Evidence for an Unusual Kinetic Phenomenon in the Metallation of Porphyrins

Francisco González-Vílchez,[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 (H_2porph) 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 (H_2porph).† 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 $R = k_e$[H_2porph] with $k_e = k$ [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 constant‡ shows a very high-order dependence on [Cu^{II}] over a limited concentration (Fig. 1) reaching a maximum value, k_e^{max} at some critical copper(II) concentration, [M]$_c$. Values of k_e^{max} and [M]$_c$ 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^{2+} beyond [M]$_c$, 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[7] and (*iii*) under the conditions of the experiment {*i.e.*, pH 7.0; $\mu = 0.15$ mol dm^{-3}; $T = 298$ K; (en)$_0 = 3$ [Cu^{II}]$_0$}, 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 [*i.e.*, Cu^{2+}, Cu(OH)$^+$, Cu(en)$^{2+}$, Cu(en)$_3^{2+}$] 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 Cu^{II}–en with the tetracationic porphyrin tetrakis (4-*N*-methylpyridyl)porphyrin, H_2tmpyp. The experiments

shown in Fig. 1(*b*) were conducted at pH 7.0, [collidine] = 2.0 × 10^{-2} mol dm^{-3}, $\mu = 0.15$ mol dm^{-3}, $T = 298$ K, [H_2tmpyp] = 3.5 × 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 × 10^{-4} mol dm^{-3}, k_e suddenly rises to a value of 9.9 × 10^{-3} s^{-1}. Further increase in [Cu^{II}] leads to a decrease in k_e until at [Cu^{II}] = 1.25 × 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, H_2tap, and the tetraanionic tetrakis(4-sulphophenyl)porphyrin H_2tpps. The maximum rate constants for metallation, k_e^{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-
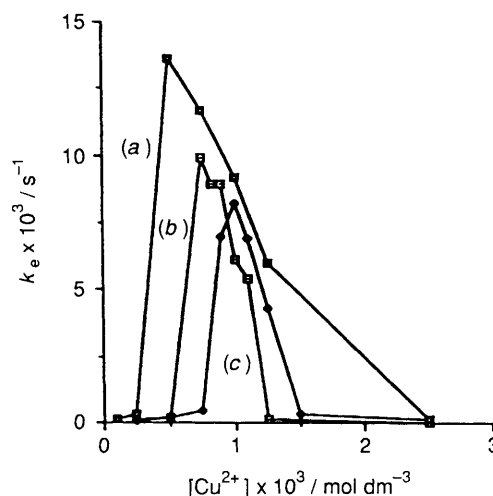
Fig. 1 Metal concentration dependence of k_e at different concentrations of H_2tmpyp: (*a*): [H_2tmpyp] = 4.10 × 10^{-5} mol dm^{-3}; (*b*): [H_2tmpyp] = 3.50 × 10^{-5} mol dm^{-3}; (*c*): [H_2tmpyp] = 1.70 × 10^{-5} mol dm^{-3}

Table 1 Variation of the experimental rate constant with metal concentration in the reaction Cu(en)$_2^{2+}$ + H_2tmpyp

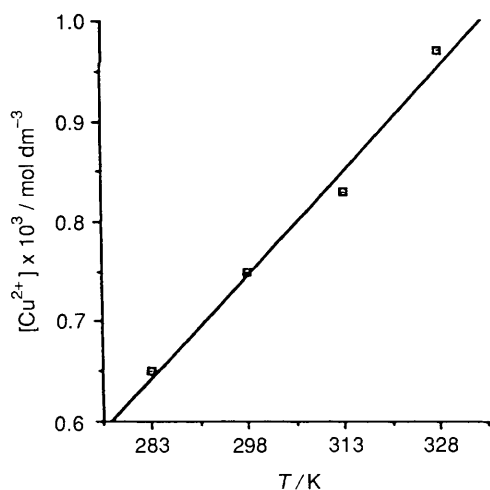| [Cu^{2+}]$_0$ × 10^3/ mol dm^{-3}	k_e × 10^3/s^{-1}
0.25	0.1
0.50	0.2
0.75	9.9
0.83	8.9
0.90	8.9
1.00	6.2
1.10	5.4
1.25	0.1
2.50	negligible

Fig. 2 Variation of the critical copper(II) concentration, $[M]_c$, with temperature

Table 2 Results of light scattering and conductivity measurements[a]

$[Cu^{2+}]_0 \times 10^3/$ mol dm^{-3}	Scattered light (arb. units)	Conductivity/ Ω^{-1} cm^{-1}
0.25	2.2	8.3
0.75	11.8	2.3
1.25	1.3	7.9

[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 $[en]_0 = 3 [Cu^{2+}]_0$.

centration, for example, leads to a larger k_e^{max} and lower values of $[M]_c$ (Fig. 1) but in all cases, the anomalous kinetic profile remains.

The reaction of Cu^{II}–ethylenediamine with H_2tmpyp was studied over a 55 °C temperature range. A kinetic profile of the type shown in Fig. 1 was found throughout and the value of k_e^{max} varied by less than 9.0%. However, $[M]_c$ increases linearly with temperature as shown in Fig. 2. The nature of the buffer (collidine tris or HEPES) influences both k_e^{max} and $[M]_c$ but not the general kinetic profile. Finally, although the

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 $[Cu^{II}] \approx [M]_c$, the scattered light intensity increases nearly sixfold (Table 2). Solutions giving rise to rapid kinetics (*i.e.*, at $[Cu^{II}] \approx [M]_c$) 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[8] having microscopic organization and macroscopic characteristics.[9]

References

1 P. Hambright, *Coord. Chem. Rev.*, 1971, **6**, 247; P. Hambright, *Ann. N.Y. Acad. Sci.*, 1973, **206**, 443; P. Hambright and P. B. Chock, *J. Am. Chem. Soc.*, 1974, **96**, 3123.
2 H. Baker, P. Hambright and L. Wagner, *J. Am. Chem. Soc.*, 1973, **95**, 5942.
3 R. F. Pasternack, G. C. Vogel, C. A. Skowronek, R. K. Harris and J. G. Miller, *Inorg. Chem.*, 1981, **20**, 3763.
4 D. K. Lavallee, *Coord. Chem. Rev.*, 1985, **61**, 55.
5 M. Tabata and M. Tanaka, *Inorg. Chem.*, 1988, **27**, 203.
6 F. R. Longo, E. M. Brown, D. J. Quimby, A. D. Adler and M. Meot-Ner, *Ann. N.Y. Acad. Sci.*, 1973, **206**, 420.
7 A. J. McHugh, M. Gouterman and Ch. Weiss, Jr., *Theor. Chim. Acta*, 1972, **24**, 346.
8 J.-M. Lehn, *Angew. Chem., Int. Ed. Eng.*, 1988, **27**, 89.
9 J. H. Fendler, *Membrane Mimetic Chemistry*, Wiley, N.Y., 1982.