Evidence For An Unusual Kinetic Phenomenon In The Metallation Of Porphyrins

F. González-Vílchez

R. A. Vilaplana

Robert F. Pasternack
Swarthmore College, rpaster1@swarthmore.edu

Follow this and additional works at: https://works.swarthmore.edu/fac-chemistry

Part of the Inorganic Chemistry Commons

Recommended Citation
https://works.swarthmore.edu/fac-chemistry/117

This work is brought to you for free and open access by . It has been accepted for inclusion in Chemistry & Biochemistry Faculty Works by an authorized administrator of Works. For more information, please contact myworks@swarthmore.edu.
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, 1-6 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

\[ R = k \ [M^2+] \ [H_2porph] \]

Pseudo-first-order conditions are usually maintained so that \( R = k_c [H_2porph] \) with \( k_c = k \ [M^2+] \). In contrast we observe in our studies at neutral pH in the presence of ethylenediamine(en), a discontinuity in the \( k_c \) vs \([CuII]\) profile. The experimental, first-order rate constants show a very high-order dependence on \([CuII]\) over a limited concentration range (Fig. 1) reaching a maximum value, \( k_{max} \), at some critical copper(II) concentration, \([M]\). Values of \( k_{max} \) 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 \([CuII]\) beyond \([M]\), the rate constant \( k_c \) decreases but more gradually than its rise.

The CuII-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 (i.e., pH 7.0; \( \mu = 0.15 \ \text{mol dm}^{-3}; T = 298 \ \text{K}; \) \( [\text{en}]_o = 3 \ [\text{CuII}]_o \)), one copper species, Cu(en)22+, predominates over the entire concentration range considered. § We calculated the concentration profiles of the various minor copper(II)-containing species \([\text{Cu}^2+; \text{Cu(OH)}^+; \text{Cu(en)}^2+; \text{Cu(en)}^2++]\) and found that none of them resembles that of the reactivity profile shown in Fig. 1.

As a specific sample of this behaviour we considered the reaction of CuII–en with the tetracationic porphyrin tetrakis(4-n-methylpyridyl)porphyrin, H2tmpyp. The experiments shown in Fig. 1(b) were conducted at pH 7.0, \([\text{collidine}] = 2.0 \times 10^{-2} \ \text{mol dm}^{-3}; \mu = 0.15 \ \text{mol dm}^{-3}; T = 298 \ \text{K}; \) \([H_2tmpyp] = 3.5 \times 10^{-5} \ \text{mol dm}^{-3}\). As shown in Fig. 1 and Table 1, the rate constant \( k_c \) is nearly zero at low values of \([CuII]\) but at \([CuII] = 7.5 \times 10^{-4} \ \text{mol dm}^{-3} \), \( k_c \) suddenly rises to a value of \( 9.9 \times 10^{-3} \ \text{s}^{-1} \). Further increase in \([CuII]\) leads to a decrease in \( k_c \) until at \([CuII] = 1.25 \times 10^{-2} \ \text{mol dm}^{-3} \), \( k_c \) is once again near zero.

The other porphyrins investigated are the tetracationic tetrakis[N,N,N-trimethyl-4-anilinium]porphyrin, H2tap, and the tetraanionic tetrakis(4-sulphophenyl)porphyrin H2tpps. The maximum rate constants for metallation, \( k_{max} \), increase in the sequence \( H_2tmpyp < H_2tap < H_2tpps \), the same order as for 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 \( H_2tmpyp \) con-

† H2porph is used to designate the free base form of the porphyrin. Charges are neglected for the sake of convenience.

‡ The slow kinetics were followed on either a Nicolet 9420 UV–VIS or a Varian 2200 recording spectrophotometer which has thermostated cell compartments. Faster reactions were observed using a Nortec stopped-flow system. The reactions were run at constant wavelength and most of the kinetic experiments were conducted under conditions such that \([CuII] \geq 10 \ [H_2porph] \); these experiments provided good first-order type kinetic profiles. However, even when the \([CuII] \geq 10 \ [H_2porph] \), such first-order profiles were obtained. Values of \( k_c \) were found to be independent of whether the disappearance of the free base–porphyrin band (518 nm for H2tmpyp) or the appearance of the metalloporphyrin peak (548 nm for CuH2tmpyp) were monitored. The existence of an isosbestic point in the visible region (λ 535 nm) implies that the porphyrin reactant and metalloporphyrin product are the only chromophores present in non-negligible concentration other than Cu(en)22+ which absorbs much further into the red of the spectrum.

§ The formation of the reactant complex Cu(en)22+ was achieved by maintaining an en-Cu ratio of 3.0 at pH 7.0. The components were added in the following sequence to avoid precipitation: CuII, en, NaNO3, milli-Q water and collidine. A stock solution (0.1 mol dm−3) of 2,4,6-collidine from Sigma Chem. Co., was prepared and used as buffer. The final pH was adjusted to 7.0 using NaOH or HNO3 if needed.

![Fig. 1](image-url)
only effect exerted by changing ionic strength is a shifting of $[M]_o$, the nature of the electrolyte has a profound influence on $k_{max}$ 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 $[Cu]_2$ concentrations both above and below $[M]_o$, the amount of light scattered is small but at $[Cu]_2 = [M]_o$, the scattered light intensity increases nearly sixfold (Table 2). Solutions giving rise to rapid kinetics (i.e., at $[Cu]_2 = [M]_o$) 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 forces8 having microscopic organization and macroscopic characteristics.9

The authors thank the NATO Postdoctoral Program and the Education Ministry of Spain for grants awarded to R. A. V. We are also indebted to the MEC Fulbright Program for a Fellowship to F. G.-V. who thanks the University of Seville for sabbatical leave. We gratefully acknowledge support of this research from the National Science Foundation (CHEM-8915264) and the Monsanto Corporation.

---

**Table 2** Results of light scattering and conductivity measurements

<table>
<thead>
<tr>
<th>$[Cu^{2+}]_o \times 10^{15}$ mol dm$^{-3}$</th>
<th>Scattered light (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 $[en]_0 = 3 [Cu^{2+}]_o$.

---

**References**


