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Kinetics and Mechanism of Cobalt(II) Incorporation into *meso*-Tetra(4-pyridyl)porphine in Acetic Acid[1)]

Shigenobu Funahashi, Keiji Saito, and Motoharu Tanaka*

Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464

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The kinetics of reactions of *meso*-tetra(4-pyridyl)porphine (H_2TPyP) with cobalt(II) acetate and cobalt(II) nitrate was studied in acetic acid spectrophotometrically. The rate of cobalt incorporation into H_2TPyP is first-order in H_2TPyP. The conditional first-order rate constants are expressed as follows: for the cobalt(II) acetate system $k_{0(\mathrm{Co})}=K[\mathrm{Co(OAc)_2}]_0(1+K[\mathrm{Co(OAc)_2}]_0)^{-1}(k_1+k_2[\mathrm{Co(OAc)_2}]_0)$, where at 25 °C $K=(5.5\pm2.0)\times10^4$ kg mol^{-1} ($\Delta H=-36\pm15$ kJ mol^{-1}, $\Delta S=-30\pm30$ J mol^{-1} K^{-1}), $k_1=(6.3\pm0.5)\times10^{-5}$ s^{-1} ($\Delta H^*=89\pm8$ kJ mol^{-1}, $\Delta S^*=-27\pm15$ J mol^{-1} K^{-1}), and $k_2=(1.17\pm0.05)\times10^{-1}$ kg mol^{-1} s^{-1} ($\Delta H^*=75\pm3$ kJ mol^{-1}, $\Delta S^*=-11\pm8$ J mol^{-1} K^{-1}); for the cobalt nitrate system $k_{0(\mathrm{Co})}=K_1[\mathrm{Co(NO_3)_2}]_0(1+K_1[\mathrm{Co(NO_3)_2}]_0)^{-1}(k_1+k_2[\mathrm{Co(NO_3)_2}]_0+k_3K_2[\mathrm{Co(NO_3)_2}]_0{}^2)$, where at 25 °C $k_1=(5.1\pm0.5)\times10^{-5}$ s^{-1}, $k_2=(2.0\pm0.1)\times10^{-1}$ kg mol^{-1} s^{-1}, $K_1=(7.2\pm2.0)\times10^4$ kg mol^{-1}, and $k_3K_2=(1.6\pm0.15)\times10^2$ kg^2 mol^{-2} s^{-1}. Formation constants of sitting-atop complexes were determined dynamically. Mechanisms are proposed for metal ion incorporation and some discussions are made on the difference in the reactivities of acetate and nitrate of cobalt(II) in acetic acid.

Metalloporphyrins are ubiquitous in living systems. For understanding the possible role of enzymatic catalysis of a variety of porphyrins related to biologically relevant material and the metalation mechanism from the viewpoint of coordination chemistry, thorough kinetic studies are required. Several reviews of metalloporphyrin formation are available.[2–4)]

Metalloporphyrins in which the metal is bonded to fewer than four nitrogen atoms, sitting-atop complexes, have been considered as models for the initial steps of the metalation of the macrocycle. Such complexes are known for rhenium and technetium,[5)] platinum,[6)] and rhodium.[7,8)] Several examples of mercury complexes have also been formulated.[9–11)]

Recently Hambright,[12)] Krishnamurthy,[13)] and Lavallee[14)] have proposed mechanisms for the formation of metalloporphyrins. Despite the numerous investigations on the formation of metalloporphyrins, many of basic features of the reaction are still conjectural.

We have investigated the rates of reaction of *meso*-tetra(4-pyridyl)porphine with cobalt(II) acetate and cobalt(II) nitrate in acetic acid. Similar measurements have been made in acetic acid/water solutions,[15)] where the nature of the metal ion reactants is often in doubt. We describe the kinetic proof for the existence of a cobalt(II) porphyrin sitting-atop complex. In acetic acid metal salts are all in the undissociated form, since it is a non-dissociating solvent having low dielectric constant ($D=6.18$ at 20 °C).[16)] Thus in this solvent we have no complication arising from the presence of dissociated anions and from ionic strentgh.

Experimental

Reagents. It is very important that all reagents be as dry as possible. Therefore, extreme care was taken in the purification and preparation of all reagents and compounds. Solutions of reagents were prepared in a glove box filled with dried air.

Anhydrous Acetic Acid: The preparation of acetic acid was described previously.[17)] The amount of water in the acetic acid was less than 9×10^{-3} %.

Porphyrin: *meso*-Tetra(4-pyridyl)porphine (Strem Chemicals) was chromatographed on an alumina column by elution with chloroform.

Cobalt(II) Acetate: Thirty grams of cobalt(II) acetate hydrate was refluxed in 300 cm^3 of acetic anhydride for 3 h. After centrifugation the precipitates were washed four times with anhydrous acetic acid. The crystals ($\mathrm{Co(OAc)_2\cdot4HOAc}$) were dried at 120 °C for 3 h to obtain $\mathrm{Co(OAc)_2}$. The quantitative change of $\mathrm{Co(OAc)_2\cdot4HOAc}$ to $\mathrm{Co(OAc)_2}$ was confirmed thermogravimetrically.

Cobalt(II) Nitrate: Reagent grade cobalt(II) nitrate hydrate was recrystallized from distilled water. The hydrate was dissolved in acetic acid. Acetic anhydride equivalent to the water involved was added to the cobalt(II) nitrate solution. Several days were required for complete reaction of water with acetic anhydride. The concentration of cobalt was standardized against EDTA using Methylthymol Blue as indicator.

Ammonium Nitrate: Reagent grade ammonium nitrate was recrystallized from water. The crystals were dried at 120 °C for 3 h under reduced pressure.

Cobalt(II) acetate, ammonium nitrate, and porphyrin solutions were prepared by weighing corresponding crystals. We use molal units (mol kg^{-1}).

Measurements. Spectral measurements were performed on a highly sensitive spectrophotometer (SM401, Union Giken Co., Ltd.). The concentration of water was determined by the Karl-Fisher aquametry. A thermogravimeter (Thermal Analyzer DT-30 Shimadzu) was used to check the thermal stability.

The reactions were followed spectrophotometrically with a Union Giken spectrophotometer with a thermostated cell compartment maintained within ±0.1 °C. All the reactions were carried out in 1.00-cm cells by mixing reactants pre-equilibrated at the reaction temperature. The metalloporphyrin Co-TPyP was made in solution by addition of a large excess of cobalt(II) to H_2TPyP. The absorption spectra as a function of time showed excellent isosbestic points within several hours. The metalloporphyrin tended to precipitate after about 20 h at room temperature. The reaction was followed at 418 nm for the $\mathrm{Co(OAc)_2}$ system and at 422 nm for the $\mathrm{Co(NO_3)_2}$ system.

Under pseudo-first-order conditions with an excess of total cobalt over porphyrin, reactions were followed and pseudo-first-order rate constants were obtained from the data. Under conditions where the cobalt concentration is about 10^{-3} mol kg^{-1}, the half-life time of formation of the metalloporphyrin is several tens of minutes. At such higher concentrations of cobalt, the linearity of first-order plot is good and gives the conditional first-order rate constant. The rate constants are obtained by an initial rate method or by the Guggenheim method,[18] which does not require a final absorbance value. Most of conditional first-order rate constants at lower concentration of cobalt were obtained by an initial rate method in order to avoid complications due to the precipitation of metalloporphyrin.

Equilibria. Recently equilibria of aquation for cobalt (II) acetate[19] and cobalt(II) perchlorate[20] in acetic acid have been studied.

$$\mathrm{Co(OAc)_2(HOAc)_4} + n\mathrm{H_2O} \overset{\beta_n}{\rightleftharpoons} \mathrm{Co(OAc)_2(H_2O)}_n\mathrm{(HOAc)}_{4-n}, \qquad (1)$$

$(\beta_1 = 6.7 \text{ kg mol}^{-1},\ \beta_2 = 11 \text{ kg}^2 \text{ mol}^{-2},\ \beta_3 = 28 \text{ kg}^3 \text{ mol}^{-3})$

$$\mathrm{Co(HOAc)_6(ClO_4)_2} + n\mathrm{H_2O} \overset{\beta_n}{\rightleftharpoons} \mathrm{Co(H_2O)}_n\mathrm{(HOAc)}_{6-n}\mathrm{(ClO_4)_2}. \qquad (2)$$

$(\beta_1 = 34 \text{ kg mol}^{-1},\ \beta_2 = 850 \text{ kg}^2 \text{ mol}^{-2})$

where equilibrium constants are given in parentheses. No data have been published for the equilibrium constant for aquation of cobalt(II) nitrate, although, presumably, it would not be much different from that of cobalt(II) perchlorate. Thus in the present systems no appreciable amount of aqua complexes was thought to be present: cobalt(II) acetate is in the form of diacetatotetrasolvatocobalt(II) and cobalt(II) nitrate exists as an ion-pair involving hexasolvatocobalt(II) $[\mathrm{Co(HOAc)_6}^{2+}][2\mathrm{NO_3}^-]$ (*vide infra*).

TPyP showed no spectral evidence for protonation in acetic acid: the spectrum of TPyP in acetic acid was the same as that in chloroform. Thus TPyP is entirely in the free base form ($\mathrm{H_2TPyP}$) in acetic acid.

Results

Reaction of H_2TPyP with $Co(OAc)_2$. Values of $k_{0(\mathrm{Co})}$ obtained at constant cobalt(II) acetate concentration (4.80×10^{-4} mol kg^{-1}) and at various concentrations of $\mathrm{H_2TPyP}$ (1.88, 2.32, 3.05, 5.37×10^{-6} mol kg^{-1}) were the same ($(1.06 \pm 0.03) \times 10^{-4}$ s^{-1}) within experimental errors. The rate for formation of metalloporphyrin (Co-TPyP) is first order in porphyrin:

$$\frac{d[\text{Co-TPyP}]}{dt} = -\frac{d[\mathrm{H_2TPyP'}]}{dt} = k_{0(\mathrm{Co})}[\mathrm{H_2TPyP'}], \qquad (3)$$

where $k_{0(\mathrm{Co})}$ is the conditional first-order rate constant involving cobalt concentration and $[\mathrm{H_2TPyP'}]$ is the total concentration of porphyrin minus the concentration of metalloporphyrin. The values of $k_{0(\mathrm{Co})}$ at 20.0, 25.0, and 30.0 °C are plotted against initial concentration of cobalt(II) acetate $[\mathrm{Co(OAc)_2}]_0$ in Fig. 1. The logarithmic relationship between rate constants and cobalt concentrations is shown in Fig. 2. As apparent from curve A in Fig. 2, at lower and higher cobalt concentration $k_{0(\mathrm{Co})}$ tends to be first order in $[\mathrm{Co(OAc)_2}]_0$, while at the intermediate cobalt concentration $k_{0(\mathrm{Co})}$ changes with $[\mathrm{Co(OAc)_2}]_0$ to a lesser extent. This kinetic behavior of formation of metalloporphyrin can be formulated by the following equation:

$$\mathrm{H_2TPyP} + \mathrm{Co(OAc)_2} \rightleftharpoons \mathrm{H_2TPyP{\cdots}Co(OAc)_2},\ K, \qquad (4)$$

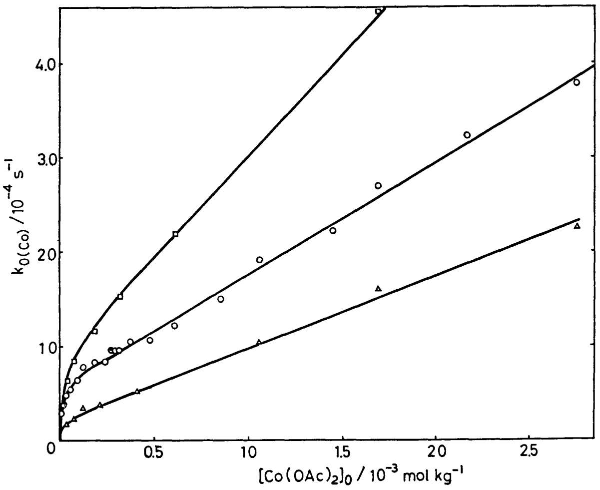

Fig. 1. Cobalt(II) acetate dependence of conditional first-order rate constants for the reaction of *meso*-tetra(4-pyridyl)porphine with cobalt(II) acetate in acetic acid.

△, 20 °C; ○: 25 °C; □, 30 °C.

The solid curves are calculated with the rate constants and formation constants obtained.

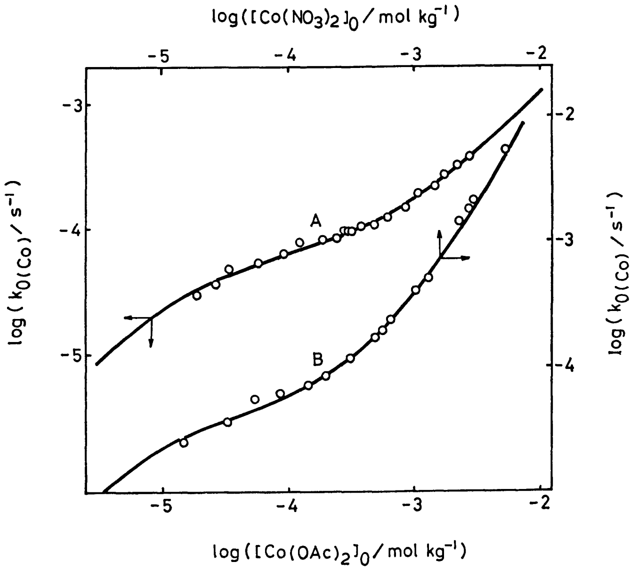

Fig. 2. Relationship between $\log k_{0(\mathrm{Co})}$ and logarithmic values of cobalt concentration.

A, TPyP–Co(OAc)$_2$ system at 25 °C; B, TPyP–Co(NO$_3$)$_2$ system at 25 °C.

The solid curves are calculated with the rate constants and formation constants obtained.

$$\mathrm{SAT} \longrightarrow \text{Co-TPyP} + 2\mathrm{HOAc}, \qquad k_1 \qquad (5)$$

$$\mathrm{SAT} + \mathrm{Co(OAc)_2} \longrightarrow \text{Co-TPyP} + \mathrm{Co(OAc)_2} + 2\mathrm{HOAc}, \qquad k_2 \qquad (6)$$

where $\mathrm{H_2TPyP{\cdots}Co(OAc)_2}$ is an intermediate which may be so-called sitting-atop complex and is denoted as SAT. For simplicity, acetic acid molecules in the reactions are omitted. If one assumes a rapid pre-equilibrium step of Eq. 4 and two parallel rate-determining steps of Eqs. 5 and 6, then an expression for $k_{0(\mathrm{Co})}$ can be derived for this mechanism and it is

Table 1. Rate constants, formation constants, and activation parameters for cobalt incorporation into H_2TPyP

	$TPyP-Co(OAc)_2$ system		
Temp/°C	k_1/s^{-1}	$k_2/kg\ mol^{-1}\ s^{-1}$	$K/kg\ mol^{-1}$
20.0	$(3.0\pm0.3)\times10^{-5}$	$(7.36\pm0.15)\times10^{-2}$	$(6.6\pm2.0)\times10^{4}$
25.0	$(6.3\pm0.5)\times10^{-5}$	$(1.17\pm0.05)\times10^{-1}$	$(5.5\pm2.0)\times10^{4}$
30.0	$(1.0\pm0.1)\times10^{-4}$	$(2.11\pm0.10)\times10^{-1}$	$(4.0\pm2.0)\times10^{4}$
	$\Delta H^{*}/kJ\ mol^{-1}=89\pm8$	$\Delta H^{*}/kJ\ mol^{-1}=75\pm3$	$\Delta H/kJ\ mol^{-1}=-36\pm15$
	$\Delta S^{*}/J\ mol^{-1}\ K^{-1}=-27\pm15$	$\Delta S^{*}/J\ mol^{-1}\ K^{-1}=-11\pm8$	$\Delta S/J\ mol^{-1}\ K^{-1}=-30\pm30$

		$TPyP-Co(NO_3)_2$ system		
Temp/°C	k_1/s^{-1}	$k_2/kg\ mol^{-1}\ s^{-1}$	$K_1/kg\ mol^{-1}$	$k_3K_2/kg^2\ mol^{-2}\ s^{-1}$
25.0	$(5.1\pm0.5)\times10^{-5}$	$(2.0\pm0.1)\times10^{-1}$	$(7.2\pm2.0)\times10^{4}$	$(1.6\pm0.15)\times10^{2}$

given below

$$k_{0(Co)}=\frac{K[Co(OAc)_2]_0}{1+K[Co(OAc)_2]_0}(k_1+k_2[Co(OAc)_2]_0). \quad (7)$$

The experimental rate data fit this expression very well as illustrated in Fig. 1. In Reaction 5, the metal ion in the sitting-atop complex just drops into the porphyrin ring, and Reaction 6 indicates that a second metal is inserted from the opposite side. Values of k_1, k_2, and K were determined by a non-linear least squares method.[21] The rate constants, formation constants, and their corresponding parameters are tabulated in Table 1.

An introduction of 0.5% water into the solvent acetic acid did not affect the rate constants within experimental errors. Errors for estimation of rate constants were within 10%. Since the water concentration of our systems is much less than 0.5%, we believe with confidence that the presence of water, if any, did not affect our results.

Reaction of H_2TPyP with $Co(NO_3)_2$. The relationship between $k_{0(Co)}$ and initial concentration of cobalt(II) nitrate is shown in Fig. 2. The cobalt dependence of $k_{0(Co)}$ at lower concentration of cobalt nitrate is similar to that in the cobalt acetate system. At higher concentration of cobalt nitrate, however, the conditional rate tends to be second-order in cobalt nitrate concentration (see curve B in Fig. 2). The mechanism of the reaction is postulated as follows:

$$H_2TPyP + Co(NO_3)_2 \rightleftharpoons H_2TPyP\cdots Co(NO_3)_2,\quad K_1 \quad (8)$$

$$SAT + Co(NO_3)_2 \rightleftharpoons SAT\cdots Co(NO_3)_2,\quad K_2 \quad (9)$$

$$SAT \longrightarrow Co\text{-}TPyP + 2HNO_3,\quad k_1 \quad (10)$$

$$SAT + Co(NO_3)_2 \longrightarrow Co\text{-}TPyP + Co(NO_3)_2 + 2HNO_3,\quad k_2 \quad (11)$$

$$SAT\cdots Co(NO_3)_2 + Co(NO_3)_2 \longrightarrow Co\text{-}TPyP + 2Co(NO_3)_2 + 2HNO_3,\quad k_3 \quad (12)$$

where $H_2TPyP\cdots Co(NO_3)_2$ is a sitting-atop complex denoted as SAT, and $SAT\cdots Co(NO_3)_2$ is a complex formed by interaction of cobalt with a nitrogen atom of pyridyl groups in porphyrin (*vide infra*). With steps 10, 11, and 12 as rate determining and steps 8 and 9 as rapid preequilibria, Eq. 13 can be readily derived.

$$k_{0(Co)}=\frac{K_1[Co(NO_3)_2]_0}{1+K_1[Co(NO_3)_2]_0+K_1K_2[Co(NO_3)_2]_0^2}\times(k_1+k_2[Co(NO_3)_2]_0+k_3K_2[Co(NO_3)_2]_0^2) \quad (13)$$

Table 2. Effect of ammonium nitrate on the rate for Co-TPyP formation

$10^5[Co(NO_3)_2]_0$ / mol kg^{-1}	$10^4[NH_4NO_3]$ / mol kg^{-1}	$10^5k_{0(Co)}$ / s^{-1}
8.81	0	6.19
8.6	0.84	6.7
8.6	1.2	5.2
8.6	1.37	4.8
14.4	0	7.1
14.4	1.4	6.9
14.4	2.23	6.1
14.4	3.73	5.7
14.4	6.78	5.5

The data obtained indicate that the third term of the denominator in Eq. 13, $K_1K_2[Co(NO_3)_2]_0^2$, is negligible all over the range of cobalt concentrations. As illustrated in Fig. 2, the empirical kinetic data are best described by Eq. 13 without the term $K_1K_2[Co(NO_3)_2]_0^2$. Constants in the $TPyP-Co(NO_3)_2$ system are tabulated in Table 1.

The kinetics of cobalt incorporation into H_2TPyP have been studied in the presence of ammonium nitrate. Conditional first-order rate constants obtained in the presence of ammonium nitrate are summarized in Table 2. Values of $k_{0(Co)}$ tend to decrease only slightly as the concentration of ammonium nitrate increases. Therefore the second order cobalt nitrate dependence is in fact due to the participation of the second cobalt and not of nitrate in the reaction.

Discussion

There have been several studies of the kinetics of metal acetate incorporation into porphyrin molecules in acetic acid.[15,22–25] The kinetic results are discouragingly inconsistent with each other. Choi and Fleisher[15] found the reaction between TPyP and manganese, cobalt, nickel, and copper in glacial acetic acid to be first order in metal in every case. Brisbin and Balahura[25] and Kingham and Brisbin[24] found the reaction between hematoporphyrin and manganese, iron, cobalt, copper, and zinc to be first order in metal and that between hematoporphyrin and nickel to be half order in metal. Brisbin and Richards[23] studied the reaction between protoporphyrin IX dimethyl ester (Proto-IX-DME) and some first-row transition metals in glacial acetic acid. The reaction appears to be half order in cobalt and nickel and close to half order in copper and shows orders between one-half and one in manganese and zinc.

The results by Choi and Fleischer[15] are inconsistent with ours. Their experiments were conducted over a very narrow range of metal concentrations: (3—6) × 10^{-3} M, and they found the reaction of cobalt(II) acetate with TPyP to be first order with respect to metal.[15] It seems quite likely that if the kinetics were investigated over a wider range of concentration, the simple rate laws would not be found to hold. In fact, it is possible to estimate the first order metal dependence from the range of (3—6) × 10^{-3} M metal concentration from Fig. 1. Moreover, assuming the similar reactivity of cobalt for TPyP and Proto-IX-DME, the decision of about half order in cobalt for the reaction of Proto-IX-DME with (2—8) × 10^{-4} M cobalt is possible, as apparent from Fig. 2. Therefore it is indispensable in these studies to conduct experiments over as wide a concentration range as possible.

The first metal ion forms a SAT complex to deform the porphyrin (Eqs. 4 and 8). This step is not rate-limiting. The metal in the SAT complex just drops into the porphyrin ring (the k_1-path given by Eqs. 5 and 10). It is the k_2-path that a second metal attacks from the opposite side (Eqs. 6 and 11). The two metals in transition state are considered to be on opposite sides of the porphyrin plane according to the crystal structure of several bi-metalloporphyrins.[26] This is also supported by results on the mechanisms of electrophilic exchange between one metal ion and another complexed in a porphyrin molecule.[27,28]

Kinetic studies[28] on the Zn/Cd–TPP (TPP: tetraphenylporphine) and Zn/Hg–TPP systems revealed rate laws of first order in each reactant. Because of their large ionic radii, cadmium and mercury can not fit as well into the plane of the four central porphyrin nitrogen atoms. It is thus considered that Hg–TPP and Cd–TPP complexes have a configuration favorable for the attack by zinc from the back. So these reactions corresponds to the k_2-path in the present systems.

Recently large metallic ions such as mercury(II), cadmium(II), and lead(II) have been found to accelerate the complex formation of manganese(II), cobalt(II), copper(II), and nickel(II) with *meso*-tetra(4-sulfonatophenyl)porphine.[29] A heterobinuclear transition state has been proposed for these systems, and it may be appropriate to postulate a homobinuclear transition state for the present system. Coordination of the first metal ion makes the configuration of porphine favorable for the attack by the second metal ion from the back. At the same time it may facilitate the dissociation of the pyrrole proton in porphine, which seems important in the formation of metalloporphyrins.

If the dissociation of solvent from metal ions were important in the formation of metalloporphyrins, $Co(OAc)_2$ should react faster than $Co(NO_3)_2$, since electron donor ability of acetate is higher than nitrate.[30,31] In this respect it is interesting to observe no appreciable difference in k_1 and k_2 between $Co(OAc)_2$ and $Co(NO_3)_2$ reactions (see Table 1).

In solvent of low dielectric constant such as acetic acid, it is valuable to consider both ionization and dissociation of reactants. Overall dissociation of AB is written as

$$AB \overset{K_i}{\rightleftharpoons} A^+B^- \overset{K_d}{\rightleftharpoons} A^+ + B^-$$

with an overall dissociation constant K_D:

$$K_D = \frac{[A^+]+[B^-]}{[AB]+[A^+B^-]} = \frac{K_iK_d}{1+K_i},$$

where K_i is an ionization constant and K_d is a dissociation constant. Available values of K_D in acetic acid are $10^{-10.1}$ for H_2O,[32] $10^{-10.1}$ for HNO_3,[33] and $10^{-7.56}$ for $Co(OAc)_2$ ($Co(OAc)_2 \rightleftharpoons CoOAc^+ + OAc^-$).[34] K_d can be calculated by an equation of the type derived by Fuoss for ion-pair formation.[35] Unknown K_d values may be predicted, at least to a correct order of magnitude. On this basis, K_d may be estimated to be about 10^{-6} M for all of these 1:1 electrolytes in acetic acid. Therefore in the concentration higher than 10^{-4} M, 1:1 electrolytes exist as undissociated ion-pair. Water, nitric acid, and cobalt acetate[36] are largely unionized, while cobalt nitrate and ammonium nitrate should be to a considerable extent in the form of undissociated ion-pair. The breaking of pyrrole type protons is involved in metalloporphyrin formation reactions. Protons released as reaction proceeds react rapidly with OAc^- and NO_3^- to form HOAc and HNO_3 molecules.

The k_3-path found for the $Co(NO_3)_2$ system is missing in the $Co(OAc)_2$ system. It may arise from the interaction of $Co(NO_3)_2$ with pyridyl nitrogen in TPyP. The interaction should lower the basicity of pyrrole 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 than the k_2-path. Since $Co(NO_3)_2$ is more electropositive than $Co(OAc)_2$, $Co(NO_3)_2$ is more reactive than $Co(OAc)_2$. Consequently the k_3-path should not be appreciable, if any, for $Co(OAc)_2$ system.

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References

1) Metal complexes in acetic acid IV. Part III: S. Funahashi, T. Nishimoto, A. Hioki, and M. Tanaka, *Inorg. Chem.*, **20**, 2648 (1981).

2) P. Hambright, "Porphyrins and Metalloporphyrins," ed by K. M. Smith, Elsevier, New York (1975), Chap. 6, pp. 233—278.

3) F. R. Longo, E. M. Brown, W. G. Rau, and A. D. Adler, "The Porphyrins," ed by D. Dolphin, Academic Press, New York (1979), Vol. V, Chap. 10, pp. 459—481.

4) W. Schneider, *Struct. Bonding (Berlin)*, **23**, 123 (1975).

5) M. Tsutsui, C. P. Hrung, D. Ostfeld, T. S. Srivastava, D. L. Cullen, and E. F. Meyer, Jr., *J. Am. Chem. Soc.*, **97**,

3952 (1975).

6) J. P. Macquet, M. M. Millard, and T. Theophanides, *J. Am. Chem. Soc.*, **100**, 4741 (1978).

7) H. Ogoshi, T. Omura, and Z. Yoshida, *J. Am. Chem. Soc.*, **95**, 1666 (1973).

8) E. B. Fleischer and F. Dixon, *Bioinorg. Chem.*, **7**, 129 (1977).

9) M. F. Hudson and K. M. Smith, *J. Chem. Soc., Chem. Commun.*, **1973**, 515.

10) A. Adeyemo and M. Krishnamurthy, *Inorg. Chem.*, **16**, 3355 (1977).

11) H. J. Callot, B. Chevrier, and R. Weiss, *J. Am. Chem. Soc.*, **101**, 7729 (1979).

12) J. Turay and P. Hambright, *Inorg. Chem.*, **19**, 562 (1980).

13) A. N. Thompson and M. Krishnamurthy, *J. Inorg. Nucl. Chem.*, **41**, 1251 (1979).

14) M. J. Bain-Ackerman and D. K. Lavallee, *Inorg. Chem.*, **18**, 3358 (1979).

15) E. I. Choi and E. B. Fleischer, *Inorg. Chem.*, **2**, 94 (1963).

16) W. Dannhauser and R. H. Cole, *J. Am. Chem. Soc.*, **74**, 6105 (1952).

17) S. Funahashi, T. Nishimoto, P. Banerjee, K. Sawada, and M. Tanaka, *Bull. Chem. Soc. Jpn.*, **53**, 1555 (1980).

18) R. G. Wilkins, "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes," Allyn and Bacon, Boston (1974), pp. 5 and 13.

19) K. Sawada and M. Tanaka, *J. Inorg. Nucl. Chem.*, **35**, 2455 (1973).

20) K. Sawada, K. Agata, and M. Tanaka, *Inorg. Chim. Acta*, **30**, 127 (1978).

21) T. Nakagawa and Y. Oyanagi, Nagoya Computation Center, Library program SALS (Statistical analysis with least-squares fitting), 1979.

22) J. James and P. Hambright, *Inorg. Chem.*, **12**, 474 (1973).

23) D. A. Brisbin and G. D. Richards, *Inorg. Chem.*, **11**, 2849 (1972).

24) D. J. Kingham and D. A. Brisbin, *Inorg. Chem.*, **9**, 2034 (1970).

25) D. A. Brisbin and R. J. Balahura, *Can. J. Chem.*, **46**, 3431 (1968).

26) D. Ostfeld and M. Tsutsui, *Acc. Chem. Res.*, **7**, 52 (1974).

27) H. Baker, P. Hambright, L. Wagner, and L. Ross, *Inorg. Chem.*, **12**, 2200 (1973).

28) C. Grant, Jr., and P. Hambright, *J. Am. Chem. Soc.*, **91**, 4195 (1969).

29) M. Tabata and M. Tanaka, *Inorg. Chim. Acta Lett*, **40**, X71 (1980); *Anal. Lett.*, **13**, 427 (1980).

30) S. Funahashi and M. Tanaka, *Inorg. Chem.*, **8**, 2159 (1969).

31) M. Tanaka and S. Yamada, *J. Chem. Soc., Chem. Commun.*, **1976**, 178.

32) S. Bruckenstein and I. M. Kolthoff, *J. Am. Chem. Soc.*, **78**, 2974 (1956).

33) W. Poscham and A. Engelbrecht, *Z. Phys. Chem., Leipzig*, **248**, 177 (1971).

34) O. W. Kolling and J. L. Lambert, *Inorg. Chem.*, **3**, 202 (1964).

35) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

36) C. F. Hendriks, H. C. A. van Beek, and P. M. Heertjes, *Ind. Eng. Chem. Prod. Res. Dev.*, **18**, 43 (1979).