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Kinetics of Pyridine Derivatives as Accelerators for the Incorporation Reaction of Cadmium(II) into Porphyrin and Association Behavior of the Accelerators with Porphyrin

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Incorporation reaction rate constants of cadmium(II) ion into 5,10,15,20-tetrakis(4-sulphonatophenyl)porphine (H_2tpps) in the presence of 8 kinds of pyridine derivatives as accelerators were determined. And association constants for 5 kinds of the accelerators with H_2tpps were also determined; the logarithmic values of which were proportional to the number of pyridine rings. The association constant is found to be one of the most important factors for controlling the acceleration effect.

A variety of functions and characteristics of porphyrin and its metal complexes have been extensively studied in many fields of chemistry. For example, analytical applications as a highly sensitive spectrophotometric reagent have been developed by using the Soret band.1) However, metal incorporation reactions into porphyrin are generally very slow, so that its applications are limited to several kinds of metal ions. In order to solve this difficulty, several kinds of acceleration methods have been developed, such as, acceleration by heating, by controlling the valence state of metal ions,1) by metal ion exchange reaction,2,3) and by using accelerator such as 2,2'-bipyridine(bpy)4) and 8-quinolinol.5) We have assumed that an extended π electron system of these ligands should be something to do with their acceleration effect. Because, it is well known that an association of reactants is an essential step for the substitution reaction of a metal complex,6) and also that porphyrin forms an self-associate by the interaction of its extended π electron system. In order to make clear this assumption, rate constants of the incorporation reaction of cadmium(II) ion into 5,10,15,20-tetrakis(4-sulphonatophenyl)porphine(H_2tpps) were determined in the presence of each 8 kinds of pyridine derivatives. Further, the association constants of H_2tpps and 5 kinds of pyridine derivatives (i.e., pyridine(py), bpy, 4,4'-bipyridine(4-bpy), 2,2',2"-tripyridine(tpy), and 2,4,6-tris(2-pyridyl)-1,3,5-triazine(tptz)) were determined. This is the first report to demonstrate the well defined correlation between the number of aromatic rings and the free energy change ($-\Delta G = RT\ln K$) in their association with porphyrin. Based on these studies, it is deduced that the association constant of pyridine derivative to porphyrin is one of the most important factors for controlling its acceleration effect.

The H_2tpps,1) N-methyl-4,4'-bipyridinium(mbpy)chloride,7) and N,N'-dimethyl-

4,4'-bipyridinium(dbpy)iodide$^{7)}$ were obtained by the method described elsewhere. All another reagents used were of analytical reagent grade. Absorbance and spectra were measured by using Simazu Model UV 365 with 1 cm quartz cells at 20 °C.

The association reaction of an accelerator ligand (L) with H_2tpps is given by

$$H_2tpps^{4-} + L \xrightleftharpoons{K_{as1}} H_2tpps(L)^{4-} \qquad (1)$$

$$H_2tpps(L)^{4-} + L \xrightleftharpoons{K_{as2}} H_2tpps(L)_2^{4-} \qquad (2)$$

The typical changes of absorption spectra with tptz at the Soret band region are shown in Fig.1. The two isosbestic points were observed in it, which shows the existence of two kinds of associates, that is, H_2tpps(L) and H_2tpps$(L)_2$. Under the conditions where only one isosbestic point was observed, preliminary values of either one of the association constants K_{as1} and K_{as2} were determined, and then their values were refined by successive approximation. As shown in Fig.2, the observed absorbance-tptz concentration relation was in very good agreement with the calculated one based on the values of $K_{as1}=10^{5.36}$ and $K_{as2}=10^{4.31}$ obtained. For the other pyridine derivatives, only one isosbestic point was observed, based

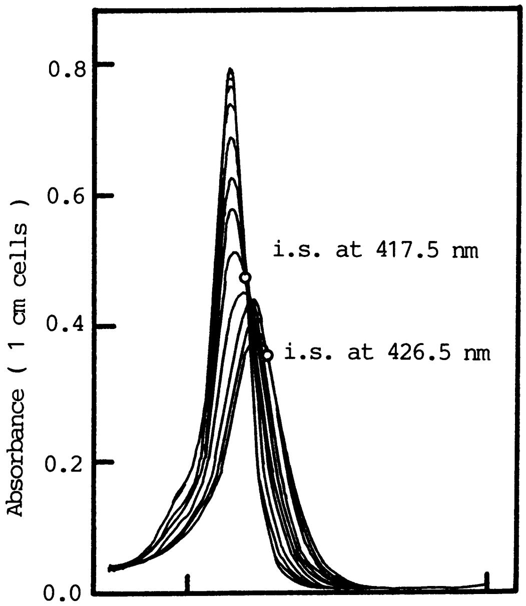

Fig.1. Absorption spectra of H_2tpps-tptz system.
$[H_2tpps]_T=1.69\times10^{-6}$ mol dm^{-3}
$[tptz]_T= 0 - 2\times10^{-4}$ mol dm^{-3}
I=0.1 (NaCl), t=20 °C, pH=8.7
Standing time = 2 min
i.s. : isosbestic point

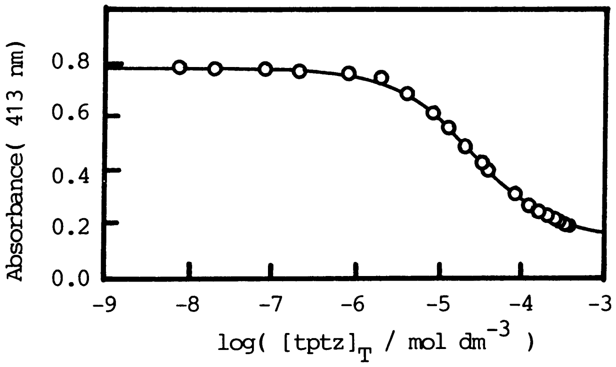

Fig.2. Absorbance vs. tptz concentration curve.
$[H_2tpps]_T=1.69\times10^{-6}$ mol dm^{-3}
$[tptz]_T= 0 - 3.6\times10^{-4}$ mol dm^{-3}
I=0.1 (NaCl), t=20 °C, pH=8.7

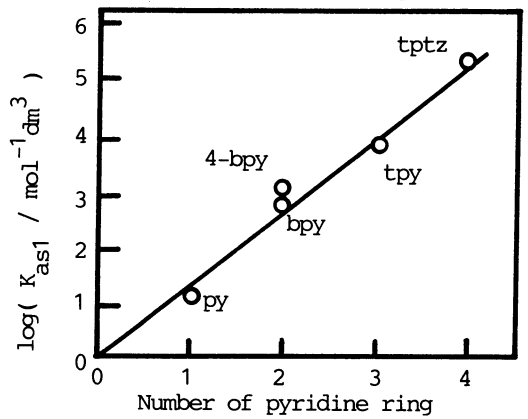

Fig.3. Log(K_{as1}/mol^{-1}dm^3) vs. number of pyridine ring curve.

on the formation of 1:1 associate. Association constants K_{as1} were determined as $10^{1.12}$ for py, $10^{2.71}$ for bpy, and $10^{3.82}$ for tpy, respectively.

The magnitude of the association constants K_{as1} increases in the order of py < bpy < tpy < tptz. As shown in Fig.3, the relationship between the logarithmic value of K_{as1} is directly proportional to the number of pyridine rings, that is, to the area of its extended π electron system. A ratio of K_{as1}/K_{as2} is 11.2 for tptz, which is somewhat larger than the value expected from a simple statistics (a factor of 4). This result indicates that an association ability of tptz-porphyrin associate toward the second tptz molecule tends to decrease, due to the π-π interaction with the first tptz molecule already associated with.

The cadmium(II) ion incorporation reaction and the apparent rate law are given by;

$$Cd^{II} + [H_2tpps(L)_x]^{4-} \xrightarrow{k_{obsd}} [Cd(tpps)]^{4-} + 2H^+ + xL \qquad (3)$$

$$\frac{d[Cd(tpps)^{4-}]}{dt} = k_{obsd}[Cd^{II}]\,[H_2tpps(L)_x{}^{4-}] \qquad (4)$$

where Cd^{II} and $[H_2tpps(L)_x]^{4-}$ indicates all the cadmium(II) species and all the porphyrin species in the solution except $[Cd(tpps)]^{4-}$, respectively.

The k_{obsd} values obtained are shown in Fig.4 as a function of the accelerator concentration. The maximum values of k_{obsd} with ligand L, $k^{max}_{obsd,L}$, are larger by a factor of 20 - 180 than the value of that in the absence of the accelerator ($k_{obsd,0}=1.11\times10^{2}$ $mol^{-1}dm^3s^{-1}$), where the predominant Cd(II) species are $[CdCl]^+$ (36%) and $[CdOH]^+$ (31%). The value of $k_{obsd,0}$ is in the same order of magnitude with the reported value of the formation rate constant of H_2tpps with Cd(II), 4.86×10^{2} $mol^{-1}dm^3s^{-1}$, I=0.1($NaNO_3$), at 25 °C, $pH\sim8$.[2] For py, bpy, and tpy, their concentration ranges where the maximum acceleration effect being observed (Fig.4), are in good agreement with the order of their formation constant

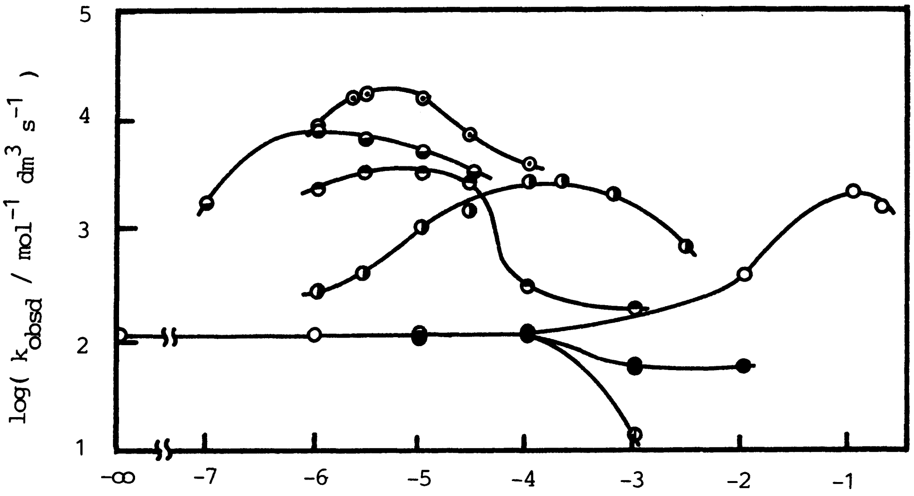

Fig.4. Log($k_{obsd}/mol^{-1}dm^3s^{-1}$) vs. log($[L]_T/mol\ dm^{-3}$) curves of Cd^{II}/ H_2tpps systems. $[Cd^{II}]_T=1.15\times10^{-6}$ mol dm^{-3}, $[H_2tpps]_T=1.69\times10^{-6}$ mol dm^{-3}, I=0.1(NaCl), t=20 °C, pH=10.0
○: py , ◐: bpy , ⊖: tpy , ⊖: phen , ◎: tptz , ⦶:4-bpy , ●: mbpy , ●: dbpy

of cadmium(II) complexes. On the other hand, the maximum values of $k^{max}_{obsd,L}$ (Fig.4) are in the order of py < bpy < tpy <tptz , which are coincide with the order of the stability of their association with H_2tpps (Fig.3).

The metal ion incorporation mechanism into porphyrin ring has been explained by combined use of the strain equilibrium model⁸⁾ and Eigen model,⁶⁾ that is, the over all rate constant is given by the product of k_d(exchange rate constant of water), K_{OS}(outersphere association constant), and K_D(strain equilibrium constant of porphine nuclear).⁸⁾ In the present system, possible contribution of pyridine derivatives on the acceleration may be attributed to the increase in the values of k_d and/or K_{OS}. In the case of k_d, the ratios of $k_{d,L}$(for $ML(H_2O)_x$ complex) / $k_{d,aq}$(for aqua complex) were reported to be 1 - 6 for bpy, tpy, and phen complexes of Ni^{2+}, Fe^{2+}, Mn^{2+}, and Co^{2+}.⁹⁾ On the other hand, the ratios of $k^{max}_{obsd,L}$ / $k_{obsd,0}$ are 21.3, 27.4, 33.1, 78.5, and 177 for py, bpy, phen, tpy, and tptz, respectively, which are remarkably larger than that of $k_{d,L}/k_{d,aq}$. Therefore, it can be concluded that the increase in k_{obsd} should largely be caused by the increase in the association ability of pyridine derivatives, which can clearly be seen in Fig.3.

On the other hand, mbpy and dbpy did not show any acceleration effects. In the case of 4-bpy, the acceleration effect was also not observed even though K_{as1} value of 4-bpy was $10^{3.13}$, which is larger than that of bpy, $10^{2.71}$. Moreover, it acted as an inhibitor at the higher concentration region (Fig.4), which indicates that the substance, which could form an associate but having poorer complexation ability, tends to interfere with the metal incorporation reaction by forming a road block associate.

Information of the association equilibria of aromatic ligands with porphyrin by $\pi-\pi$ interaction is not only essential for designing an accelerator for the metal incorporation into porphyrin, but also for developing a capturing method for the some aromatic mutagens, which has been proposed by using the complex of porphyrin-like compound, such as copper(II)-phthalocyanine complex.¹⁰⁾

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