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The Liquid-Phase Oxidation of Aldehydes with Metal Tetra(*p*-tolyl)porphyrins

Yasukazu Ohkatsu and Tetsuo Osa
Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo,
Bunkyo-ku, Tokyo 113

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The effects of the kind of metal of metal porphyrins and the substituent of the phenyl group of porphynato plane were discussed, using them as catalysts in the autoxidation of aldehydes. The effect of the solvent and the additive on the above-mentioned catalytic activity of the porphyrins was put into order by means of their pK_a(BH$^+$) and pK_a(H$^+$) values; the increased pK_a(BH$^+$), namely, the electron-donating power of solvents, seemed to lead to their strong coordination, followed by the initiation of the coordination of oxygen. On the other hand, the oxygen which had been activated on the porphyrins was estimated to react with or be stabilized by a solvent with a low pK_a(H$^+$); it could not initiate the autoxidation with ease.

The interaction of molecular oxygen with hemoproteins is important in respiratory and metabolic processes. Many investigators have studied this interaction using a metal porphyrin as a model of such hemoproteins as hemoglobin and myoglobin. It has been one of their most important aims to ioslate a so-called dioxygen complex, such as the "picket fence porphyrin" obtained by Collman *et al.*[1] On the other hand, there have been reported[2,3] a number of studies of Fe(II) dioxygen complexes in terms of the effect of the environmental conditions of dioxygen complexes on their stability or instability—the concept of axial bases and hydrophobic circumstances.

Welscher and Anderson[4] reported the *trans* effect of axial bases on the dissociation of Fe(TPP)(base)($\mathrm{O_2}$), namely, the reversible liberation of the oxygen of the dioxygen complex, to be in the order of pyridine$>$ piperidine$\gg$1-methylimidazole, and concluded that π-donating ability of an axial base was responsible for the instability of the dioxygen complex. Bringer, Chang, and Traylor[5] showed the effect of the basicity of the media on the oxygenation of porphyrin.

The above-mentioned papers, however, offer no detailed information about whether axial bases help the stabilization of the oxygen of the dioxygen complex, or whether they act as activating agents of such an oxygen molecule for a substrate approaching from the outside. We have tried to make it clear, in the autoxidation of organic compounds, how oxygen molecule behaves on complexes such as metal polyphthalocyanines and cobalt tetra(*p*-tolyl)porphyrin in its interaction with cumene,[6] and aldehydes[7–10] as proton donors. In these studies, it has been found that the interactions among all chemical species including an oxygen molecule, a substrate to be oxidized, and a solvent are of importance.[10] However, there remain a few points to be clarified, because Taft's equation, which is considered in these experiments to show, only incompletely, the direct correlation with the electron-donating and electron-accepting natures of chemical species, has been used in the measurements.

In this paper, the interactions among all of chemical species are more distinctly discussed using the acidity and basicity of the chemical species in place of the σ^* and ρ^* values of Taft's equation. It is also discussed how the concentrations of chemical species are important in addition to their electron-donating and electron-accepting properties.

Experimental

Materials. Metal tetra(*p*-substituted phenyl)porphyrins used for this study were metal tetra-(*p*-methoxyphenyl)-, -(*p*-tolyl)-, -phenyl-, and -(*p*-chlorophenyl)-porphyrins, which were prepared according to the procedure described in an earlier paper.[11] As metals, nickel, copper, manganese, and cobalt were introduced.[12]

Aldehydes, such as acetaldehyde and benzaldehyde, were purified under nitrogen by the conventional methods just before use in order to avoid the formation of the corresponding peracids.

Solvents, such as ethyl acetate and ethyl isobutyrate, and additives as a part of the solvents, such as pyridine, *N*,*N*-dimethylformamide, water, acetone, ethanol, trichloroethanol, nitroethane, succinic acid, benzoic acid, trichloroacetic acid, benzamide, urea, quinoline, benzylamine, piperidine, and acridine, were purified by standard methods.

Procedure. The oxidation of aldehydes with a porphyrin complex catalyst and the titration of peracids and hydrogen peroxide were carried out as has been described in a previous paper.[10]

Results and Discussion

General Aspect of Oxidation. The liquid-phase oxidation of aldehyde with a porphyrin complex catalyst proceeds according to the autoxidation mechanism represented by the rate equation,

$$-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = k[\mathrm{RCHO}]^{3/2}[\text{porphyrin}]^{1/2}[\mathrm{O_2}]^{1/2}, \qquad \text{(I)}$$

as has been described before.[10] The rate of initiation can be written as

$$R_\mathrm{i} = k'[\mathrm{RCHO}][\text{porphyrin}][\mathrm{O_2}]. \qquad \text{(II)}$$

According to the ESR study by many investigators[13,14] and by us,[15] porphyrins can activate molecular oxygen as superoxide ions, which abstract hydrogen atom from a substrate to be oxidized, initiating autoxidation as follows:[16,17]

$$\mathrm{Co(II)TPP} + \mathrm{O_2} \rightleftharpoons \mathrm{Co(III)TPP}\cdots\mathrm{O_2}^-, \qquad (1)$$

$$\mathrm{Co(III)TPP}\cdots\mathrm{O_2}^- + \mathrm{RCHO} \rightarrow \mathrm{Co(III)TPP}\cdots\mathrm{O_2H}^- + \mathrm{R\dot{C}O}. \qquad (2)^*$$

The nature of the central metal of a porphyrin

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[*] Step (2) may be followed by

$$\mathrm{Co(III)TPP}\cdots\mathrm{O_2H}^- \rightarrow \mathrm{Co(II)TPP} + {}^{\cdot}\mathrm{O_2H}, \qquad (3)$$

$$\mathrm{RCHO} + {}^{\cdot}\mathrm{O_2H} \rightarrow \mathrm{R\dot{C}O} + \mathrm{H_2O_2}. \qquad (4)$$

TABLE 1. EFFECT OF THE METAL ION OF TETRAPHENYLPORPHYRINS ON THE OXIDATION RATE

Metal ion	($\times 10^3$ M)	Acetaldehyde (M)	$-d[O_2]/dt$ ($\times 10^6$ M s^{-1})
Ni(II)	5.0	0.5	3.1
Cu(II)	5.0	0.5	3.4
Mn(II)	5.0	0.5	3.5
Co(II)	5.0	0.5	2.6
Co(II)	6.7	0.1	3.6

Reaction conditions: solvent, ethyl acetate; temperature, 10 °C; $[O_2]$, 1 atm.

TABLE 2. EFFECT OF THE SUBSTITUENT OF THE PHENYL GROUP OF COBALT TETRAPHENYLPORPHYRINS ON THE OXIDATION RATE

Substituent	$-d[O_2]/dt$ ($\times 10^6$ M s^{-1})	Relative activity for oxidative dehydrogenation[a)]
p-OCH_3	4.2	1.18
p-CH_3	81	1.44
H	2.6	1.00
p-Cl	1.2	—
p-NO_2	—	0.82

Reaction conditions: Acetaldehyde, 0.5 M; catalyst, 5.0×10^{-3} M; solvent, ethyl acetate; temperature, 10 °C; (O_2), 1 atm.

a) Details of the reaction are unknown.

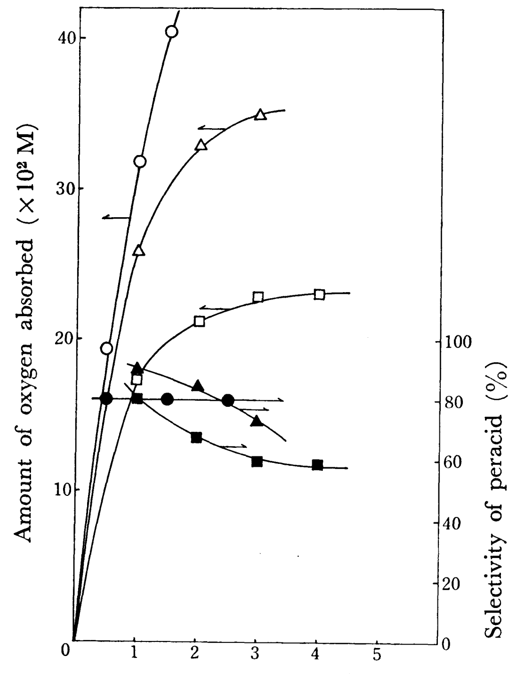

Fig. 1. Amount of oxygen absorbed and selectivity of peracid.

Catalyst	Solvent	AcH	Temp	Ref.
○, ● Co tetra(*p*-tolyl)-porphyrin, 5×10^{-3} M	ethyl acetate	1.0 M	10 °C	This work
□, ■, Fe,Cu-polyphthalocyanine 5×10^{-3} M	ethyl acetate	0.45 M	10 °C	9
△, ▲, Fe,Cu-polyphthalocyanine 5×10^{-3} M	bromobenzene	0.45 M	10 °C	9

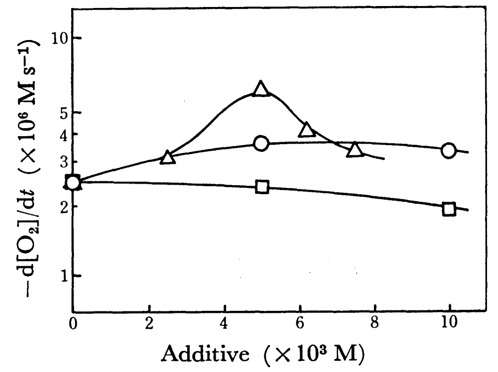

Fig. 2. Effective of some additives on oxidation rate. Reaction conditions: Co tetra(*p*-tolyl)porphyrin, 5.0 $\times 10^{-3}$ M; acetaldehyde, 0.5 M; solvent, ethyl acetate; temperature, 10 °C; (O_2), 1 atm.

△: Pyridine, ○: *N*,*N*-dimethylformamide, □: water.

affected its activity little, compared with the case of metal polyphthalocyanine (Table 1), but the substituents of the phenyl group in the porphynato plane had a considerable effect (Table 2); the effects of substituents on the rate of oxidation were in the order of $CH_3 \gg CH_3O > H > Cl$. This order, though it cannot be easily explained by only the electron-donating and electron-attracting properties of the substituent, coincides with that of the influence of chemical substituents on the catalytic activity for oxidative dehydrogenation, as studied for tetra(*p*-substituted phenyl)porphyrins by Manassen (see Column 3 in Table 2).[18)]

A metal porphyrin had little activity to decompose a peracetic acid as one of oxidation products and produced the peracid quantitatively, as is in the case of a metal polyphthalocyanine (Fig. 1). Hydrogen peroxide was also considerably stable in the presence of the porphyrin at 10 °C. This result suggests that the formation of free radicals by the redox decomposition of peracid with a metal porphyrin, if any, is less important as an initiation reaction in this oxidation.

The addition of a small amount of pyridine, *N*,*N*-dimethylformamide, or water to a main solvent such as ethyl acetate used in the reaction system affected the activity of the catalyst, as is observed in the case of a metal polyphthalocyanine (Fig. 2). Water did not affect, or was apt to decrease the oxidation rate upon addition, whereas pyridine or *N*,*N*-dimethylformamide gave the maximum rate when the catalytic amount was added. A small addition of such an electron-donating additive is likely to increase the catalytic activity, which depends on the characteristic donating power of the additive. The effect of additives was of the order of pyridine > *N*,*N*-dimethylformamide > water.

The increase in the catalytic activity of a metal porphyrin can be well explained by the coordination of an additive to the metal, resulting in the activation of oxygen molecule at the trans-position, as has been reported with respect to a metal polyphthalocyanine.[6)] The decrease upon the addition of more than a catalytic amount of the additive, on the contrary, may be ascribed to the occupation of both axial positions by the additive. The effect of the additive on the decrease mentioned

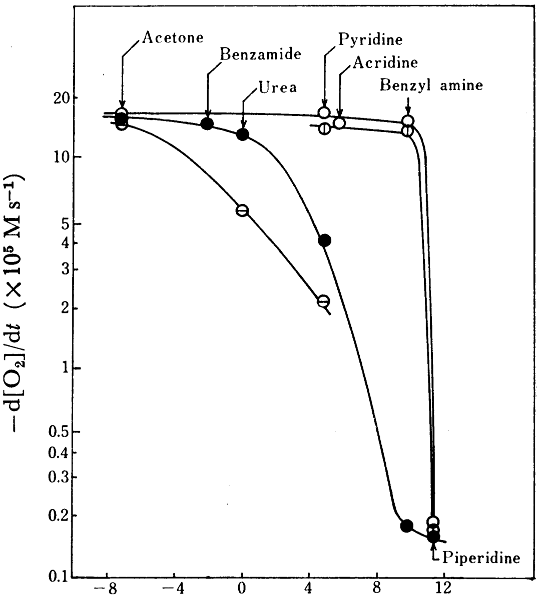

Fig. 3. Effect of pK_a(BH$^+$) of basic additive on oxidation rate. Reaction conditions: Co tetra(*p*-tolyl)porphyrin, 2.5×10^{-3} M; benzaldehyde, 0.4 M; solvent, ethyl isobutyrate; temp, 10 °C; (O_2), 1 atm; additive ○: 2.5×10^{-3} M, ⦶: 6.0×10^{-3} M, ●: 2.5×10^{-2} M, ⊖: 4.0×10^{-2} M.

above will be discussed in the next paragraph.

Effect of Additives. *Effect of Bases*: An additive with an elctron-donating or electron-accepting ability was added to the oxidation system consisting of cobalt tetra(*p*-tolyl)porphyrin as a catalyst, benzaldehyde, and oxygen, with ethyl isobutyrate as the main solvent. Figure 3 shows the relation of the pK_a(BH$^+$) of an additive as a conjugated acid to the oxidation rate under same concentrations of acetaldehyde and a catalyst, and oxygen pressure. The additive with a higher pK_a(BH$^+$) value—that is, a stronger electron-donating ability, suppressed the oxidation by preventing the oxygen from coordinating, depending on the amount present. Based on the mole of the catalyst, the catalytic and 2.4 times as much of the additive gave the point of the abrupt suppression of the rate near pK_a(BH$^+$)=10; 10 times, near pK_a(BH$^+$)=−2, and 160 times, pK_a(BH$^+$)=−8. In addition, it is very surprising that a small change in the pK_a(BH$^+$) values near 10 brought about a sudden decrease in the oxidation rate, even in the presence of a catalytic amount of the additive.

The effect of the additive concentration on the rate is illustrated in Fig. 4. The pK_a(BH$^+$) of the oxygen molecule is not known. However, it is considered to be under about 5, because the pK_a(BH$^+$) of the superoxide ion has been reported as 4.8.[19] Acetone with a pK_a(BH$^+$) of −7.2 did not affect the rate even if it was present in an amount 100 times that of the moles of the catalyst. The additive of a relatively high pK_a(BH$^+$), such as quinoline (4.83), pyridine (5.21), or acridine (5.50), reduced the rate gradually when the concentration went over a certain amount. However, an additive such as benzylamine of pK_a(BH$^+$)=9.33 lowered the oxidation rate abruptly, and piperidine (11.12) inhibited the oxidation almost completely even if there was only a little more than the catalytic amount. In other words, as the pK_a(BH$^+$) of the additive became higher, the degree of competitive coordination between an additive and the molecular oxygen increased. In the case of piperidine, almost all substances added seem to occupy the coordination sites of the catalyst because of its high pK_a(BH$^+$) value.

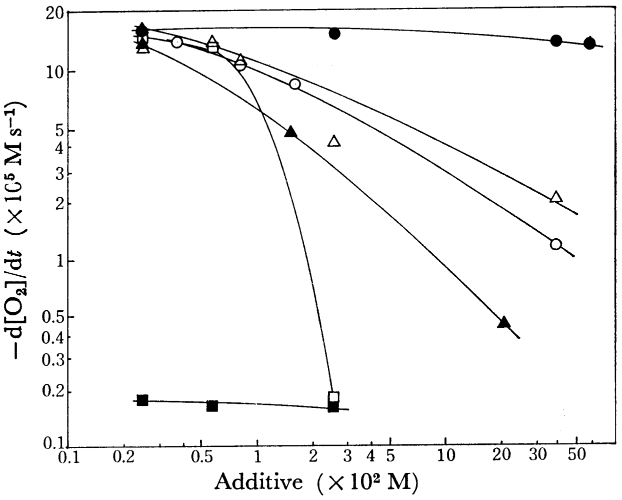

Fig. 4. Effect of the amount of basic additive on oxidation rate. Reaction conditions: Cobalt tetra(*p*-tolyl)-porphyrin, 2.5×10^{-3} M; benzaldehyde, 0.4 M; solvent ethyl isobutyrate; temperature, 10 °C; (O_2), 1 atm; additive, ●: acetone (pK_a(BH$^+$)=−7.2), ○: quinoline (4.83), △: pyridine (5.21), ▲: acridine (5.50), □: benzylamine (9.33), ■: piperidine (11.12).

The competitive reaction can be successfully explained by the above-mentioned results and discussion. However, a minor effect, namely, the steric effect of an additive, may be observed. On quinoline, pyridine, and acridine, the respective pK_a's are 4.81, 5.21, and 5.50. These additives, accordingly, would lead to the lowering of the oxidation rate in the order of: quinoline > pyridine > acridine when present in inhibitive amounts. However, the experimental order was reversed in quinoline and pyridine. This may be due to the difference in steric bulkiness on gaining access to the central metal of catalyst: quinoline>pyridine.

Effect of Acids. For the start of oxidation, it is essential for the substrate to be oxidized to approach and react with the activated oxygen. The ease of approach will be discussed using the electron-attracting, namely, the proton-giving, property of the chemical species in the reaction system, such as an aldehyde, a solvent, and an additive. Such a point of view with respect to aldehydes has been previously reported.[12] The role of the last additive is shown in Fig. 5. The figure shows that a decrease in the oxidation rate was observed below pK_a(H$^+$) of 4 on the addition of a proton-donating substrate corresponding to the amount of a catalyst, below pK_a(H$^+$)=6 on the addition of 10 times the amount, and below pK_a(H$^+$)=10 on the addition of 100 times the amount. It is also well known in the field of electrochemistry that the superoxide ion, which is fairly stable under an alkaline condition,

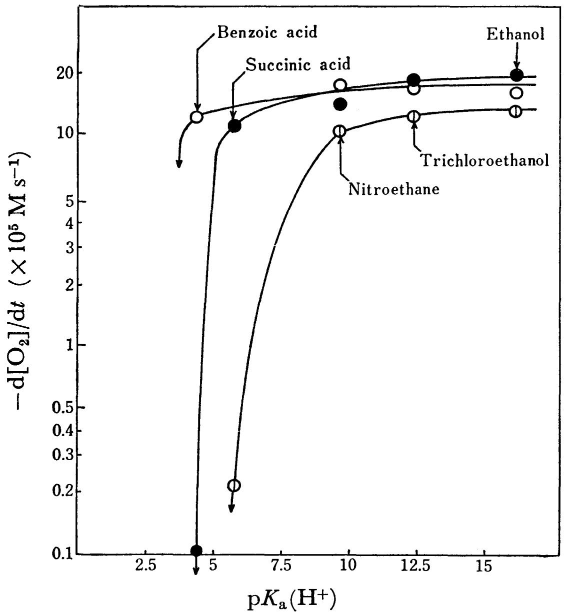

Fig. 5. Effect of pK_a(H$^+$) of protic additive on oxidation rate. Reaction conditions: Co tetra(*p*-tolyl)-porphyrin, 2.5×10^{-3} M; benzaldehyde, 0.4 M; solvent, ethyl isobutyrate; temp, 10 °C; (O_2), 1 atm; additive, ○ 2.5×10^{-3} M, ● 2.5×10^{-2} M, ⦶ 2.5×10^{-1} M. Arrow (↓) means no absorption of oxygen in trichloroacetic acid (pK_a(H$^+$) = 0.65).

reacts easily with a proton-giving substrate thus:

$$O_2 + e + H^+ \rightarrow HO_2^{\cdot}, \quad (5)$$

$$HO_2^{\cdot} + e + H^+ \rightarrow H_2O_2. \quad (6)^{20)}$$

These facts imply that the oxygen activated on porphyrin is deactivated by a protic substrate. If its acidity is stronger than that of benzaldehyde, it obstructs the hydrogen abstraction of benzaldehyde and converts the activated oxygen into the other form which interacts with the aldehyde only with difficulty.

This may be explained by plotting the oxidation rate against the amount of an additive added (Fig. 6). In the presence of ethanol (pK_a(H$^+$) = 15.9) or trichloroethanol (pK_a(H$^+$) = 12.24), the oxidation rate begins to be suppressed only after the addition of approximately the same amount of the additive as benzaldehyde. This means that the solvent with a pK_a(H$^+$) over about 12 has no power to compete with benzaldehyde in approaching to the activated oxygen because of its lower electrophilic property: the pK_a(H$^+$) of aldehyde is from about 10 to about 13.5; that of formaldehyde, 13.29, and that of chloralaldehyde, 10.03. On the other hand, benzoic acid (pK_a(H$^+$) = 4.20) inhibited the oxidation considerably even if only 2.5×10^{-2} M was present, corresponding to 10 times the catalytic amount. Trichloroacetic acid (pK_a(H$^+$) = 0.65) prevented the oxidation almost completely in the presence of the catalytic amount.

These experimental facts coincide well with the curve of oxygen absorption (Fig. 1). The oxidation of acetaldehyde and benzaldehyde produces acetic and benzoic acids respectively as follows:

$$RCOOOH + RCHO \rightarrow 2RCOOH. \quad (7)$$

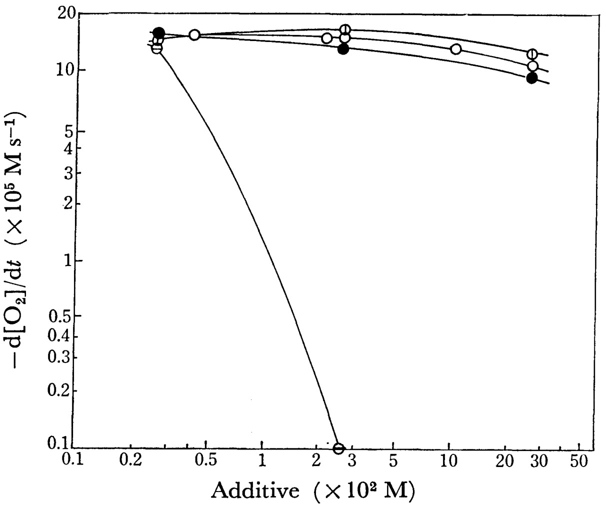

Fig. 6. Effect of the amount of protic additive on oxidation rate. Reaction conditions: Cobalt tetra(*p*-tolyl)-porphyrin, 2.5×10^{-3} M; benzaldehyde, 0.4 M; solvent ethyl isobutyrate; temperature, 10 °C; (O_2), 1 atm; additive, ⦶: ethanol, ○: trichroloethane, ●: nitroethane, ○: benzoic acid.

These acids may deactivate the activated oxygen; the pK_a(H$^+$) values of these acids are 4.76 and 4.20 respectively.**

Conclusion

As an additive included in a solvent has some parallel interaction with a porphyrin and its active intermediate, its pK_a plays an important role in the initiation reaction in terms of change of the rate. The concentration of the solvent relative to other chemical species is also important. These results and this dicussion can considerably clarify the questionable aspects proposed by other investigators.

F. A. Walkner, for example, studied the thermodynamics of the reaction of molecular oxygen with a cobalt porphyrin.[21] The thermodynamics data of the reaction,

$$CoP\cdot B + O_2 \rightleftarrows CoP\cdot B\cdot O_2, \quad (8)$$

in which B represents an axial base, probably corresponding to the activation of the oxygen molecule, were measured at −65 °C for bases such as pyridine, 4-picoline, 3,4-lutidine, 4-methylimidazole, and piperidine. He could not find any direct relationship between the pK_a of the coujugated acids of amines and the equilibrium constants of Scheme 8 or the ΔH of the formation of the Co–O bond. In this paper, moreover, there remain a few questions with respect to the following points: (A) The stabilization of coordinated oxygen by the base $CoP\cdot O_2\cdot B$ was not taken into account in the kinetical treatment of formation of oxygen complexes. This action of the amine cannot always be neglected, though; Pauling[22] and others[23,24] suggest that a more distinct imidazole from

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** The sudden decrease in the oxidation rate after a certain amount of oxygen has been absorbed (Fig. 1) may be attributed to the formation of such an acid.

the histidine residue (E-7) projecting into the oxygen-binding pocket in the oxygen-carrying protein may somehow stabilize the coordinated dioxygen by hydrogen bonding. (B) The sample used in his experiments contained cobalt tetra(*p*-tolyl)porphyrin in a concentration of $(8-9)\times10^{-4}$ M and the above-mentioned amine in a concentration of $1\times10^{-2}-1\times10^{-1}$ M. In other words, the ratio of the amine to porphyrin was from about ten to one hundred. This ratio is considered to be in the range of concentration ratios in which some bases can stop the oxidation completely (see Fig. 4) and the formation of dioxygen complex may be suppressed, and in which only 0.8% of the cobalt would be in the form of the oxygen adduct under an atmosphere in the presence of 4-dimethylaminopyridine or *N*-methylimidazole as an axial base. The ratio seems to be too high for us to dicuss the formation of the oxygen complex kinetically. In autoxidation under such a ratio, a difference in the slopes of the straight parts of the graphs in relation with pK_a was observed, namely, the equilibrium constants, as shown in Figs. 4 and 6, and the straight parts sometimes crossed each other. A discussion based on the special ratio may, therefore, misunderstand the actual phenomena. The results reported by Stynes and Ibers[25] for the similar cobalt protoporphyrin IX dimethyl ester·B system, including pyridine, 4-butylpyridine, *N*-methylimidazole, and several others as axial bases, showed a direct relationship between the $pK_a(BH^+)$ of the base and the formation of the Co–O bond. The ratio of 2—3 which they used will be suitable for a discussion of the interaction of porphyrin with the oxygen molecule. (C) Though the steric hindrance of bases is probably small, it should also be considered.

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