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Kinetics of Incorporation of Manganese(II), Cobalt(II), and Nickel(II) into Tetraphenylporphine in Dimethylformamide. Effect of the Acetate Anion

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The kinetics of incorporation of Mn(II), Co(II), and Ni(II) into *meso*-tetraphenylporphine (H_2TPP) in N,N-dimethylformamide (DMF) at 50° were dependent on the metal salts employed. The reaction was first order in total concentration of Mn(II) acetate, but half order in Co(II) and Ni(II) acetate. In DMF solutions of the metal acetate, an equilibrium exists between the dimer and monomer; $M_2(OAc)_4 \rightleftarrows 2M(OAc)_2$. The half-order dependence can be explained as being due to predissociation of the dimer followed by reaction of a monomer with H_2TPP. The kinetic results show that Co(II) and Ni(II) acetate exist to a greater extent as the dimer, while Mn(II) acetate exists predominantly as the monomer. The reaction with perchlorate salts was first order in total concentration of Mn(II) and half order in that of Co(II) or Ni(II). The reaction with mixtures of perchlorate and acetate was most rapid at an $[OAc]_T/[M(II)]_T$ ratio of 1.0—1.5 at constant $[M(II)]_T$, where the subscript T indicates total concentrations. It can be concluded that the species $M(OAc)^+$ is more reactive than the fully solvated metal species or the monomeric metal acetate species, $M(OAc)_2$, and their reactivities follow the order Cu(II)>Zn(II)>Co(II)>Ni(II)~Mn(II).

Keywords——kinetics of metal complexation; metalloporphyrin; tetraphenylporphine; N,N-dimethylformamide; dimer-monomer equilibrium of metal acetate; Mn(II) acetate; Ni(II) acetate; Co(II) acetate; monoacetato metal(II) ion

We have been studying the kinetics of incorporation of metal ions into *meso*-tetraphenylporphine (H_2TPP) in N,N-dimethylformamide (DMF).[2-4] The kinetics were dependent on the metal salts employed. The copper(II) incorporation reaction was first order in total concentration of Cu(II) perchlorate, but half order in that of Cu(II) acetate.[2]

In contrast, the zinc(II) incorporation reaction was half order in total concentration of its perchlorate and first order in that of its acetate salt.

The half-order dependence on Cu(II) acetate was explained on the basis of its dimeric nature, and that on Zn(II) perchlorate was ascribed to the formation of the reactive monohydroxo species.

The apparent contradiction between the kinetic dependences with Cu(II) and Zn(II) salts prompted us to investigate other bivalent transition metals. The present paper describes the kinetics of incorporation of manganese(II), cobalt(II), and nickel(II) ions into H_2TPP in DMF at 50°. The kinetic properties are correlated with the metal species present under the conditions used.

Experimental

meso-Tetraphenylporphine was prepared as reported elsewhere.[5] DMF was dried over solid KOH and distilled prior to use. Inorganic chemicals were of reagent grade.

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Kinetic procedures were essentially the same as those described previously.[2-4] Since the reactions were slow with the metal ions studied here, the kinetics were measured at 50°. The kinetics were followed under pseudo-first-order conditions with an excess of total metal ions relative to the initial concentration of H_2TPP, which was 4×10^{-5} M in most runs. Total concentrations of the metal ions were in at least twenty-five fold, one hundred and twenty-five fold, and two hundred and fifty fold excess over that of H_2TPP for Co(II), Ni(II), and Mn(II), respectively.

The spectral changes accompanying the reaction showed distinct isosbestic points, indicating the absence of any long-lived intermediate species detectable under these conditions. The reactions were monitored in terms of the absorptions due to H_2TPP (514, 646 nm). Monitoring the absorptions of the metallotetraphenylporphine complexes (MTPP) gave identical kinetic results.

Concentrated DMF solutions of Mn(II) salts gradually became colored on standing at 50° for several hours. This phenomenon interfered with the estimation of H_2TPP or MTPP concentration by direct measurements of the reaction mixture. In such cases, an aliquot was drawn from the reaction mixture and H_2TPP and MTPP were precipitated by the addition of water. The precipitate, after washing with water, was extracted with $CHCl_3$. The concentration of H_2TPP was measured from the absorption spectra of the $CHCl_3$ solutions.

The first-order plots were linear over three half-lives and the pseudo-first-order rate constants, k_0, were calculated from the slopes. k_0 was independent of the total concentration of H_2TPP over the range of $2.0—8.0\times10^{-5}$ M.

Results

For the overall reaction

$$M^{2+} + H_2TPP \longrightarrow MTPP + 2H^+$$

the kinetics were measured using solutions of metal perchlorates, metal acetates, and mixtures of the two. With a constant H_2TPP concentration, the pseudo-first-order rate constant, k_0, was dependent on the metal salt employed and was a function of its total concentration.

When $Mn(ClO_4)_2\cdot6H_2O$ or $Mn(OAc)_2\cdot4H_2O$ was used, k_0 was proportional to the total concentration of the Mn(II) salt. The second-order rate constant, k_{II}, was calculated from the slope of a plot based on the equation

$$k_0 = k_{II}[Mn(II)]_T$$

where the subscript T indicates the total concentration of the substance in brackets.

k_0 was not proportional to the total concentration of $Co(OAc)_2\cdot4H_2O$, $Ni(OAc)_2\cdot4H_2O$ or $Ni(ClO_4)_2\cdot6H_2O$. Plots of k_0 against the square root of the salt concentrations were linear. Thus, the half-order rate constant, $k_{1/2}$, was calculated from the slope of a plot based on the following equation.

$$k_0 = k_{1/2}[M(II)]_T^{1/2}$$

Table I. Rate Data for the Reaction of H_2TPP and M(II) Salts

Salt	Reaction order	Rate constant	Temperature	Reference[a]
Cu (II) perchlorate	1	1.03×10^{-1} M^{-1} sec^{-1}	30°	2
Cu (II) acetate	1/2	4.19×10^{-4} M$^{-1/2}$ sec^{-1}	30°	2
Zn (II) perchlorate	1/2	1.63×10^{-4} M$^{-1/2}$ sec^{-1}	30°	3
Zn (II) acetate	1	2.95×10^{-3} M^{-1} sec^{-1}	30°	3
Mn (II) perchlorate	1	4.39×10^{-5} M^{-1} sec^{-1}	50°	p
Mn (II) acetate	1	8.25×10^{-5} M^{-1} sec^{-1}	50°	p
Co (II) perchlorate	1/2	2.43×10^{-5} M$^{-1/2}$ sec^{-1}	50°	p
Co (II) acetate	1/2	3.36×10^{-5} M$^{-1/2}$ sec^{-1}	50°	p
Ni (II) perchlorate	1/2	1.22×10^{-5} M$^{-1/2}$ sec^{-1}	50°	p
Ni (II) acetate	1/2	8.70×10^{-6} M$^{-1/2}$ sec^{-1}	50°	p

a) The numbers 2 and 3 indicate references 2 and 3 in the text, respectively, and p denotes the present work.

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The values of the rate constants thus calculated are listed in Table I. The values for Cu(II) and Zn(II) are included for comparison.

The kinetics of the reaction were not affected by the presence of less than 0.1 M $KClO_4$ or acetic acid. The use of the hydrate salt introduced less than 1% water into the solvent. An additional 1% water did not significantly affect the kinetic results. Kinetic runs were not carried out in completely dehydrated DMF.

Since Co(II) perchlorate of the desired purity was unobtainable, a solution of Co(II) acetate and two equimolar amounts of $HClO_4$ was used. The solution should contain the same Co(II) species as a solution of Co(II) perchlorate. A similar experiment with Ni(II) acetate gave a result identical with that obtained for the perchlorate. The Co(II) incorporation reaction was half order with respect to Co(II) under these conditions. The calculated rate constant is included in Table I. Since a set of clear isosbestic points was observed during the reaction, the formation of Co(III)-TPP complex[6] must be negligible under these experimental conditions.

A series of DMF solutions containing definite concentrations of metal ions and various concentrations of acetate anions was made up by mixing appropriate amounts of solutions of metal perchlorate and acetate. The kinetics of MTPP formation were measured with these solutions. Plots of k_o against $[OAc]_T/[M(II)]_T$ are shown in Fig. 1. Bell-shaped k_0-ratio profiles were obtained for the three metal ions, as in the cases of Cu(II) and Zn(II).[2,3] In the Mn(II) and Ni(II) reactions, the maximal rates were attained in an equimolar mixture of perchlorate and acetate. The Co(II) reaction was most rapid at a $[OAc]_T/[Co(II)]_T$ ratio of about 1.5.

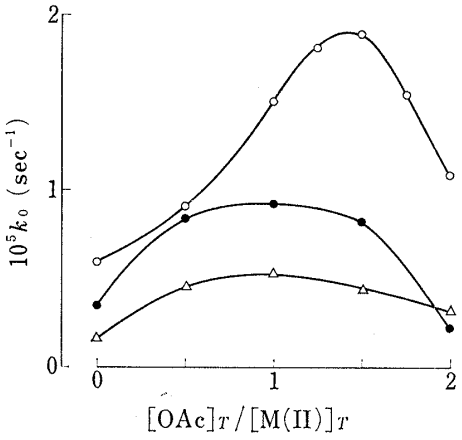

Fig. 1. Effect of Acetate Concentration on the H_2TPP–M(II) Reaction

$[H_2TPP]_T=4\times10^{-5}$ M.
—△—, $[Mn(II)]_T=4\times10^{-2}$ M;
—○—, $[Co(II)]_T=2\times10^{-3}$ M;
—●—, $[Ni(II)]_T=8\times10^{-2}$ M.

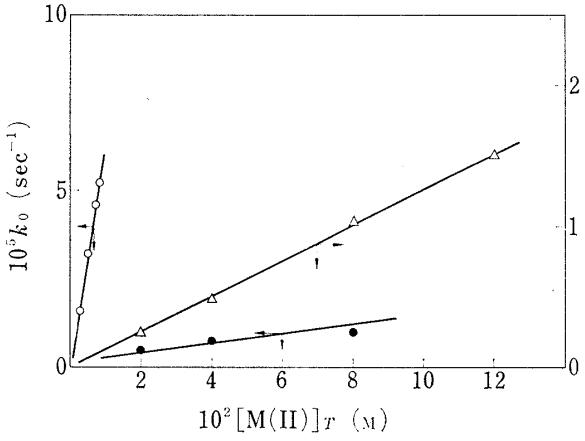

Fig. 2. The Pseudo-first-order Rate Constants of the H_2TPP–M(II) Reaction in the Presence of Equimolar Acetate Anion and M(II)

$[H_2TPP]_T=4\times10^{-5}$ M.
—○—, Co(II); —●—, Ni(II); —△—, Mn(II).

At a ratio of unity, the kinetics were measured at various values of $[M(II)]_T$. As shown in Fig. 2, k_0 was roughly proportional to $[M(II)]_T$ in the presence of an equimolar amount of acetate anions. The second order rate constants measured under these conditions were 1.35×10^{-4}, 7.32×10^{-3}, and 1.46×10^{-4} M^{-1} sec^{-1} for Mn(II), Co(II), and Ni(II), respectively.

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

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Discussion

Copper acetate exists in the crystalline phase as a dimeric entity.[7] This dimeric structure has been shown to persist in nonaqueous solvents and quantitative investigations on the monomer-dimer equilibrium in acetic acid[8] and DMF[9] have been reported.

$$2M(OAc)_2 \rightleftharpoons M_2(OAc)_4$$

The half-order dependence of the H_2TPP–Cu(II) acetate reaction could be explained on the assumption that the monomeric species reacts with H_2TPP in a rate determining step.[2,10] The rate constant of the reaction involving $Cu(OAc)_2$ species was calculated based on the equilibrium data in DMF.[2,9] The kinetic results for Co(II) and Ni(II) acetate in the present investigation suggest a similar mechanism of incorporation. Dimer species similar to that of Cu(II) acetate are known to exist for Co(II) and Ni(II).[11] However, no quantitative study on the dimer-monomer equilibrium in DMF has yet appeared. The assumptions that the monomer species, $M(OAc)_2$, is in rapid equilibrium with the predominant dimer species, $M_2(OAc)_4$, and that the former species is reactive in the incorporation reaction can well account for the half-order dependence. Calculation of the individual rate constants is impossible due to the lack of equilibrium data in DMF.

The reaction was first order with respect to the total concentration of Mn(II) acetate. This result indicates that the monomeric species, $Mn(OAc)_2$, is predominant and reactive. It can be concluded from the previous[2,3] and present studies that Cu(II), Co(II), and Ni(II) acetate all exist to a greater extent as the dimer, while Mn(II) and Zn(II) acetate exist predominantly as the monomer in DMF.

Brisbin and Richards[6] studied the kinetics of incorporation of metal ions into protoporphyrin dimethylester in acetic acid. The reaction was half order in Co(II) and Ni(II) and close to half order in Cu(II). With Mn(II) and Zn(II), the reaction orders were reported to be between one-half and one. The apparent discrepancy may be due to the nature of the media. It seems likely that acetic acid shifts the equilibrium towards the formation of the dimer.

In DMF solutions of $Mn(ClO_4)_2$, Mn(II) must be present as a monomeric fully solvated species. This species should be involved in the reaction with H_2TPP. The first-order kinetics with this salt can be understood on this basis. The results show that this species is half as reactive as the acetate-coordinated species, $Mn(OAc)_2$.

The half-order dependence on perchlorate with Co(II) and Ni(II) cannot be readily understood in terms of a mechanism involving the monomeric fully solvated metal species. It is unlikely that this species is not predominant under the conditions used. The formation of a species much more reactive than the fully solvated one, such as monohydroxo species, $M(OH)^+$, can account for the kinetics.[3] However, detailed kinetic studies are not required.

The bell-shaped relationships shown in Fig. 1 suggest that the species coordinated by an acetate anion, $M(OAc)^+$, is reactive in the incorporation reaction. Though quantitative rate data for individual species are unobtainable, $M(OAc)^+$ may be more reactive than $M(OAc)_2$ and the fully solvated species.

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Similar bell-shaped relationships were observed for Cu(II) and Zn(II).[2,3] The reactivity of $M(OAc)^+$ for incorporation into H_2TPP follows the order Cu(II)>Zn(II)>Co(II)>Ni(II)-~Mn(II) among the bivalent metals studied.

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