KINETICS OF METALLOPORPHYRIN FORMATION WITH PARTICULAR
REFERENCE TO THE METAL ION ASSISTED MECHANISM

Motoharu Tanaka

Laboratory of Analytical Chemistry, Faculty of Science,
Nagoya University, Chikusa, Nagoya, 464 Japan

Abstract - A classification of kinetics of metalloporphyrin
formation is presented according to the composition of the
activated complex involved in the reaction. In the reaction
of large metal ions, such as mercury(II) and cadmium(II),
with porphyrins, these metal ions can not fit into the
porphyrin nucleus and they are out-of-plane in the metallo-
porphyrin. In this case the reaction is relatively fast and it
proceeds through a pathway involving a mononuclear activated
complex. At higher metal ion concentration, a dinuclear
product results. In the incorporation of metal ions of medium
size, such as cobalt(II) and copper(II), the first metal ion
weakly bound to porphyrin deforms the porphyrin nucleus, thus
making easy the attack from the back by another metal ion.
This reaction thus involves a homodinuclear species as an
activated complex. In the presence of large metal ions like
mercury(II), the mercury(II)-porphyrin is formed rapidly and
it is more reactive than the free porphyrin. This is the
reason why a small amount of mercury(II) or cadmium(II) acts
as a catalyst in the formation of metalloporphyrins involving
transition metal ions of medium size such as manganese(II),
cobalt(II) and nickel(II). A heterodinuclear activated complex
is involved in this metal ion assisted formation of metallo-
porphyrins. *N*-methyl-*meso*-tetraphenylporphine is favorably
deformed and it is more reactive than the non-*N*-methylated
analogue. For *N*-methylated porphyrins the reaction proceeds
through a pathway involving a mononuclear activated complex:
no homodinuclear activated complex is observed and the forma-
tion rate is always proportional to the metal ion concentra-
tion.

INTRODUCTION

Because of the widespread occurrence and the biological importance of metallo-
porphyrins in plants and animals, chemistry of metalloporphyrins is a matter
of concern to bioinorganic chemists. Kinetic studies of metalloporphyrin
formation are of course indispensable in order to understand the *in vivo* metal
incorporation processes leading to the heme and chlorophylls. When Philips has
published a review article dealing with the coordination behavior of porphyrin
(Ref.1), little physico-chemical information was available on kinetics of
porphyrin metal ion interactions. It was in the same year that Fleischer and
Wang have proposed a reaction intermediate, called the sitting-atop complex
(SAT), leading to the metalloporphyrin(Ref.2). The Philips review and the
proposal of the SAT concept no doubt have very much stimulated the work in
the field. Since 1960 more than hundred papers including several important
review articles on the subject(Ref.2-4) have appeared.

In 1963 Choi and Fleischer reported a kinetic study on the incorporation of
several bivalent transition metal ions into *meso*-tetra-4-pyridylporphine
(TPyP)(Ref.5). According to their detailed study on the copper(II) porphyrin
formation, the copper(II) incorporation rate was first order in both porphyrin
and copper(II). In the following year Fleischer and his co-workers found the
rate law for the metal ion incorporation into TPyP with an unusual square term
in metal ion concentration(Ref.6). They were successful in interpreting

their results assuming a SAT complex, which reacts with another metal ion to form the product metalloporphyrin.

Later Hambright studied the effect of lithium ion on the incorporation of copper(II) and zinc(II) by TPyP, and he obtained the rate law similar to the previous one(Ref.6) with an additional term proportional to copper and lithium ion concentration(Ref.7). The same author proposed the importance of porphyrin deformation caused by the weak coordination of a metal ion in the metal ion incorporation into porphyrins by the attack from the back(Ref.8). In fact the predeformed N-methylated porphyrin incorporates metal ions up to five orders of magnitude faster than the corresponding non-N-methylated species(Ref.9). The incorporation of copper by $meso$-tetrakis(4-N-methylpyridyl)porphine(TMPyP) was found to be first order in the copper(II) concentration(Ref.10). With the same porphyrin Baker et $al.$ reported a rate law including an anion term: The rate of copper incorporation was proportional to both copper and nitrate concentrations(Ref.11). They attributed the SAT phenomenon to an unusual anion term in the rate law and the salt effect on the basicity of porphyrin. Nevertheless they still considered the SAT complex as a probable configuration of the system along the reaction coordinate towards metalloporphyrin formation.

Baum and Plane reported the incorporation of magnesium into a variety of porphyrins catalyzed with pyridine and certain other nitrogenous bases(Ref.12). Zinc ion incorporation into a water soluble synthetic porphyrin was found to be also catalyzed with pyridine and its derivatives(Ref.13).

According to kinetic studies by Brisbin and her associates(Ref.14-16) on the incorporation of several transition metal ions into hematoporphyrin in glacial acetic acid, the rate is first order in metal ion concentration for all but nickel acetate for which they observed the half order dependence. Berezin and his coworkers have made extensive studies on the formation of a variety of metal pheophytins in different solvents(Ref.17). Though they analyzed their kinetic data assuming the first order in metal concentration, the rate constant varied with metal ion concentration in most cases. Based on the extensive study including at least 30 different porphyrins in the incorporation of 16 different transition metal ions, in 7 different solvent systems, Longo and others(Ref.18) have found the rate of metal ion incorporation simply proportional to the metal ion concentration. These results are well documented in Ref.2,4,19,20.

Now the brief survey of the literatures shows that some authors proposed the kinetics of metalloporphyrin formation first order in the metal concentration and that the other reported the rate law involving a square term in the metal ion concentration. In some instances the fractional order in metal ion concentration was said to be relevant to the metalloporphyrin formation. Under the circumstances, we would like to present a unified overview of the subject.

FORMATION OF A METALLOPORPHYRIN THROUGH A PATHWAY INVOLVING
A HETERODINUCLEAR ACTIVATED COMPLEX(Ref.21,22)

The rate of the incorporation of manganese(II) by $meso$-tetrakis(p-sulfonatophenyl)porphine(H$_2$TPPS) is very slow, and little spectral change is observed even 60 minutes after the initiation of the reaction at 25°C(Fig.1a). The reaction proceeds only by 25% after two days. However in the presence of mercury(II) or cadmium(II) a rapid spectral change is observed: the absorbance at 413 nm decreases and the absorbance at 467 nm increases(Fig.1b). Mercury-(II) also accelerates the complex formation reaction of TPPS with nickel(II), cobalt(II) and copper(II). The formation rate of Mn-TPPS is first order in concentrations of mercury(II), manganese(II) and TPPS. A large metallic ion such as mercury(II) can not fit into the porphyrin nucleus, and just sits on the nucleus. Thus the complex formation of mercury with TPPS is fast, and the coordination of mercury(II) seems to make the configuration of TPPS favorable for the attack by manganese(II) from the back as suggested by Khosropour and Hambright(Ref.23). We postulate the following mechanism:

$$Hg(II) + H_2TPPS \rightleftharpoons Hg(II)-TPPS + 2H^+ \tag{1}$$

$$Hg(II)-TPPS + Mn(II) \longrightarrow Mn-TPPS + Hg(II) \tag{2}$$
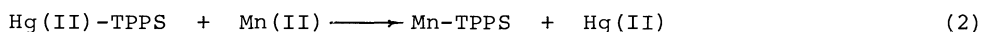
with a heterodinuclear activated complex involving mercury(II) and manganese. Reaction(1) is a labile equilibrium(Ref.24) preceding the rate-determining step(2). Mercury(II) released in reaction(2) is repeatedly involved in the reaction(1) and it acts as a catalyst in the formation of Mn-TPPS.

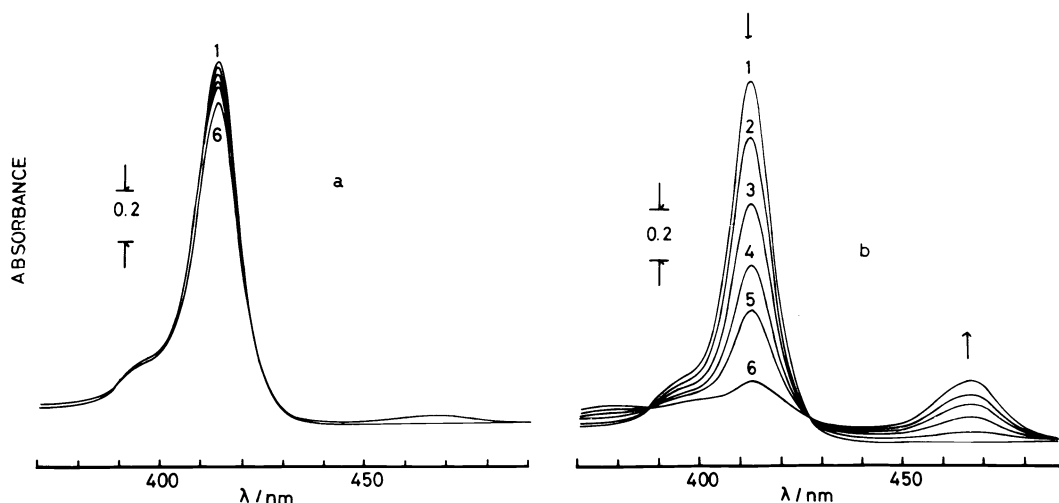Metal ion incorporation into porphyrins is also assisted by other metal ions

Fig. 1. Spectral change during the reaction of manganese(II)
with H_2TPPS in the absence and the presence of cadmium(II).
a: absence of Cd, b: Cd 4.88×10^{-7}, H_2TPPS 2.55×10^{-6}, Mn 2.27
$\times 10^{-4}$, NH_2OH 9.44×10^{-3}(unit = M = mol dm^{-3}). pH = 8.01. Reaction
time/min: (1) 0, (2) 3, (3) 10, (4) 20, (5) 30, (6) 60.

such as cadmium(II) and lead(II). The catalytic effect of these metal ions
on the complex formation of H_2TPPS with manganese(II) is illustrated in Fig. 2.
As shown in Fig. 2, mercury(II) exerts the largest catalytic effect among
them. In the complex formation reaction of H_2TPPS catalyzed by a metal ion,
the ionic radius of the metal ion acting as a catalyst appears to be an
important factor: Hg(II)>Cd(II)>Pb(II). The manganese(II) incorporation into
H_2TPPS in the presence of cadmium(II) has been studied in more detail(Ref.22).
In the presence of about 10^{-7} M cadmium(II), a rapid spectral change was
observed as in the presence of mercury(II) with distinct isosbestic points
at 388 nm and 426 nm(Fig. 1). The disappearance of H_2TPPS at 413 nm was
monitored. We determined the conditional rate constant involving concentra-
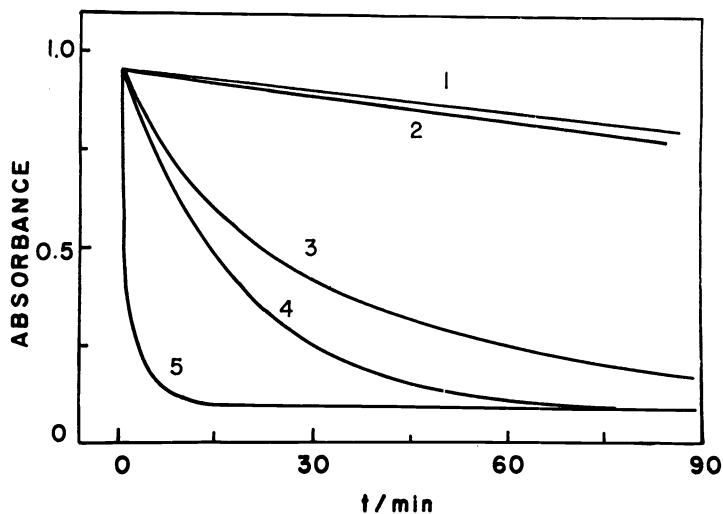tions of hydrogen ion, cadmium(II) and manganese(II), k_0, which is defined
as follows:

Fig. 2. Catalytic effect of some metals on the manganese(II)
complexation. Metals 4.0×10^{-7} except for (1). (1) In the
absence of any metals. (2) Zn, (3) Pb, (4) Cd, (5) Hg.
TPPS 1.80×10^{-6}, Mn 1.10×10^{-4}, pH = 6.9(PIPES buffer).
Unit = M = mol dm^{-3}.

$$-d[H_2TPPS]/dt = k_0[H_2TPPS]$$

In Fig. 3 k_0 is plotted *versus* pH. The rate of formation of Mn-TPPS in the absence of cadmium(II) is independent of pH. On the other hand, the rate in the presence of cadmium(II) depends on pH. Cadmium(II) accelerates the formation of Mn-TPPS at pH higher than 6. The conditional rate constant increases with increasing pH and then levels off. k_0 is proportional to the cadmium ion concentration. We postulate the following reaction scheme for
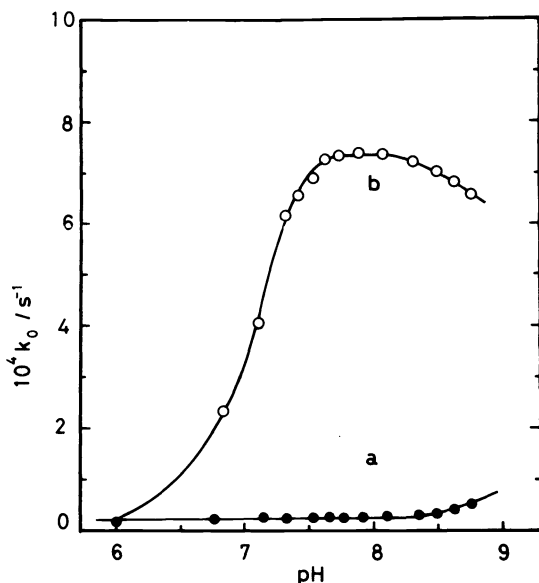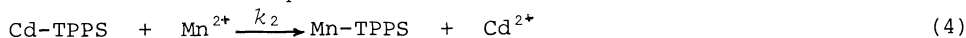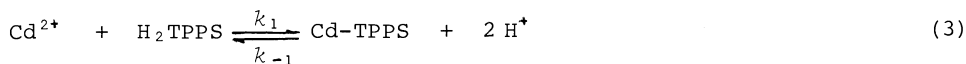

Fig. 3. Effect of pH on the formation of Mn-TPPS in the absence and presence of cadmium(II). a: absence of cadmium(II), b: Cd 4.88×10^{-7} M, TPPS 2.10×10^{-6} M, Mn 2.27×10^{-4} M.

the Mn-TPPS formation in the presence of cadmium(II):

$$Cd^{2+} + H_2TPPS \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cd\text{-}TPPS + 2 H^+ \tag{3}$$

$$Cd\text{-}TPPS + Mn^{2+} \xrightarrow{k_2} Mn\text{-}TPPS + Cd^{2+} \tag{4}$$

Applying the steady-state approximation for Cd-TPPS, we have the following:

$$k_0 = k_1 k_2 [Mn^{2+}][Cd^{2+}]/(k_{-1}[H^+]^2 + k_2[Mn^{2+}]) \tag{5}$$

At higher pH where $k_{-1}[H^+]^2 << k_2[Mn^{2+}]$, the rate equation(5) simplifies to the following form:

$$k_0 = k_1[Cd^{2+}] \tag{6}$$

Under this condition, the rate constant is independent of both hydrogen ion and manganese(II) concentrations. The rate constants at pH from 7.8 to 8.1 in Fig. 3 are given by equation(6). The rate constants are independent of manganese(II) at concentration higher than 1.13×10^{-4} M as expected from equation(6). Kinetic data are analyzed according to equation(5): $k_1 = (4.86 \pm 0.16) \times 10^2$ $M^{-1}s^{-1}$ and $k_{-1}/k_2 = (2.98 \pm 0.14) \times 10^{10}$ M^{-1} at 25°C and at an ionic strength of 0.1 M(NaNO$_3$). By an independent experiment, it was revealed that manganese in the product is in the trivalent state and that the rate of oxidation of Mn(II)-TPPS to Mn(III)-TPPS is rapid compared to the complex formation.

In the incorporation of manganese(II) into TPPS in the presence of cadmium(II) Cd-TPPS was postulated to form as an intermediate. Then we studied the substitution reaction of Cd-TPPS with manganese(II). The reaction rate is proportional to concentrations of both reactants. Over a pH range from 7.9 to 8.4 the reaction is independent of pH. At lower pH, Cd-TPPS is demetallized by acid. This reaction corresponds to the k_{-1} path of reaction(3). The value of k_2 was determined as $(1.98 \pm 0.10) \times 10^2$ $M^{-1}s^{-1}$. With this value k_{-1} is determined from the previously determined value of k_{-1}/k_2: $k_{-1} = (5.9 \pm 0.2) \times 10^{12}$ $M^{-2}s^{-1}$.

From the above experimental results the incorporation of manganese(II) into H_2TPPS in the presence of cadmium(II) may be summarized as follows:
1) At higher pH and/or higher manganese(II) concentration, that is $k_{-1}[H^+]^2 \ll k_2[Mn^{2+}]$, the rate-determining step is the formation of Cd-TPPS and the rate law is given by equation(6): The activated complex involves only cadmium(II) and it is of course mononuclear.
2) At lower pH and/or lower manganese(II) concentration, that is $k_{-1}[H^+]^2 \ll k_2[Mn^{2+}]$, the demetallation of Cd-TPPS by proton is appreciable and the formation of Mn-TPPS proceeds through a heterodinuclear activated complex involving cadmium(II) and manganese(II).

FORMATION OF A METALLOPORPHYRIN THROUGH A PATHWAY INVOLVING A HOMODINUCLEAR ACTIVATED COMPLEX(Ref.25)

Baker *et al.* found the rate of copper(II) incorporation into *meso*-tetrakis-(*N*-methyltetrapyridyl)porphine(TMTPyP) proportional to both copper(II) and nitrate concentration(Ref.11). Since acetic acid is a non-dissociating solvent having low dielectric constant, metal salts are all in the undissociated form(Ref.26-28). Thus any complications arising from the presence of anions may not be present in this solvent. This is why we have undertaken a study on the reaction of *meso*-tetra(4-pyridyl)porphine(H_2TPyP) with cobalt-(II) acetate and cobalt(II) nitrate in acetic acid.

The rate of formation of metalloporphyrin(Co-TPyP) is first order in porphyrin:

$$d[Co\text{-}TPyP]/dt = k_0[H_2TPyP] \tag{7}$$

where k_0 is the conditional first order rate constant involving cobalt(II) concentration. The logarithmic relationship between rate constants and cobalt(II) concentrations is given in Fig. 4. As evident from this figure, at lower and higher cobalt(II) concentration k_0 tends to be first order in $[Co(OAc)_2]$, while at the intermediate cobalt(II) concentration k_0 changes with $[Co(OAc)_2]$ to a lesser extent. This kinetc behavior of metalloporphyrin formation can be formulated by the following equations:
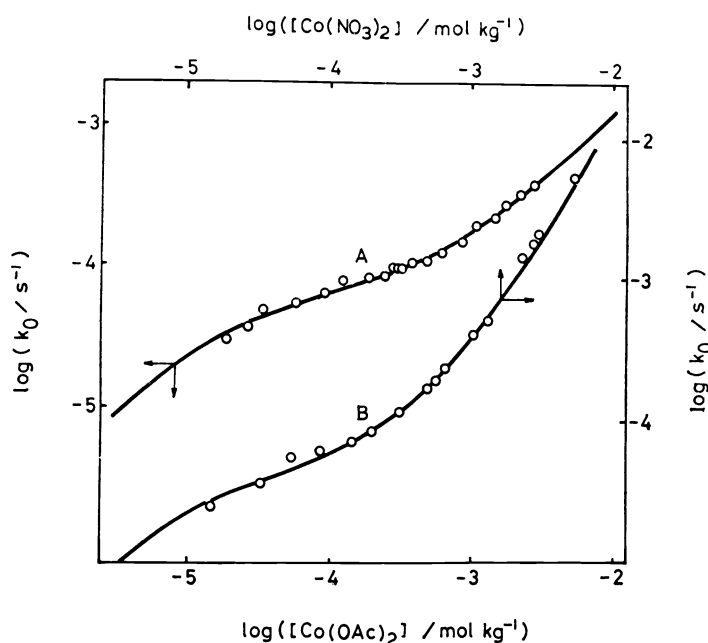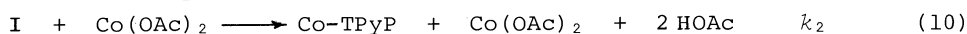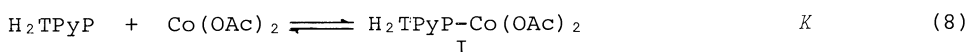
$$H_2TPyP + Co(OAc)_2 \rightleftharpoons \underset{I}{H_2TPyP\text{-}Co(OAc)_2} \qquad K \tag{8}$$

$$I \longrightarrow Co\text{-}TPyP + 2\,HOAc \qquad k_1 \tag{9}$$

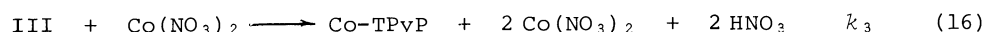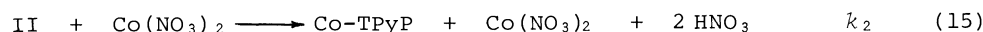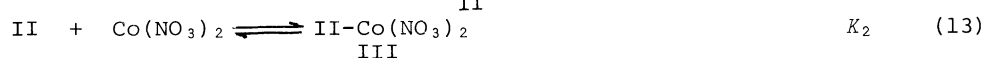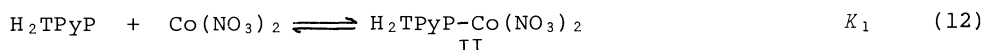$$I + Co(OAc)_2 \longrightarrow Co\text{-}TPyP + Co(OAc)_2 + 2\,HOAc \qquad k_2 \tag{10}$$

Fig. 4. Relations between $\log k_0$ and logarithmic cobalt(II) concentration. A: $Co(OAc)_2$ system; B: $Co(NO_3)_2$ system. At 25°C. The solide curves are calculated with the rate constants and formation constants obtained.

where I is an intermediate, in which cobalt is weakly bound with the porphyrin. If one assumes a rapid pre-equilibrium(8) and two parallel pathways leading to the final product Co-TPyP, the following expression is derived for k_0:

$$k_0 = K[Co(OAc)_2](k_1 + k_2[Co(OAc)_2])/(1 + K[Co(OAc)_2]) \qquad (11)$$

Experimental rate data fit this expression very nicely as illustrated in Fig. 4. The rate equation(11) is similar to that proposed by Fleischer *et al.*(Ref.6), but it involves an additional term first order in cobalt(II) concentration in the numerator. In reaction(5) the metal ion in I just drops into the porphyrin ring, while in reaction(6) a second metal ion attacks I from the back. The rate constants, formation constants, and associated thermodynamic parameters are summarized in Ref.25.

The conditional rate constant k_0 for the cobalt nitrate incorporation into TPyP tends to be first order in $[Co(NO_3)_2]$ at lower cobalt concentration as in the cobalt acetate case, while at higher cobalt concentration it tends to be second order in $[Co(NO_3)_2]$. Therefore we postulate additional pathway(k_3) for the cobalt nitrate incorporation, in which cobalt nitrate is bound to the peripheral pyridyl nitrogen. The interaction of pyridyl nitrogen should be

$$H_2TPyP + Co(NO_3)_2 \rightleftharpoons H_2TPyP\text{-}Co(NO_3)_2 \qquad K_1 \qquad (12)$$
$$ II$$

$$II + Co(NO_3)_2 \rightleftharpoons II\text{-}Co(NO_3)_2 \qquad K_2 \qquad (13)$$
$$ III$$

$$II \longrightarrow CoTPyP + 2 HNO_3 \qquad k_1 \qquad (14)$$

$$II + Co(NO_3)_2 \longrightarrow Co\text{-}TPyP + Co(NO_3)_2 + 2 HNO_3 \qquad k_2 \qquad (15)$$

$$III + Co(NO_3)_2 \longrightarrow Co\text{-}TPyP + 2 Co(NO_3)_2 + 2 HNO_3 \qquad k_3 \qquad (16)$$

greater for $Co(NO_3)_2$ which is more electropositive than $Co(OAc)_2$. The interaction should lower the basicity of pyrrole nitrogen in TPyP through the change of peripheral charge. This may make easy the deprotonation of H_2TPyP and thus the k_3-path requires lower activation energy. According to the mechanism(12) - (16), we obtain the rate law similar to equation(11) with additional terms $k_3 K_1 K_2 [Co(NO_3)_2]^3$ in the numerator and $K_1 K_2 [Co(NO_3)_2]^2$ in the denominator. As apparent from Fig. 4 this equation describes nicely the kinetic data for the cobalt nitrate system over a whole range of cobalt concentration.

Choi and Fleischer(Ref.5) found the reaction of TPyP with manganese, cobalt, nickel and copper in glacial acetic acid to be first order in metal in every case. Brisbin and Richards(Ref.16) also studied the reaction between proto-porphyrin IX dimethyl ester(Proto-IX-DME) and some first-row transition metal ions in glacial acetic acid. In this case the reaction appears to be half order for cobalt, nickel and copper and fractional order for manganese and zinc. It is noticed that in these studies experiments were carried out over a very narrow range of metal ion concentration: for example $(3 - 6) \times 10^{-3}$ M (Ref.5). It seems likely that if the kinetics were investigated over a wider range of concentration in these studies the simple rate law would not have been found to hold. In fact it would be possible to conclude the first order dependence of $Co(OAc)_2$ for the range of cobalt concentration $(3 - 6) \times 10^{-3}$ M from Fig. 4, while for the range of cobalt concentration $(2 - 8) \times 10^{-4}$ M the apparent order in cobalt would be about half(see Fig. 4). Therefore it is indispensable in these studies to carry out kinetic experiments over as wide a concentration range as possible.

The reaction mechanism may be summarized as follows: the first metal ion forms a weakly bound complex(SAT complex) to deform the porphyrin(equations (8) and (12))(Ref.23). This step is not the rate-determining step. The metal in this complex just drops into the porphyrin ring(k_1-path, equations(9) and (14)). In k_2-path a second metal ion attacks the SAT complex(I in equation (10) and II in equation(15)) from the back. In this pathway the reaction proceeds through a homodinuclear activated complex, in which the two metal ions are on the opposite side of porphyrin plane to each other. Recently the mechanism formulated by equations(8) - (10) has been found to apply also for the incorporation of copper(II) and zinc(II) into *meso*-tetraphenylporphine (TPP) in *N,N*-dimethylformamide(Ref.29).

METALLOPORPHYRIN FORMATION WITH A PATHWAY INVOLVING A MONONUCLEAR ACTIVATED COMPLEX

Large metal ions, such as mercury(II) or cadmium(II) form metalloporphyrins involving these metal ions out-of-plane: these metal ions can not fit the porphyrin nucleus. A dinuclear structure was proposed for the bischloro-

mercury(II) complex of *N*-tosylaminooctaethylporphine(Ref.30). Cadmium(II) reacts readily with a variety of porphyrins to form corresponding metalloporphyrins. Cadmium(II) and mercury(II) porphyrins are in general labile and they have been the subject of equilibrium study(Ref.31,32). Linear relations between basicity and logarithmic formation constant are presented(Ref.31,32). Electrophilic substitution of cadmium porphyrin with another metal ion proceeds smoothly and has been the subject of kinetic study(Ref.33,34). At lower cadmium concentration the rate of metalloporphyrin formation is proportional to both cadmium and porphyrin concentrations. At higher cadmium concentration, however, spectral change becomes complicated and dinuclear product yields as in the case of mercury(II)(Ref.24,35). The rate constant of formation of the mononuclear cadmium complex with TPPS is 5.1×10^2 M^{-1} s^{-1} at 25°C and I = 0.1 M(NaNO$_3$)(Ref.35). The metal incorporation rate relative to the water exchange rate at metal ions is $(1-3) \times 10^{-6}$ for nickel, cobalt, copper and zinc TPPS(Ref.36,37), while it is 3×10^{-4} for cadmium TPPS formation. This may be resulted from the fact that cadmium ion just sits on with a low activation energy and it does not fit into the porphyrin nucleus.

Because of the presence of a bulky methyl group, *N*-methyltetraphenylporphine (CH$_3$-TPP) is deformed favorably for the metal ion incorporation. So the reaction of this porphyrin with various metal ions is relatively fast and it is always first order in the metal ion concentration(Ref.9,29,38).

ACTIVATION VOLUME FOR THE METAL ION INCORPORATION INTO PORPHYRINS

Activation volume is useful in diagnosing the reaction mechanism. By means of the high-pressure stopped-flow apparatus exploited in our laboratory(Ref. 39) the determination of activation volume is being carried out for various reactions involving metal ions and metal complexes(Ref.40-43). In the course of these studies, the activation volume for the incorporation of cobalt(II) nitrate into CH$_3$TPP was investigated in *N,N*-dimethylformamide(DMF) at various temperatures and pressures(Ref. 43).

The rate is first order in cobalt(II) ion over a wide range of concentration: $3 \times 10^{-4} - 7 \times 10^{-2}$ mol kg^{-1}. The values of activation enthalpy(72 ± 5) kJ mol^{-1} and entropy(-12 ± 8) J mol^{-1} K^{-1} were estimated. According to the transition state theory the change in rate constant with pressure is given as follows:

$$(\partial \ln k / \partial P)_T = -\Delta V^{\ddagger} / RT \tag{17}$$

Since the plot of ln*k versus* P is linear, the activation volume is independent of pressure. It was determined to be 8.0 ± 0.3 cm^3 mol^{-1}. The positive activation volume strongly points to a dissociative character of the activation process. Recently Merbach *et al.*(Ref.44) have reported the activation volume for the solvent exchange of cobalt(II) in DMF: 6.7 cm^3 mol^{-1} at 296 K and 9.2 cm^3 mol^{-1} at 253 K. They proposed a dissociative interchange mechanism for the solvent exchange reaction. In fact the activation volume for the cobalt porphyrin formation is about the same as for the exchange of DMF at cobalt. Thus the mechanism involves solvent dissociation from the cobalt(II) ion as an important rate-determining factor. Moreover the rates for complexation of CH$_3$TPP are slower than for corresponding solvent exchange, while they are faster than rates for complexation of planer TPP(Ref.9,18,29,38). These facts point to the deformation of porphyrin as an important rapid process before the rate-determining step(Ref.23,38). Recently Pasternack and his coworkers suggested the SAT complex as a convenient model for the transition state complex rather than the pre-equilibrium structure(Ref.45). This proposal seems to be based on the small formation constant of the SAT complex (Cu-H$_2$TPP) in Me$_2$SO. In acetic acid, however, the formation constant as high as 6.6×10^4 has been obtained for cobalt acetate - H$_2$TPyP system(Ref.25). Further investigations in different solvents for different pairs of metal ions and porphyrins would be required to make this point clearer.

ACKNOWLEDGMENTS

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