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F. González-Vílchez
R. A. Vilaplana
Robert F. Pasternack
Swarthmore College, rpaster1@swarthmore.edu

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Evidence for an Unusual Kinetic Phenomenon in the Metallation of Porphyrins

Francisco González-Vilchez, a Rosario A. Vilaplana a and Robert F. Pasternack b

a Departamento de Química Inorgánica, Facultad de Química, Universidad, 41071 Sevilla, Spain
b Chemistry Department, Swarthmore College, Swarthmore, PA 19081, USA

Reaction of copper(ii) with water soluble porphyrins (H₂porph) in the presence of ethylenediamine shows an unusual and so far unreported kinetic phenomenon that can be explained in terms of supramolecular assembly formation apparently involving all solute species as confirmed via light scattering and conductivity measurements.

In this contribution we present an anomalous and so far unreported kinetic phenomenon that occurs when copper(ii)-ethylenediamine complexes react with water soluble synthetic porphyrins (H₂porph). Other reports of porphyrin metallation reactions in aqueous solutions, generally conducted at low pH to avoid hydrolysis of metal ions and precipitation of hydroxy species, are consistent with a rate law of the form \( R = k \ [M^{2+}][H₂porph] \). Pseudo-first-order conditions are usually maintained so that \( R = k_0[H₂porph] + k \ [M^{2+}] \). In contrast we observe in our studies at neutral pH in the presence of ethylenediamine(en), a discontinuity in the \( k_e vs [Cu^{II}] \) profile. The experimental, first-order rate constants show a very high-order dependence on \([Cu^{II}]\) over a limited concentration (Fig. 1) reaching a maximum value, \( k_{emaX} \), at some critical copper(ii) concentration, \( [M_{ic}] \). Values of \( k_{emaX} \) and \([M_{ic}] \), depend on solution conditions as described below but the profile shown in Fig. 1 persists for a variety of electrolytes, buffers and porphyrins. At concentrations of \( Cu^{II} \) beyond \([M_{ic}] \), the rate constant \( k_e \) decreases but more gradually than its rise.

The \( Cu^{II} \)-ethylenediamine system was selected because (i) the rate of copper(ii) insertion into porphyrins is in a convenient range for study, (ii) the free ligand shows no reactivity with the water soluble porphyrins investigated here and (iii) under the conditions of the experiment \( \mu = 0.15 \) mol dm⁻³, \( T = 298 \) K, \( [en] = 5 \ [Cu^{II}] \), one copper species, \( Cu(en)₂^{2+} \), predominates over the entire concentration range considered. We calculated the concentration profiles of the various minor copper(ii)-containing species \([H₂porph] \), \( Cu(OH)⁺ \), \( Cu(en)₂^{2+} \) and \( Cu(en)₂^{2+} \) and found that none of them resembles that of the reactivity profile shown in Fig. 1.

As a specific example of this behaviour we considered the reaction of \( Cu^{II} \)-en with the tetracationic porphyrin tetrakis(4-N-methylpyridyl)porphyrin, \( H₂tmpyp \). The experiments shown in Fig. 1(b) were conducted at \( \phiH \ 7.0 \), \( [collidine] = 2.0 \times 10^{-2} \) mol dm⁻³, \( \mu = 0.15 \) mol dm⁻³, \( T = 298 \) K, \( [H₂tmpyp] = 3.5 \times 10^{-5} \) mol dm⁻³. As shown in Fig. 1 and Table 1, the rate constant \( k_e \) is nearly zero at low values of \( [Cu^{II}] \) but at \( [Cu^{II}] > 7.5 \times 10^{-4} \) mol dm⁻³, \( k_e \) suddenly rises to a value of \( 9.9 \times 10^{-3} \) s⁻¹. Further increase in \( [Cu^{II}] \) leads to a decrease in \( k_e \) until at \( [Cu^{II}] = 1.25 \times 10^{-3} \) mol dm⁻³, \( k_e \) is once again near zero.

The other porphyrins investigated are the tetracationic tetrakis(N,N,N-trimethyl-4-anilinium)porphyrin, \( H₂tap \), and the tetracationic tetrakis(4-sulphophenyl)porphyrin \( H₂tpps \). The maximum rate constants for metallation, \( k_{emaX} \), increase in the sequence \( H₂tmpyp < H₂tap < H₂tpps \), the same order as porphyrin basicity. For the last of these compounds, stopped-flow methods must be employed for kinetic measurements. Charge and basicity of the porphyrin therefore play a role in determining the value of the rate constant. The concentration of the porphyrin also in part determines the critical parameters in the process. Increasing \( H₂tmpyp \) con-
only effect exerted by changing ionic strength is a shifting of $[M_c]$, the nature of the electrolyte has a profound influence on $k_{e,max}$ and even the breadth of the profile.

To probe the nature of the species in solution giving rise to these unusual kinetic effects, we have performed light scattering and conductance measurements on these systems. We find that at Cu$^{II}$ concentrations both above and below $[M_c]$, the amount of light scattered is small but at $[Cu^{II}] = [M_c]$, the scattered light intensity increases nearly sixfold (Table 2). Solutions giving rise to rapid kinetics (i.e., at $[Cu^{II}] = [M_c]$) have much lower conductivities than solutions on either side of these critical concentrations (Table 2). These results provide evidence for the formation of some type of composite in solution at the critical conditions. Based upon the evidence, we propose that the unusual kinetic effect found here is attributable to the existence of molecular assemblies of a supramolecular nature formed by association of the metal complex, porphyrin and other solute species and held together by intermolecular forces having microscopic organization and macroscopic characteristics.9

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References

Table 2 Results of light scattering and conductivity measurements$^a$

<table>
<thead>
<tr>
<th>$[Cu^{II}]$ $\times 10^{-3}$ mol dm$^{-3}$</th>
<th>Scattered light intensity (arb. units)</th>
<th>Conductivity/Ω$^{-1}$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>2.2</td>
<td>8.3</td>
</tr>
<tr>
<td>0.75</td>
<td>11.8</td>
<td>2.3</td>
</tr>
<tr>
<td>1.25</td>
<td>1.3</td>
<td>7.9</td>
</tr>
</tbody>
</table>

$^a [H_2tmpyp] = 3.50 \times 10^{-5}$ mol dm$^{-3}$; pH = 7.0; $\mu = 0.15$ mol dm$^{-3}$; $T = 298$ K; collidine $= 2.0 \times 10^{-2}$ mol dm$^{-3}$. In all experiments $[en]_0 = 3 [Cu^{II}]$.