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Kinetics of Incorporation of Zinc(II) into Tetraphenylporphine in N,N-Dimethylformamide. I. Monohydroxo and Acetato Complexes

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The kinetics of incorporation of zinc(II) into *meso*-tetraphenylporphine in N,N-dimethylformamide (DMF), at 30°, were affected by the trace water in the solvent and by the presence of acetate ion (OAc^-). The reaction was one half order in $Zn(ClO_4)_2 \cdot 6H_2O$, whereas first order in $Zn(ClO_4)_2 \cdot 6DMF$. Addition of $HClO_4$ to the water containing system retarded the reaction rate and converted the kinetics to the first order with respect to total Zn(II). The main path for the reaction of $Zn(ClO_4)_2 \cdot 6H_2O$ was concluded to be that involving the monohydroxo species, $Zn(OH)^+$. Addition of acetate anion increased the rate, until at a ratio $[OAc^-]/[Zn]$ of unity the rate reached a maximum; an increase of the ratio past unity caused a rate decrease. The species, $Zn(OAc)^+$, is concluded to be more reactive than the fully solvated Zn(II) species and $Zn(OAc)_2$.

Keywords——kinetics of metal complexation; metalloporphyrin; tetraphenylporphine; Zn-tetraphenylporphine; hexakis(dimethylformamide)zinc perchlorate; zinc acetate; monohydroxo zinc ion; monoacetato zinc ion; N,N-dimethylformamide

Although a great many works have been concerned with the kinetics of metal ion incorporation into porphyrins,[2] little attention has been paid on the effect of the coordination sphere of the inserting metal ions. In the previous paper,[3] we reported an unusual effect of carboxylate anions on the rate of copper (II) incorporation into *meso*-tetraphenylporphine (H_2TPP) in N,N-dimethylformamide (DMF). First-order kinetics in total concentration of Cu perchlorate, one half-order dependence on that of Cu acetate, the acceleration of the reaction in an equimolar mixture of Cu perchlorate and Cu acetate and the effects of water content in the solvent led to the conclusion that the monopositive Cu(II) species with an acetate anion in the coordination sphere is more than twenty times as reactive as the fully solvated Cu(II) species and the dimeric copper acetate is unreactive.[3]

Kinetics of Zn(II) incorporation into H_2TPP under similar conditions gave results quite different from those of Cu(II). The present paper describes the results and the arguments as to the reactive metal species for the metalloporphyrin formation.

Experimental

Kinetic procedures were essentially the same as described in the previous paper.[3] Zinc perchlorate hexahydrate and zinc acetate were reagent grade chemicals. Hexakis(N,N-dimethylformamide)zinc perchlorate was prepared by the method of Lo and Swaddle.[4] *Anal.* Calcd. for $C_{18}H_{42}Cl_2N_6O_{14}Zn$: C, 30.76; H,6.02; N, 11.96. Found: C, 28.96; H, 6.39; N, 11.49.

Results

For the overall reaction

$$Zn^{2+} + H_2TPP \longrightarrow ZnTPP + 2H^+$$

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[2] P. Hambright, *Coord. Chem. Rev.*, **6**, 247 (1971); P. Hambright, "Porphyrins and Metalloporphyrins," ed. by K.M. Smith, Elsevier, Amsterdam, 1975, Chapter 6.

[3] S. Sugata and Y. Matsushima, *J. Inorg. Nucl. Chem.*, **39**, 729 (1977).

[4] S.T.D. Lo and T.W. Swaddle, *Inorg. Chem.*, **14**, 1878 (1975).

kinetic measurements were made at 30° under various conditions. The kinetics were followed under pseudo-first-order conditions with at least twenty-five fold excess of total Zn(II) to the initial concentrations of H_2TPP. The rate obtained by monitoring the absorptions due to H_2TPP and ZnTPP were identical. The pseudo-first-order rate constant, k_0, was independent of total H_2TPP over a four-fold range (2.0×10^{-5}—8.0×10^{-5} M). k_0 was dependent on Zn(II) salt employed and on solvent composition and was a function of total concentration of Zn(II) ($[Zn]_T$).

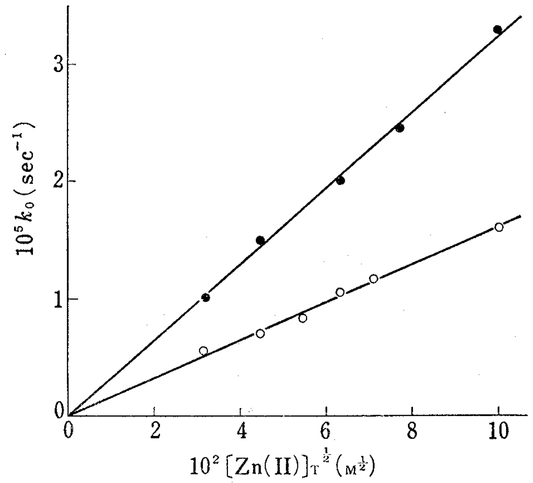

Fig. 1. The One Half Order Dependence of Zn Perchlorate-H_2TPP Reaction on Total Zn(II) Concentration

○ in DMF without the addition of water; ● in DMF containing 8% water.

Reaction of Zn Perchlorate

Figure 1 illustrates plots of k_0 against the square root of total Zn perchlorate, $Zn(ClO_4)_2\cdot6H_2O$. The reaction was one-half-order with respect to total Zn perchlorate in DMF. The kinetics of the reaction was unaffected by $KClO_4$. The rate law is

$$\text{rate} = k_1[H_2TPP][Zn]_T^{1/2}$$

The constant, k_1, calculated from the slopes are 1.63×10^{-4} sec^{-1} M$^{-1/2}$ in DMF without the addition of water and 3.25×10^{-4} sec^{-1} M$^{-1/2}$ in DMF containing 8% water.

The effect of the content of water in DMF on k_1 was examined. The rate constant, k_1, increased up to almost double with an increase of the water content until it was made 2%, whereas k_1 was independent of the water content, when it lies in the range 2.0—10.0%. Crystal water contained in Zn perchlorate is introduced into the solvent, hence DMF contained 0.01—0.1% water even without the addition of water. To see the effect of the trace water on the kinetics, hexakis (DMF) zinc perchlorate was used in completely dehydrated DMF. The data gave a good first order plot under the conditions.

$$\text{rate} = k_2[H_2TPP][Zn]_T$$

The second order rate constant, k_2, was 1.25×10^{-3} sec^{-1} M^{-1}.

The half order dependence on $[Zn]_T$ in DMF containing trace water suggests that Zn(II) species other than the fully solvated one plays an important role. The hydrolysis of the fully or partially hydrated Zn(II) shown in equation (1) may take place in the medium.

$$Zn(OH_2)^{2+} \rightleftarrows Zn(OH)^{+} + H^{+} \qquad (1)$$

The half order dependence becomes reasonable, if we assume that $Zn(OH)^+$ is very reactive. If it is the case, the addition of acid should result in a decrease in the rate, as the equilibrium (1) should be shifted to the left.

Figure 2 is a plot of the pseudo-first-order constant, k_0, against the concentration of added $HClO_4$. The rate was greatly retarded in the presence of 2×10^{-5} M $HClO_4$. The rate was hardly affected by the acid concentration in the range 2×10^{-4}—2×10^{-3} M $HClO_4$, where the spectra indicated that tetraphenylporphine was still mainly in the free base species (H_2TPP) and not in the protonated species (H_3TPP^+, H_4TPP^{2+}).

The first order dependence on zinc perchlorate hexahydrate was found in this region and the rate is expressed as

$$\text{rate} = k_3[H_2TPP][Zn]_T$$

The calculated second order rate constant, k_3, was 1.65×10^{-4} and 1.60×10^{-4} sec^{-1} M^{-1} in the presence of 1×10^{-3} M and 2×10^{-3} M $HClO_4$, respectively.

The addition of trace amount of alkali resulted in unreproducible kinetics or in the precipitation of Zn salt.

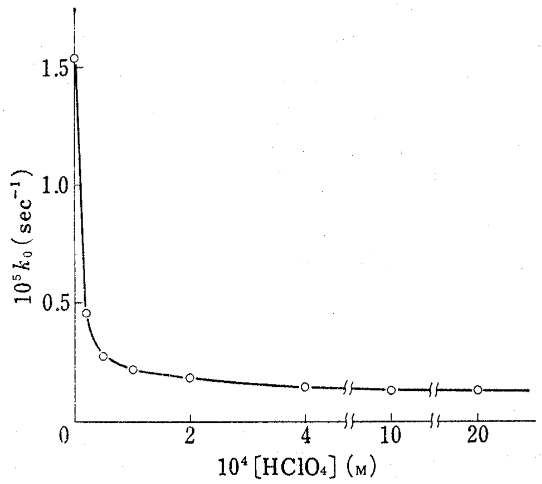

Fig. 2. Effect of the Concentration of $HClO_4$ on Zn Perchlorate-H_2TPP Reaction

[H_2TPP]$=4\times10^{-5}$ M; [$Zn(ClO_4)_2\cdot6H_2O$]$=8\times10^{-3}$ M.

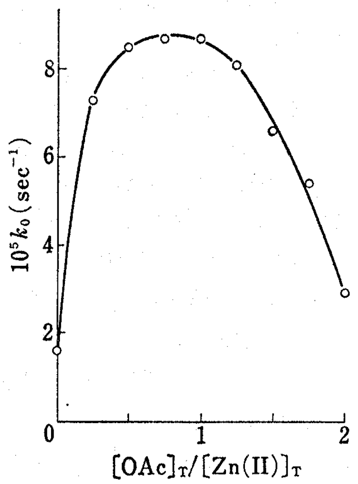

Fig. 3. Effect of Acetate Concentration on the Rate of the Zn-H_2TPP Reaction

[H_2TPP]$=4\times10^{-5}$ M; [Zn]$_T$$=1\times10^{-2}$ M.

Effect of Acetate Anion

When zinc acetate, $Zn(OAc)_2\cdot2H_2O$ was used, the pseudo-first-order rate constant, k_0, was proportional to the concentration of the zinc salt. The rate law is

$$\text{rate} = k_4[\text{H}_2\text{TPP}][\text{Zn}]_\text{T}$$

The second-order rate constant, k_4, was calculated as 2.95×10^{-3} sec^{-1} M^{-1}.

Solutions of zinc acetate and zinc perchlorate were mixed so as to contain 1×10^{-2} M Zn(II) and varying amounts of acetate. Figure 3 is the results of the kinetic studies carried out with these Zn(II) solutions. Under a constant [Zn]$_T$, maximal rate was attained in an equimolar mixture of Zn perchlorate and Zn acetate.

The bell-shaped k_0–[OAc^-]$_T$ profile similar to that obtained in the reaction of Cu(II) suggests that the species $Zn(OAc)^+$ is more reactive than the predominant species in Zn perchlorate and Zn acetate solutions.[3] k_0 was roughly proportional to [Zn]$_T$ in the presence of an equimolar amount of acetate. The second order rate constant measured under the conditions was approximately 7.9×10^{-3} sec^{-1} M^{-1}.

Discussion

For the Zn(II) incorporation into H_2TPP, kinetic dependence was different in anhydrous DMF and in DMF containing trace water. This fact suggests different reaction mechanisms between the media. In the pure DMF solution of $Zn(ClO_4)_2\cdot6$DMF, Zn(II) should be present as a monomeric species fully solvated with DMF. This should be the species that reacts with the porphyrin in the medium and the second order rate constant, k_2, is concerned with the reaction.

The half order dependence in the water containing medium may be brought up for further discussion. In the Zn(II) incorporation into mesoporphyrin dimethyl ester in pyridine containing 11% water, Khosropour and Hambright[5] found one-half-order dependence in zinc chloride. They ascribed the phenomenon to the formation of a tightly bound ion pair, $[ZnCl_3(py)]^-[Zn(py)_3Cl]^+$, in the medium, where py indicates pyridine. $[Zn(py)_3Cl]^+$ in equilibrium with the ion pair was thought to be a reactive species. Such an ion pair can not exist

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[5] R. Khosropour and P. Hambright, *J.C.S. Chem. Comm.*, **1972**, 13.

in the present reaction system, since no coordinating anion was added. Dimeric μ-hydroxo species might be present in a minute amount, but this species can not be a reactive one.

The predominant species in the present medium may be the partly or fully hydrated divalent ion, $Zn(OH_2)^{2+}$. This species, however, can not account for the kinetics. The half-order dependence may be best explained in terms of the formation of the monohydroxo species, $Zn(OH)^+$. As the extent of hydrolysis of the aquo ion, $Zn(OH_2)^{2+}$, may be small, the concentration of the monohydroxo species should be low and be expressed as $[Zn(OH)^+]=K^{1/2}[Zn(OH_2)^{2+}]^{1/2}$. K is the dissociation constant for the equilibrium (1); $K=[Zn(OH)^+][H^+]/[Zn(OH_2)^{2+}]$. It is assumed here that $[Zn(OH)^+]\simeq[H^+]$.

The pseudo-first-order rate constant, k_0, may be expressed as

$$\begin{aligned} k_0 &= k_a[Zn(OH_2)^{2+}] + k_b[Zn(OH)^+] \\ &= k_a[Zn(OH_2)^{2+}] + k_bK^{1/2}[Zn(OH_2)^{2+}]^{1/2} \\ &= k_bK^{1/2}[Zn(OH_2)^{2+}]^{1/2}(1+[Zn(OH_2)^{2+}]^{1/2}\cdot k_a/k_bK^{1/2}) \end{aligned}$$

k_a and k_b are the second order rate constants for $Zn(OH_2)^{2+}$ and $Zn(OH)^+$, respectively. The second-order rate constant determined in the presence of dilute $HClO_4$ may be regarded as k_a.

The experiment showed that k_0 was proportional to the square root of the total Zn concentration.

$$k_0 = k_1[Zn]_T^{1/2}$$

The comparison of the above equations and the assumption $[Zn]_T\simeq[Zn(OH_2)^{2+}]$ lead to $k_1=k_bK^{1/2}$. From the values $k_1=3.25\times10^{-4}$ $\text{sec}^{-1}\text{M}^{-1/2}$, $k_a=k_3=1.60\times10^{-4}$ $\text{sec}^{-1}\text{M}^{-1}$ and $[Zn]_T<1\times10^{-2}\,\text{M}$, the term $[Zn]_T^{1/2}\cdot k_a/k_bK^{1/2}$ is calculated to be less than 0.05 and, thus, is proved to be negligible.

For the estimation of k_b, the knowledge on K is indispensable. The exact value may be hard to obtain and has never described in the literature. On the assumption that the value is essentially the same as that reported for aqueous solution ($pK=9.25$),6) k_b is calculated to be 6.9 $\text{sec}^{-1}\text{M}^{-1}$. Although the estimation lacks sound basis, it may be inferred that the main path of the reaction in the water containing DMF involves the monohydroxo species, $Zn(OH)^+$.

Kinetic dependence on metal acetate in DMF solution was first order in Zn salt, whereas it was half order in Cu(II) salt.3) The result on Cu(II) acetate was interpreted in terms of the dimeric nature of this salt in DMF solution.7) Unlike Cu(II), Zn acetate must be present as the monomeric species to a greater extent. The main path in the reaction of Zn acetate may involve $Zn(OAc)_2$, as this species is predominant and is expected to be reactive.3) In mixtures of Zn perchlorate and Zn acetate, $Zn(OAc)^+$ may be present besides solvated Zn(II), the monohydroxo species, and $Zn(OAc)_2$. The concentrations of the solvated and hydroxo species should decrease with an increase of the ratio $[OAc^-]_T/[Zn]_T$. At around the ratio of unity, $[Zn(OAc)^+]$ should be largest under the constant $[Zn]_T$.

The bell-shaped relationship between k_0 and the ratio suggests that $Zn(OAc)^+$ is a reactive species. Since the equilibrium data in this solvent are unknown, the concentration of the species and, hence, the individual rate constants were unobtainable. But it can be assumed from the results that $Zn(OAc)^+$ is at least several times as reactive as $Zn(OAc)_2$.

It is concluded from the previous3) and present results that the monopositive species of divalent metal ions coordinated by an anion such as carboxylate and hydroxide is more reactive than solvated dipositive species and neutral species with two anionic ligands. The replacement of a solvent molecule in the coordination sphere of the divalent metals by a monovalent anion should reduce the charge repulsion between the porphyrin and the metal species and promote the metalloporphyrin formation.

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6) G. Schorsch, *Bull. Soc. Chim. Fr.*, **1965**, 988.
7) S. Sugata and Y. Matsushima, *Yakugaku Zasshi*, **96**, 1356 (1976).