Polarographic Reduction of Porphyrins and Electron Spin Resonance of Porphyrin Anions[1]

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Received October 8, 1965

Abstract: Polarographic measurements have been made on a number of tetraphenylporphyrin and etioporphyrin complexes, in DMF or DMSO solution. The polarograms are characterized by two main waves corresponding, for the most part, to one-electron reductions. This is confirmed by the optical and esr absorption of porphyrin monoanions, prepared by electrochemical reduction at the first half-wave potential. Evidence is given that addition of both electrons generally occurs into orbitals belonging mainly to the porphyrin ring, except for cobalt tetraphenylporphyrin, in which reduction appears to occur in a metal-centered orbital. These results, and the observed order of increasing negative half-wave potentials (corresponding to the calculated order of over-all negative charge on the ring), are in agreement with recent theoretical results of Zerner and Gouterman. The monoanion esr spectra fall into two classes, differing sharply in line breadth and *g* value.. The line widths are discussed.

The oxidation–reduction properties of the porphyrins play a key role in their biological function. To clarify these properties further, an extended study of the electrochemistry of the porphyrins and the spectra of their negative ions is in progress.[2] As part of this work, we present here polarographic and esr data and interpretations on a number of porphyrins. The first systematic polarographic studies of porphyrins and chlorins were done by Hass[3] and Gilman[4] in buffered ethanol solution. The work described here was carried out in dimethylformamide or dimethyl sulfoxide solvent, in which complications arising from proton-transfer reactions at the electrode do not occur. Related studies on chlorophyll and derivatives in these solvents have been published elsewhere.[5a] Similar independent polarographic studies have been reported recently by Clack and Hush.[5b]

Experimental Section

(a) **Materials.** Dimethylformamide (DMF, reagent grade) was refluxed over CaH_2 and fractionated. Dimethyl sulfoxide (DMSO) was similarly purified over hydride and distilled at low pressure. Tetra-*n*-propylammonium perchlorate[6] and tetrahydrofuran (THF)[7] were purified and stored as described previously.[6,7] Prepurified nitrogen was deoxygenated and dried by passage through chromous chloride solution over zinc amalgam, CO_2 traps, and potassium terphenylide solution in THF, and finally presaturated with DMF or DMSO. The anthracene used in porphyrin reductions was scintillation grade (Pilot Chemical Co., Waltham).

Etioporphyrin I was kindly supplied by Dr. J. G. Erdman. Metalloetioporphyrins were prepared by the method of Erdman and Corwin,[8] using THF in place of chloroform as solvent, and were purified by chromatography on alumina with 1:1 benzene–THF. Free base $\alpha,\beta,\gamma,\delta$-tetraphenylporphine ($H_2TPP$) was prepared by condensation of pyrrole and benzaldehyde[9,10] and was purified by chromatography on acid alumina with 1:1 chloroform–benzene and recrystallization from benzene–methanol solvent. ZnTPP and zinc tetraphenylchlorin (ZnTPC) were obtained by condensation in the presence of zinc acetate, in a manner analogous to that used for H_2TPP. The salts were separated by chromatography on alumina with benzene, followed by elution of the chlorin with ether. The remaining metallotetraphenylporphyrins were prepared from the free base by established methods[9] and purified by repeated chromatography and recrystallization from benzene–methanol. To obtain pure CoTPP, it was necessary to chromatograph on $CaCO_3$ with benzene.

The composition of tin tetraphenylporphyrin is somewhat uncertain. *Anal.* Calcd for SnTPP: C, 72.25; H, 3.86. Found: C, 68.75; H, 4.30; Cl, 0.0. Although Rothemund and Menotti[10] reported this compound as SnTPP dichloride, while Dorough, *et al.*,[9] refer to it as stannous tetraphenylporphyrin, all the visible spectra agree. Our analyses correspond to the diacetate, SnTPP-$(C_2H_3O_2)_2$ (Calcd C, 67.52; H, 4.08.), and we will assume that the oxidation state of tin is four in its TPP complex. Tin etioporphyrin II has been made as the diacetate or dichloride.[11]

(b) **Polarographic Technique.** Dc polarograms were recorded with a calibrated Sargent Model XXI polarograph and dropping mercury electrode (capillary constant at 1 v in DMSO = 1.33 mg/sec). A conventional H-cell was used with a coarse fritted disk between the anode and cathode compartments, and 0.1 *M* tetra-*n*-propylammonium perchlorate as the supporting electrolyte. The anode was an aqueous saturated calomel electrode with connecting KCl–agar salt bridge. The bridge deteriorates rapidly in organic solvents and was frequently replaced. Polarographic half-waves and slopes (Table I) were corrected for *IR* drop.

(c) **Chemical Reductions.** Reductions with alkali metal were carried out in sealed-off ampoules, by bringing the dye, dissolved in carefully degassed THF, into contact with a sodium or potassium mirror deposited by previous distillation in a side arm. The reaction was followed spectrophotometrically in an absorption cell carried on another side arm, or in a capillary tube which could be inserted in an esr spectrometer. Reductions using sodium anthracenide were done in essentially the same apparatus. A solution of sodium anthracenide was first prepared by reacting anthracene in THF solution with the metal mirror, and then decanting this into the side arm carrying porphyrin and the absorption cell.

(d) **Electrochemical Reductions.** These were done at inert mercury or platinum gauze electrodes, in cells mounted either in a Cary Model 14 spectrophotometer or the esr spectrometer. Working and reference calomel electrodes were also provided for potentiometric control of the effective reduction potentials. For the esr experiments reported here, the apparatus used was that of Maki and Geske.[6]

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[1] This work was supported by grants from the National Institutes of Health (GM 10833) and the U. S. Atomic Energy Commission (AT-30-1-2003).

[2] R. H. Felton, Thesis, Harvard University, 1964.

[3] M. Hass, Thesis, Syracuse University, 1952.

[4] S. Gilman, Thesis, Syracuse University, 1956.

[5] (a) R. H. Felton, G. M. Sherman, and H. Linschitz, *Nature*, **203**, 637 (1964); (b) D. W. Clack and N. S. Hush, *J. Am. Chem. Soc.*, **87**, 4238 (1965).

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[8] J. G. Erdman and A. H. Corwin, *J. Am. Chem. Soc.*, **68**, 1885 (1946).

[9] G. Dorough, J. Miller, and F. Huennekens, *ibid.*, **73**, 4315 (1951).

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[11] A. Corwin and O. Collins, *J. Org. Chem.*, **27**, 3060 (1962).

Table I. Polarographic Results on Porphyrins[a]

Compound	$-E_{1/2}$[b] (pre-wave)	$-E_{1/2}$ (1)[b]	Slope, mv	$-E_{1/2}$ (2)[b]	Slope, mv	Δ[c]
MgTPP	0.67	1.35	57	1.80	62	0.45
ZnTPP	0.71	1.31	59	1.72	63	0.41
CdTPP	0.67	1.25	59	1.70	68	0.45
CuTPP[f]	0.72	1.20	64	1.68	62[g]	0.48
NiTPP[h]	...	1.18	...	1.75	...	0.57
PbTPP[e]	0.83	1.10	58	1.52	62	0.42
H_2TPP	0.70	1.05	61	1.47	65	0.42
CoTPP	Absent	0.82	65	1.87	68	1.05
SnTPP(OAc)$_2$	0.5	0.81	61	1.26	65[g]	0.45
ZnEtio I[d]	0.89	1.60	57	1.95	85[g]	0.35
CuEtio I[d]	0.95	1.46	62	2.05	...	0.54
H_2Etio I[d]	0.92	1.34	63	...	...	...
CoEtio I[d]	Absent	1.04	62	1.57	75[g]	0.53
ZnTPC	0.72	1.33	66	1.70	65	0.37
ZnTPP	Over the concentration range 0.37 to 1.3 m*M*, diffusion current constants for the first and second waves were constant at 0.89 and 0.90, respectively. Plots of wave height *vs.* square root of corrected Hg head (20–60 cm) were linear for both waves, with zero current intercept. Higher waves were seen in DMSO solvent at −2.36 and −2.58 v.					
H_2TPP	Heights of both waves were equal, proportional to concentration (0.2 to 1.4 m*M*) and linear in square root of Hg head. An extended wave at −1.87 v was present.					
SnTPP	Higher wave at −2.14 v.					
PbTPP	Higher wave at −2.34 v.					
CoTPP	First wave has a small maximum, 5% of total height.					
ZnTPC	Shows small wave at −2.07 v.					
CoEtio I	Second wave at −1.57 v was half the height of the first wave. First wave had maximum, independent of dye concentration.					
Na$_2$TPP	No wave was observed up to reduction wave of NaClO$_4$ (−1.7 v).					

[a] Unless otherwise specified, the solvent system was 0.1 *N* tp-NClO$_4$ in DMSO. [b] Volts *vs.* saturated calomel electrode (aq). [c] $E_{1/2}(1) - E_{1/2}(2) = \Delta$. [d] DMF solvent. [e] 1:3 THF–DMSO solvent. [f] 1:3 THF–DMF solvent. [g] Estimated from $E_{3/4} - E_{1/4}$. [h] Benzene–DMF solvent.

Results and Discussion

1. Polarographic Results. Table I summarizes the polarographic data and analysis. The polarograms of H_2TPP and all the metal TPP and TPC complexes examined here show two well-defined waves of equal height and slopes corresponding to one-electron reduction. Two main waves are also found for the etioporphyrins, but the second wave tends to be sensitive to concentration, increasing in height and shifting to more negative potentials with added dye. For ZnEtio I and CoEtio I, the second wave characteristics are believed to be reliable, but the corresponding waves for H_2Etio I and CuEtio I are several times the height of the first wave and evidently represent rather complicated reductions. Similar concentration shifts and overlapping multiple reductions were found by Gilman, in TPP complexes.[4] A small prewave is also associated with all the porphyrins except the nickel and cobalt salts. This prewave is not due to an impurity and does not increase linearly with dye concentration.

In attempting to assign the waves of Table I to specific reduction processes, we note first a constant difference in the potentials of the first waves, between corresponding pairs of TPP and etioporphyrins, as follows: (1) H_2TPP–H_2Etio I, 0.29 v; (2) ZnNTPP–ZnEtio I, 0.29 v; (3) CuTPP–CuEtio I, 0.26 v. If the electron were added to an orbital primarily centered on the metal, such constancy could hardly be expected for such highly diverse accepters as protons, filled d-shell ions, and transition metal ions. Moreover, the positive sign of the difference agrees with the expected decrease in electron affinity of the porphyrin nucleus on the substitution of eight alkyl groups. Table I shows also a strikingly constant difference between the potentials of the first and second waves, $\Delta = E_{1/2}(1) - E_{1/2}(2) = 0.44 \pm 0.04$, in the group H_2TPP and the magnesium, zinc, cadmium, copper, lead, and tin(IV) TPP complexes. This suggests that in these compounds the second electron is also being added to the ring, to produce a porphyrin dianion. Finally, it is instructive to compare the experimental diffusion current constant, $I_d = i_d c^{-1} m^{-2/3} t^{-1/6}$, with the Ilkovic expression,[12] $I_d = 607nD^{1/2}$, estimating the diffusion constant at 25° from the Walden relation,[12] $D = 2.96 \times 10^{-7} \eta^{-1} V_m^{-1/3}$. For ZnTPP in DMSO, we take η = 19.6 mpoise[13] and the molar volume V_m = 442 cm^3/mole,[14] and obtain for the diffusion current constant $I_d = 0.855n$. Comparing this with the experimental constants for the first and second waves of ZnTPP (0.89 and 0.90, respectively) verifies the one-electron nature of both reduction processes.

The value of Δ for CoTPP, 1.05 v, is sharply different from that for the other porphyrins of Table I. This implies a difference in the nature of the reductive process in this compound and suggests that the site of primary reduction in this case may be the metal ion rather than the ring.

These views are generally supported by the results of our chemical and electrochemical reduction experiments. The characteristic near-infrared bands of the monoanions of ZnTPP,[15] ZnEtio I,[16] SnTPP, and CuTPP were obtained by chemical reductions using sodium metal, anthracenide, or ketyl. Similar bands were observed in electrochemical reductions at controlled potentials 0.2 v more cathodic than the $E_{1/2}(1)$'s of Table I. However, for CoTPP both sodium (THF) and controlled-potential (DMSO) reductions yield the same optical spectrum which is quite different from the typical spectra of the monoanions; peaks are found at 365, 425, and 510 mμ, and no infrared bands are seen. Moreover, sodium reduction of CoTPP proceeds much more slowly than that of the other complexes and, unlike them, does not go beyond the first reduction stage. Clearly, the reduction reaction in CoTPP differs markedly from that in the other porphyrins.

An interpretation of these results may be given on the basis of recent extended Hückel calculations by Zerner and Gouterman[17] which indicate that, for a series of metalloporphyrins, the sequence Ni $\lesssim$ Cu < Zn < Mg corresponds to the order of increasing negative charge on the ring. This order corresponds exactly to that found polarographically for the first reduction potentials (Table I). Zerner and Gouterman thus

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(14) E. Fleischer, *J. Am. Chem. Soc.*, **85**, 1353 (1963).

(15) G. Closs and L. Closs, *ibid.*, **85**, 818 (1963).

(16) J. Dodd and N. Hush, *J. Chem. Soc.*, 4607 (1964).

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assign the increasing difficulty of reduction in this series to increasing Coulomb repulsion between the ring charge and the added electron. This view does not ascribe shifts in half-wave potential to changes in energy of the lowest unfilled molecular orbital. Indeed, the calculations cited show that, for the above series of compounds, the energy of this orbital remains stationary. In the case of H_2TPP, the particularly low value of $E_{1/2}(1)$ is explained by the presence of nodes in the wave function of the lowest split e_g level. The incoming electron can thus better avoid regions of high electron density. It is particularly noteworthy that for the cobalt complex, Zerner and Gouterman find the lowest available level to be the half-filled cobalt a_{1g} (d_{z^2}) orbital, which lies well below the lowest porphyrin e_g (π) orbital. Thus preferential reduction of the metal in this complex is reasonable.

The constant difference, Δ, between the first and second half-wave potentials may be understood by considering a relation used by Hoijtink, *et al.*,[18] to discuss the free energy of disproportionation of aromatic anions

$$\Delta = J + \Delta E_s^{2-} - 2\Delta E_s^{-}$$

Here, J is the Coulomb integral corresponding to electron repulsion in the lowest filled orbital of the dianion, ΔE_s^{-} and ΔE_s^{2-} are the solvation energies of the mononegative and dinegative ions, respectively, and entropy and possible ion-pairing effects are taken to be equal for both reduction stages. Because the lowest unfilled porphyrin orbital is a degenerate e_g level,[19] the above equation is slightly modified, as

$$\Delta = J_{xy} \pm K_{xy} + \Delta E_s^{2-} - 2\Delta E_s^{-}$$

The exchange integral K_{xy} is taken between degenerate components of the e_g level and allows for formation of the dianion in a singlet (positive sign) or triplet (negative sign) ground state. We now observe that none of the quantities on the right side of the equation should be markedly sensitive to changes in the central metal ion of the complex. For J_{xy} and K_{xy}, this insensitivity follows from the nonbonding nature of the e_g orbitals,[19] and for the ΔE_s's because these energies refer to solvation of the entire anion, not of the complexed metal.

2. **Esr Spectra.** For the majority of metalloporphyrin radical-anion spectra, listed in Table II, g factors were equal to the free-spin value (2.0023), and total widths[20] were in the range 15–20 gauss. However, for Na^+ ZnEtio I^- and n-pr_4 N^+ $ZnTPP^-$ the g factors were significantly less than 2.0023, and total widths were about 80 and 100 gauss, respectively. No hyperfine structure was found in any of the spectra at concentrations near 10^{-3} M, and for Na^+ ZnEtio I^- down to 10^{-4} M. Spectra were symmetrical about the center. Representative examples ($ZnTPP^-$ and $ZnTPC^-$) are shown in Figure 1.

Table II. Esr Spectral Characteristics of Porphyrin Anions in DMSO

Compound	g value	Width between inflection points, gauss	Total width, gauss
ZnTPP	2.0000 ± 0.0004	20	100
ZnEtio[b]	2.0002 ± 0.0003	17	80
CdTPP	2.0025 ± 0.0003	7	22
MgTPP	2.0024 ± 0.0003	4.7	15
ZnTPC	2.0023 ± 0.0003	8.2	22
H_2TPP[a]	2.0027 ± 0.0003	3.8	15

[a] Solvent, DMF. [b] Reduced with Na in THF.

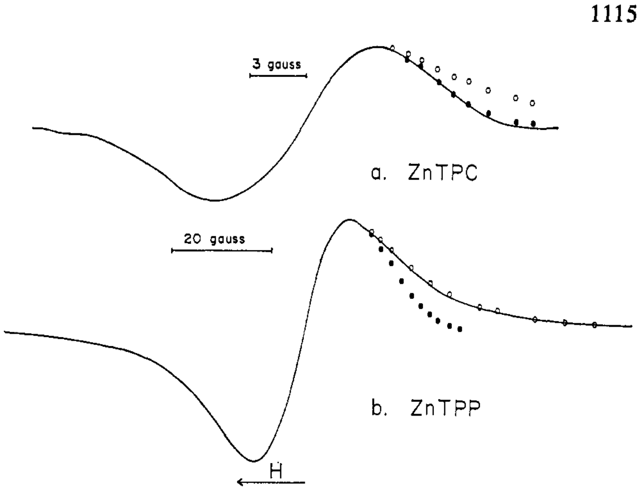

Figure 1. Porphyrin monoanion esr spectra: (a) ZnTPC; (b) ZnTPP; solid line, experimental; ○, Lorentzian fit; ●, Gaussian fit.

The observed line widths are not influenced by modulation broadening or saturation effects, which were specifically avoided in these measurements. Moreover, exchange broadening by electron transfer between charged and neutral species[21] is much too small, at the concentrations used here to account for the observed widths. In fact, solutions of Na^+ $ZnTPP^-$ in THF, prepared from the pure solid salt[15] show spectral widths (26 gauss between points of maximum slope) which are comparable to those observed here (Table II) for n-pr_4 N^+ $ZnTPP^-$ in DMSO.

In order to discuss the width of the porphyrin anion spectrum, we calculate the hyperfine spectrum. Hyperfine coupling constants in Table III are found from the relations: $a_H^i = Q_H\rho_{CH}^i$, $a_N = Q_N\rho_N$, and $a_{CH_3} = Q_{CH_3}\rho_{CCH_3}$. Here, a_H^i, a_N, and a_{CH_3}, are, respectively, the coupling constants for equivalent hydrogens of the ith class, bonded to sp^2-hybridized carbon atoms, for nitrogen atoms and for methyl protons (present in etioporphyrin I); ρ_N, ρ_{CH}, and ρ_{CCH_3} denote π spin densities on nitrogen and carbon atoms to which the respective protons or methyls are bonded. The spin density was set equal to the extra electron distribution on the appropriate atom. Orbital coefficients were those of Kobayashi[22] and correspond to two sets of calculations with $\delta_N = 0$ and $\delta_N = 1.0$, where $\alpha_N = \alpha_c + \delta_N\beta_{cc}$. Here, α_N is the nitrogen Coulomb parameter and β_{cc} is the carbon–carbon bond integral. Values of Q

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(20) "Total widths" were taken to be the extent of the spectrum measured between field strengths corresponding to about 5% of the derivative peak heights.

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in gauss were $Q_H = -25$,[23] $Q_N = 30$,[24] and $Q_{CH_3} = 25$.[25,26] The spectrum of etioporphyrin I anion was calculated assuming the methyl group to be ethyl, thus retaining D_{4h} symmetry.

Table III. Calculated Hyperfine Coupling Constants (gauss)

	δ_N					
	ZnTPP⁻		ZnEtioI⁻		Zn porphine⁻	
	1.0	0.0	1.0	0.0	1.0	0.0
a_H (methine)	0	0	2.25	2.58	2.25	2.58
a_N	0.725	1.36	0.725	1.36	0.725	1.36
a_H (pyrrole)	0.976	0.875	1.95	1.75	0.976	0.875
Total width	13.6	17.9	30.4	35.2	22.6	28.2

Since the ground state of metalloporphyrin anion is ^2E_g, spin distribution will be affected by both external perturbations, such as interaction with the polar solvent or a cation, and by vibronic coupling. If the degenerate components of the ground state are mixed by perturbations at a frequency which is greater than the separation of hyperfine components ("fast switching"), then large fluctuations in spin density will be averaged to yield a hyperfine spectrum reflecting molecular symmetry.[27]

Values of a_N, a_H, and a_{CH_3} appropriate to this fast switching case are calculated by determining these values for one component, say E_{gx}, of the ^2E_g state followed by averaging. To illustrate, we note that for a molecule fixed in the E_{gx} state, only two nitrogen orbitals will have spin density (there is a symmetry node through the remaining pair of nitrogens). From this coupling and using the previous parameters, one obtains a five-line spectrum with 5.8 gauss between the outermost components ($M_I = +2$ and $M_I = -2$). For fast switching in which all four nitrogens become equivalent, a nine-line spectrum results with 5.8 gauss separating outer components, and the appropriate coupling constant for nitrogen is 5.8/8 = 0.725 gauss. No attempt was made to ascertain what contribution was made to the total width by negative spin density.

Total widths, listed in Table II for radical anions of MgTPP, zinc tetraphenylchlorin, CdTPP, and H_2TPP, are in accord with the computations as summarized in Table III. The lack of resolved hyperfine structure is to be expected in view of line widths associated with hyperfine components of molecule with degenerate electronic states[28,29] and the expected number of hyperfine components in tetraphenylporphyrin and etioporphyrin radical anions.

At present, we do not have an unambiguous explanation for zinc porphyrin monoanion spectra. Correlation between low *g* values and broadened lines suggests spin relaxation phenomena. However, it is difficult to understand the narrow line of CdTPP anion compared with ZnTPP, if only a heavy atom effect is operative. It is possible that we are observing the spin-orbit relaxation mechanism suggested by McConnell,[30] in which the component of unquenched ring orbital momentum perpendicular to the porphyrin plane couples with the spin. If so, spin relaxation must be more efficient in, say, ZnTPP than in benzene anion, which has a normal *g* value and line width.[28] Here again, one must explain the difference between the esr spectra of CdTPP or MgTPP anion and that of ZnTPP. These may arise from different distortions of the porphyrin ring out of planarity,[31] perhaps associated with complexing of solvent molecules at the central metal ion.[32] Such distortion would strongly modify the ring angular momentum but not the electronic spectrum, thus accounting for the spectral similarity of ZnTPP and MgTPP anions.[16] In any case, it is clear that relaxation times must be determined.

Acknowledgment. It is a pleasure to acknowledge the assistance and cooperation of Professor M. Gouterman in this work. We wish to thank Professor J. G. Erdman for a generous sample of etioporphyrin and Professor A. Maki, for hospitably allowing us the use of his esr equipment.

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