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Kinetic Evidence for the Existence of a Heterodinuclear Reaction Intermediate in the Mercury(II) Catalyzed Formation of Metalloporphyrins

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A reaction intermediate of a heterodinuclear metalloporphyrin involving mercury(II) and zinc(II) was kinetically observed as a two-step reaction pathway and confirmed by both the rate equation and the change in absorption spectra in the reaction of dimercury(II)porphyrin with aquazinc(II).

The rate of metalloporphyrin formation is very slow compared with that of metal complex formation of open-chain ligands.[1,2] This slow reaction, however, is accelerated by the presence of mercury(II), cadmium(II) and lead(II) even at concentrations as low as 10^{-8} mol dm^{-3}.[3-6] Because of their large ionic radii, large metal ions such as mercury(II) can not fit well into the porphyrin nucleus, and are displaced from the porphyrin plane. The coordination of mercury(II) causes the porphyrin nucleus to deform favorably for the attack of other metal ion from the back side. This is the reason why the large metal ions catalyze the formation of the metalloporphyrins.[3,7-9] In this reaction, we have proposed the formation of a heterodinuclear metalloporphyrin as a reaction intermediate, in which both a large metal ion such as mercury(II) and a medium-size metal ion like zinc(II) are bound simultaneously to a porphyrin on the opposite sides.[3,9]

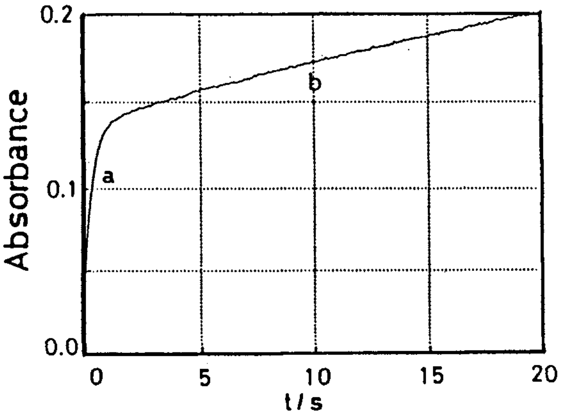

Fig. 1. A typical kinetic run showing a two-step reaction for the reaction of $Hg_2(tpps)^{2-}$ with zinc(II) at pH 5.92, 25 °C and $I = 0.1$ mol dm^{-3} ($NaNO_3$). $C_{Hg} = 1.00 \times 10^{-4}$, $C_{Zn} = 2.00 \times 10^{-3}$, $C_{H2(tpps)} = 4.04 \times 10^{-6}$. Unit of concentration is mol dm^{-3}.

The present paper describes an evidence for the formation of the heterodinuclear metalloporphyrin from a kinetic study of the reaction of zinc(II) with the dimercury(II) complex of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphine (H_2tpps^{4-}):

$$Hg_2(tpps)^{2-} + Zn^{2+} \longrightarrow Zn(tpps)^{4-} + 2Hg' \qquad (1)$$

where Hg' denotes the total mercury(II) ion not bound to the porphyrin. The molar-ratio method and the equilibrium studies show the formation of a 2:1 mercury(II) porphyrin complex, $Hg_2(tpps)^{2-}$, for the reaction of H_2tpps^{4-} with aquamercury(II) ion.

Kinetic studies were carried out in the pH range 4.5 - 6.5 (2-(N-morpholine)ethanesulfonic acid; MES buffer, 10^{-2} mol dm^{-3}) under various concentrations of mercury(II) nitrate (10^{-5} - 10^{-3} mol dm^{-3}) and zinc(II) nitrate (10^{-4} - 10^{-2} mol dm^{-3}), and at 25 °C and $I = 0.1$ mol dm^{-3} ($NaNO_3$). Since the reverse reaction of Eq. 1 is negligible in excess of zinc(II), the kinetics of the reaction was the pseudo-first order. The reaction was started by mixing a $Hg_2(tpps)^{2-}$ (4.0×10^{-6} mol dm^{-3}) solution containing a large excess of mercury(II) ion with a zinc(II) solution. The change in absorbance at 421 or 551 nm (λ_{max} of $Zn(tpps)^{4-}$ at Soret- or Q-band) was monitored as a function of time using a Otuka Denshi RA401 spectrophotometer. Biphasic kinetic behavior was observed as shown in Fig.1. The first-step reaction was completed in a few seconds, and was followed by the second-step with a half-life of about a few minutes.

The obseved first-order rate constants, k_0^f, for the firststep reaction were plotted against the concentrations of zinc(II) and mercury(II) in Fig. 2(a). The rate constants increase with zinc(II) concentration to reach a plateau, and decrease with the concentration of mercury(II).

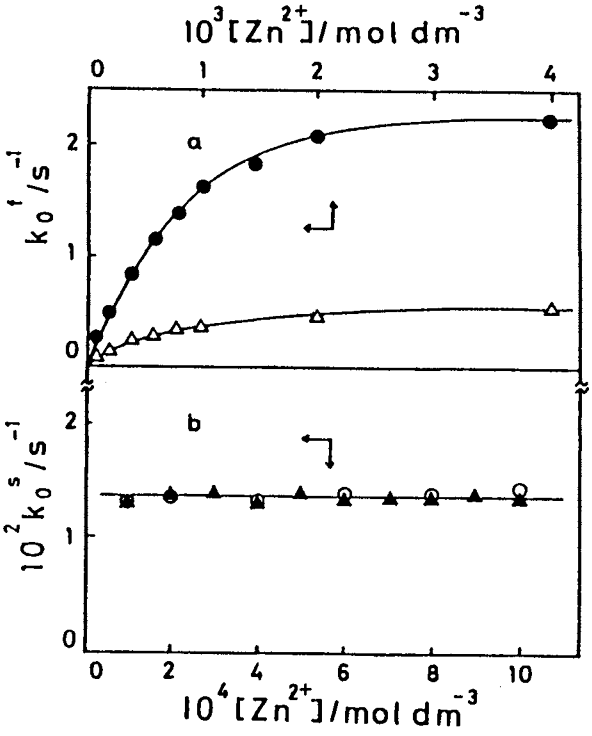

Fig. 2. Dependence of rate constants for the first-step (a) and the second step (b) reactions on the concentrations of mercury(II) and zinc(II) at 25 °C and $I = 0.1$ mol dm^{-3}($NaNO_3$). $C_{Hg} = 1.00 \times 10^{-4}$ (●) and 5.02×10^{-4} (△) for the first-step reaction, and $C_{Hg} = 5.02 \times 10^{-5}$ (▲) and 9.58×10^{-5} (○) for the second-step reaction. Unit of the concentration is mol dm^{-3}.

The observed first-order rate constants, k_0^{s}, for the second-step reaction were plotted against the concentrations of zinc(II) and mercury(II) in Fig. 2(b). The rate constants are independent of concentrations of mercury(II) and zinc(II) ions. The results indicate the unimolecular reaction, i.e. the self-dissociation of the reaction intermediate, $Hg(tpps)Zn^{2-}$. These kinetic results for the two-step reaction are consistent with the reaction mechanism shown in Eqs. 2-4.

$$Hg_2(tpps)^{2-} + OH^- \rightleftharpoons Hg(tpps)^{4-} + Hg(OH)^+;\ k_1,\ k_{-1} \qquad (2)$$
$$Hg(tpps)^{4-} + Zn^{2+} \longrightarrow Hg(tpps)Zn^{2-};\ k_2 \qquad (3)$$
$$Hg(tpps)Zn^{2-} \longrightarrow Zn(tpps)^{4-} + Hg(OH)^+;\ k_3 \qquad (4)$$

The reaction-paths 2 and 3 correspond to the first-step reaction, and the reaction-path 4 does to the second-step reaction. Since zinc(II) can not directly attack $Hg_2(tpps)^{2-}$, zinc(II) reacts with the 1:1 $Hg(tpps)^{4-}$ formed by the dissociation of one molecule of mercury(II) of $Hg_2(tpps)^{2-}$. Then the formation of the heterodinuclear metalloporphyrin of $Hg(tpps)Zn^{2-}$ in which zinc(II) and mercury(II) are bound simultaneously to the porphyrin is followed (Eq. 3). The heterodinuclear metalloporphyrin dissociates to form $Zn(tpps)^{4-}$ and $Hg(OH)^+$. The reaction mechanism shown in Eqs. 2-4 leads to the following rate equations for k_0^{f} and k_0^{s}:

$$k_0^{f} = (k_1k_2[Zn^{2+}][OH^-])(k_{-1}[Hg(OH)^+] + k_2[Zn^{2+}])^{-1} \qquad (5)$$
$$k_0^{s} = k_3 \qquad (6)$$

The rate constants of the first-step reaction were determined by plotting $(k_0^{f})^{-1}$ vs. $[Zn^{2+}]^{-1}$, and the values of $k_1 = 1.56 \times 10^{8}$ mol^{-1} dm^3 s^{-1} and $k_2/k_{-1} = 9.62 \times 10^{-2}$ were obtained. The rate constant of the second step reaction was found to be $k_0^{s} = k_3 = 9.2 \times 10^{-3}$ s^{-1}.

A series of absorption spectra were taken to confirm the reaction mechanism using a rapid-scan spectrophotometer. The typical spectral change is given in Fig. 3 for the first-step reaction. The change in absorption at 564 nm (Q-band of $Hg_2(tpps)^{2-}$) was smaller than that of of the second-step reaction. That indicates still binding of one molecule of mercury(II) in the reaction intermediate. Furthermore,

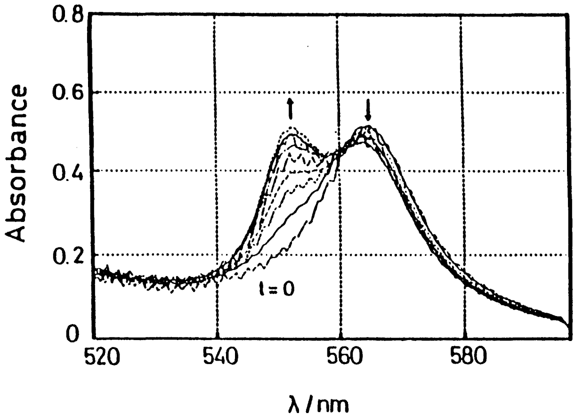

Fig. 3. The change in the absorption spectra during the reaction of $Hg_2(tpps)^{2-}$ with Zn^{2+} observed at a 200 ms interval for the first-step reaction.

the increase of the absorbance at 551 nm (Q-band of $Zn(tpps)^{4-}$) for the first-step reaction suggests the bonding of zinc(II) in the formation of the heterodinuclear metalloporphyrin. Similar behavior was also found at Soret band of $Zn(tpps)^{4-}$ (421 nm) and $Hg_2(tpps)^{2-}$ (434 nm). These results strongly support the formation of $Hg(tpps)Zn^{2-}$ at the first-step reaction.

The present kinetic data reveal the following features for the formation of heterodinuclear metalloporphyrin ($Hg(tpps)Zn^{2-}$). (1) The reaction of $Hg_2(tpps)^{2-}$ with Zn^{2+} proceeds through a two-step reaction. (2) For the first-step reaction, the rate constants reach a plateau at high concentration of zinc(II), and $Hg(tpps)Zn^{2-}$ is formed by the replacement of one mercury(II) of $Hg_2(tpps)^{2-}$ by zinc(II). (3) For the second-step reaction, the rate constants are independent of both zinc(II) and mercury(II) concentrations, that is, the reaction pathway is a unimolecular reaction.

Present paper, for the first time, clearly shows the formation of heterodinuclear metalloporphyrin based on the two-step reaction, and the rate equation for each reaction pathway and the spectral change at the first-step reaction. Since we also observed the similar two-step reaction for the reaction of $Hg_2(tpps)^{2-}$ with copper(II) or nickel(II), the formation of the heterodinuclear metalloporphyrins seems to be a general feature for the metalloporphyrin formation catalyzed by large metal ions such as mercury.

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