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Kinetics of Copper Incorporation into a *Meso*-substituted Trimethylanilinium Water Soluble Porphyrin

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The most detailed studies of the pathways for metal ion incorporation into porphyrin molecules to form metalloporphyrins come from work in aqueous solution using the monomeric and water soluble porphyrin [1–3] TMPyP(4), tetra(4-N-methylpyridyl)porphyrin. This tetrapositive porphyrin, with its pyridyl groups conjugated with the ring showed a strong dependence of its protonation constants and metal ion rate behavior on ionic strength. We wish to report the kinetics of copper incorporation into tetra-(4-(N,N′,N″-trimethylanilinium)porphyrin, H_2-TAP, a new water soluble tetrapositive [4] porphyrin of higher basicity and presumably less charge delocalization than found in TMPyP(4).

Experimental

The iodide salt of H_2-TAP was synthesized by literature methods [4], and converted to its perchlorate salt by precipitation from aqueous solution with sodium perchlorate. At an ionic strength of 0.1 ($NaNO_3$), pH = 7, H_2-TAP followed Beer's Law over a hundred fold dilution (10^{-4} to 10^{-6} *M*). As reported earlier [4], protonation titrations of H_2-TAP with HNO_3 followed in the visible region showed a lack of pH independent isosbestic points, indicating the existence of a monocation, H_3-TAP$^+$ porphyrin form. The kinetics were studied under pseudo-first order conditions with an excess of (H^+) and (Cu^{2+}) to total porphyrin at $\mu = 0.1(HNO_3/NaNO_3)$, 25 °C), in unbuffered solutions. The incorporation kinetics were followed at the Cu–TAP 541 nm peak.

Results and Discussion

At constant pH and ionic strength, copper porphyrin formation was first order in porphyrin and first order in copper (1.5 to 8 × 10^{-3} *M*). From pH 4.9 to 2.7, the rate decreased with a decrease in pH. The following mechanism is assumed:

$$H_4\text{-}TAP^{2+} = H_3\text{-}TAP^+ + H^+ \qquad K_4 \quad (1)$$

$$H_3\text{-}TAP^+ = H_2\text{-}TAP + H^+ \qquad K_3 \quad (2)$$

$$H_2\text{-}TAP + Cu^{2+} \longrightarrow Cu\text{–}TAP + 2H^+ \qquad k \quad (3)$$

The diacid (H_4-TAP^{2+}) and monocation porphyrins are in equilibrium with the free base, and only the free base (H_2-TAP) form reacts with Cu^{2+}. The observed rate constant, k_{obs} is thus:

$$k_{obs} = k(Cu^{2+})_0/(1 + (H^+)_0/K_3 + (H^+)_0^2/K_3K_4) \quad (4)$$

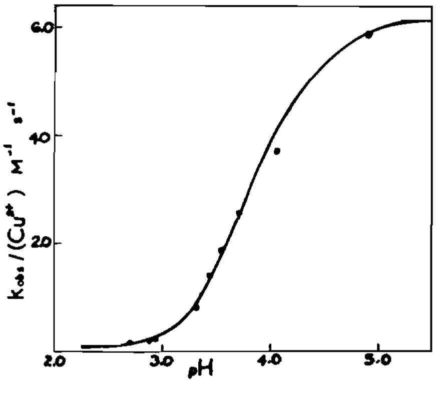

Fig. 1. Specific rate–pH profile of the reaction of Cu^{2+} with H_2-TAP. Ionic strength = 0.1($NaNO_3$), T = 25 °C. Dots are experimental points and the solid line is drawn based on eq. 4 and the rate and equilibrium constants in the text.

It was found that k = 6.2 M^{-1} s^{-1}, $pK_3 = 3.64$ and $pK_4 = 3.62$. A plot of the specific rate constant *vs.* pH is shown in Fig. 1. In qualitative agreement with previous workers [4], pK_3 and pK_4 are close to one another for H_2-TAP, while [1] TMPyP(4) shows $pK_3 = 1.7$ and $pK_4 = 0.7$ at $\mu = 0.2$. More basic porphyrins tend to incorporate metal ions faster [3, 5], and indeed H_2-TAP reacts about thirty times more rapidly with copper than does TMPyP(4) (k = 0.23 M^{-1} s^{-1} at $\mu = 0.1$) [1]. Both porphyrins incorporate metal ions only through the free base form [6].

At pH = 2.3, titration of tetra(4-pyridyl)porphyrin with $NaNO_3$ produced color changes (red to green) and spectral behavior that were initially interpreted [7] as the formation of Sitting-Atop complexes, 1:1 adducts between cations and free base porphyrins (M–PH_2). With the same porphyrin, other workers [8] have postulated by mass law considerations, the formation of similar (M–PH_2) and (M–PH_3) species. Due to the insolubility of this porphyrin at high pH, both studies were done in pH regions near pK_3 and pK_4. Although similar spectral changes (which resemble porphyrin acid–base titrations) with ionic strength were noted with TMPyP(4) at pH 2.3, at

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pH 7, well out of the range of the pK values, such changes of spectra with ionic strength are not noted [1]. The indication was that pK_3 and pK_4 increase at constant pH with an increase in ionic strength, and thus the postulated Sitting-Atop complexes were perhaps the di- and monocation porphyrins found at constant pH due to the sensitivity of such positive porphyrin protonation equilibria to ionic medium effects. The present H_2-TAP behaves in the same way. At pH 3.5, with no added electrolyte, H_2-TAP shows the characteristic free base spectrum. Addition of $NaNO_3$ leads to the mono- and dication spectra, as the ionic strength increases. Such changes are not found at pH = 7.

The rate of Cu–TAP formation at constant pH increases with an increase in ionic strength. No linear dependence of the specific rate constants on ionic strength, or Log k *vs.* $\mu^{1/2}$ could be fitted. At constant pH, an increase in μ will decrease the rate due to the decrease in concentration of the free base H_2-TAP reactant (as pK_3 and pK_4 increase). This is apparently offset by the rate increase expected with ionic strength due to the reaction of two positively charged species. The interplay of both factors complicates the rate, ionic strength interpretations.

At $\mu = 1.0(NaNO_3)$, H_2-TAP does not follow Beer's Law at pH 7, and the rate of Cu–TAP formation is not first order in copper at lower pH values. The indication is that dimerization or polymerization occurs at high ionic strength, as found for other rather basic porphyrin types [9].

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