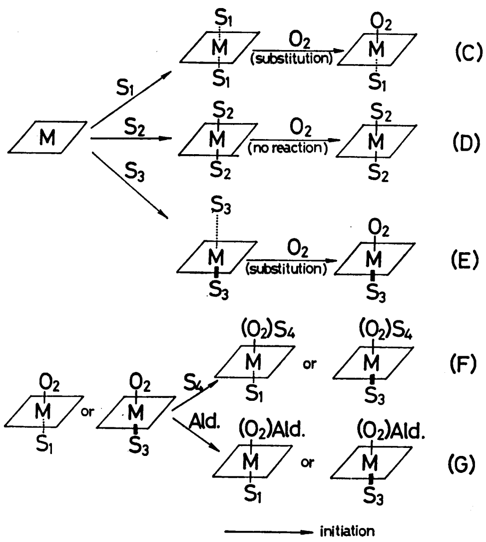
menon is not fully understood, but it may be related to the fact that the maximum points of the rate of oxidation seem to shift against the σ^* values of alkyl groups of esters, depending on the kind of aldehydes (see Fig. 1). The oxidation rates of all aliphatic aldehydes except for unsaturated ones are arranged against the σ^* values of the aliphatic residues as in Fig. 2. The lower the σ^* value was the higher the oxidation rate was. If an aldehyde is taken account of as a part of a solvent, this result seems to be the reverse of that shown in Fig. 1 with respect to the σ^* values of alkyl substituents of aldehydes. This may be explained as follows, not by the steric hindrance of aldehyde, but by the electron-donating property of aldehyde.

The value of σ^* of the alkyl residue has, in general, some relation with the steric hindrance factor (E_s). The E_s is considered to show the possibility for an aldehyde occupying the coordination site of oxygen sterically to prevent it from access to the site. However, this explanation is the just reverse of the inclination against σ^*, as is shown in Fig. 2.

In previous papers[5,7] we have reported that a strong electron-donating additive such as pyridine could accelerate the rate of oxidation if it is present in a catalytic amount. This was well interpreted by the idea that the additive could activate the oxygen molecule at the axial position through electron donation. The complexes used in this oxidation have vacant axial positions, which are probably solvated by a solvent in solution. The aldehyde with a stronger electron-donating power compared with an ester solvent may substitute the solvating ester or may occupy the coordination site in preference over the solvent molecule. Consequently, an aldehyde such as isobutyraldehyde is considered to assist the activation of oxygen, as does pyridine. The first coordination of an aldehyde with an electron-rich carbonyl group, that is, with an alkyl residue with a lower σ^* value makes its second coordination difficult because of the repulsion of electrons between the central metal of the complex given by the first aldehyde and of the carbonyl group of the second aldehyde approaching from the axial trans position. Thus, the electrophilic coordination and activation of the oxygen molecule at the second site is accomplished more easily, and the oxidation of isobutyraldehyde, for example, is initiated more easily and faster.

The difference as a catalyst between Fe,Cu-polyphthalocyanine and cobalt tetra-*p*-tolylporphyrin was also observed (Table 4 and Fig. 1). Though it is difficult to compare the two catalysts simply because of their probable different behavior in response to peracids, the latter catalyst, unlike the former, did not give mountain-shaped lines, but lost its oxygen-activating performance in the limited number of solvents used as the σ^* values of the ester solvents increase. This may be ascribed to the concept that cobalt tetra-*p*-tolylporphyrin is probably affected only with difficulty by solvents with electron-donating ability, compared with a metal polyphthalocyanine as may be seen in the comparable data of the effects of additives such as pyridine on the rate of oxidation.[2,7]

From the above-mentioned results and discussion, the behavior of chemical species present in the reaction system may be deduced in terms such scheme as shown on the next page. In the scheme, ------ indicates a weak coordination; ——, medium coordination; ━━, strong coordination; S_1—S_3, an ester solvent and/or an aldehyde; S_4, the solvent, and Ald., an aldehyde. Fe,Cu-polyphthalocyanine and cobalt tetra-*p*-tolylpophyrin can initially activate an oxygen molecule to abstract the hydrogen atom from a substrate to be oxidized, and then initiate the autoxidation. The presence of a chemical species (S_1) which has a week interaction with the catalyst facilitates the coordination and activation of oxygen by substitution



(Scheme C), whereas a chemical species (S_2) with a medium interaction obstracts the coordination of oxygen by its occupation of both trans-positioned sites, depending on the capacity of electron donation (Scheme D). However, a chemical species (S_3) including an aldehyde to be oxidized with a suitable capacity can activate oxygen more easily than in the absence of such a species because of the delivery of an electron to the trans-position through the central metal of the catalyst Subsequently, the chemical species (S_4) solvating strongly to the coordinated oxygen inhibits the approach of an aldehyde to be oxidized, resulting in a decrease in the rate of oxidation (Scheme F). When an aldehyde can react with the activated oxygen, the autoxidation is initiated (Scheme G).

To utilize polyphthalocyanines and porphyrins as oxidation catalysts, we must carefully select the reaction conditions, especially the circumstances of the oxidation reaction.

We should like to express our thanks to Professor Teiji Tsuruta for his fruitful discussions and suggestion throughout our work of this paper.

Rerences

1) R. V. Norton, Am. Chem. Soc. Chicago Meeting, Sept., 1970, Session of Petrochem., B 18.

2) Y. Ohkatsu and T. Osa, *Bull. Chem. Soc. Jpn.*, submitted for publication.

3) H. Inoue, Y. Ikeda, and E. Imoto, *Bull. Chem. Soc. Jpn.*, **41**, 684, 692 (1968)

4) Y. Ohkatsu, T. Hara, and T. Osa, *Bull. Chem. Soc. Jpn.*, **50**, 696 (1977).

5) T. Hara, Y. Ohkatsu, and T. Osa, *Chem. Lett.*, **1973**, 103.

6) T. Hara, Y. Ohkatsu, and T. Osa, *Chem. Lett.*, **1973**, 953.

7) T. Hara, Y. Ohkatsu, and T. Osa, *Bull. Chem. Soc. Jpn.*, **48**, 85 (1975).

8) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsvier, Amsterdam (1964).

9) P. Rothemund and A. R. Menotti, *J. Am. Chem. Soc.*, **70**, 1808 ((1948).

10) A. Misono, T. Osa, Y. Ohkatsu, and M. Takeda, *Kogyo Kagaku Zasshi*, **69**, 2129 (1966).

11) F. P. Greenspan, *Anal. Chem.*, **20**, 1061 (1948).

12) G. E. Zaikov, J. A. Howard, and K. U. Ingold, *Can. J. Chem.*, **47**, 3017 (1969).

13) T. Hara, Y. Ohkatsu, and T. Osa, *Bull. Chem. Soc. Jpn.*, **47**, 156 (1974).

14) Y. Ohkatsu and T. Osa, to be contributed.

15) Japan Chem. Soc., "Zikken Kagaku Koza," **18**, 357, Maruzen, Tokyo (1958).

16) Y. Ohkatsu, T. Osa, and A. Misono, *Bull. Chem. Soc. Jpn.*, **40**, 2111 (1967).