Oxidation of Acetaldehyde Catalyzed by Cobalt(II) Tetraphenylporphyrin

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(Received August 7, 1975)

Cobalt(II) tetraphenylporphyrins catalyzed the autoxidation of acetaldehyde giving peracetic acid quantitatively. The *p*-substituents of phenyl groups of tetraphenylporphyrin influenced the catalytic activity, cobalt(II) tetra(*p*-methylphenyl)porphyrin being remarkably active. The effect of the base added into the reaction system was such that an appropriate quantity of the base gave rise to a maximum rate of oxidation. The rate equation was determined experimentally. From the results of kinetics and ESR study, it was concluded that an oxygen molecule activated through the electron transfer from a cobalt(II) ion abstracted the hydrogen of acetaldehyde to initiate the autoxidation.

So far, a number of studies have been made with regard to various porphyrins, especially from the viewpoint of a model compound of oxygen carrier in living system such as hemoglobin.[1)]

On the other hand, as the model of heterogeneous catalysts, the thermostable and easily accessible tetraphenylporphyrins of phthalocyanines have been investigated,[2)] since the compounds, where every metal ion is surrounded by the same ligand, are convenient for catalytic research of the metal ion. Cobalt(II) tetraphenylporphyryin (CoTPP) is well known to take up an oxygen molecule reversibly.[3)] However, the reactivity of coordinated oxygen has been scarcely investigated. In the case of metal phthalocyanine or polyphthalocyanine, the low-valent metal ion activates oxygen molecule to catalyzed the autoxidation of cumene, acetaldehyde, and so on.[4)] Therefore, it is expected that metal porphyrin behaves similarly because of the analogy of the structure of both compounds.

We have confirmed that an oxygen molecule activated to the superoxide through the electron transfer from CoTPP abstracts the hydrogen of acetaldehyde to initiate the auoxidation. The effect of the *p*-substituents of phenyl rings (Fig. 1) was examined and cobalt(II) tetra(*p*-methylphenyl)porphyrin [Co-(*p*-CH_3)-TPP] was found to be remarkably active. The effect of the base added into the reaction system was explained in terms of porphyrin-base complex from the ESR study.

Experimental

Synthesis of Catalysts. Tetraphenylporphyrin (H_2TPP) was prepared according to the method by Falk.[5)] Pyrrole (0.8 mol) and benzaldehyde(0.8 mol) were refluxed in 3 l of propionic acid for one-half hour under nitrogen atmosphere. On being left to stand, H_2TPP was precipitated. The crystals were filtered, washed several times with methanol and then with hot water, and dried; yield, approximately 20%.

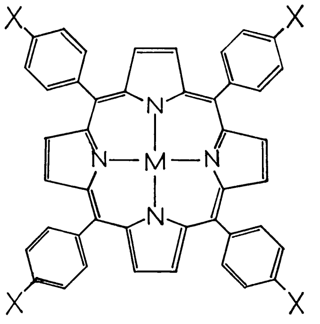

Fig. 1. Metal tetra(*p*-substituted phenyl)porphyrin.

Cobalt(II) tetraphenylporphyrin (CoTPP) was prepared according to the method by Rothemund and Menotti.[6)] Five hundred mg of H_2TPP was refluxed in 50 ml of chloroform and 50 ml of glacial acetic acid saturated with cobalt(II) acetate for two hours, then 100 ml of methanol being added. The crude CoTPP precipitated on cooling was filtered, washed several times with methanol, and dried; yield, approximately 80%. The crude CoTPP prepared above was repeatedly treated with cobalt(II) acetate by a similar method except for the use of the CoTPP in place of H_2TPP to complete the complexation. The product was then subjected to the Soxhlet extraction with methanol, the unreacted materials being removed. Cobalt(II) tetra(*p*-methylphenyl)porphyrin [Co(*p*-CH_3)TPP], tetra(*p*-methoxyphenyl)prophyrin [Co(*p*-OCH_3)TPP], and tetra(*p*-chlorophenyl)porphyrin [Co(*p*-Cl)TPP] were also synthesized by the method described above from *p*-tolualdehyde, *p*-anisaldehyde, and *p*-chlorobenzaldehyde, respectively, in place of benzaldehyde as the starting material. The reagents used in the synthesis of catalysts had been purified by the ordinary methods.

Oxidation of Acetaldehyde. The oxidation of acetaldehyde was carried out in ethyl acetate at 10 °C using a closed oxygen-circulating system, similar to that described previously.[7)] The reaction was started by the addition of a certain amount of acetaldehyde to the solution. The amount of oxygen absorbed during the course of the reaction was pursued by means of a gas burrete. Acetaldehyde was distilled under nitrogen atmosphere just before use. Ethyl acetate was purified by distillation. Pyridine and *N*,*N*-dimethylformamide as additive were also distilled under reduced pressure.

Analysis. All the peroxides in the liquid phase were estimated by an iodometric titration designed to determine the separate concentrations of hydrogen peroxide, peracetic acid and other peroxides.[8)] Hydrogen peroxide was first estimated by charging 1 to 2 ml of an accurately weighed sample into an Erlenmeyer flask containing 150 ml of 5% sulfuric acid and sufficient cracked ice; the temperature of the mixed solution was maintained at 0 to 5 °C; titration was carried out with 0.1 N ceric sulfate until the salmon color of the ferroin indicator disappeared. The concentration of hydroperoxide in the feedstock of the solution obtained after oxidation was below 3×10^{-3} wt% in every experiment. To the resulting mixture was added 10 ml of a 10% potassium iodide solution, and the iodine liberated was titrated with 0.1 N sodium thiosulfate. Peracetic acid was thus estimated. The solution was then for 5 to 10 min, and the liberated iodine was titrated with sodium thiosulfate. The active oxygen in various peroxides other than hydrogen peroxide and peracetic

TABLE 1. OXIDATION OF ACETALDEHYDE BY Co(*p*-CH_3)TPP CATALYST

Concn of acetaldehyde (M)	Concn of catalyst (mM)	Concn of oxygen (mM)	$-d[O_2]/dt$ ($\times 10^4$ M s^{-1})	k[a] ($\times 10^2$ $M^{-3/2}$ s^{-1})	R_i[b] ($\times 10^7$ M s^{-1})	Chain-length[c]
0.50	5.0	11.5	0.81	2.9	2.0	400
1.00	5.0	11.5	2.20	2.8	3.7	590
1.25	5.0	11.5	3.30	3.0	5.4	620
1.00	0.8	11.5	0.75	2.4	0.44	1700
1.00	1.4	11.5	1.1	2.7	0.95	1200
1.00	2.0	11.5	1.5	3.0	1.8	870
1.00	4.0	11.5	2.1	3.0	3.4	620
1.00	10	11.5	3.0	2.7	6.9	430
1.00	5.0	4.6	1.1	2.3	0.95	1200
1.00	5.0	7.5	1.8	3.0 (Av. 2.8)	2.5	720

In ethyl acetate at 10 °C. a) Calcd according to Eq. 3. b) Calcd according to Eq. 8. c) Calcd according to $(-d[O_2]/dt)/R_i$.

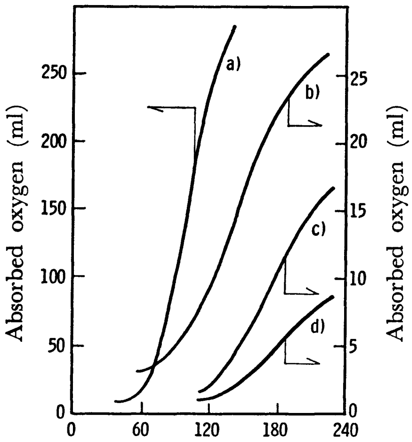

Fig. 2. Oxidation of acetaldehyde by cobaltous tetra-(*p*-substituted phenyl)porphyrin catalysts in ethyl acetate at 10 °C.
Acetaldehyde (0.5 M). Catalysts (5 mM). X: a) $-CH_3$, b) $-OCH_3$, c) -Cl, d) -H.

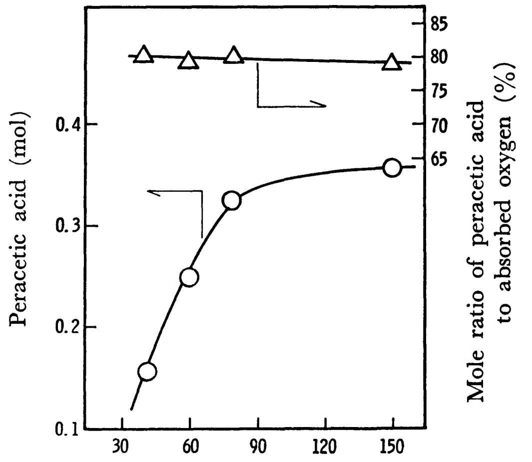

Fig. 3. Peracetic acid produced in oxidation of acetaldehyde by Co(*p*-CH_3)TPP catalyst in ethyl acetate at 10 °C.
Acetaldehyde (1.0 M). Catalyst (5 mM).

acid was thus estimated. From preliminary experiments, the titration was confirmed to be suitable. Peracetic acid could be completely analyzed at 0 to 5 °C, and any other peroxides which might be formed during the reaction were titrated in the last titration step. Neither separate quantification of acetaldehyde monoperacetate (AMP nor analysis of acids which might be formed) was made.

ESR Study. The ESR spectra of a solution of Co(*p*-CH_3)TPP in ethyl acetate were recorded at −196 °C with a JEOL Model JES-PE-IX spectrometer. The solution was prepared by the complete removal of dissolved oxygen according to the usual freeze-pump-thaw method. Oxygen or air was subsequently introduced little by little, when necessary, to get signals of the activated oxygen. The spectra were also measured in the presence of pyridine as an additive. The *g*-factors and coupling constants of the spectra were determined in comparison with those of Mn^{2+} marker.

Results and Discussion

In the absence of a catalyst, acetaldehyde was not oxidized within three hours at 10 °C. However, as shown in Fig. 2, the presence of CoTPP caused the absorption fairly soon, indicating the occurrence of the autoxidation of acetaldehyde. The *p*-substituents attached to the phenyl groups of porphyrin ring influenced the catalytic activity, the *p*-methyl group in particular making the corresponding porphyrin remarkably active. The activity of Co(*p*-CH_3)TPP was ten times as much as that of the other porphyrins. The order of activity was $-CH_3 \gg -CHO_3 > -Cl > -H$. This does not correspond to that of oxidation potentials of *p*-substituted porphyrins obtained by a cyclic voltammetric method.[9] This shows that the effect of the *p*-substituent cannot be explained only from the viewpoint of the electron-donating or attracting property of the substituent.

In the autoxidation, peracetic acid was obtained selectively and accumulated as the reaction proceeded. Hydrogen peroxide or any other peroxides could not be detected by titration (see Experimental). The mole ratio of peracetic acid formed to oxygen molecule absorbed remained constant *ca.* 0.8 in the course of the oxidation (Fig. 3). This suggests that Co(*p*-CH_3)-TPP has no ability to decompose peracetic acid substantially under the reaction conditions, in contrast to the fact that general transition metal salts and complexes can decompose peroxides heterolytically:

$$\mathrm{ROOH} + \mathrm{M}^{(n+1)+} \longrightarrow \mathrm{ROO}\cdot + \mathrm{M}^{n+} + \mathrm{H}^+ \qquad (1)$$

$$\mathrm{ROOH} + \mathrm{M}^{n+} \longrightarrow \mathrm{RO}\cdot + \mathrm{M}^{(n+1)+} + \mathrm{OH}^- \qquad (2)$$

This also indicates that the initiation of autoxidation does not involve the formation of free radicals by the decomposition of peracetic acid.

The catalytic effect of Co(p-CH$_3$)TPP is deduced by kinetic consideration. The rate equation was (Table 1):

$$-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = k[\mathrm{CH_3CHO}]^{1.5}[\mathrm{O_2}]^{0.5}[\mathrm{Co}(p\text{-}\mathrm{CH_3})\mathrm{TPP}]^{0.5} \qquad (3)$$

in which k was obtained as $2.8\times10^{-2}\ \mathrm{l}^{3/2}\ \mathrm{mol}^{-3/2}\ \mathrm{s}^{-1}$ over the range of concentration of acetaldehyde (0.5 to 1.25 M) and Co(p-CH$_3$)TPP (0.8 to 10 mM) and the partial pressure of oxygen (0.4 to 1.0atm) in the oxidation system.

For autoxidation under the conditions of fairly long chain-length and sufficient partial pressure of oxygen,

$$\mathrm{RH} \longrightarrow \mathrm{R}\cdot \quad R_\mathrm{i} \qquad (4)$$

$$\mathrm{R}\cdot + \mathrm{O_2} \longrightarrow \mathrm{RO_2}\cdot \qquad (5)$$

$$\mathrm{RO_2}\cdot + \mathrm{RH} \xrightarrow{k_\mathrm{p}} \mathrm{ROOH} + \mathrm{R}\cdot \qquad (6)$$

$$2\mathrm{RO_2} \xrightarrow{k_\mathrm{t}} \text{non-radicals} \qquad (7)$$

the rate equation is

$$-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = k_\mathrm{p}k_\mathrm{t}^{-1/2}[\mathrm{RH}]R_\mathrm{i}^{1/2} \qquad (8)$$

in which RH, R_i, k_p, and k_t, represent acetaldehyde, the initiation rate, the propagation rate constant and the termination rate constant, respectively.[10]

Comparison of Eq. 3 with Eq. 8 leads to Eq. 9 as the expression of the initiation rate:

$$R_\mathrm{i} = k_\mathrm{i}[\mathrm{CH_3CHO}][\mathrm{O_2}][\mathrm{Co}(p\text{-}\mathrm{CH_3})\mathrm{TPP}] \qquad (9)$$

where k_i denotes $k^2k_\mathrm{p}^{-2}k_\mathrm{t}$. As regards acetaldehyde, the constant k_p at 10 °C is approximately calculated to $3.6\times10^3\ \mathrm{l\ mol^{-1}\ s^{-1}}$ from k_p at 0 °C ($2.7\times10^3\ \mathrm{l\ mol^{-1}\ s^{-1}}$)[11] and the activation energy of k_p (4.2 kcal/mol), which is assumed to be equal to that of n-decanal.[12] The constant k_t may be $1.04\times10^8\ \mathrm{l\ mol^{-1}\ s^{-1}}$ which is reported for the value of k_t at 0 °C of acetaldehyde,[11] since the value can be considered to be almost independent on the temperature. Therefore, $k_\mathrm{p}k_\mathrm{t}^{-1/2}$ for acetaldehyde can be calculated to be $0.36\ \mathrm{l^{1/2}\ mol^{-1/2}\ s^{-1/2}}$ at 0 °C. As the concentration of oxygen dissolved in ethyl acetate at 10 °C and at atmospheric pressure is $1.15\times10^{-2}\ \mathrm{mol\ l^{-1}}$,[13] the constant k_i is calculated to be approximately $0.6\times10^{-2}\ \mathrm{l^2\ mol^{-2}\ s^{-1}}$. This value is slightly smaller than that of Fe or Fe, Co polyphthalocyanine catalyst but much smaller than that of Fe, Cu polyphthalocyanine catalyst.[14] We see from Table 1 that the chain of the autoxidation is long enough to satisfy Eq. 8.

Equation 9 suggests that the initiation mechanism can be described as follows:

$$\mathrm{Co^{2+}}(p\text{-}\mathrm{CH_3})\mathrm{TPP} + \mathrm{O_2} \rightleftharpoons [\mathrm{Co^{3+}}(p\text{-}\mathrm{CH_3})\mathrm{TPP}]\cdots\mathrm{O_2}^- \qquad (10)$$

$$[\mathrm{Co^{3+}}(p\text{-}\mathrm{CH_3})\mathrm{TPP}]\cdots\mathrm{O_2}^- + \mathrm{CH_3CHO} \longrightarrow [\mathrm{Co^{3+}}(p\text{-}\mathrm{CH_3})\mathrm{TPP}]\cdots\mathrm{O_2H}^- + \mathrm{CH_3\dot{C}O} \qquad (11)$$

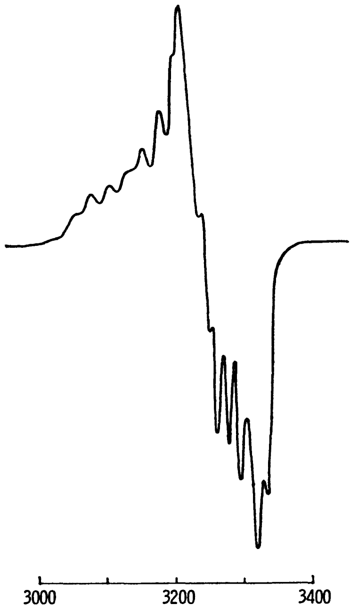

Fig. 4. ESR spectrum of Co(p-CH$_3$)TTP in ethyl acetate containing oxygen (*ca.* 0.02 atm.) at −196 °C. ν=9.262 GHz, field in gauss.

An evidence of the activation of oxygen molecule, namely, the formation of superoxide through the electron transfer, might be given by ESR study. In the absence of oxygen, Co(p-CH$_3$)TPP in ethyl acetate gave a complex pattern of lines at −196 °C. This could be attributed to the overlapping spectra of Co(p-CH$_3$)TPP in ethyl acetate glass and the polycrystals due to the segregation of Co(p-CH$_3$)TPP.[15] After the contact with oxygen, a new type of singal appeared in addition to the original spectrum (Fig. 4). The new signal of the hyperfine splittings due to cobalt(II) was attributed to the superoxide formed through the electron transfer from the d$_{z^2}$ orbital of cobalt to 2pπ* orbital of oxgen molecule according to the investigations relating to porphyrin–oxygen complex.[15–19] The electro-generated superoxide ion gave a similar spectrum except that it did not display the hyperfine lines.[20–22] These results seem to support firmly the step expressed in Eq. 10.

After the completion of the oxidation, the catalyst was recovered almost quantitatively and could be used with the same activity in the subsequent experiment as in the previous run. This suggests the regeneration of the catalyst as follows.

$$[\mathrm{Co^{3+}}(p\text{-}\mathrm{CH_3})\mathrm{TPP}]\cdots\mathrm{O_2H}^- \longrightarrow \mathrm{Co^{2+}}(p\text{-}\mathrm{CH_3})\mathrm{TPP} + \mathrm{HO_2}\cdot \qquad (12)$$

The hydroperoxy radical can also abstract the hydrogen atom from acetaldehyde to initiate the oxidation forming hydrogen peroxide.

$$\mathrm{HO_2}\cdot + \mathrm{CH_3CHO} \longrightarrow \mathrm{CH_3\dot{C}O} + \mathrm{H_2O_2} \qquad (13)$$

Although no hydrogen peroxide could be detected by titration throughout this study, the step 13 may be another initiation reaction step in the autoxidation. In either case, it is concluded that an oxygen molecule activated by Co(p-CH$_3$)TPP can abstract the hydrogen of acetaldehyde. The hydroperoxy radical, in addition

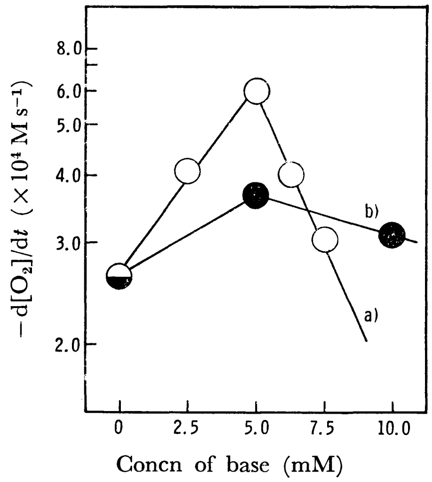

Fig. 5. Effect of base on oxidation of acetaldehyde by Co(p-CH_3)TPP catalyst in ethyl acetate at 10 °C. Acetaldehyde (1.0 M). Catalyst (5 mM). Base: a) pyridine, b) N,N-dimethylformamide.

to reaction 13, may react with other free radicals to become inert compounds.

$$HO_2\cdot + R\dot{C}O \longrightarrow RCOO_2H \quad (14)$$

$$HO_2\cdot + RCOO_2\cdot \longrightarrow RCOO_2H + O_2 \quad (15)$$

Addition of a base such as pyridine or N,N-dimethylformamide into the reaction system influenced the rate of oxidation (Fig. 5). The rate increased with the addition of pyridine, becoming maximum at 5×10^{-3}M concentration. The maximum rate was about 2.5 times of that in the absence of the base. In contrast, further addition caused a decrease in the rate. A similar phenomenon was observed also with regard to N,N-dimethylformamide, although it was not so prominent as in the case of pyridine. A similar effect of the base was found in the study of polyphthalocyanine catalyst.

The effect of the base was also examined by ESR study. Figure 6 shows the spectra of Co(p-CH_3)TPP in ethyl acetate containing pyridine. At low concentration of pyridine (0.1 vol%), a spectrum was obtained which displayed superhyperfine splittings due to the interaction with one nitrogen (Fig. 6a). This indicates that the species present at this concentration of pyridine is a 1 : 1 complex, where pyridine coordinates to the cobalt(II) ion as a fifth ligand. The result given in Fig. 6b was obtained for higher concentration of pyridine (5 vol%). Although the spectrum lacks superhyperfine lines, it would be reasonably ascribed to a 2 : 1 pyridine–Co(p-CH_3)TPP complex, where pyridine occupies both the fifth and sixth coordination sites, as discussed in detail by Walker[15,17,19] in his study on Co(p-OCH_3)TPP–amine complex on toluene glass. After contact with oxygen, a spectrum similar to that in Fig. 4 was also obtained in the presence of pyridine, the amount of which was approximately such an amount as to produce the 1:1 complex. This may be attributed to the complex of Co(p-CH_3)TPP with one pyridine and one oxygen molecule as the fifth and sixth ligands, respectively. Therefore, from the result of ESR study,

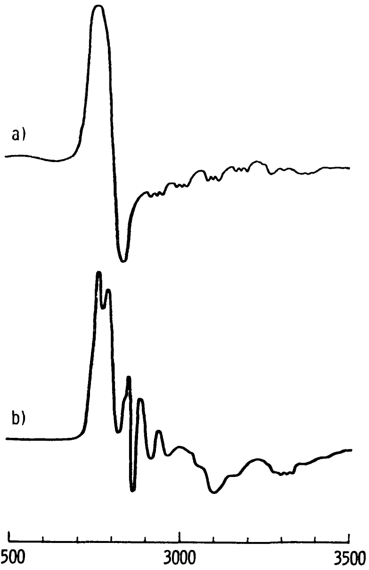

Fig. 6. ESR spectrum of Co(p-CH_3)TPP in ethyl acetate containing pyridine [a) 0.1, b) 5.0 vol %] at −196 °C. ν: a) 9.250, b) 9.238 GHz, field in gauss.

the effect of the base on the rate of oxidation (Fig. 5) could be explained by the concept that an appropriate amount of base would coordinate to the central cobalt(II) ion of the planar porphyrin molecule as a fifth ligand, facilitating the electron transfer from the cobalt(II) ion to the oxygen molecule as the sixth ligand. However, the excess base prevents the oxygen molecule from the coordination sites. The effect of the excess base, especially pyridine, is partly ascribed to the deactivation of the peroxy radical, namely the chain-carrier of autoxidation by the complex formation,[23] resulting in a decrease in the rate of oxidation.

From the results described above it would be most accepted that the catalyst activates an oxygen molecule to superoxide, which abstracts the labile hydrogen from acetaldehyde to initiate autoxidation.

We would like to express our thanks to Prof. Taiseki Kunugi for his valuable advice and discussion.

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