Inorg. Chem. **1981**, *20*, 1274-1277

Contribution from the Department of Chemistry,
University of Houston, Houston, Texas 77004

Reactions of Metalloporphyrin π Radicals. 1. Complexation of Zinc Tetraphenylporphyrin Cation and Anion Radicals with Nitrogenous Bases

K. M. KADISH,* L. R. SHIUE, R. K. RHODES, and L. A. BOTTOMLEY

Received July 24, 1980

Stability constants for TPPZn with 20 nitrogenous bases were obtained by the method of proportional absorbances. These results were combined with electrochemical data to obtain stability constants for the reaction of TPPZn radical cations and radical anions with ligands. Values of log β_1 ranged from 1.64 to 4.59 for ligand addition to $[TPPZn]^+$ and from 1.47 to 3.50 for addition to $[TPPZn]^-$. Only five-coordinate complexes were observed. These measurements represented the first values of stability constants obtained for nitrogeneous base addition to porphyrin π radicals. The changes in stability constants observed as a function of ligand pK_a allowed the "tuning" of the zinc radical cation half-wave potential between 0.83 and 0.74 (vs. SCE) and the radical anion potential between −1.38 and −1.49 V. The ligand additions proceeded in a chemically reversible fashion over the experimental time frame. Thin-layer spectra for oxidations showed slight spectral differences between $[TPPZn]^+$ and $[TPPZn(L)]^+$ but were almost totally insensitive to a specific L. The possibility of an alternate oxidative pathway to the β-substituted pyrrole product was examined and found not to be operative for this time frame and solvent system.

Introduction

The understanding of metalloporphyrin redox properties in relation to biological processes is of great importance.[1-3] Depending on the type of porphyrin and its specific function, this redox reaction will be reflected in either metal-centered or ring-centered electron transfers.[4,5] With use of simpler synthetic porphyrins to model the more complicated biological systems, several strategies have been developed in our laboratories to investigate these electrochemical reactions. These have included making systematic variations in porphyrin ring substituents,[6,7] centeral metal ion,[8,9] axial ligation,[10,11] and solvent or counterion coordinated to the metal.[12,13]

Prior to this study, all electrochemical investigations of axial ligand binding by metalloporphyrins have involved transition-metal complexes with uncharged porphyrin π systems. It is well-known that nitrogenous bases will readily bind to metalloporphyrins having uncharged conjugated π systems and that some anions may bind to porphyrin π-cation radicals.[3] Several spectroscopic studies of cation radicals with axially bound solvent molecules, ligands, or counterions have been published.[14-17] However, it was not evident what the stoichiometry, stability constants for axial ligand addition, or electrochemical reactivity would be for cation radicals which were electrochemically generated from neutral complexes already axially bound by nitrogenous bases. Likewise, prior to this study, there was almost no data of any kind on porphyrin π-anion radicals which were axially complexed at the central metal.

In this paper, we present the first evidence for axial ligand binding of zinc porphyrin radicals by nitrogenous bases. Stability constants are presented for the binding of 20 different nitrogenous bases in methylene chloride. $[TPPZn]^+$ and $[TPPZn]^-$ were selected for our initial investigations of radical binding by axial ligands because of the extensive spectroscopic data available on TPPZn[18-21] and the fact that only 1:1 complexes may be formed with axial ligands.[18,19] Likewise, there is extensive ESR[22] data on complexes of $[TPPZn^{II}]^+X^-$, where X = Br^-, Cl^-, I^-, F^-, or ClO_4^-, and the X-ray structure of $[TPPZn^{II}]^+ClO_4^-$ has been published.[23]

In the absence of ligands, on the cyclic voltammetry time scale, TPPZn is known to undergo two reversible one-electron ring oxidations[9,16] (eq 1) and two reversible one-electron ring

$$TPPZn \underset{}{\overset{-e^-}{\rightleftharpoons}} [TPPZn]^{+\cdot} \overset{-e^-}{\rightleftharpoons} [TPPZn]^{2+} \qquad (1)$$

reductions[9,24] (eq 2). In addition, the cation and anion radicals

$$TPPZn \overset{e^-}{\rightleftharpoons} [TPPZn]^- \overset{e^-}{\rightleftharpoons} [TPPZn]^{2-} \qquad (2)$$

can be reversibly produced by bulk electrolysis[25] and thin-layer techniques[26] to allow for both optical and ESR spectroscopic

---

(1) H. A. Harbury and R. H. L. Marks in "Inorganic Biochemistry", Vol. 2, G. E. Eichorn, Ed., Elsevier, Amsterdam, 1973, Chapter 26.
(2) J. M. Rifkind in "Inorganic Biochemistry", Vol. 2, G. E. Eichorn, Ed., Elsevier, Amsterdam, 1973, Chapter 25.
(3) R. H. Felton in "The Porphyrins", Vol. 5, D. Dolphin, Ed., Academic Press, New York, 1979, Chapter 3.
(4) C. E. Castro in "The Porphyrins", Vol. 5, D. Dolphin, Ed., Academic Press, New York, 1979, Chapter 1.
(5) D. Dolphin and R. H. Felton, *Acc. Chem. Res.*, **7**, 26 (1974).
(6) F. A. Walker, D. Beroiz, and K. M. Kadish, *J. Am. Chem. Soc.*, **98**, 3484 (1976).
(7) K. M. Kadish, L. A. Bottomley, and D. Beroiz, *Inorg. Chem.*, **17**, 1124 (1978).
(8) J. Fuhrhop, K. M. Kadish, and D. G. Davis, *J. Am. Chem. Soc.*, **95**, 5140 (1973).
(9) K. M. Kadish and M. M. Morrison, *Bioinorg. Chem.*, **7**, 107 (1977).
(10) K. M. Kadish and L. A. Bottomley, *Inorg. Chem.*, **19**, 832 (1980).
(11) K. M. Kadish, L. A. Bottomley, and J. S. Cheng, *J. Am. Chem. Soc.*, **100**, 2731 (1978).
(12) K. M. Kadish, R. K. Rhodes, and L. A. Bottomley in "Symposium on Interaction Between Iron and Proteins in Oxygen and Electron Transport", Airlie, Va., 1980.
(13) K. M. Kadish and L. A. Bottomley, *Inorg. Chem.*, in press.
(14) G. M. Brown, F. R. Hopf, J. A. Ferguson, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **95**, 5939 (1973).
(15) N. Farrell, D. H. Dolphin, and B. R. James, *J. Am. Chem. Soc.*, **100**, 324 (1978).
(16) J. Fajer, D. C. Borg, A. Forman, D. Dolphin, and R. H. Felton, *J. Am. Chem. Soc.*, 92, 3451 (1970).
(17) C. Mengersen, J. Subramanian, J. H. Fuhrhop, and K. M. Smith, *Z. Naturforsch.* **429**, 1827 (1974).
(18) C. H. Kirksey, P. Hambright, and C. B. Storm, *Inorg. Chem.*, **8**, 2141 (1969).
(19) M. Nappa and J. S. Valentine, *J. Am. Chem. Soc.*, **100**, 5075 (1978).
(20) S. J. Cole, G. S. Curthoys, E. A. Magnusson, and J. H. Phillips, *Inorg. Chem.*, **5**, 1024 (1972).
(21) (a) G. C. Vogel and L. A. Searby, *Inorg. Chem.*, **12**, 936 (1973); (b) G. C. Vogel and B. A. Beckmann, *ibid.*, **15**, 483 (1976). (c) G. C. Vogel and J. R. Stahlbush, *ibid.*, **16**, 950 (1977).
(22) (a) A. Forman, D. C. Borg, R. H. Felton, and J. Fajer, *J. Am. Chem. Soc.*, **93**, 2790 (1971); (b) J. Fajer, D. C. Borg, A. Forman, A. D. Adler, and V. Varadi, *ibid.*, **96**, 1238 (1974).
(23) L. D. Spalding, P. G. Eller, J. A. Bertrand, and R. H. Felton, *J. Am. Chem. Soc.*, **96**, 982 (1974).
(24) D. W. Clack and N. S. Hush, *J. Am. Chem. Soc.*, **87**, 4283 (1965).
(25) A. Wolberg and J. Manassen, *J. Am. Chem. Soc.*, **92**, 2982 (1970).
(26) J. G. Lanese and G. S. Wilson, *J. Electrochem. Soc.*, **119**, 1039 (1972).

0020-1669/81/1320-1274\$01.25/0

measurements. The dication can also be produced under rigorously clean conditions, but the presence of trace water, methanol, or strong nucleophiles can lead to the formation of isoporphyrins.[27] Reduction to the dianion, even on a thin-layer time scale, is believed to result in the formation of the phlorin anion.[28] Due to the possibility of mechanistic complications with the short-lived dication and dianion species, we have restricted this paper to measurements involved only complexes generated from the first ring oxidation or the first ring reduction in the presence of nitrogenous bases. With one or two exceptions, all electrochemical reactions were well defined and free of side reactions on the time scale of our measurements.

Experimental Section

Materials. (5,10,15,20-Tetraphenylporphinato)zincate (TPPZn) was obtained from Strem Chemicals and also prepared by the method of Adler et al.[29] Both lots gave comparable electrochemical and spectral characterizations. Methylene chloride, CH_2Cl_2, was of reagent grade, doubly distilled from P_2O_5, and stored over 4-Å Linde molecular sieves prior to use. The supporting electrolyte, tetrabutylammonium perchlorate (TBAP), was obtained from Eastman Chemical, recrystallized once from ethyl acetate–pentane solution, and dried under reduced pressure at 40 °C until used. The nitrogenous bases used as ligands (L) in this study consisted of a series of substituted pyridines and imidazoles. These were obtained from Fisher Scientific and Aldrich Chemical Co. and were purified by standard literature methods.

Instrumentation. Cyclic voltammetric measurements using a three-electrode system were made with a Princeton Applied Research (PAR) Model 174A polarographic analyzer. A platinum button served as the working electrode with a platinum wire as the counterelectrode. A saturated calomel electrode (SCE), separated from the bulk solution by a fritted supporting electrolyte/solvent bridge, was used as the reference electrode. Current–voltage curves were collected on a Houston Instruments Omnigraphic 2000 X-Y recorder at scan rates of from 0.020 to 0.500 V/s. The electrochemical titiation data was acquired at 0.200 V/s.

Thin-layer spectrocoulometry was performed with use of a PAR model 179 coulometer in conjunction with a model 173 potentiostat/galvanostat. The thin-layer cell consisted of a 1000 1pi gold minigrid working electrode sandwiched between two glass slides (1 × 2.5 cm) and assembled in a three electrode configuration similar to Murray et al.[30] The path length of this cell was found to be 1.2×10^{-2} cm by both spectrophotometric and electrochemical calibration. This system was coupled with a Tracor Northern 1710 holographic optical spectrometer/multi-channel analyzer to obtain time-resolved spectra data for electrochemical oxidations. Spectra result from the signal averaging of 100 sequential 5-ms spectral acquisitions. Each acquisition represents a single spectrum from 325 to 950 nm, simultaneously recorded by a diode-array detector with a resolution of 1.2 nm per channel. Spectra were taken at both 2.5×10^{-4} and 1.0×10^{-3} M porphyrin in the thin-layer cell. The supporting electrolyte was 1.0×10^{-1} M TBAP, and ligand concentration was adjusted as described later.

Method of Calculation. Stability constants for nitrogenous base addition to TPPZn were calculated spectrophotometrically by the method of proportional absorbances as originally described by Budesinsky[31] and improved upon by Leggett et al.[32] The measurements were made at 25.0 ± 0.5 °C on a Cary 14 spectrometer using porphyrin concentrations of 4.5×10^{-4} M and 9.0×10^{-4} M in ionic strength solutions of 0.0 and 0.1 M. Stability constants for the radical reactions and changes in axial ligation were determined by monitoring shifts in half-wave potential as a function of free [L]. These potentials were measured by cyclic voltammetry for the uncomplexed TPPZn and for complexed TPPZn in the presence of free-ligand concentrations of 1×10^{-3}–1 M. Plots of $E_{1/2}$ vs. log [L] were constructed and, from the plot slopes, the change in axial ligand coordination number was determined by using eq 3 and 4, where $(E_{1/2})_c$ and $(E_{1/2})_s$ are the

$$(E_{1/2})_c = (E_{1/2})_s - (0.059/n)\log(\beta_1{}^{+}/\beta_1{}^{0}) - (0.059/n)\log[\mathrm{L}]^{p-q} \quad (3)$$

$$(E_{1/2})_c = (E_{1/2})_s - (0.059/n)\log(\beta_1{}^{0}/\beta_1{}^{-}) - (0.059/n)\log[\mathrm{L}]^{q-v} \quad (4)$$

half-wave potentials of the complexed species and uncomplexed species, respectively, [L] is the free-ligand concentration, n is the number of electrons transferred in the diffusion-controlled reaction, and p, q, and v are the number of ligands bound to the cation radical, neutral, and anion radical species. For each ligand $\beta_1{}^0$ was determined spectrophotometrically with use of proportional absorbances and combined with the electrochemical data to calculate values for $\beta_1{}^+$ and $\beta_1{}^-$.

Results and Discussion

Spectra of TPPZn(L). The electronic absorption spectrum of TPPZn is strongly dependent on axial interaction. In the absence of coordinating ligands the reported[19] normal metalloporphyrin spectrum was obtained. This included a Soret band at 420 nm and two visible bands at 547 and 584 nm. Additions of aliquots of substituted pyridines to solutions of TPPZn in CH_2Cl_2 produced red shifts in the visible absorption spectrum and changes in the ratio of the visible absorption band heights as reported by previous investigations.[18,19] Spectral comparison of solutions containing TPPZn with and without ligand allowed calculation of stability constants by the method of proportional absorbances.[31,32] This method is reliable and reproducible but has not, to our knowledge, been used to determine stability constants of porphyrin nitrogenous base adducts. The method of proportional absorbances is particularly suited for the study of TPPZn complexation because only monoligated complexes have been identified in solution.

The results of our calculations are shown in Table I. Twenty different ligands were investigated including nonsterically hindered substituted pyridines (**1**–**14**), sterically hindered pyridines (**15**, **16**), nonsterically hindered imidazoles (**17**, **18**), and sterically hindered imidazoles (**19**, **20**). Eight literature values[18] are presented in Table I, and, in all cases, the values obtained in this study are within experimental error of those reported earlier. The range of log $\beta_1{}^0$ in this study was from 2.50 to 5.57, with imidazoles giving the largest formation constants.

In order to directly compare results obtained by electrochemical techniques and those by spectroscopic methodologies, we have made measurements both in the presence and in the absence of supporting electrolyte (0.1 M TBAP, $\mu = 0.1$). For all ligands investigated, the measured stability constants are slightly higher in solutions without supporting electrolyte, a trend observed before for the case of pyridine binding to TPPZn.[19] This effect is believed to be due to competitive binding between the ligand and the supporting electrolyte anion, ClO_4^-. This would imply that the reaction in the absence of supporting electrolyte is given as a simple addition reaction (eq 5) while in the presence of 0.1 M TBAP a displacement reaction may result (eq 6). This would imply that

$$\mathrm{TPPZn} + \mathrm{L} \rightleftarrows \mathrm{TPPZn(L)} \quad (5)$$

$$[\mathrm{TPPZn(ClO_4)}]^- + \mathrm{L} \rightleftarrows \mathrm{TPPZn(L)} + \mathrm{ClO_4}^- \quad (6)$$

the binding constant of ClO_4^- to TPPZn is extremely small as indicated by the large quantity of the electrolyte (0.1 M) required to produce small changes in log $\beta_1{}^0$.

Electrode Reactions of TPPZn and TPPZn(L). In CH_2Cl_2 containing 0.1 M TBAP, half-wave potentials for cation and anion radical formation were 0.78 and −1.38 V, respectively.

---

(27) D. Dolphin, R. H. Felton, D. C. Borg, and J. Fajer, *J. Chem. Soc.*, **92**, 743 (1970).

(28) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85**, 818 (1963).

(29) A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).

(30) R. W. Murray, W. R. Heineman, and G. W. O'Dom, *Anal. Chem.*, **39**, 1666 (1967).

(31) B. Budesinsky, *J. Inorg. Nucl. Chem.*, **31**, 1345 (1969).

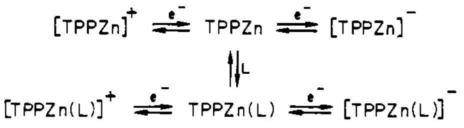
(32) D. J. Leggett and W. A. E. McBryde, *Talanta*, **22**, 781 (1975).

Table I. Formation Constants for Ligand Addition

no.	ligand	pK_a[a]	$\log \beta_1^{+}$[b]	$\log \beta_1^{-}$[c]	$\log \beta_1^{0}$, $\mu = 0.1$[d]	$\log \beta_1^{0}$, $\mu = 0.0$[e]	lit.[f] value
1	3,5-dichloropyridine	0.67	1.64	1.47	2.50 ± 0.03	2.45 ± 0.05	
2	3-cyanopyridine	1.45	2.04	1.70	2.70	2.82	2.80 ± 0.04
3	4-cyanopyridine	1.86	2.23	1.60	2.84	3.00	2.9 ± 0.1
4	3-chloropyridine	2.81	2.85	1.61	3.00	3.11	
5	3-bromopyridine	2.84	2.87	1.92	3.06	3.14	
6	3-acetylpyridine	3.18	3.14	1.99	3.19	3.31	
7	4-acetylpyridine	3.51	3.25		3.27	3.51	
8	pyridine	5.29	3.98	2.06	3.62	3.82	3.78 ± 0.02
9	3-picoline	5.79	4.00	1.90	3.76	3.92	3.82 ± 0.07
10	4-picoline	5.98	4.41	2.09	3.82	3.96	4.02 ± 0.05
11	3,4-lutidine	6.46	4.59	2.10	3.98	4.15	
12	4-aminopyridine	9.17			4.49	4.67	4.65 ± 0.04
13	4-(*N,N*-dimethylamino)pyridine	9.71			4.61	4.84	
14	piperidine	11.1		2.75	4.90	5.09	5.05 ± 0.05
15	2-picoline	5.96	2.10	0.78	2.25	2.36	2.30 ± 0.04
16	2-aminopyridine	6.82			2.76	2.87	
17	imidazole	6.65			5.11 ± 0.06	5.28 ± 0.08	
18	1-methylimidazole	7.33		3.02	5.16	5.38	
19	2-methylimidazole	7.56			5.32	5.45	
20	1,2-dimethylimidazole	7.85		3.50	5.47	5.57	

[a] K. S. Schoefield, "Hetero-Aromatic Nitrogen Compounds", Plenum Press, New York, 1967, p 146. [b] Reaction: $[TPPZn]^+ + L \rightleftarrows [TPPZnL]^+$. [c] Reaction: $[TPPZn]^- + L \rightleftarrows [TPPZnL]^-$. [d] Reaction: $TPPZn + L \rightleftarrows TPPZnL$ (in CH_2Cl_2, 0.1 M TBAP). [e] Reaction: $TPPZn + L \rightleftarrows TPPZnL$ (in CH_2Cl_2, no supporting electrolyte). [f] Reference 18.

Scheme I



Cyclic voltammograms were recorded for oxidation and reduction of TPPZn before and after additions of each ligand listed in Table I. No change was observed in either the shape or the heights of current–voltage curves until a concentration consistent with ligand binding by TPPZn was attained. At this point a shift of the reduction and oxidation peak potentials occurred. For all ligands the reduction process initially shifted cathodically by 80–150 mV and was then invariant with further increases in ligand. The oxidation peak initially shifted in a cathodic or anodic direction depending upon the ligand by up to 60 mV and was then invariant with further ligand additions. The final $E_{1/2}$ at high ligand concentration is listed in Table II.

These electrochemical results are consistent with the spectroscopic results and can be explained by Scheme I. At low ligand concentrations TPPZn is uncomplexed and the electrode reactions proceed as shown in the top part of the scheme. At high ligand concentrations TPPZn(L) is formed in solution. This species can form $[TPPZn(L)]^-$ and $[TPPZn(L)]^+$ as shown in the lower part of Scheme I.

Complexation of neutral TPPZn was monitored spectrophotometrically. Complexation of $[TPPZn]^+$ and $[TPPZn]^-$ by nitrogenous bases was monitored electrochemically and verified spectrophotometrically. Both the oxidation and reduction process proceed from reversible at low [L] to slightly quasireversible at high [L] (peak separation = 100 mV), but in neither case did this complicate the calculation of $E_{1/2}$. Regions of half-wave potential independence at highest [L] indicate no change in ligand axial coordination (L = 1) between the neutral TPPZn(L) and the radicals $[TPPZn(L)]^+$ and $[TPPZn(L)]^-$ (i.e., $p = q = v$ in eq 3 and 4). Formation constants were calculated for each radical complex and are listed in Table I along with the spectrophotometrically determined β_1^0 values at $\mu = 0.1$ and 0.0.

Table II. Half-Wave Potentials[a] for Oxidation and Reduction of TPPZn(L) in CH_2Cl_2 Containing 0.1 M TBAP and 1.0 M Ligand

no.	ligand	pK_a[b]	$E_{1/2}$(ox)	$E_{1/2}$(red)
	neat CH_2Cl_2		0.78	−1.38
1	3,5-dichloropyridine	0.67	0.83	−1.42
2	3-cyanopyridine	1.45	0.82	−1.42
3	4-cyanopyridine	1.86	0.82	−1.44
4	3-chloropyridine	2.81	0.79	−1.44
5	3-bromopyridine	2.84	0.79	−1.43
6	3-acetylpyridine	3.18	0.78	−1.43
7	4-acetylpyridine	3.51	0.78	*c*
8	pyridine	5.28	0.76	−1.46
9	3-picoline	5.77	0.77	−1.47
10	4-picoline	5.98	0.74	−1.46
11	3,4-lutidine	6.46	0.74	−1.47
14	piperdine	11.1	*c*	−1.49
15	2-picoline	5.96	0.77	−1.45
18	1-methylimidazole	7.33	*c*	−1.49
20	1,2-dimethylimidazole	7.85	*c*	−1.48

[a] $E_{1/2}$ was measured in volts vs. SCE. [b] K. Schoefield, "Hetero-Aromatic Nitrogen Compounds", Plenum Press, New York, 1967, p 146. [c] Reaction not observable within the solvent range.

Thin-layer spectrocoulometry for the electrode reaction $[TPPZn(L)]^0 \rightleftarrows [TPPZn(L)]^+ + e^-$ was performed when possible. Free-ligand concentrations were adjusted, by using calculated β_1^+ values, to levels which would provide greater than 99% complexation. The oxidative coulometry showed 1.0 ± 0.1 electrons transferred for ligands with pK_a values less than 3,4-lutidine. The ligands of highest pK_a showed increasing oxidation behavior which thin-layer ligand blanks verified as ligand oxidation. The uncertainty in the coulometry for these ligands precludes the reporting of *n* values.

Time-resolved thin-layer spectra were also obtained for the oxidation to the cation radical in both the presence and absence of ligand. As opposed to the spectra of TPPZn, which in the presence of ligand is red shifted 5–8 nm in the Soret region and 8–15 nm in the visible region, the radical cation spectra are rather insensitive to the presence of ligand. The Soret change is less than 1 nm while the visible changes are primarily in intensity rather than wavelength. As seen in Figure 1 for the oxidation of TPPZn(py) the appearance of clean isosbestic points indicates no intermediate products. These thin-layer oxidations required only 30 s for complete conversion to the ligated cation radical and are spectrally reversibly upon the reverse reduction. On this 1-min time scale there is no spectral

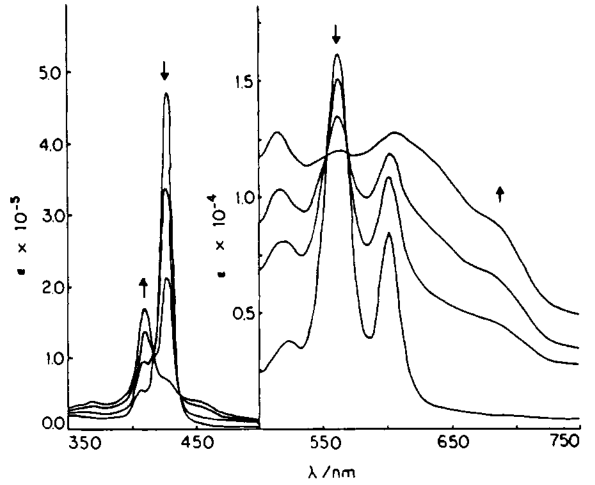


Figure 1. Time-resolved spectra for the reaction TPPZn(py) ⇄ $[TPPZn(py)]^+ + e^-$.

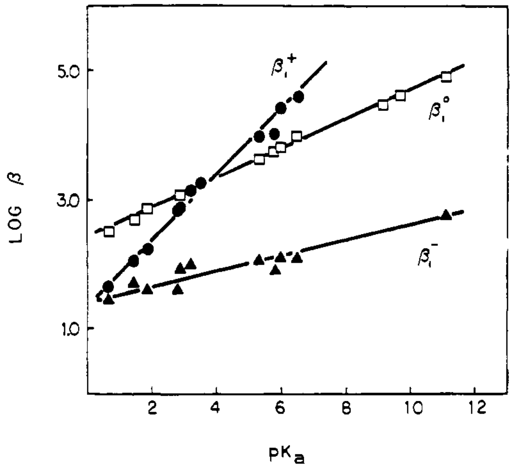


Figure 2. Plot of log β_1^+, log β_1^0, and log β_1^-, as a function of pK_a of the substituted pyridine. The ligands are identified in Table I.

evidence for the $TPPZn(\beta\text{-py})^+ClO_4^-$ product obtained by Shine[33] in acetonitrile for the reaction of the $TPPZnClO_4$ with pyridine.

Linear Free-Energy Relationships. Plots of log β_1^+, log β_1^0, and log β_1^-, vs. pK_a of the substituted pyridine are shown in Figure 2. The increase of log β_1^+, log β_1^0, and log β_1^- with pK_a suggests, for all three reactions, that σ bonding dominates the ligand to metal interaction for the pyridine system. The fit of piperidine to the log β_1^0 vs. pK_a trace confirms this assignment since the piperidine N can only σ bond to the metal. Formation constant magnitudes for the imidazoles investigated are 1 order of magnitude greater than for the pyridines studied with comparable pK_a's (Table I). This behavior has been previously observed for other porphyrin systems and can be attributed to an increase in the Zn–N bond order due to ligand π donation onto the imidazole N.

Comparison of the formation constant magnitudes for 4-picoline (ligand **10**) and 2-picoline (ligand **15**) yields an intriguing result. Both ligands have essentially the same pK_a value yet the formation constants for 2-picoline are between 1 and 2 orders of magnitude less than 4-picoline. This behavior has been previously observed for iron porphyrins[34] and has been attributed to steric hindrance by the methyl group in the 2 position. However, the difference in formation constant magnitude attributable to steric effects increases with increasing charge on the porphyrin; that is, $\Delta \log \beta_1^- = 1.31$, $\Delta \log \beta_1^0 = 1.57$, and $\Delta \log \beta_1^+ = 2.31$. The reason behind this behavior is not clear at the present time. Experiments with other sterically hindered ligands binding to TPPZn and other metalloporphyrins are presently underway to evaluate whether the observed differences are due only to this particular system or are, in fact, a general phenomena.

Finally, complexation of the zinc porphyrin with the 20 nitrogenous bases studied has permitted the first redox "tuning" of a porphyrin π-radical reaction. By variation of the pK_a of the ligand, the potential of the TPPZn(L) oxidation process has been shifted over a 90-mV range ($0.83 \geq E_{1/2} \geq 0.74$ V) whereas the potential of the TPPZn(L) reduction process has been shifted over a 110-mV range ($-1.38 \geq E_{1/2}$ -1.49 V). Although the observed potential shifts are small with respect to the shifts observed for metal-centered porphyrin electron transfers,[10] the shifts clearly demonstrate that the potential for π-radical formation is affected by the central metal stoichiometry.

Acknowledgment. The support of this research from the National Science Foundation (Grant CHE-7921536) and the Robert A. Welch Foundation (Grant E-680) is gratefully acknowledged.

Registry No. **1**, 2457-47-8; **2**, 100-54-9; **3**, 100-48-1; **4**, 626-60-8; **5**, 626-55-1; **6**, 350-03-8; **7**, 1122-54-9; **8**, 110-86-1; **9**, 108-99-6; **10**, 108-89-4; **11**, 583-58-4; **12**, 504-24-5; **13**, 1122-58-3; **14**, 110-89-4; **15**, 109-06-8; **16**, 504-29-0; **17**, 288-32-4; **18**, 616-47-7; **19**, 693-98-1; **20**, 1739-84-0; $[TPPZn]^+$, 39732-73-5; $[TPPZn]^-$, 34465-10-6; TPPZn, 14074-80-7; TPPZn(**1**), 76377-09-8; TPPZn(**2**), 24315-64-8; TPPZn(**3**), 24315-63-7; TPPZn(**4**), 76377-10-1; TPPZn(**5**), 76377-11-2; TPPZn(**6**), 68932-66-1; TPPZn(**7**), 68932-67-2; TPPZn(**8**), 24389-79-5; TPPZn(**9**), 24389-78-4; TPPZn(**10**), 24315-61-5; TPPZn(**11**), 76377-12-3; TPPZn(**14**), 24315-59-1; TPPZn(**15**), 24315-65-9; TPPZn(**18**), 67820-10-4; TPPZn(**20**), 76377-13-4.

---

(33) H. J. Shine, A. G. Padilla, and S. M. Mu, *J. Org. Chem.*, **44**, 4069 (1979).

(34) F. A. Walker, E. Hui, and J. M. Walker, *J. Am. Chem. Soc.*, **97**, 2390 (1975).