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Acid Solvolysis Reaction Kinetics of Copper and Nickel Porphyrins: A Rate-Stability Index Correlation

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The majority of the kinetic studies of acid catalyzed solvolysis reactions of water soluble metalloporphyrins (eqn. 1) have involved

$$M{-}P + 4H^+ \rightarrow M^{2+} + H_4{-}P^{2+} \qquad (1)$$

Zn^{2+} [1–3], Mn^{2+} [4, 5] and Cd^{2+} [6] porphyrins, for which the metals are removed with rates readily measured below 1 *M* H^+ concentration. Kinetic work with Zn^{2+} [7] and Mg^{2+} [8] complexes of water-insoluble porphyrins have been run in alcohol media. Acid demetallation of W(V)–porphyrin in water [9] is preceded by oxidation to W(VI), and Fe(III)–porphyrins in acetic acid [10] can be solvolyzed by prior reduction to Fe(II)–P forms. Higher acidities are required with more inert metalloporphyrins, and for Cu–etioporphyrin in acetic acid/H_2SO_4, the unusual rate law $R = k(Cu{-}P)^2(h_0)^4$ was followed [11]. Reynolds and co-workers [12, 13] measured solvolysis kinetics for Fe(III)–tetra(4-sulfonatophenyl)porphyrin in acid–alcohol–water media, where, in H_2SO_4, alcohol was necessary to prevent porphyrin precipitation and possibly monomerize Fe–$TPPS_4$.

We report a study of the kinetics of acid solvolysis reactions of Cu^{2+} and Ni^{2+} complexes of tetra(4-N,N,N-trimethylanilinium)porphyrin, M–TPA [14, 15], and qualitative results for tetra(N-methyl-4-pyridyl)porphyrin M–TMPYP [16] in hydrochloric acid. A literature review [17] indicates that contradictory claims have been advanced as to whether Cu–P or Ni–P is the more stable in acid. Our work answers this question for the porphyrins considered, gives relative solvolysis rates, and develops an interesting correlation between solvolysis rates and the stability index of metal ions.

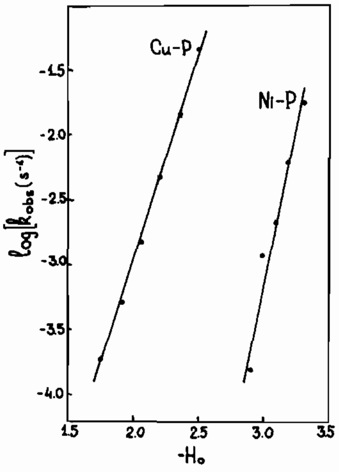

Fig. 1. Plot of the log of the observed first order acid solvolysis rate constants of copper and nickel porphyrins *vs.* the Hammett constant $-H_0$ for reactions in hydrochloric acid at 25 °C.

Experimental

The porphyrins and metalloporphyrins were prepared by standard procedures [3, 16] and changed by ion-exchange methods into their chloride forms for kinetic studies. The acid concentrations were determined by both titrations and density measurements. The kinetics, followed spectrophotometrically, were run at 25 °C.

Results and Discussion

Acid solvolysis reactions of metalloporphyrins generally increase in rate with an increase in free-base porphyrin basicity towards protons [7]. H_2–TMPYP is less basic (pK_3 = 1.5 [18]) than H_2–TAP (pK_3 = 4.1 (14, 19]), and the solvolysis of Cu–TAP in 11 *M* HCl is over within the time of mixing. Under the same conditions, the disappearance of Cu–TMPYP is first order in porphyrin, with $t_{1/2}$ = 60 minutes. Qualitatively, Ni–TMPYP reacts much more slowly than does Cu–TMPYP.

The kinetics of solvolysis of Cu–TAP were followed in the visible region (700–500 nm) with Cu–TAP concentrations *ca.* 4 × 10^{-5} *M*. The reactions were neither first nor second order in porphyrin, nor were isosbestic points found during the course of the reaction. In this connection, Paquette and Zador [20] found in a study of the kinetics of incorporation of Cu^{2+} into an ethylenediammine substituted protoporphyrin, that as Cu–P formed, it inter-

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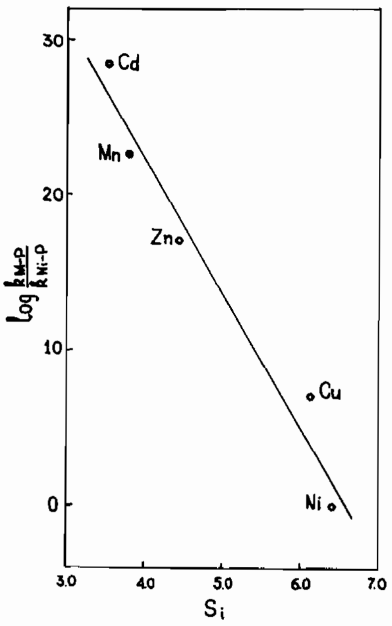

Fig. 2. Plot of the log of the acid solvolysis rates of various metalloporphyrins relative to the nickel porphyrin calculated at 1.0 *M* H^+ concentration, *vs.* the stability index of a metal ion, S_i.

acted with the reactant H_2–P to produce a species of lower reactivity. Attempts to analyze our high concentration Cu–TAP data with a two-term rate law, one involving Cu–TAP, and the second with a (Cu–TAP)(H_4–TAP) term were not particularly encouraging over a wide range of porphyrin concentrations.

When monitoring the Cu–TAP reactions in the Soret at *ca.* 10^{-7} *M* Cu–TAP levels, however, the reactions were cleanly first order in porphyrin over three half-lives, and the isosbestic points found indicated that Cu–TAP and H_4–TAP^{2+} were the major absorbing species. Figure 1 shows the linear plots of the logarithms of the first order solvolysis rate constants, k_{obs}, *vs.* $-H_o$, the Hammett acidity function [21]. The rate law is thus of the form Rate = $k(M{-}P)(h_o)^n$. The value of n = 3.1 and k = 1.7 × 10^{-10} was found for Cu–TAP between 5 and 7 *M* HCl. With Ni–TAP, from 8 to 9 *M* HCl, least-squares methods gave n = 4.7 and k = 1.5 × 10^{-17}.

The acid solvolysis rates of Zn–TMPYP [1, 16] and Fe(III)$TPPS_4$ [13] depended strongly on the nature of the anion associated with the acid, whereas no anion effect was noted in the demetallation reaction [3] of Zn–TAP. Our attempts to study the Cu–TAP reactions in various acids were unproductive, in that $HClO_4$ and HI immediately precipitated from solution this positively charged porphyrin. Above 5 *M* HNO_3, the Cu–TAP is apparently rapidly oxidized producing bleached solutions.

For the range of acid strengths investigated, the large 'n' values for both Cu and Ni–TAP (also found with Cu–Etio [11]) could indicate a multi-proton stepwise solvolysis process, in agreement with Zn^{2+} [7], Fe^{2+} [10] and Mn^{2+} [4] porphyrin studies done under moderate acidities, where values of n from 1 to 3 have been found*. There is general agreement that strongly basic Cu and Ni porphyrins are Class II metalloporphyrins (completely demetallated by 100% H_2SO_4 [17]), and the present results give the stability order Ni–P > Cu–P for both M–TAP and M–TMPYP.

A consideration of published metalloporphyrin solvolysis kinetic data [3, 4, 6] with the rates extrapolated to 1 *M* H^+ concentration, gives the acid kinetic stability order $Ni^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+} > Cd^{2+}$ in the ratios $1 : 10^7 : 10^{17} : 10^{22.6} : 10^{28.5}$ for M–TAP. Buchler [17] has developed a 'stability index' parameter S_i for metal ions in porphyrins. $S_i = 100\ Z(E_N)/r_i$, where Z is the charge of the ion, E_N the Pauling electronegativity, and r_i the ionic radius (in pm units). S_i values correlate well with the strength of acid needed to fully or partially demetallate metalloporphyrins under stated conditions [17]. Figure 2 shows a plot of the log of the relative acid solvolysis rate constants, log (k_{M-P}/k_{Ni-P}) of the M–TAP species *vs.* the stability index S_i. A linear relationship of the form

$$\mathrm{Log}\,(k_{M-P}/k_{Ni-P}) = 56.9 - 8.62\,(S_i) \tag{2}$$

is obtained. While this correlation may be fortuitous considering the variety of reaction conditions and rate laws observed for each metal ion, it nevertheless provides impetus for further study.

Acknowledgements

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*Unknown H_{4+} functions would be more appropriate than H_o values, which are for reactions between acids and neutral bases.

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