Rate constants for the primary reactions were obtained by extrapolation to zero time. Agreement between extrapolated values derived from replicate runs was within 10%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

The specific rate for Eu(II) reduction of ligand IX to its radical was estimated by using this ligand as a catalyst in the Eu(II) reduction of excess $Co(NH_3)_5(py)^{3+}$. Under the conditions used, reduction of the ligand, which is the rate-determining step in the catalytic sequence,[10] is monitored by following the disappearance of Co(III) at 475 nm. As in earlier work,[10] k_{Eu} values obtained from replicate runs agreed to better than 8%.

Results and Discussion

Specific rates of Cr^{2+} reduction of Co(III) complexes of N-substituted ligands appear in Table II. These are compared with rate constants for the 1e reduction of the free ligands to their radicals (obtained from past catalytic studies)[4,10] and with values for Eu^{2+} reductions of the complexes. Where the latter are available, they are seen to lie remarkably near k_{Eu}'s for the ligands, reminding us that the rate-determining steps for the two classes of Eu^{2+} reduction are closely related, i.e., that reductions of these Co(III) complexes are initiated by acceptance of an electron by the isonicotinoyl ring system (the chemical mechanism).[5] In the absence of accelerating groups, this transfer is seen to proceed with a specific rate in the range 2–15 $M^{-1}\ s^{-1}$ (25 °C, $\mu = 1.0$). In a single instance (ligand II), the Co(III) complex is found to be reduced significantly more slowly than the parent ligand; here Co^{III} is positioned unusually close to the ring, and electrostatic repulsion between metal centers may be playing a part.

By affixing strongly electron-attracting substituents to the ring nitrogen, k_{Eu} may be made to approach 10^3. Units that function in this manner are *N*-carboxymethyl (I), *N*-aryl (XI),[11,12] and *N*-carbamoylmethyl (XII). It has been shown[13] that replacement of a γ-$CONH_2$ group (as in I) by a γ-$COOCH_3$ group (as in XI) results in only a 3-fold increase in k_{Eu}. Since ligand XI is here likewise found to be reduced just 3 times as rapidly as ligand I, we may infer that no special advantage results from incorporation of a carboxyl (rather than a phenyl) into the N-bound group.

Rate-enhancing effects for Cr^{2+} reductions are seen, however, to be considerably more specific. In the absence of a carboxyl group (oxidant XIV), k_{Cr} values drop close to the range characteristic of outer-sphere reductions of $(NH_3)_5Co^{III}$ derivatives of N-donor ligands (10^{-4}–10^{-3} $M^{-1}\ s^{-1}$).[8a] Moreover, only modest increases (in comparison to those for the *N*-methyl complex, II) result from attachment of those *N*-bound substituents that are most effective for Eu^{2+}. The $^{+}NCH_2CONH_2$ group (complex XII), which is closely related structurally to $^{+}NCH_2COOH$ (complex I), exhibits only a marginal effect with Co(III) absent from the side chain. The most rapid oxidants, by far, are those that feature the ring-bound $^{+}NCHCOOCo^{III}$ unit (I and XIII). Only from these may the doubly bridged precursor, V, be assembled. The latter structure then remains a reasonable intermediate for rapid reductions by Cr^{2+}, although it can no longer be taken to be essential for those by Eu^{2+}.

The difference in structural requirements may be considered in conjunction with differences in attenuation patterns associated with the two reductants. It has been reported[14] that k_{Cr} values in homologues of complex I and related oxidants fall off very sharply as the chain between the pyridine ring and $-COOCo^{III}$ is lenghened by interposition of additional carbon atoms, whereas k_{Eu} values decline much more gradually. Moreover, in some carboxyl-free systems marked isonicotinoyl-related enhancements of k_{Eu} (but not k_{Cr}) may persist even though the activated ring is separated from the Co^{III} center by as many as seven atoms.[5] It has been proposed[14] that the different symmetry character of the donor orbitals for these two reducing centers is reflected in differences in their mode of action, i.e., that transmission of spin density between the activated ring and Co^{III} operates mainly through the intervening bonds in Cr(II) systems but principally through space in Eu(II) systems. The present findings appear to be consistent with this suggestion.[15,16]

Registry No. II, 74911-56-1; IX, 90219-69-5; X, 90219-63-9; XI, 90219-65-1; XII, 90219-67-3; XIV, 90219-70-8; Cr, 7440-47-3; Eu, 7440-53-1.

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(9) Barber, J. R., Jr.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 4045.

(10) See, for example: Fanchiang, Y.-T.; Carlson, R. R.; Thamburaj, P. K.; Gould, E. S. *J. Am. Chem. Soc.* **1977**, *99*, 1973. The catalytic sequence is

$$\mathrm{Lig} \underset{Eu^{3+},\ k_{-1}}{\overset{Eu^{2+},\ k_1}{\rightleftharpoons}} \mathrm{Lig}\cdot \xrightarrow[k_2]{Co^{III}} \mathrm{Lig} + Co^{2+}$$

The ratio k_2/k_{-1} (but not individual values for each) may be obtained from experiments with Eu(II) in excess and in the presence of Eu(III).[4] This ratio, for ligand IX, is 18 (25 °C, 1.0 M $HClO_4$).

(11) The largest k_{Eu} value for an isonicotinoyl derivative is 1.1×10^3 $M^{-1}\ s^{-1}$, reported for the *N*-(2-naphthyl) derivative of methyl isonicotinate.[4] Still larger values result from incorporation of a second, but not a third, carboxyl group in the ring.[12]

(12) See, for example: Fanchiang, Y.-T.; Heh, J. C.-K.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 1142.

(13) Radlowski, C. A.; Chum, P.-W.; Hua, L.; Heh, J.; Gould, E. S. *Inorg. Chem.* **1980**, *19*, 401. Values of k_{Eu} reported by these workers are 2.0 $M^{-1}\ s^{-1}$ for isonicotinamide and 6.2 $M^{-1}\ s^{-1}$ for ethyl isonicotinate (25 °C, 1.0 M $HClO_4$).

(14) Srinivasan, V. S.; Radlowski, C. A.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 2094.

(15) A reviewer has asked how certain we are that the Cr(II) reductions of the (carboxylato)cobalt(III) complexes in this study proceed by the inner-sphere route. Although we have characterized the Cr(III) product only from oxidant I, we cite the study by Fan,[16] who has estimated outer-sphere contributions to reactions of this type as 10^{-5}–10^{-2} times the observed rates. Reduction of complex XIV, in which the carboxyl cannot assume a lead-in function toward Co(III), would be expected to be outer sphere.

(16) Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2647.

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Magnitudes of Ionic Strength Effects in Porphyrin Metalation and Acid Solvolysis Reactions

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Received April 26, 1983

In metalation and acid-catalyzed solvolysis reactions of porphyrins and metalloporphyrins, certain peripherally positively charged porphyrins have been reported to have anion terms in their rate laws, while other positive and negative derivatives lack such features. The following analysis indicates that anion catalysis is partially (but not exclusively) attributable to ionic strength effects.

For a number of positively charged water-soluble porphyrins (H_2–P) such as tetrakis(*N*-methyl-4-pyridyl)porphyrin[1] and its 3- and 2-pyridyl analogues[2] studied in nitrate media, the kinetics of divalent metal ion incorporation show rate = k_f $[H_2\text{–}P][M^{2+}][NO_3^-]$. The rate law for the solvolysis of the corresponding zinc porphyrins[3] at high acidities in HNO_3 is rate = $k_D[Zn\text{–}P][H^+]^2[NO_3^-]$. The unusual first-order term in nitrate was suggested by the fact that plots of the observed specific rates ($k_{obsd}/[M^{2+}]$ or $k_{obsd}/[H^+]^2$) vs. $[NO_3^-]$ were

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(1) Hambright, P.; Chock, P. *J. Am. Chem. Soc.* **1974**, *96*, 3123.

(2) Reid, J.; Hambright, P. *Inorg. Chem.* **1977**, *16*, 968.

(3) Shah, B.; Hambright, P. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3240.

0020-1669/84/1323-1990$01.50/0

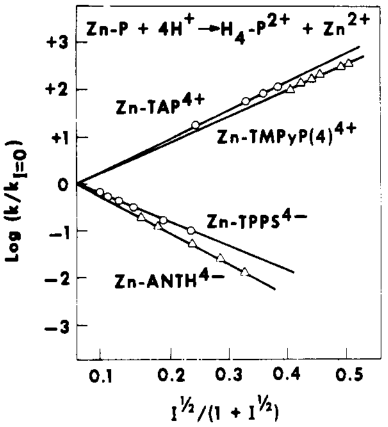

Figure 1. Brønsted–Bjerrum plots for the acid solvolysis reactions of positive and negatively charged zinc porphyrins (25 °C, in $HNO_3/LiNO_3$ (or $NaNO_3$)). See text for the porphyrin abbreviations.

linear over wide ranges and had apparent zero intercepts; i.e., the specific rates went to zero as $[NO_3^-]$ approached zero. Tetrapositively, but not monopositively, charged porphyrins in detergent solutions exhibited such anion effects.[4] This anion catalysis for positive porphyrins has been variously viewed as the necessity for charge reduction in the activated complex,[1] the association of anions[5] and cations[6] with the positive porphyrins, and the reactants being inner sphere ($ZnNO_3^+$) in character.[7]

However, it was also noted that for positive porphyrins reacting with positive (M^{2+}, H^+, $M-P^+$) reactants,[1,2,8,9] the rates should in fact increase with an increase in ionic strength (here, $NaNO_3$ concentration). The observations that metal incorporation[8] and acid solvolysis reactions[3] of positive porphyrins, run at the same ionic strength with differing neutral salts, showed markedly different specific rates, while the same acid solvolysis reactions of a negative porphyrin[10] had rates relatively independent of the nature of the salt at the same ionic strength, led to the belief that positive porphyrins were somehow different in character and mechanistic behavior from negative porphyrins.

We have now studied the ionic strength (I) dependence ($HNO_3/LiNO_3$) of the acid solvolysis reactions of the zinc complexes of the negatively charged tetrakis(4-sulfonatophenyl)porphyrin ($Zn-TPPS_4^{4-}$) and the tetrasulfonated 9-anthracene porphyrin. The quantity $k_{obsd}/[H^+]^2$ was found to be constant at constant ionic strength,[11] and as the ionic strength decreased, the specific rate increased. The Brønsted–Bjerrum equation[12] is of the form given by eq 1,

$$\log k_I = \log k_{I=0} + QI^{1/2}/(1 + I^{1/2}) \qquad (1)$$

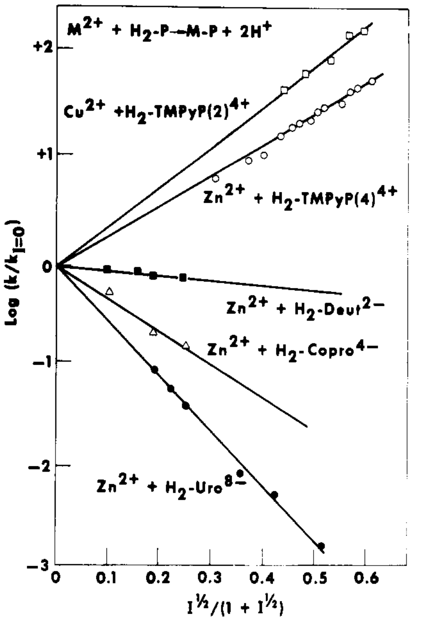

Figure 2. Brønsted–Bjerrum plots for metal incorporation reactions of positive and negatively charged porphyrins, in $HNO_3/NaNO_3$ or $HClO_4/NaClO_4$ media. All data are at 25 °C except for the $Cu^{2+}/H_2-TMPyP(2)^{4+}$ results at 65 °C.

Table I. Summary of Rate Data Extrapolated to $I = 0$, 25 °C

reacn[a]	$k_{I=0}$[b]	Q_{obsd}[c]	Q_{calcd}[c]	ref[d]
$Cu^{2+}/H_2-TMPyP(2)^{4+}$	6.7×10^{-5}	3.8	8	2
$Zn^{2+}/H_2-TMPyP(4)^{4+}$	1.8×10^{-3}	2.9	8	1
$Zn^{2+}/H_2-Deutero^{2-}$	6.0×10	−0.53	−4	15
$Zn^{2+}/H_2-Copro^{4-}$	1.6×10^3	−3.2	−8	15
Zn^{2+}/H_2-Uro^{8-}	3.6×10^4	−5.4	−16	15
$Zn-TMPyP^{4+}/H^+$	6.0×10^{-5}	4.5	9	3
$Zn-TAP^{4+}/H^+$	1.4×10^{-2}	4.7	9	13b
$Zn-Anth^{4-}/H^+$	4.0	−5.5	−7	tp
$Zn-TPPS_4^{4-}/H^+$	8.6×10	−4.2	−7	tp

[a] The $Cu^{2+}/H_2-TMPyP(2)^{4+}$ reaction in Figure 2 is at 65 °C, having $k_I = 1.3 \times 10^{-3}$ M^{-2} s^{-1}. The known activation parameters from ref 2 were used to calculate k_I at 25 °C in this table. [b] $k_I = k_{obsd}/[M^{2+}]$ (in M^{-1} s^{-1}) for the incorporation reactions and $k_I = k_{obsd}/[H^+]^2$ (in M^{-2} s^{-1}) for the acid solvolysis reactions. [c] Q_{obsd} is the observed slope of the Brønsted–Bjerrum plots, and Q_{calcd} is the slope ($0.5(\Delta z^2)^{\ddagger}$) calculated with use of the stated porphyrin nominal charges and eq 1. [d] tp = this paper.

where $Q = 0.5(\Delta z^2)^{\ddagger}$. $(\Delta z^2)^{\ddagger}$ here is equal to the square of the charge of the metalloporphyrin or metalloporphyrin–proton activated complex minus the sum of the squares of the charge of each reactant. For the two tetrasulfonated zinc porphyrins, plots of log ($k_{obsd}/[H^+]^2$) vs. the ionic strength function were linear and could be extrapolated to $I = 0$, giving $k_{I=0}$. Results for the two negative porphyrins plotted according to eq 1 are in Figure 1. Literature data for the acid solvolysis reactions of several positively charged porphyrins in nitrate media ($Zn-TMPyP(4)^{4+}$, which was reportedly nitrate catalyzed[3] and $Zn-TAP^{4+}$, the tetrakis(*N*,*N*,*N*-trimethyl-4-aniliniumyl)porphyrin complex, where the rate increase with I was treated as a salt effect[13]) are also presented in Figure 1. The linearity for both positive and negative porphyrins implies that the nitrate term in the solvolysis rate law is more profitably treated as an ionic strength rather than a specific anion catalysis phenomenon. However, the fact[3] that, at the same concen-

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(4) Williams, G.; Williams, R. F. X.; Lewis, A.; Hambright, P. *J. Inorg. Nucl. Chem.* **1979**, *41*, 41.

(5) Schneider, W. *Struct. Bonding (Berlin)* **1975**, *16*, 64.

(6) Rao, W.; Longo, F. *Inorg. Chem.* **1977**, *16*, 1372.

(7) Longo, F. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 5, Chapter 10.

(8) Baker, H.; Hambright, P.; Wagner, L. *J. Am. Chem. Soc.* **1973**, *95*, 5942.

(9) Baker, H.; Hambright, P.; Wagner, L.; Ross, L. *Inorg. Chem.* **1973**, *12*, 2200.

(10) Cheung, S. K.; Dixon, F. L.; Fleischer, E. B.; Jeter, D. Y.; Krishnamurthy, M. K. *Bioinorg. Chem.* **1973**, *2*, 281.

(11) $Zn-TPPS_4^{4-}$ was studied over the range 9.8×10^{-2} to 3.5×10^{-3} M in H^+ at $I = 0.3$, while $Zn-Anth^{4-}$ was followed between 4.0×10^{-1} and 2.5×10^{-2} M in H^+ at $I = 0.5$. The quantities $k_{obsd}/[H^+]^2$ for each porphyrin varied by less than 7% from one another in these ranges. No terms higher or lower in H^+ concentration were required to fit the data in the intervals studied. For $Zn-TPPS_4^{4-}$ at $I = 0.1$ ($HNO_3/LiNO_3$) and 25 °C, we find $k_{obsd}/[H^+]^2 = 9.8$ M^{-2} s^{-1}, as compared to 10.9 M^{-2} s^{-1} ($I = 0.1$ $HClO_4/NaClO_4$) at 30 °C.[10] The $Zn-Anth^{4-}$ porphyrin gave essentially the same specific rates in $HNO_3/LiNO_3$ as in $HClO_4/NaClO_4$.

(12) Espenson, J. H. "Chemical Kinetics and Reaction Mechanisms"; McGraw-Hill: New York, 1981; p 176.

(13) (a) Thompson, A.; Krishamurthy, M. K. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1251. (b) Thompson, A. Ph.D. Thesis, Howard University, 1979.

tration of HX, the solvolysis of Zn–TMPyP(4)$^{4+}$ is 675 times faster in HCl than in HI, while minimal changes in rate are found for Zn–TPPS$_4^{4-}$ with the same reagents,[10] suggests that strong specific salt effects occur for positive porphyrins, as well as negative porphyrins containing certain metal ions.[14]

We then reconsidered the published data[1,2,15] on metal ion incorporation reactions for both porphyrin charge types as a function of ionic strength in terms of eq 1. As shown in Figure 2, the nitrate term for both positive porphyrins again appears to be an ionic strength effect, in line with the results shown for the negative porphyrins.

As shown in Table I and as noted before,[16] both positive and negative porphyrins behave kinetically as if they carried less charge than predicted by their overall nominal charges. The lack of notable anion effects in the metalation of the formally monopositive triphenyl(*N*-methyl-4-pyridyl)porphyrin[4] is now understandable for a porphyrin having an effective charge $Z_A \approx 0$ and, as such, parallels the results found for the formally dinegative deuteroporphyrin (Figure 2), where the rate shows little variation with I, due to $Z_A \simeq -0.2$.

The important conclusion is that these positive and negative porphyrins have the same observed incorporation (rate = $k_I[H_2–P][M^{2+}]$) and acid solvolysis (rate = $k_D[Zn–P][H^+]^2$) rate laws under the conditions studied. The magnitudes of the extrapolated specific rates are shown in Table I. At I = 0, the octanegative uroporphyrin is predicted to incorporate zinc over 2×10^7 times faster than the less basic tetrapositive H_2–TMPyP(4)$^{4+}$, while the tetranegative Zn–TPPS$_4^{4-}$ is predicted to be solvolyzed over 10^6 times more rapidly than the less basic Zn–TMPyP(4)$^{4+}$. Plots of log k vs. the ionic strength function indicate that (1) the metalation rates of positive and negative porphyrins approach one another as I increases, (2) while Zn–TPPS$_4^{4-}$ is predicted to solvolyze 600 times faster than Zn–TAP^{4+} at I = 0, the rates become equal at I = 0.5, and Zn–TAP^{4+} reacts faster than Zn–TPPS$_4^{4-}$ above this level, and (3) the more basic Zn–TAP^{4+} solvolyzes 200 times faster than Zn–TMPyP(4)$^{4+}$ at any ionic strength.

The trends of reaction rates upon ionic strength are of importance in understanding water-soluble porphyrin reactivities, where the usual tendency of comparing different porphyrins under one set of conditions can often be misleading. As a general trend at low ionic strengths, it appears that the higher the basicity of the metal-free porphyrin, the faster the acid solvolysis,[17] metal ion incorporation,[18] metal ion exchange,[19] and ligand exchange[20] reactions.

Acknowledgment. This work was supported by the Howard University NIH Biomedical Research Grant 5-SO-6-RR-08016-9.

Registry No. Zn-TPPS$_4^{4-}$, 80004-36-0; Zn-ANTH^{4-}, 90245-31-1.

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(14) In^{3+}–TPPS$_4$ is stable for hours in 5 M HClO$_4$ and solvolyzes rapidly to the diacid when the solution is made 0.01 N in NaCl. For SCN catalysis of the In–TPPS$_4$ reaction, see: Hambright, P. J. *Coord. Chem. Rev.* **1983**, *12*, 279. Reynolds, W. C.; Gall, P.; Arndt, P. *Int. J. Chem. Kinet.* **1982**, *14*, 849.

(15) Shamim, A.; Hambright, P. *Inorg. Chem.* **1983**, *22*, 649.

(16) Pasternak, R. F.; Sutin, N.; Turner, D. H. *J. Am. Chem. Soc.* **1976**, *98*, 1908. See also ref 13a and 15.

(17) Shah, B.; Shears, B.; Hambright, P. *J. Am. Chem. Soc.* **1971**, *93*, 776.

(18) Ademyemo, A.; Shamim, A.; Hambright, P. *Indian J. Chem., Sect. A* **1982**, *21A*, 763.

(19) Reid, J.; Hambright, P. *Inorg. Chim. Acta* **1979**, *33*, L135.

(20) Williams, G. N.; Hambright, P. *Inorg. Chem.* **1978**, *17*, 2687.