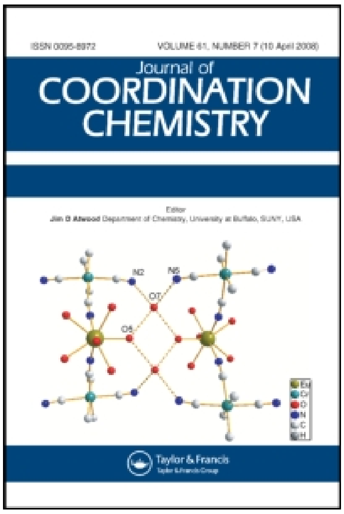

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

ANION CATALYZED ACID SOLVOLYSIS OF INDIUM(III) PORPHYRINS

Peter Hambright[a]
[a] Department of Chemistry, Howard University, Washington, DC, USA

To cite this Article Hambright, Peter(1983) 'ANION CATALYZED ACID SOLVOLYSIS OF INDIUM(III) PORPHYRINS', Journal of Coordination Chemistry, 12: 4, 297 — 301

To link to this Article: DOI: 10.1080/00958978308073861

URL: http://dx.doi.org/10.1080/00958978308073861

J. Coord. Chem., 1983, Vol. 12, pp. 297–302
0095-8972/83/1204-0297 $18.50/0

ANION CATALYZED ACID SOLVOLYSIS OF INDIUM(III) PORPHYRINS

PETER HAMBRIGHT

Department of Chemistry, Howard University, Washington, DC 20059, USA

(Received August 2, 1981)

Solvolysis of several water soluble indium(III) porphyrins is catalyzed by both protons and anions. For indium(III)–*tetrakis*–(4-sulfonato–phenyl)porphyrin, the anion effect is in the order Cl^-, Br^-, $SCN^- \gg ClO_4^-$, BF_4^-, HSO_4^-. In $HClO_4/NaCl$, Rate = $k(In^{3+}{-}P)\,(Cl^-)^2\,(h_0)^{2.2}$.

INTRODUCTION

The kinetics of the acid catalyzed solvolysis of Cu^{2+}, Co^{2+} and Ni^{2+} coordinated to positively charged[1,2] *tetrakis*-(4-*N, N, N*-trimethylanilinium)porphyrin (M^{2+}–TAP) in HCl required acid concentrations above the 1 M level for convenient rates, and could be described by the rate law Rate = k (M^{2+}–TAP) $(h_0)^n$, where the Hammett acidity function H_0 (= $-\log h_0$) measures the tendency of the solution to transfer a proton to a neutral base.[3] The "n" values were found to be above 2, and while suggesting multiple protonation of the metalloporphyrin,[4] the possible role of anions in the overall solvolysis process was obscure for several reasons. Thus the positively charged porphyrins studied were insoluble or rapidly oxidized in high concentrations of mineral acids containing weakly coordinating anions. In addition, the large dependence of rate upon $(h_0)^n$ and the small changes in total acid concentration needed to produce large changes in h_0 made it experimentally difficult to vary the HX concentration by amounts sufficient to separate the effect of h_0 from that of X^-.

To study such anion effects, we have used indium(III)–*tetrakis*–(4-sulfonatophenyl)–porphyrin, In^{3+}–$TPPS_4$, which is found to be stable for hours in $HClO_4$ below 6 M acid levels at 25°. The addition of low concentrations of NaX salts to such solutions leads to rapid acid solvolysis, and provides an opportunity to probe h_0 and X^- independently. The positively charged In^{3+}–TAP and indium(III)–*tetrakis*–(*N*-Methyl-4-pyridyl)porphyrin, In^{3+}–TMPYP, both slow to be solvolyzed in $HClO_4$, were compared with In^{3+}–$TPPS_4$ in HCl media.

EXPERIMENTAL

The synthesis of water soluble indium(III) porphyrins has not been described. Briefly, H_2–TMPYP and an excess of $InCl_3.nH_2O$ were refluxed overnight in HCl at pH 2. The solution was cooled, filtered, and the porphyrin precipitated with $NaClO_4$, washed with water and air-dried. For In^{3+}–TMPYP.$2H_2O$: Calcd. for $In(C_{44}H_{26}N_8).5ClO_4.2H_2O$: C, 39.89; H, 3.04; N, 8.46%. Found: C, 39.86; H, 2.98; N, 8.32%. In 10^{-2} M HCl, λ_{max} 424 mm (ϵ = 3.9 x 10^5 M^{-1} cm^{-1}), 518 nm (3.7 x 10^3), 558 nm (2.3 x 10^4) and 597 nm (4.7 x 10^3). In^{3+}–TAP was prepared in a similar fashion: 416 nm (5.4 x 10^5), 514 nm (3.3 x 10^3), 553 nm (2.0 x 10^4) and 609 nm (7.5 x 10^3). For In^{3+}–$TPPS_4$, the Na salt of H_2–$TPPS_4$ was refluxed overnight with an excess of $InCl_3$.n H_2O at pH *ca.* 7, and no reaction occurred. The addition of 10 cm^3 of acetic acid to 100 cm^3 of the hot solution led to the immediate formation of the purple In^{3+}–$TPPS_4$, from the green free base/di-acid mixture. The solution was cooled, filtered, and passed through a cation column in the Na^+ form at pH 7, and evaporated. The solid was extracted into methanol, concentrated, and the porphyrin precipitated with acetone. [λ_{max} at 417 nm (7.0×10^5), 516 nm (3.6×10^3), 554 nm (2.3×10^4) and 607 nm (1.1×10^4)]. The spectra of all three porphyrins were similar[5] to that of indium(III)-tetraphenylporphyrin chloride, In(TPP)Cl.

The kinetics were followed spectrophotometrically at 25° in the Soret region at porphyrin concentrations of *ca.* 10^{-6} M. Isosbestic points were found at 700, 575, 495, 435 and 390 nm as In^{3+}–TMPYP transformed into the di-acid H_4–TMPYP in 4 M HCl, and other porphyrins showed similar isosbestic behavior in the Soret region.

RESULTS AND DISCUSSION

The kinetics of the acid solvolysis reactions of the three indium porphyrins were first-order with respect to porphyrin concentration over three half-lives in all of the solvents.

$$In\text{–}P^+ + 4\,HX \longrightarrow In^{3+} + 4\,X^- + H_4\text{–}P^{2+} \qquad (1)$$

The reactions were studied as a function of HCl concentration (and HNO_3 for In^{3+}–$TPPS_4$) and plots of the log of the observed rate constant k_o *vs* $-H_o$ were linear. The rate law in the neat solvents were thus of the form Rate = k (In^{3+}–P) $(h_o)^n$, and the results are shown in Table I.

In 5.3 M $HClO_4$, the concentration of In^{3+}–$TPPS_4$ decreased by less than 1% after 5.5 hours, indicating that a first order solvolysis half-life would be greater than 380 hours. Making this solution 0.1 M in $NaClO_4$, NaCN, Na_2SO_4 or $NaBF_4$ was without effect, while the addition of 0.1 M NaCl led to a solvolysis half-time of 160 seconds. Figure 1 (top), shows that in 5.3 M $HClO_4$, the reaction was second order in added chloride from 5×10^{-2} to 4×10^{-1} M, and $k_o/(Cl^-)^2 = (4.3 \pm 0.3) \times 10^{-1}\ M^{-2}\ s^{-1}$. The same was found for added NaSCN, where $k_o/(SCN^-)^2 = (3.7 \pm 0.4) \times 10^{-1}\ M^{-2}\ s^{-1}$. With NaBr, while the reaction was neither first nor second order in bromide, the rates were of a similar order of magnitude. In a solution of 0.29 M NaCl, the In^{3+}–$TPPS_4$ reactions were studied as a function of $HClO_4$ concentration. The linear plot of $\log(k_o/(Cl^-)^2)$ *vs* $-H_o$ is also shown in Figure 1. It was found that Rate = k (In^{3+}–$TPPS_4$) $(Cl^-)^2$ $(h_o)^{2.2}$, with k = $(8.6 \pm 0.7) \times 10^{-7}\ M^{-4.2}\ s^{-1}$, with a correlation coefficient of r = 0.9962.

Low concentrations of the positive porphyrins In^{3+}–TAP and In^{3+}–TMPYP were soluble in $HClO_4$. In 5.3 M $HClO_4$, the acid solvolysis reactions were similarly slow, and orders of magnitude faster after the addition of NaCl.

In HCl, the three indium porphyrins have "n" values ranging from 2.2 to 2.4, presumably indicating that two protons are required for the solvolysis reaction, a result similar

TABLE I

Indium(III)–porphyrin acid solvolysis kinetic parameters at 25°

Porphyrin	Solvent	n^a	k^a	r^b
In^{3+}–TMPYP	HCl	2.2	1.1×10^{-6}	0.9998
In^{3+}–TAP	HCl	2.4	8.7×10^{-6}	0.9987
In^{3+}–$TPPS_4$	HCl	2.4	9.3×10^{-6}	0.9996
In^{3+}–$TPPS_4$	HNO_3	2.1	2.3×10^{-6}	0.9986

[a] Rate = k (In^{3+}–P) $(h_o)^n$; k ± 10% in units of $M^{-n}\ s^{-1}$ (n ± 0.1). [b] Correlation coefficient.

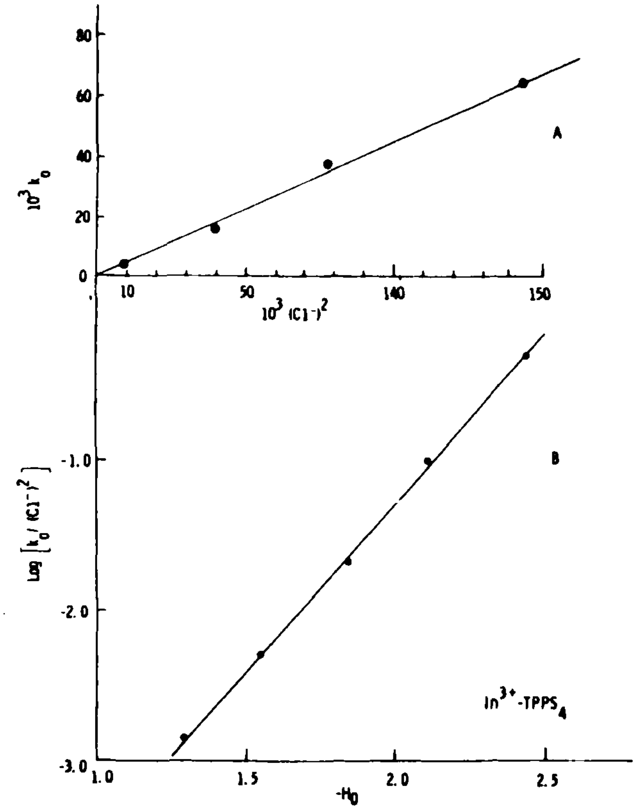

FIGURE 1 Top: Plot of the observed rate constant k_0 (s^{-1}) vs. $(Cl^-)^2$ for In^{3+}–TPPS$_4$ in 5.3 M $HClO_4$. Bottom: Plot of log $(k_0/(Cl^-)^2$ vs. $-H_0$ for In^{3+}–TPPS$_4$ in 0.29 M NaCl with $HClO_4$.

to that found for Fe^{2+}, Mg^{2+}, Zn^{2+} and Cd^{2+} porphyrins,[2,6] where, at lower acidities, the rates are proportional to $[H^+]^2$. The In^{3+}–TAP and In^{3+}–TMPYP porphyrins have an overall formal charge of 5+. Benzenesulfonic acid is half dissociated in 1.1 M acid, and thus the sulfonic acid groups on In^{3+}–TPPS$_4$ may be partially protonated under the reaction conditions (2 to 6 M acid). H_0 probably does not truly describe proton donation to such charged species. Nevertheless, the order of the k values, as noted before,[4] indicates that the least basic porphyrin is solvolyzed the slowest.

At an ionic strength of 0.1 ($HClO_4$/$NaClO_4$), the rate law[8] for the acid catalyzed solvolysis of Zn^{2+}–TPPS$_4$ was found to be first-order in porphyrin and second order in $[H^+]$. The addition of NaCl, NaBr and NaI at constant pH and overall ionic strength produced only small rate effects, and the same rate law and absence of strong anion terms[9] was found for Zn^{2+}–TAP in HNO_3/ $NaNO_3$. In contrast, In^{3+}–TPPS$_4$ (and In^{3+}–TAP) is stable for long periods of time in $HClO_4$/$NaClO_4$, and the marked catalytic effects of added NaCl and NaSCN (HSCN) indicates that the zinc(II) and indium(III) porphyrins are solvolyzed by rather different mechanisms. The composition of the activated complex is $\{2H^+, Zn\text{–}TPPS_4\}$ for the former, and $\{2H^+, 2Cl^-, In^{3+}\text{–}TPPS_4\}$ for the latter. Such anion catalysis has been found[10] before for Zn^{2+}–TMPYP, where Rate = k (Zn–P) $(H^+)^2$ $(X^-)^n$, with n = 2 for Cl^-, Br^- and I^-, and n = 1 for NO_3^-. The present In^{3+}–TMPYP reaction is also strongly anion dependent. However, anion catalyzed reactions are usually found for the TMPYP ligand (for example metal incorporation[11] and metal exchange processes[12]), and it is not clear to what extent the catalysis is due to the metal, the positive porphyrin type, or ion atmosphere requirements. The metal-porphyrin formation reactions of H_2–TPPS$_4$ and H_2–TAP are relatively anion insensitive[8,11] and these In^{3+}–P acid solvolysis results possibly provide evidence that protonation of the porphyrin as well as ligation of the metal (which lowers the overall charge, may increase metal-porphyrin bond lengths, stabilize the solvolyzed product ion and prevent reformation of metal-porphyrin bonds) assist one-another in porphyrin deformation and metal ion removal.

The formation constants for aquo-In^{3+}–anion addition[7] parallel the In^{3+}–TPPS$_4$ solvolysis rates; Cl^-, Br^-, SCN^- > NO_3^- > ClO_4^-. In this connection, Reynolds[13] also found the rate order HCl > H_2SO_4 > $HClO_4$ for the acid solvolysis of Fe^{3+}–TPPS$_4$ in alcohol-water-acid media, where log k_o was proportional to $-H_o$ only in H_2SO_4, and where the alcohol appeared to be necessary for rapid solvolysis in $HClO_4$.

The In^{3+}–TPPS$_4$ reactions in HCl followed in 3 to 5 M HCl vary in rate by a factor of 25, and are adequately described in this range by $k_o = 9.3 \times 10^6 (h_o)^{2.4}$. While no hint of anion catalysis appears, the fact that k is smaller in HNO_3 than in HCl, and not measurable in neat $HClO_4$ indicates the hidden information in the HCl data. Assuming a $(Cl^-)^2$ dependence in neat HCl, recalculation gives $k_o/(Cl^-)^2 = 4.4 \times 10^{-6} (h_o)^{1.8}$, with, therefore, rather different parameters than those found in $HClO_4$ with small added amounts of NaCl. While it is known that NaX additions to HX solutions increases or decreases h_o, this effect is linear in NaX, and would be small for the concentrations used in this study.[3] It must be concluded that such simple $(h_o)^n$ data for metalloporphyrin acid solvolyses for a given acid are simply empirical correlations which may obscure interesting mechanistic features if the reactions are not studied in a range of solvents.

The fact that In^{3+} is 0.61 Å above the porphyrin plane[14] in In(TPP)Cl, while the corresponding distance is 0.38 Å in Fe(TPP)Cl, 0.27 Å in Mn(TPP)Cl and 0.74 Å in Tl(TPP)Cl correlates with the acid solvolysis rate order $Tl^{3+} > In^{3+} > Fe^{3+} > Mn^{3+}$ that we find for M^{3+}–TAP complexes. Al^{3+} and Ga^{3+}–TMPYP compounds are stable for days in concentrated HCl. We also note that In^{3+}–TPPS$_4$ was destroyed (oxidized) in 5.3 M $HClO_4$ containing 0.1 M $NaNO_3$, and similar behavior was found for In(TPP)Cl in $NaNO_3$/HAc media at higher temperatures.[15]

ACKNOWLEDGEMENT

This work was supported by the Howard University NIH Biomedical Research Grant, 5-SO6-RR-08016-9.

REFERENCES

1 A. Adeyemo, A. Valiotti, C. Burnham and P. Hambright, *Inorg. Chim. Acta Letters*, **54**, L63 (1981).
2 A. Valiotti, A. Adeyemo and P. Hambright, *Inorg. Nucl. Chem. Letters*, 17, 213 (1981).
3 C.H. Rochester, Acidity Functions, Academic Press, London, 1970.
4 B. Shah, B. Shears and P. Hambright, *J. Amer. Chem. Soc.*, **93**, 776 (1971).
5 M. Bhatti, W. Bhatti and E. Mast, *Inorg. Nucl. Chem. Letters*, **8**, 133 (1972).
6 A. Shamim and P. Hambright, *Inorg. Chem.*, **19**, 564 (1980).
7 L.G. Sillen and A. Martell, Stability Constants, and Stability Constants, Supplement 1, The Chemical Society, London, 1964.
8 S. Cheung, F. Dixon, E. Fleischer, D. Jeter and M. Krishnamurthy, *Bioinorg. Chem.*, **2**, 281 (1973).
9 A. Thompson and M. Krishnamurthy, *J. Inorg. Nucl. Chem.*, **41**, 1251 (1979).
10 B. Shah and P. Hambright, *J. Inorg. Nucl. Chem.*, **32**, 3420 (1970).
11 H. Baker, L. Wagner and P. Hambright, *J. Amer. Chem. Soc.*, **95**, 5942 (1973).

12 H. Baker, L. Wagner, L. Ross and P. Hambright, *Inorg. Chem.*, **12,** 2200 (1973).
13 W. Reynolds, K. Kooda, B. Florine, N. Johnson and K. Thielman, Int. J. Chem. Kinetics, **22,** 97 (1980).
14 R. Ball, K. Lee, A. Marshall and J. Trotter, *Inorg. Chem.*, **19,** 1463 (1980).
15 A. Nunn, *J. Radioanalytical Chem.*, **53,** 291 (1979).