Electrochemical studies of some porphyrin IX derivatives in aprotic media

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calculation of the A_o values, and estimated to be 2% for the beam-intensity monitor and Faraday cup calibration, and about 2% for errors in timing for the ^{20}F experiments. The accuracy of the absolute excitation function is about 5%.

DISCUSSION

Interferences. By using ^{20}F activity, fluorine analyses are relatively free from interferences produced either directly or indirectly by other elements present in the sample. The direct interference is caused by the same-isotope (^{20}F) production; the only obvious interference would be ^{20}F activity produced by any ^{18}O present in the sample. The excitation function of $^{18}O(^3He, p)^{20}F$ is shown in Figure 5; the cross section at 17 MeV is about 50 mb, rising to 100 mb at 10 MeV. The isotope abundance, however, for ^{18}O in natural oxygen is only 0.2%. As the $^{19}F(^3He, 2 p)^{20}F$ and $^{18}O(^3He, p)^{20}F$ cross sections are comparable between 12 to 17 MeV, at equal concentration of fluorine and oxygen impurities is a given matrix, only 0.2% of the ^{20}F activity will have been caused by an interfering ^{18}O. An analysis based upon the production of ^{18}F is also feasible in some cases, but the chances for interference are much greater with ^{18}F as the "signal" than with ^{20}F because ^{16}O would induce a direct interference. This possible interference would be caused by the $^{16}O(^3He, p)^{18}F$ reaction whose cross section below 10 MeV is about 20 times greater than the $^{19}F(^3He, 2 p)^{20}F$ reaction. Indeed, *oxygen* analysis *via* the former reaction has been previously described (*12*).

Sodium might be a possible interference due to the $^{23}Na(^3He, \alpha \, 2 \, p)^{20}F$ reaction. Although the cross sections

have not been measured, the threshold is 13.2 MeV; therefore, sodium would be eliminated as an interference by bombardments near or below this energy.

Indirect interferences (nuclides emitting gamma rays about 1.6 MeV) would have to be sufficiently close to 10.8-sec half-life and sufficiently great in quantity to prevent resolution of the ^{20}F 1.63 MeV decay curves. High atomic-number impurities or target matrices will not induce any radioactivities if the ^3He energy is controlled to be below the Coulomb barrier.

Estimate of Detection Limit. Under the following conditions: Beam current 1 μA, cross section 70 millibarns, length of bombardment 10.8 seconds; we found D_o (disintegration rate at end of bombardment) to be 5.7 $\times$ 10^5 dps per mg/cm^2 of F. With our overall detection coefficient of only 1.6%, this gives about 10^4 counts per second in the gamma photopeak. As the background was about 40 cps, this corresponds to a factor of about 250 times background. At equal signal and background rates, under our easy conditions, we could detect $\sim$4 $\mu g/cm^2$ F. Because the beam intensity can be increased to 10 μA (or greater), and the detection coefficient can be easily doubled, the detection limit can be lowered to 0.2 $\mu g/cm^2$ F. If the matrix in which the F is imbedded is 10 to 100 mg/cm^2 thick, the concentration limit would therefore be 20 ppm to 2 ppm, respectively. With more care for shielding, the background and therefore the detection limit could be further lowered. The sensitivity, of course, will depend upon the presence of interferences and the matrix.

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Electrochemical Studies of Some Porphyrin IX Derivatives in Aprotic Media

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The electrochemical reduction of deuteroporphyrin (DPDME) and mesoporphyrin (MPDME) IX dimethyl esters was investigated in dimethyl formamide. Under polarographic conditions both compounds exhibit three waves, the first two being reversible one-electron steps, the third an irreversible two-electron process. The anion radical of DPDME can be shown by *in situ* generation in a thin-layer cell with an optically transparent electrode to undergo slow disproportionation. The products of this reaction can be further reduced. The di-anion of DPDME when formed rapidly abstracts a proton from the solvent medium. Although very similar in structure, MPDME undergoes the described reactions much more slowly, thereby facilitating observation. Mechanisms and spectral evidence are presented. Effect of controlled proton addition was also noted.

THE PORPHYRIN NUCLEUS forms one of the most important structures in biological electron transport systems. Because it is frequently complexed with a metal as a metalloporphyrin, there is a tendency to overlook the capability of the porphyrin

ring itself as an electron donor or acceptor. Because porphyrins can exist in a large number of oxidation states (at least six are known), electrochemical investigation is particularly useful in sorting out the many species which can be produced. The effectiveness of electrochemical generation of porphyrin species is greatly enhanced by simultaneous spectral measurements.

Porphyrin and metalloporphyrin electrochemistry have been studied in aqueous solution (*1–3*). In virtually every case, the pH has had a strong influence on the course of the electrochemical reaction. The presence of a proton, however, tends to promote disproportionation and cause overlap of electron transfer steps. Aqueous studies are further plagued by the well-known aggregation of porphyrin species (*4*).

[1] To whom communications concerning this paper should be addressed.

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Figure 1. Porphyrin IX structures

DPDME — A,B = H;
MPDME — A,B = C₂H₅

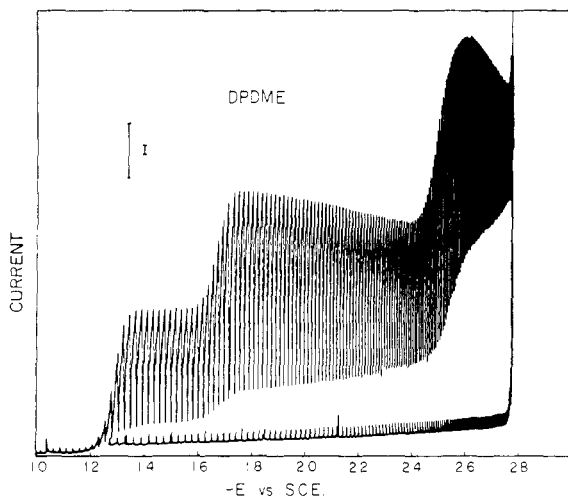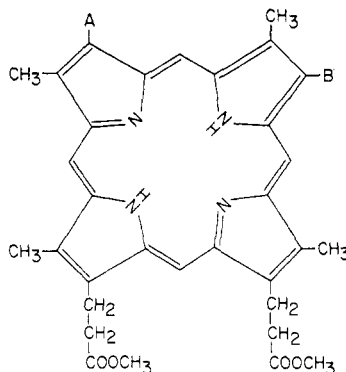**Figure 2. Polarography of DPDME in DMF 0.1M TEAP**

Concentration $1.2 \times 10^{-3}M$. $I = 0.5\ \mu A$. Residual current curve: $I = 0.2\ \mu A$

Figure 3. Cyclic voltammetry of DPDME in DMF 0.1M TEAP at HMDE

Concentration $8.0 \times 10^{-4}M$. Scan rate 0.10 V/sec. A. Single scan. B. Hold at −1.8 V followed by anodic scan

Nonaqueous electrochemical studies of porphyrins have been mostly restricted to polarographic measurements accompanied by some EPR and spectral data (5, 6). The main interest, however, in these studies, has been the correlation of half wave potentials with molecular orbital calculations rather than with the details of the electron transfer reactions themselves. Inhoffen and coworkers have identified controlled potential electrolysis products by NMR (7). In the present study, the electrode reactions are examined in detail in an aprotic solvent [dimethylformamide (DMF)]. To this solvent a proton donor is added, and the changes in the overall electron transfer reactions are noted.

EXPERIMENTAL

Materials. Deuteroporphyrin IX and mesoporphyrin IX dimethylester free base (DPDME and MPDME, respectively) were obtained from the Pierce Chemical Company and were used without further purification.

SOLVENT. Spectrograde DMF was refluxed for 8 hr with crushed calcium hydride under nitrogen. It was distilled at about 12 mm (43 °C) under vacuum using a 3-foot Vigreux column under 20:1 reflux ratio. This procedure was carried out 3 times. Collection of fractions and other transfer operations were carried ou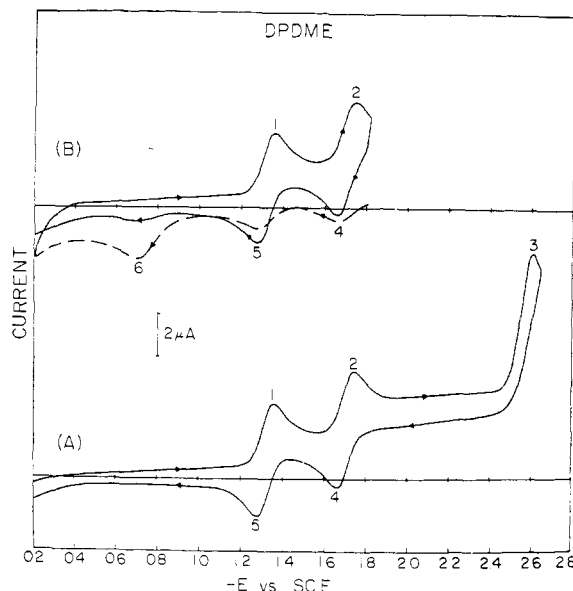t under nitrogen atmosphere. If properly purified solvent and supporting electrolyte are used, less than 0.1 μA residual current is observed between +0.2 V and −2.8 V vs. SCE with no evidence of waves. Karl Fischer titration of the purified solvent gave a water concentration of 0.1–0.3 millimolar. To our knowledge this is the lowest reported level (8).

SUPPORTING ELECTROLYTE. Tetraethylammonium perchlorate (TEAP) (Eastman) was recrystallized twice from methanol and dried under vacuum overnight at 80–100 °C.

NITROGEN. An inert atmosphere was provided by passing tank nitrogen through a tower containing BTS catalyst (BASF Colors and Chemicals), a Cu-Ni formulation which removes oxygen from the gas stream by reduction at room temperature. This is followed by a tower containing phosphorus pentoxide. The purified nitrogen was then presaturated in a gas wash bottle containing TEAP and DMF.

Apparatus and Methods. Polarographic and cyclic voltammetric data were obtained using a Heath EUA19-2 polarographic analyzer and EUA 19-4 stabilizer. A triangular wave generator as described by Weir and Enke (9) was employed. Current voltage curves were obtained using a Moseley 7001A x-y recorder or a digital data acquisition system described previously (10). A standard hanging mercury drop electrode (HMDE) was employed. A polarographic cell described elsewhere (11) was maintained at a constant temperature of 25 ± 0.1 °C. All potential measurements were made with respect to an aqueous saturated calomel electrode (SCE).

Near infrared and visible spectra were recorded using a Cary 14R spectrophotometer. In situ generation of porphyrin species was accomplished using a thin-layer cell (about 0.09-mm path length) of a design similar to that given by Heineman et al. (12). EPR spectra were generated in situ at 25 °C in the cavity of a Varian E-3 EPR spectrometer in a cell similar to that described by Visco (13).

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(12) W. R. Heineman, J. N. Burnett, and R. W. Murray, ANAL. CHEM., **40**, 1974 (1968).
(13) R. E. Visco, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1962.

Figure 4. Spectra of DPDME in DMF 0.1M TEAP (thin-layer cell)

Concentration 1.1 × $10^{-3}M$. P(———); P ⁻ (- - -); PH⁻ (— · —·); $PH_{n+1}^{[4-(n+1)-]}$ (-O-O-O-); $PH_{n+m+1}^{[4-(n+m+1)]-}$ (-■-■-■-).
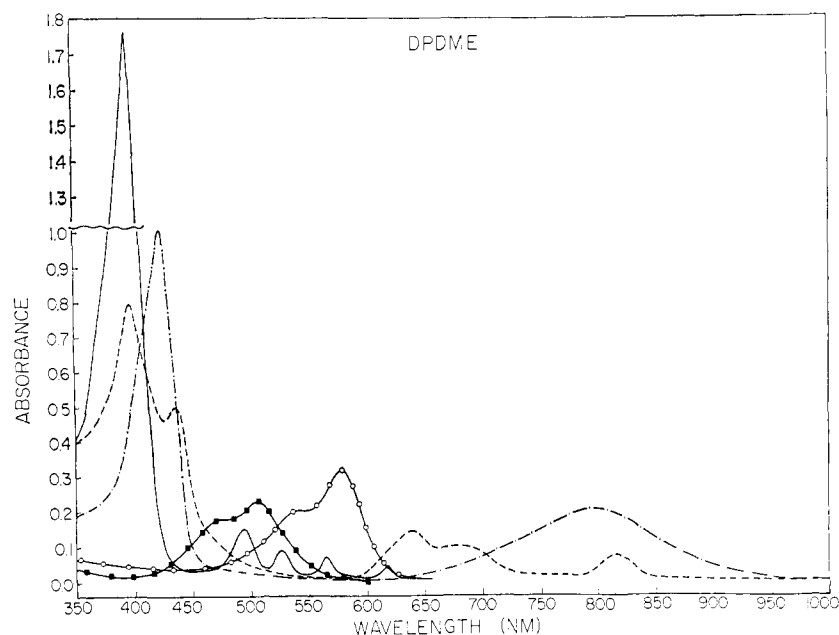
Table I. Electrochemical Data for Porphyrin IX Derivatives[a]

	Wave	$-E_{1/2}$	Slope, mV[b]	$-E_{pc}$[c]	$-E_{pa}$
DPDME	1	1.29	60	1.36	1.27
	2	1.68	65	1.74	1.65
	3	2.53	45	2.62	...
MPDME	1	1.34	58	1.39	1.31
	2	1.73	62	1.79	1.70
	3	2.57	41	2.64	...

[a] Data obtained in DMF, 0.1M TEAP. Potentials measured vs. aqueous SCE.
[b] Slope = $E_{3/4} - E_{1/4}$.
[c] Scan rate 0.100 V/sec.

RESULTS

Polarography and Cyclic Voltammetry. Deuteroporphyrin IX dimethylester (DPDME), whose structure is shown in Figure 1, yields in DMF three well defined polarographic waves with heights in the ratio of 1:1:1.6 when corrected for drop time. The peak-like appearance of the third wave is due to the fact that the DME is dropping very rapidly at the negative potentials applied. All three waves as shown in Figure 2 are diffusion controlled and show linear dependence on concentration. Analysis of the rising portion of the waves indicates that the first two steps are nearly reversible one-electron processes. The slope of 45 mV for the third wave clearly indicates that more than one electron is involved. The third step is irreversible. No prewaves are observed. Cyclic voltammetry confirms the polarographic conclusions given above. The first two steps are shown to be nearly reversible if the cathodic scan limit is set just beyond the second step. The third step is irreversible as shown in Figure 3A. The pertinent data for these experiments are summarized in Table I. Similar results were obtained for MPDME.

A series of experiments was conducted in which the hanging drop electrode was polarized at various potentials to produce the reduced DPDME product. This was then followed by an anodic scan. If the electrode is polarized at −1.8 V (just beyond the second step) followed by an anodic scan, an additional anodic peak (Peak 6, Figure 3B) is observed at −0.7 V. It is tempting to conclude that this peak is as-

sociated with the second cathodic step, but as we shall show later, it is, in fact, also associated with the first. No new peaks appear on polarization after the third step.

Because water is an ever-present contaminant and because it has undoubtedly affected previously reported results, the effect of the addition of water on the characteristics of DPDME reduction was investigated. Addition of less than 0.5% v/v water causes no great changes in the first two waves except to make the former somewhat more reversible. The third wave, however, increases in height and is shifted to more positive potentials. This wave is at all times diffusion-controlled. Further addition of water produces no change in the first wave, a more reversible second wave, and a third wave which is about twice as high as the original wave and shifted to yet more positive potentials. In cyclic voltammetry, this wave also grows to twice its original height. Between the original second and third waves, two new waves appear at about −1.82 and −2.05 V, respectively. The first of these is identified as an adsorption controlled wave on the basis of mercury column height dependence studies and the variation of peak height with scan rate. The wave at −2.05 V is probably due to hydrogen ion which is reducible at this potential. If more water is added (1.8% v/v), the adsorption wave becomes more pronounced, the third original wave decreases to its original height, but is drawn-out and ill-defined. It is shifted to more positive potentials.

If degassed water is added to DMF containing supporting electrolyte, a single small wave is observed at about −2.0 V which does not exceed 0.1 μA even at water concentrations of 15% (v/v). The height of the wave increases with increasing concentration, but not linearly. Comparable concentrations of formic or perchloric acid give a wave at the same potential, but greatly increased amplitude. The above observations support the idea that water is a very weak acid in this solvent and that the observed wave is due to a dissociated proton form. It should be noted, however, that water will cause the hydrolysis of DMF to form formic acid and dimethylamine. Under such conditions, an increase in the wave with time is observed.

Thin-Layer Electrochemistry. Electrochemical generation of DPDME species in the thin-layer cell proved invaluable in the characterization of reduced species. Although the resistance of the cell was high (10–20 K), it was still easy to correlate
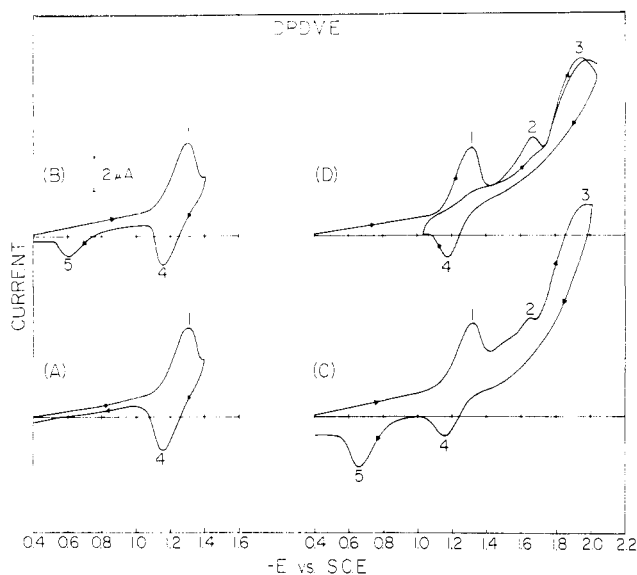
**Figure 5.** Thin-layer cyclic voltammetry for DPDME $0.1M$ TEAP

Concentration $1.1 \times 10^{-3}M$. Scan rate -0.05 V/min. *A.* In presence of room light. *B.* Same as *A* but in dark. *C.* Same as *B* but with extended scan limit. *D.* Multiple cycle

thin-layer potentials with those of polarography and cyclic voltammetry although the values were shifted to some extent. If the gold minigrid electrode is polarized at the top of the first wave, a change in the five-band spectrum of the original porphyrin, designated P, is noted in Figure 4. A five-banded species is formed, which is designated P^{τ} and which is distinguished by two Soret bands at 396 and 436 nm, respectively, and new bands at 640 nm, 685 nm, and 815 nm. As expected, this product is paramagnetic and exhibits an EPR spectrum. Consistent with previous observations of other porphyrins (5), the spectrum shows a single line with no hyperfine splitting. The line width (difference between inflection points) was 6.5 gauss. The line shape was not affected by modulation amplitude, microwave power, concentration variation, or the addition of water. No other products observed in this study were found to exhibit EPR spectra.

The anion radical, P^{τ}, is green in color and is slowly converted (over a period of 5 minutes) to a yellow-green form designated PH^-. The justification for this designation will be given subsequently. This species has a considerably simpler two-peak spectrum characterized by a new Soret band at 423 nm and a very broad band in the near infrared at about 800 nm. During the conversion of P^{τ} to PH^- with current flowing in the cell, three isosbestic points are observed at about 410, 436, and 705 nm, indicating the existence of two distinct species. The rate of formation of PH^- does not appear to depend on added water. It is stable to electrochemical oxidation at the potential of the first wave but can be quantitatively oxidized to the original porphyrin at about -0.6 V. Thus the anodic peak observed in cyclic voltammetry at -0.7 V is due to the oxidation of PH^- to the original porphyrin. There is a slight difference between the thin-layer and cyclic voltammetry potentials because of the high cell resistance and the difference in electrode material. This oxidation is incidentally electrochemically irreversible as expected (Figure 3*B*). If the minigrid electrode is polarized on the rising portion of the first wave below the half wave potential, a mixture of P, P^{τ}, and PH^- results which is stable with time. If P^{τ} is present, it can be oxidized to P at -1.1 V, indicating the reversibility of this process. If P^{τ} is generated at the first step and the current then turned off, one observes

the disappearance of P^{τ} and the formation of a mixture of P and PH^-.

No spectral changes occur between the top of the first wave and the foot of the second. Just beyond the top of the second wave, a purple species $PH_{n+1}^{[4-(n+1)]-}$ is produced. It has a band at 580 nm with a shoulder at 540 nm and is lacking a Soret band. If the course of the direct reduction of P is observed spectrally just beyond the top of the second wave, the process appears to proceed according to the scheme

$$P \rightarrow P^{\tau} \rightarrow PH^- \rightarrow PH_{n+1}^{[4-(n+1)]-}$$
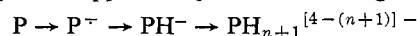
once again yielding the purple form. When the potential is stepped back to the top of the first wave, PH^- and not P^{τ} is observed. Quantitative conversion from PH^- back to the parent porphyrin can only be achieved at potentials more positive than -0.6 V. P^{τ} is not observed as an intermediate.
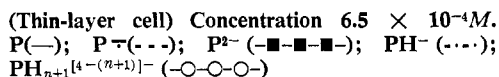
To permit correlation of thin-layer spectrometry and cyclic voltammetry, current–voltage curves were obtained at low scan rates in the thin-layer cell. Because the path length of the thin-layer cell is short, the electrochemical processes occurring at the minigrid electrode are easily affected by light as shown in Figures 5*A* and 5*B*. In the presence of laboratory fluorescent lighting, it is possible to reduce P to P^{τ} and reoxidize the latter without forming PH^- as shown in Figure 5*A*. In darkness PH^- is formed as shown by the appearance of Peak 5 in Figure 5*B*. Spectral measurements in the Cary 14R therefore undoubtedly affect the extent of this conversion. Such observations demonstrate the danger of misleading results caused by photochemical influence on electron transfer. Because of the above observations, subsequent current–voltage data were obtained in darkness.

Polarography and ordinary cyclic voltammetry suggested that it should be possible to observe the dianion, P^{2-}, in the thin-layer cell. Figure 5*C* shows possible formation of P^{2-} (Peak 2), but only in small quantities as indicated by the size of the peak. We have demonstrated by spectral measurements that $P^{\cdot-}$ is formed at Peak 1 and is converted by chemical reaction into PH^- which is reduced to $PH_{n+1}^{[4-(n+1)]-}$ at Peak 3. Thus Peaks 1 and 3 constitute an ECE mechanism. This is not observed in ordinary cyclic voltammetry because the intermediate chemical step is too slow. It will be shown subsequently that Peaks 2 and 3 constitute a second ECE mechanism leading to the same product, $PH_{n+1}^{[4-(n+1)]-}$. Peak 4 is not due to the oxidation of P^{τ} to P. If it were, Peak 1 would be observed on the second cycle of Figure 5*D*. After the first cycle, therefore, this current–voltage curve is interpreted as the cyclic conversion of PH^- to $PH_{n+1}^{[4-(n+1)]-}$. This conclusion is confirmed by spectral measurements.

Thin-layer electrolysis at the potential of the third polarographic wave (Figure 2) produces disappearance of all spectral bands between 390 and 1000 nm. It is possible to regenerate P at a potential of $+1.5$ V.

Electrogeneration at the top of the first wave in the presence of water produces no changes in the spectral or electrochemical behavior. On the second wave, however, an orange product $PH_{n+m+1}^{[4-(n+m+1)]-}$ is produced. As it is produced in the presence of 2% (v/v) water P^{τ}, PH^-, and $PH_{n+1}^{[4-(n+1)]-}$ are first observed to form in sequence. Reoxidation of the orange product to the original porphyrin results first in the formation of PH^-, then P. As noted previously, P^{τ} is not observed on reoxidation. At more negative potentials, the orange compound is reduced to a colorless product. This also occurs at the second wave in the presence of large amounts (6%) of water.

As noted earlier, the polarographic characteristics of MPDME are essentially the same as those of DPDME. The

Figure 6. Spectra of MPDME in DMF 0.1M TEAP

(Thin-layer cell) Concentration 6.5 $\times$ $10^{-4}M$.
P(—); P$\overline{\cdot}$(- - -); P^{2-} (-■-■-■-); PH$^-$ (-·-·-);
PH$_{n+1}^{[4-(n+1)]-}$ (-O-O-O-)

Table II. Spectral Data for Porphyrin IX Derivatives

	DPDME λ_{max}(NM)	DPDME $\epsilon \times 10^{-3}$	MPDME λ_{max}(NM)	MPDME $\epsilon \times 10^{-3}$		DPDME λ_{max}(NM)	DPDME $\epsilon \times 10^{-3}$	MPDME λ_{max}(NM)	MPDME $\epsilon \times 10^{-3}$
P	396	170	397	190	P^{2-}			426	88
	495	14.7	496	16.5				535	24
	526	8.2	529	11.2				580	33
	565	6.7	566	8.0	PH$^-$	423	95	426	110
	618	4.2	620	6.1		800	22	800	29
P$\overline{\cdot}$	396	78	397	97	PH$_{n+1}^{[4-(n+1)]-}$	540 s	21	545 s	26
	436	48	435	59		580	33	585	37
	640	15	642	16.5	PH$_{n+m+1}^{[4-(n+m+1)]-}$	475 s	18		
	685	10	690	12.8		505	23		
	815	8	815	12.0					

cyclic voltammetry is similar except in one respect—electrolysis after the second step, followed by an anodic scan, results in a very much diminished anodic process analogous to Peak 6, Figure 3B. Unlike DPDME, the anion radical P$\overline{\cdot}$ produced in the thin-layer cell is stable and does not undergo conversion to PH$^-$. Further, at the second step, the dianion, P^{2-}, is easily observed. With time, however, it is slowly converted by chemical reaction to PH$^-$. At slightly more negative potentials, the conversion of PH$^-$ to PH$_{n+1}^{[4-(n+1)]-}$ can also be observed. If water is added to a MPDME solution, the P$\overline{\cdot}$ becomes unstable and the electrochemistry is essentially identical to DPDME.

The spectra for MPDME are shown in Figure 6 and the spectral data for both compounds are summarized in Table II.

CONCLUSIONS

The observations described above are consistent with the following scheme (potentials given are for DPDME):

The parent porphyrin is reduced in a reversible one-electron step to the anion radical. In the presence of available protons, the radical undergoes the disproportionation reaction

$$2P^{\overline{\cdot}} + H^+ \rightarrow PH^- + P$$

The formation of PH$^-$ and P from the radical are observed in the thin-layer cell. This reaction has previously been demonstrated to occur (14). Further, the spectrum of PH$^-$ is characteristic of a phlorin anion (15, 16). If P$^{\overline{\cdot}}$ can be reduced to the dianion, P^{2-}, before the former has a chance to disproportionate, then PH$^-$ can be formed by a different route. Since PH$^-$ is diamagnetic, it cannot be mistaken for PH· the phlorin radical, which should have produced an

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EPR signal. We are unable to observe this latter species even in the course of oxidation of PH$^-$ back to P.

The phlorin anion can be further reduced by a two-electron step to a porphomethene (15). The spectrum shows no Soret band indicating a high degree of ring saturation. The conclusion of a two-electron process is based on thin-layer current–voltage curves, on the spectral characteristics, and on the fact that the purple product is diamagnetic. It is not possible at this point to specify the number of protons associated with the purple form but there is at least one, possibly two. In the presence of water, a blue shift occurs in the spectrum producing the orange species. This is no doubt due to uptake of further protons. Both the orange and purple forms are oxidized to PH$^-$ at essentially the same potential. The product of the direct reduction of the dianion PH$_b^{(4-b)-}$ has not as yet been isolated, however its electrochemical characteristics are quite different from the orange and purple forms. It cannot be oxidized to PH$^-$ within the normal potential region.

The orange and purple porphomethenes can be further reduced by two more electrons to the colorless porphyrinogen. This is consistent with spectral observations. Such a process must involve the addition of a total of six electrons to the parent porphyrin. This is possible only if electron transfer is associated with electrophilic attack on the porphyrin ring, since without this, the lowest lying orbital can accommodate only four electrons (17). The polarography and cyclic voltammetry of MPDME and DPDME show the addition of a total of four electrons at the third step. However, the third step must involve reduction to the porphomethene level under polarographic conditions. Limited protonation is the most likely cause of the irreversibility of this process. In the thin-layer cell, where more time is allowed for the relatively slow acid–base reactions to take place, reduction to the porphyrinogen can occur. The thin-layer conditions can be approximated polarographically if water is added, although in the latter case, the reactions are complicated and undoubtedly lead to a variety of products. Thus in the water-free solvent, the extent of porphyrin reduction is limited kinetically by the supply of protons.

(17) N. S. Hush, Theor. Chim. Acta, 4, 108 (1966).

Electrochemical Studies of Tetraphenylporphin, Tetraphenylchlorin, and Tetraphenylbacteriochlorin

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The electrochemical reductions of tetraphenylporphin (TPP), tetraphenylchlorin (TPC) and tetraphenylbacteriochlorin (TPB) were investigated in aprotic media (dimethylformamide). TPP shows four well-defined polarographic waves. The first two waves are reversible one-electron steps with half-wave potentials at −1.08 V and −1.45 V, while the last two are irreversible two-electron processes at −2.36 V and −2.48 V. TPC gives three polarographic waves at −1.12 V, −1.52 V, and −2.43 V. The first two are reversible one-electron processes, the latter two-electron irreversible. TPB exhibits two one-electron reversible processes at −1.10 V and −1.55 V. In all three cases, the final electron transfer step gives a product isoelectronic with a porphyrinogen (six-electron reduced porphin). The two-electron irreversible processes noted were shown to involve proton abstraction from the solvent medium. Electrochemical products were observed directly using an optically transparent electrode. Optical and EPR spectra are reported. Effect of controlled proton addition to the solvent was also noted.

SINCE THE TOTAL SYNTHESIS of chlorophyll a by Woodward (1), there has been an intensive effort directed toward the characterization of this intriguing compound by physical and chemical means. Closely related to this are the developments in the area of porphyrin chemistry which is equally important to the understanding of biological electron transfer reactions.

Much of the investigation in this latter area has concerned itself with the influence of particular metals and their ligands (metalloporphyrins) on the observed electrochemical behavior (2, 3). Since it now is clear that metalloporphyrin electrochemistry involves not only the metal but also the porphyrin ring itself (4), studies have been conducted in this laboratory on the metal-free porphyrins. An understanding of the behavior of these latter compounds in comparison to metalloporphyrins will aid in clarifying the role of the central metal atom, particularly for such cases as magnesium.

As has been pointed out (1), the reduction of a porphyrin by the addition of two electrons and two protons results in the formation of two classes of isomeric dihydroporphyrins—chlorins and phlorins, shown in Figure 1. These two classes have quite different chemical and physical properties. For example, the chlorins (the class to which chlorophyll belongs) are relatively stable to air-oxidation; the phlorins are not. Further reduction of the dihydroporphyrins by two more electrons and two protons produces three classes of isomeric tetrahydroporphyrins–bacteriochlorins, chlorin–phlorins (5), and por-

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