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Kinetics of Interaction of Zn(II) with Hematoporphyrin IX in Basic Aqueous Solution

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The formation of metalloporphyrins has been mainly studied in organic or mixed solvents [1], due to the poor solubility of most porphyrins in water. The use of these solvents presents several problems related to the nature of the reacting species of the metal ion.

The present report deals with the reaction between Zn(II) and hematoporphyrin IX, in basic aqueous solution ($0.05 \leqslant [NaOH] \leqslant 0.25$ *M*), where this porphyrin is fairly soluble. As in our earlier work on the reaction of Cu(II) with the same porphyrin in acetic acid–water solvent [3], the main purpose of this work concerns the nature of the reacting species of the metal ion.

Results and Discussion

The kinetics were followed spectrophotometrically by monitoring the increase of absorbance due to the appearance of the metalloporphyrin band at 407 nm. In all experiments the Zn(II) concentration was kept in great excess with respect to the porphyrin; under these conditions first order kinetics were observed over three half-lives. The reaction was first order in Zn(II) over a more than 100 fold concentration range, as shown by the plot of k_{obs} *vs.* Zn(II) in Figure 1. These results lead to the usual rate law:

$$\text{Rate} = k_{obs}[HPH_2] = k[Zn(II)][HPH_2]$$

where $k_{obs} = k[Zn(II)]$.

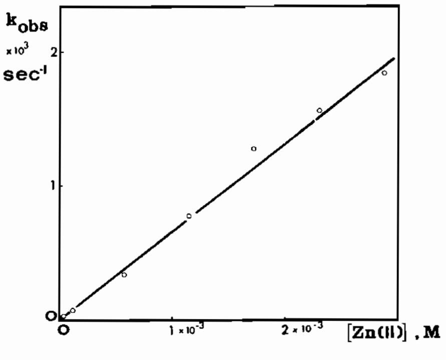

Figure 1. Influence of Zn(II) on k_{obs}. (T = 25 °C; $[HPH_2]$ = 5.0×10^{-6} *M*; [NaOH] = 0.25 *M*; ionic strength = 0.3 *M*).

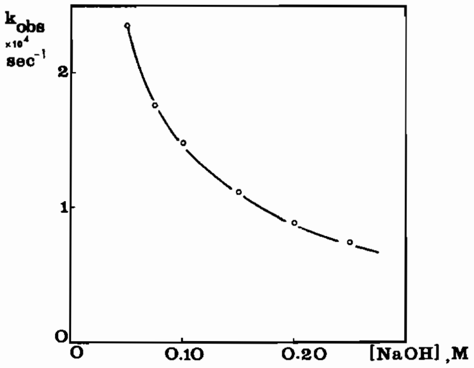

Figure 2. Influence of hydroxyl ions on k_{obs}. (T = 25 °C; $[HPH_2]$ = 5.0×10^{-6} *M*; [Zn(II)] = 1.15×10^{-4} *M*; ionic strength = 0.3 *M*; the open circles represent experimental data; the curve is calculated).

The influence of hydroxyl ions has been investigated. The results show (Figure 2) that there is a marked decrease in k_{obs}, at constant Zn(II) concentration, with hydroxyl ion concentration. This effect cannot be attributed to any change in acid–base or monomer–dimer equilibria of the porphyrin, since the characteristic four band visible spectrum of the free base [2] is observed over the whole pH range studied.

This effect is however well explained taking into account the changes in the concentration of different reacting species of Zn(II).

The influence of ligands on the rate of metallation of porphyrins has been observed previously, and a rate-law of the type: Rate = $k_1[M][P] + k_2[M][P][L]$ has been obtained. The second term represents the catalytic effect of ligand L [4–6]. This catalysis is thought to be of the general base type and applies to both nitrogen bases [4, 5] and acetate ions [6].

Another hypothesis consists to take into account the change in coordination of the metal ion. This was done in the case of the reaction of Cu(II) and hematoporphyrin IX by Margerum *et al.* in basic aqueous solution [7] and in our earlier work using acetic acid–water solvent [3].

It is known that in basic medium $Zn(OH)_2$, $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ are the species in solution related by the following equilibria:

$$Zn(OH)_2 + OH^- \overset{K_1}{\rightleftharpoons} Zn(OH)_3^- \qquad (2)$$

$$Zn(OH)_3^- + OH^- \overset{K_2}{\rightleftharpoons} Zn(OH)_4^{2-} \qquad (3)$$

The kinetics observed can thus be explained by postulating three pathways for the reaction:

$$Zn(OH)_2 + HPH_2 \xrightarrow{k_1} Zn\cdot HP + 2H_2O \qquad (4)$$

$$Zn(OH)_3^- + HPH_2 \xrightarrow{k_2} Zn\cdot HP + 2H_2O + OH^- (5)$$

$$Zn(OH)_4^{2-} + HPH_2 \xrightarrow{k_3} Zn\cdot HO + 2H_2O + 2OH^- \qquad (6)$$

This yields a multiterm expression for k_{obs}:

$$k_{obs} = k_1[Zn(OH)_2] + k_2[Zn(OH)_3^-] + k_3[Zn(OH)_4^{2-}] \qquad (7)$$

The individual rate constants of equation 7 have been resolved by means of a multiple linear regression program, using literature values of the equilibrium constants of equations 2 and 3 ($K_1 = 160\,M^{-1}$ and $K_2 = 16\,M^{-1}$ [8]).

The following rate constants have been obtained at 25 °C: $k_1 = 10.3\,M^{-1}\,s^{-1}$; $k_2 = 2.5\,M^{-1}\,s^{-1}$; $k_3 = 0.125\,M^{-1}\,s^{-1}$. The agreement of equation 7 with the experimental results is very good as shown by the calculated curve in Figure 2.

The results show that the reactivity of Zn(II) decreases with the number of OH^- coordinated, *i.e.* $k_1 > k_2 > k_3$. This is similar to the reaction of Cu(II) with hematoporphyrin IX and several macrocyclic polyamines in basic media, where $k_{Cu(OH)_3^-} > k_{Cu(OH)_4^{2-}}$ [7].

It is quite significant that the rate constant of metallation of $Zn(OH)_3^-$ ($k_2 = 2.5\,M^{-1}\,s^{-1}$) is about one order of magnitude greater than the corresponding rate constant obtained under identical conditions for $Cu(OH)_3^-$ ($k = 0.2\,M^{-1}\,s^{-1}$ [7]), whereas for the aquo-ions the contrary is always observed, *i.e.* $k_{Cu^{2+}} \gg k_{Zn^{2+}}$ [9, 10]. This reversal of reactivity shows the extreme importance of the coordination of the metal ion in the metallation of porphyrins. A meaningful interpretation of this effect is not yet possible, due to the complexity of the metallation, implying the breaking and the forming of several bonds.

The decrease of the rate constants with increasing hydroxyl ion concentration gives another valuable information: it rules out any mechanism involving a deprotonation of the pyrrole nitrogens preceding the rate-determining step even at high pH, because the increase in pH would highly favor this mechanism.

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