Electrooxidation of porphyrin free bases: fate of the π-cation radical

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In contrast to metalloporphyrins with non-electroactive metal centres, the π-cation radicals of porphyrin free bases (H_2OEP, H_2TPP, H_2CdiE) electrogenerated in strictly anhydrous solvents are not stable and give rise to a quantitative chemical reaction. Conjunction of electrochemical and spectroscopic data (UV/VIS, EPR and NMR) demonstrates unambiguously that the porphyrin skeleton is not modified during the chemical reaction. The reaction product is the protonated free base, and thus the free base can be regenerated by reduction of the protons.

π-Cation radicals of porphyrins and metalloporphyrins have been very long recognized as very important mediators in bioenergetic processes such as electron transfer in Photosynthetic Reaction Centres (PRCs).[1–5] This explains the large interest devoted to this aspect of the chemical and electrochemical reactivity of the ubiquitous porphyrin pigment.[6,7] However compared to metalloporphyrins, interest for the metal-free macrocycles, the so-called free base, bearing two central hydrogen atoms on the pyrrolic nitrogens, has remained elusive.[6–11] The oxidized forms of the porphyrins, and especially the π-cation radical, have been reported as extremely reactive intermediates, and in most cases only their oxidation potentials are reported. Their transient formation has been proposed as the initial step in the formation of meso or β-substituted or other modified forms of the porphyrin's core, such as isoporphyrins, chlorins, bilitrienes.[3,11–20] Interestingly, this reactivity of the π-cation radical has been taken advantage of recently for the electrochemical substitution of the porphyrin rings and more especially the electrochemical generation of covalently linked porphyrin dimers.[19,20] However the π-cation radical of the free bases has never been isolated, neither have its spectral properties been established. From its EPR spectra, it has been reported to have a very short half live;[9,11,21,22] and an UV/VIS spectrum was reported for this species produced by flash photolysis.[23] Surprisingly, its very high reactivity is often pointed out, but the initial fate of this π-cation radical in the absence of any 'added' substrate has never been discussed in detail.

Recent progress has been made in the modelling of the PRCs, and especially of the 'Special Pair', with an increasing number of synthetic compounds in which two porphyrins interact strongly in a cofacial configuration either by covalent linkage[24] or by spontaneous dimerization in solution.[25] The involvement of the free bases in the photosynthetic systems and their models urges a good knowledge of the properties of their oxidized forms. In a continuation of our study of the interacting processes between close face-to-face porphyrin rings as a model for electronic delocalization in dimers and electron-transfer processes,[24] we have been confronted by the question of the fate of the free base π-cation radical.[26] Interestingly, it was recently reported that, in contrast to thermodynamic expectation, no redox reaction is observed between the free base radical and the neutral less oxidant more electron-rich metallic derivatives of porphyrins. Surprisingly the unexpected converse reaction was observed.[25] Moreover, while free base type derivatives are considered as the primary electron acceptor in the electron-transfer chain of the PRCs, the free base is regenerated in its neutral state after the subsequent electron transfer.[4,5] The interaction between the neutral free base and the delocalized π-cation radical of the porphyrin dimer 'Special Pair' is of significance when addressing the question of back electron transfer.

The purpose of the present article is the examination of the oxidative electrochemical behaviour of the free base restricted to the formation of the π-cation radical. The oxidation was performed in organic solvent (mainly benzonitrile, PhCN) in drastic conditions for the water and dioxygen contents in the medium (nitrogen dry box). The product of the reaction was characterized by electrochemistry, UV/VIS spectroelectrochemistry, EPR and ^{1}H NMR spectroscopies, and the physico-chemical data were compared to those observed for the protonated forms of the corresponding porphyrins. The porphyrins examined in this study are shown in Scheme 1.

Results

Electrochemistry

As well documented the voltammograms of the neutral derivatives of the free bases display two reversible oxidation processes and two reduction processes, corresponding respectively to the formation of the π-cation radical and dication, and to the π-anion radical and dianion.[6,8–14] Data are summarized in Table 1. The RDE (rotating disk electrode) voltammograms for H_2C_2DiE and H_2TPP in solution in PhCN are shown in Fig. 1. In the case of H_2C_2DiE the second reduction wave is out of the solvent electrochemical range. Departure from

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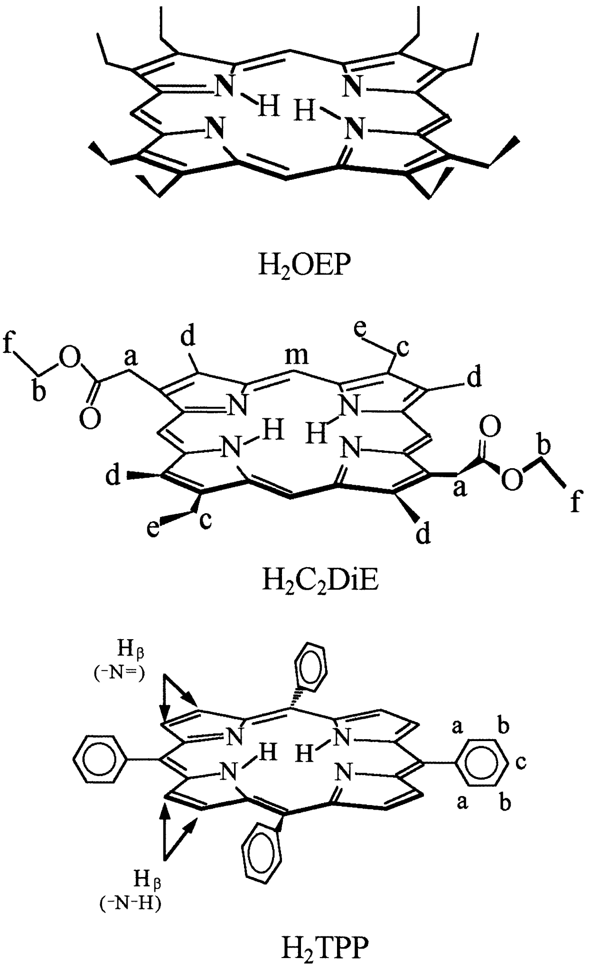

Scheme 1 Porphyrins examined in this study and numbering scheme for the assignments of ^1H NMR spectra for H_2C_2DiE and H_2TPP

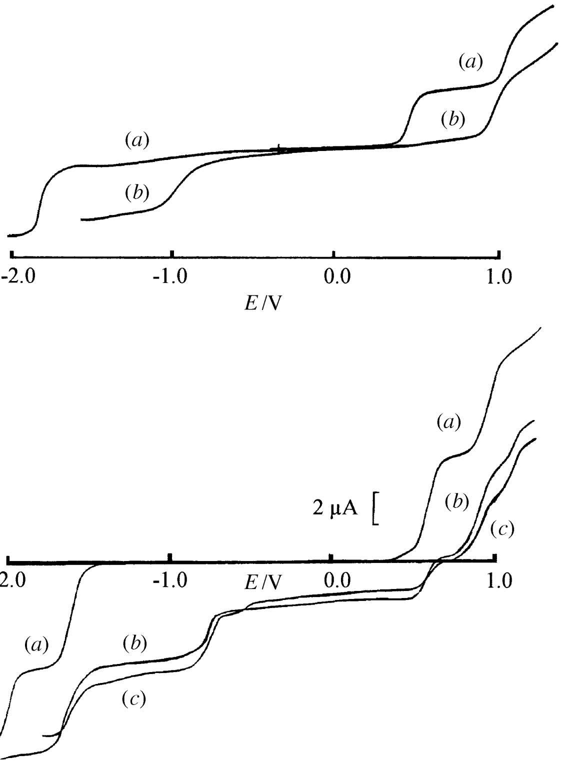

Fig. 1 Rotating disk electrode voltammograms of the porphyrin free bases at different stages of coulometry during an oxidation at a potential on the first wave. (Pt electrode, PhCN, 0.2 mol dm^{-3} Bu_4NPF_6, scan rate 0.01 V s^{-1}, ref. *vs.* Fc^+/Fc). Top: H_2C_2DiE (7 × 10^{-4} mol dm^{-3}) (*a*) neutral (*b*) 1 electron oxidized; bottom: H_2TPP (7 × 10^{-4} mol dm^{-3}) (*a*) neutral (*b*) 1 electron oxidized (*c*) 1.7 electron oxidized

reversibility is observed for the second oxidation process (Table 1); the CV (cyclic voltammogram, not shown) displays a larger peak-to-peak separation (140 mV) and a ratio $i_{pa}/i_{pc} > 1$. This illustrates the well-known high reactivity of the dication derivatives even in these experimental conditions; only the first oxidation process is scrutinized in this study.

Contrary to what is observed for non–electroactive metals, the free base porphyrin π-cation radical is not stable. The voltammetry of solutions after an exhaustive electrolysis at a potential more anodic than the first process reveals an evolution of the π-cation. Moreover, the behaviour depends on the nature of the porphyrin macrocycle and is different in the case of 'flat' porphyrins such as H_2C_2DiE and H_2OEP and in the case of meso-substituted porphyrins such as H_2TPP.

In the case of H_2C_2DiE and H_2OEP an exhaustive electrolysis, performed at the first-wave potential, gives a coulometric value of one Faraday per mole of porphyrin, with an exponential decrease of the oxidation current *versus* time. This indicates a simple electron exchange in a first step. In Fig. 1, it is shown that the first oxidation wave has vanished after the electrolysis and is replaced by a new wave at $E_{1/2} \approx -1.0$ V (Table 1). This wave corresponds to an irreversible peak by CV. An exhaustive electrolysis at a potential on the new reduction wave, as well as a CV scan more cathodic than the first cathodic reversible reduction processes ($E < -2.0$ V), regenerate the original CV. This indicates the chemical reversibility of the oxidation process. During this process, no change is observed for the second oxidation.

In the case of the H_2TPP free base, the electrolysis at a potential corresponding to the formation of the π-cation radical follows a different course. In an apparent first step, after an exchange of one electron per molecule of porphyrin after *ca.* 2 h (as for the H_2C_2DiE and H_2OEP study), the current value is close to 5% of the initial value with an exponential decrease. This step gives rise to a split of the RDE oxidation wave into two reduction waves of equal heights (Fig. 1). The first is at the same potential as the original oxidation wave and the second wave is at $E_{1/2} = -0.7$ V. The total height of these two waves is equal to that of the original oxidation wave. Moreover, a reduction electrolysis at a potential more cathodic than the reduction wave at -0.7 V regenerates the initial voltammogram. The second oxidation wave is left unchanged during this step. This solution evolves spontaneously, the reduction wave at $E_{1/2} = 0.6$ V producing the original oxidation wave at the same halfwave potential in part, plus an increase of the more cathodic reduction wave, this observation after a few hours (typically 1–2 h). In agreement with this observation, if electrolysis is performed in the same conditions as above up to 5% of the initial current level, after about 2 h *ca.* 1.7 electron per molecule is exchanged and the wave at 0.6 V has almost disappeared with a concomitant increase of the more cathodic reduction wave, at $E_{1/2} = -0.7$ V (Fig. 1). During this second oxidation step, the wave of the second oxidation process shifts anodically ($E_{1/2} = 1.1$ V). Also, in this case, an electrolysis at a potential more cathodic than the reduction wave ($E_{1/2} = -0.7$ V) regenerates the porphyrin in its initial form with little degradation; a CV scan of the reduced solution at a potential more cathodic than that of the formation of the radical anion restores the original CV. This illustrates the chemical reversibility of the process.

These observations demonstrate that the π-cation radicals of both types of porphyrin seem stable on the CV time scale (0.1 V s^{-1}), but they give rise to a chemical reaction on the electrolysis time scale (1–2 h), and the course of the reaction is different depending on the type of porphyrin (OEP or TPP). It has been checked that, under the same experimental conditions, the π-cation radicals of metalloporphyrins (M = Zn, Cu, Ni, Co,. . .) are stable for hours.

Table 1 Electrochemical data for neutral, oxidized and protonated forms of the free base porphyrins

Compound		Reduction E'^0/V,[a](ΔE_p/mV),[b] n_e[c]							Oxidation E'^0/V,[a](ΔE_p/mV),[b]n_e[c]			
H_2C_2DiE	neutral	−2.14(70)1	−1.78(60)1						+0.44(60)1	+0.92(140)1		
	1 e$^-$ oxidized[e]	−2.11(80)1	−1.76(60)1			$E_{pc} = -0.96$[d]				+0.92(200)1		
	monoprotonated		−1.77(60)1		$E_{pc} = -1.07$[d]	$E_{pc} = -0.96$[d]				+0.92(140)1		
	diprotonated		−1.76(60)1	$E_{pc} = -1.52$[d]	$E_{pc} = -1.12$[d]	$E_{pc} = -0.94$[d]	$E_{pc} = -0.68$[d]					
H_2OEP	neutral	−2.31(60)1	−1.90(60)1						+0.39(60)1	+0.89(60)1		
	1 e$^-$ oxidized[e]	−2.29(70)1	−1.88(60)1		$E_{pc} = -1.11$[d]					+0.89(70)1		
	monoprotonated	−2.29(70)1	−1.90(60)1		$E_{pc} = -1.16$[d]	$E_{pc} = -1.04$[d]				+0.87(60)1		
	diprotonated	$E_{pc} = -2.32$[d]	−1.81(60)1	$E_{pc} = -1.57$[d]		$E_{pc} = -0.99$[d]	$E_{pc} = -0.89$[d]					
H_2TPP	neutral	−2.00(80)1	−1.61(70)1						+0.60(70)1	+0.93(100)1		
	1 e$^-$ oxidized[e]	−1.99(60)1	−1.61(70)1			$E_{pc} = -0.76$[d]		+0.58(60)1		+0.92(90)1	+1.08(60)1	+1.30(80)1
	1.7 e$^-$ oxidized[e]	−1.97(60)1	−1.60(60)1			$E_{pc} = -0.76$[d]	$E_{pc} = -0.55$[d]	+0.59(60)1		+0.93(80)1	+1.09(60)1	+1.34(100)1
	monoprotonated	−1.94(60)1	−1.60(60)1			−0.74(60)1					+1.08(60)1	+1.30(80)1
	diprotonated	−2.03(70)	−1.57(80)			−0.74(60)1	−0.56(60)1				+1.06(60)1	+1.29(80)1

[a] Obtained from cyclic voltammetry in PhCN + Bu_4NPF_6; Pt electrode; 100 mV s^{-1}, E'^0 *versus* Fc^+/Fc. [b] $\Delta E_p = E_{pa} - E_{pc}$. [c] n_e = number of electrons exchanged. [d] E_{pc} = Cathodic peak potential for irreversible systems. [e] Electrolysis on the first oxidation wave.

UV/VIS spectrophotometry

The formation of the oxidized species of the porphyrins have been monitored by UV/VIS spectrophotometry in a spectroelectrochemical cell.† The UV/VIS spectroscopic data are reported in Table 2.

The evolution of the visible spectra for H_2C_2DiE oxidation is shown in Fig. 2; similar changes are observed for H_2OEP (Table 2). The evolution of the spectra for both oxidation steps has been followed for the purpose of comparison with H_2TPP (*vide infra*). The observation of two isosbestic sets of spectra [$\lambda_{isosbestic}(1^{st}$ oxidation step) = 514, 616 nm; $\lambda_{isosbestic}(2^{nd}$ oxidation step) = 542, 558, 584 nm] for the two oxidation steps illustrates the formation of two distinct species. No evolution of the spectra is observed if the potential is maintained at the potential of the first oxidation and the original spectrum is restored by setting the potential at a value corresponding to the reduction wave reported above ($E < -1$ V). The spectrum after reduction of the species obtained at a potential of the second oxidation step displays a noticeable degradation.

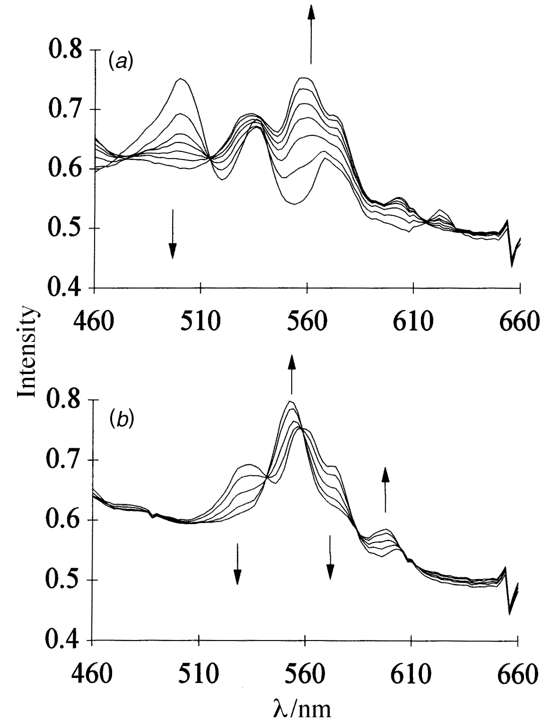

Fig. 2 Visible spectra for H_2C_2DiE mono- and di-oxidation processes followed by spectroelectrochemistry ($[H_2C_2DiE] = 7 \times 10^{-4}$ mol dm^{-3} in PhCN, 0.2 mol dm^{-3} Bu_4NPF_6): (*a*) neutral to 1 electron oxidized species; (*b*) 1 to 2 electron oxidized species

In the case of H_2TPP, the spectral changes are different from what is observed for the H_2C_2DiE and H_2OEP porphyrins, as seen in Fig. 3 and Table 2. Noticeably, and according to the above-described electrochemical behaviour, the first oxidation step leads directly to the two-electron oxidized species. As shown in Fig. 3 the two-electron oxidation of the porphyrin involves only one isosbestic set [$\lambda_{isosbestic} = 424$ nm (Soret), $\lambda_{isosbestic} = 505$ (visible)] indicating that during the two-electron oxidation process of the H_2TPP, no intermediate species can be detected. It was also checked that a reduction at the potential of the cathodic reduction wave regenerates the original spectrum; only a partial degradation was observed.

The spectral characteristics obtained after oxidation are close to those typical of the $^2A_{2u}$ and $^2A_{1u}$ ground states for H_2C_2DiE and H_2TPP, respectively;[3,7] the spectrum of the present oxidized form of H_2TPP is also close to that ascribed to the π-cation radical $H_2TPP^{\cdot +}$ prepared by photooxidation.[23] These spectra were also surprisingly similar to those long assigned to the protonated form of the unoxidized

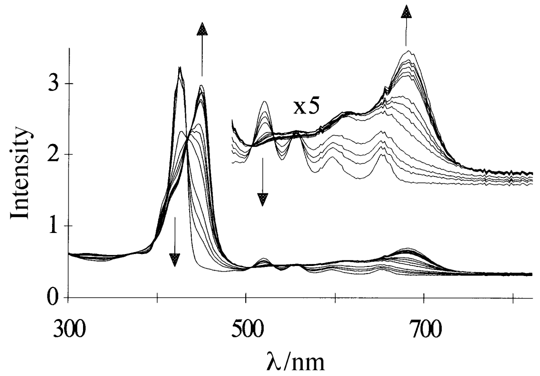

Fig. 3 UV/VIS spectra for H_2TPP oxidation process followed by spectroelectrochemical technique ($[H_2TPP] = 7 \times 10^{-4}$ mol dm^{-3} in PhCN, 0.2 mol dm^{-3} Bu_4NPF_6): neutral to 2 electron oxidized species

Table 2 UV/VIS spectrophotometric data for neutral, oxidized and protonated forms of the free-base porphyrins [λ_{max}/nm ($\varepsilon/10^{-3}$ dm^3 mol^{-1} cm^{-1})]

Porphyrin	State	Soret[a]	Visible region[b]
H_2C_2DiE	neutral	404 (142.4)	502 (13.6), 536 (8.7), 568 (5.7), 622 (3.0)
	1 e$^-$ oxidized	398 (115.5)	534 (10.4), 558 (12.6), 574 (10.5), 602 (4.4)
	2 e$^-$ oxidized		552 (14.9), 598 (3.3)
	monoprotonated		480 (5.9), 534 (8.3), 556 (10.8), 574 (8.2), 604 (3.2)
	diprotonated		482 (5.2), 552 (11.9), 594 (4.6)
H_2OEP	neutral	402 (165.8)	498 (13.1), 532 (10.4), 568 (6.8), 622 (4.9)
	1 e$^-$ oxidized	398 (108.0)	532 (5.6), 560 (6.3), 570 (5.6), 602 (2.9)
	monoprotonated		536 (9.2), 556 (12.8), 570 (9.6), 602 (4.0)
	diprotonated		550 (15.5), 594 (4.0)
H_2TPP	neutral	422 (330.9)	516 (22.3), 552 (16.9), 592 (12.6), 650 (13.7)
	2 e$^-$ oxidized	448 (287.8)	614 (7.9), 672 (26.2)
	diprotonated	444 (284.7)	664 (57.2)

[a] In PhCN–Bu_4NPF_6, conc. = 7×10^{-5} mol dm^{-3}, obtained by dilution of oxidized or protonated solutions. [b] In PhCN–Bu_4NPF_6, conc. = 7×10^{-4} mol dm^{-3}, obtained directly from studied solutions.

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† In the spectroelectrochemical cell the concentration was the same as that used for the electrochemical experiments in order to correlate exactly the observations by both techniques. This concentration precludes the recording of the Soret bands, and only the visible part of the spectra are recorded. However, it was checked independently on dilute solution by bulk electrolysis in the classical electrochemical cell that the dilution did not affect the visible spectra, and this gave the characteristics of the Soret Bands.

porphyrin, but not distinctly different from some described for modified porphyrin.[1]

EPR

The one-electron oxidized solutions for the H_2OEP or H_2C_2DiE do not show the reduction wave or peak corresponding to the π-cation radical, but a cathodic shifted reduction. Accordingly, the EPR spectra of the these solutions only display a residual signal typical of a π-cation ($g = 2.004$),[22] accounting for only a 0.5–0.1% concentration of this species as compared to a standard. (The integration value is calculated taking $ZnTPP^{\bullet +}$ as a standard, which gives an intense and reproductive signal.[24]) According to the electrochemical observations, this confirms that the transient π-cation radical is not stable.

Conversely, in the case of H_2TPP, the π-cation radical can be detected by its typical EPR spectrum ($g = 2.004$, linewidth = 6 G) in a ratio corresponding to the height of its RDE reduction wave ($E_{1/2} = 0.6$ V) obtained after the first one-electron oxidation step: *ca.* 50% of the total concentration of H_2TPP was detected in the radical $H_2TPP^{\bullet +}$ form. After a longer oxidation (*vide supra*), the intensity of the signal decreases to a residual value with a concomitant disappearance of the corresponding RDE reduction wave of the π-cation at +0.6 V.

These observations indicate that the π-cation radicals give rise to a follow-up reaction, but do not give any direct indication on the nature of the product of this reaction. The EPR silent product could suggest the formation of associated or aggregated species with spin coupling such as dimer formation. The only alternative would involve a redox reaction of the intermediate π-cation radical so as to produce a diamagnetic species.

Protonation of the porphyrin free bases

This study indicates that the protonated form of the free base could be one of the final products of the reaction of oxidation as previously suggested for metallic derivatives.[20] The electrochemical and spectroscopic characteristics of the oxidized solutions of the free bases have been compared to those of the protonated forms obtained by addition of up to 2 equiv. of protons in solution. In any case, the similarity of the data between the mono- or di-oxidized species and the mono- or di-protonated forms is striking.

As shown in Fig. 4, the evolution of the RDE voltammogram of H_2TPP when protons are added to the medium parallels the evolution observed during the porphyrin oxidation (Fig. 1). The protonated species displays a reduction wave at *ca.* $E_{1/2} = -0.7$ V, and shifted oxidation waves (Table 1). The evolution of the voltammogram is continuous for the addition of 0–2 protons, as is the case for the oxidation process. For H_2C_2DiE and H_2OEP, the same similarity between protonation and oxidation is evidenced from the voltammograms of the protonated species (Fig. 4 and 1, Table 1). However, for these porphyrins two consecutive evolutions are observed for the addition of the first and the second protons, paralleling again the oxidation process as shown by coulometry and spectroelectrochemistry.

The UV/VIS spectra of the protonated and oxidized species are also similar (see Table 2). The evolution of the electrolysis parallels the protonation reactions. The addition of one proton to H_2C_2DiE or H_2OEP generates an isosbestic set of spectra corresponding to the same observation by spectroelectrochemistry for the abstraction of one electron; a second isosbestic set of spectra is observed for the addition of a second proton as for the second electron oxidation. In the case of H_2TPP, a direct di-protonation is evidenced by a lone isosbestic set, paralleling the two-electron oxidation. Addition of protons to solution of the free base did not generate any EPR signal, even at residual level. This indicates that there is no oxidation of the porphyrin by protons.

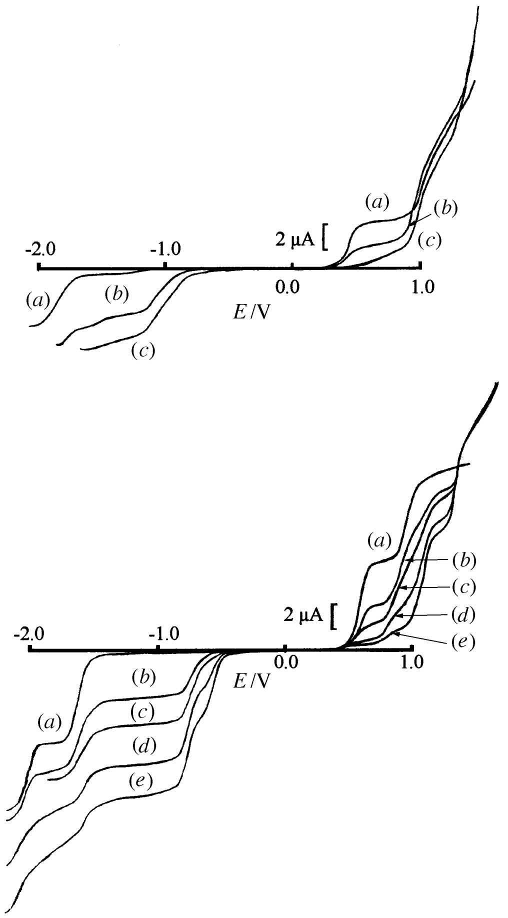

Fig. 4 Rotating disk electrode voltammetry of free-base porphyrins after protonation by diluted $HClO_4$ (Pt electrode, PhCN, 0.2 mol dm^{-3} Bu_4NPF_6, scan rate 0.01 V s^{-1}, ref *vs.* Fc^+/Fc). Top: $[H_2C_2DiE] = 7 \times 10^{-4}$ mol dm^{-3} (*a*) neutral, (*b*) 0.6 equiv., (*c*) 1 equiv. H^+. Bottom: $[H_2TPP] = 7 \times 10^{-4}$ mol dm^{-3} (*a*) neutral, (*b*) 0.6 equiv., (*c*) 1 equiv., (*d*) 1.6 equiv., (*e*) 2 equiv. $HClO_4$

NMR

The apparent diamagnetism of the product of the reaction suggested the use of NMR for unequivocal characterization and determination of its structure, especially as regards to possible substitution reactions or modifications of the porphyrin core. The spectra of the oxidized species have also been compared to those of the protonated forms in the same solvent.

It was necessary, therefore to obtain the NMR spectra of the electrolysed solutions so as to correlate them validly with the electrochemical and spectral characterization. Experimental conditions were defined to allow direct recording of the NMR spectra from the electrolysed solutions. As d_6-PhCN was not available, another electrolyte solution was selected, namely CD_2Cl_2–Et_4NClO_4. Beforehand, the oxidative behaviour of the two types of porphyrins, H_2C_2DiE–H_2OEP and H_2TPP, was analyzed in CH_2Cl_2. H_2TPP displays exactly the same behaviour as in PhCN, while H_2C_2DiE behaves differently from its behaviour observed in PhCN, but exactly in the same fashion as H_2TPP. The ^1H NMR spectra of the oxidized solutions are obtained directly by transfer of CD_2Cl_2 electrochemical solutions in an NMR tube. The data for both porphyrins are reported in Table 3. Only data for H_2C_2DiE are given, owing to insufficient solubility of the H_2OEP derivatives. For comparison, the data of the neutral derivatives in the same solutions are also reported.[1]

Table 3 ^1H NMR data for the porphyrin free bases [δ/ppm[a] (multiplicity)[b] integration]. Assignments of protons are as displayed in Scheme 1

	neutral[c]		dioxidized[d]		diprotonated[c]	
H_2C_2DiE	+25 °C		+40 °C		+25 °C	
H_{meso}	10.14(2s)4		10.88(s)2		10.87(s)2	
			10.89(s)2		10.78(s)2	
H_a	5.02(s)4		5.10(s)4		5.11(s)4	
H_b	4.23(q)4		4.27(q)4		4.27(q)4	
H_c	4.15(q)4		4.18(q)4		4.18(q)4	
H_d	3.67(s)6		3.75(s)6		3.75(s)6	
	3.68(s)6		3.70(s)6		3.71(s)6	
H_e	1.87(t)6		1.79(t)6		1.80(t)6	
H_f	1.26(t)6		[e]—		1.27(t)—	
H_N	−3.96(broad)		−4.56(s)2		−4.54(s)0.9	
			−4.66(s)2		−4.71(s)0.7	
H_2TPP	+25 °C	−60 °C	+25 °C	−60 °C	+25 °C	−60 °C
$H_{\beta(-NH)}$	8.85(s)8	8.97(s)4	8.83(s)8	8.86(s)8	8.83(s)8	8.87(s)8
$H_{\beta(-N=)}$		8.76(s)4				
H_a	8.22(m)8	8.19(m)8	8.63(m)8	8.65(m)8	8.64(m)8	8.66(m)8
H_b and H_c	7.75(m)12	7.75(m)12	8.02(m)12	8.03(m)12	8.04(m)12	8.01(m)12
H_N	−2.86(s)2	−3.11(s)2	−2.53(s)3.5	−2.71(s)3.6	−2.53(s)4	−2.75(s)4

[a] TMS is the internal standard. [b] s = singlet; t = triplet; q = quadruplet; m = multiplet. [c] conc. = 5×10^{-3} mol dm^{-3} in CD_2Cl_2. [d] conc. = 5×10^{-3} mol dm^{-3} in CD_2Cl_2/Et_4NClO_4. [e] Electrolyte.

The NMR data indicate that the spectra of the oxidized derivatives are very close to those of the protonated forms. No dramatic change is observed compared with the data for the neutral species.[1,27] In the case of H_2TPP, the H_N protons of the oxidized form are less shielded (by *ca.* 0.33 ppm) than in the neutral forms. This effect is more pronounced at low temperature. The integration of these signals gives values close to 4 protons, but the peaks are large and ill-resolved. The H_β protons are practically unshifted compared to the neutral derivatives. However, the two types of H_β proton for the oxidized and protonated forms are no longer differentiated at low temperature. This observation leads to two possible interpretations for the porphyrins in the oxidized forms, either the pyrrolic protons remain labile at low temperature, or the four N are protonated. The last hypothesis is in agreement with the integration values. The low-temperature spectra of the H_2C_2DiE could not be obtained owing to its low solubility (Table 3). The room-temperature spectra are, however, well resolved. The integration values for the two types of N pyrrolic protons at 25 °C are low [$n_{H(total)} < 4$] in both oxidized ($n_H = 1.51 + 1.65$) and protonated forms ($n_H = 0.9 + 0.7$), but they are not reliable owing to the broadness of the peaks. This is particularly evident from the later values obtained for the protonated derivative. However, at 40 °C, the integration value for the N pyrrolic protons is in agreement with 4 protons.

Therefore while the integration values of the N pyrrolic protons are only indicative of protonation for the oxidized species, the quasi-perfect match between the characteristics of this species with those of the protonated forms, and their close resemblance to those of the neutral form appears as definite evidence that there is no modification of the porphyrin core during the oxidation process and its follow-up reaction.

Discussion

The well-known reactivity of the π-cation radical of free base porphyrin is confirmed by our electrochemical study, which moreover shows that the reaction process of the free base is chemically reversible. The initial product is regenerated by a counterelectrolysis. Electrochemical and UV/VIS spectrophotometric characterizations were insufficient to rule out the possibility of porphyrins with a modified skeleton, *e.g.*, β- or meso-substituted porphyrins, isoporhyrins, dimers, bilitriens. However, this hypothesis is ruled out by the NMR and EPR studies which show that the final product of the reaction is diamagnetic and consequently that the protons do not oxidize the free base porphyrins. Also the NMR study clearly establishes that the porphyrin core is not modified during the process.[1,27] It is unambiguously demonstrated that the oxidation products are the protonated forms of the free base. The different ways of oxidation followed by the two types of porphyrin, either 'flat' porphyrin (OEP type) one-electron oxidation, or hindered porphyrin (TPP type) two-electron oxidation, result from the stabilization of the protonated form of the free base.[1,27] When the monoprotonated one is the stable form, one-electron oxidation (OEP) is observed. When the monoprotonated form is not stable, it gives rise to disproportionation leading to the diprotonated derivative, and consequently a two-electron oxidation process.

The cyclic voltammetry indicates that the π-cation radical is formed transiently in a first step; so the final production of the only protonated form of the free base infers that a reduction + protonation chemical step of this radical follows the initial electrochemical oxidation; this necessarily involves the reaction with an oxidizable and protic substrate SH.

The reaction process could therefore be written as follows for H_2OEP type:

$$H_2P \overset{-1e}{\rightleftharpoons} H_2P^{\cdot +}$$
$$H_2P^{\cdot +} + S-H \rightleftharpoons H_3P^+ + S^\cdot$$
$$H_3P^+ \rightleftharpoons H_2P + H^+$$

for H_2TPP type:

$$H_2P \overset{-1e}{\rightleftharpoons} H_2P^{\cdot +}$$
$$2H_2P^{\cdot +} + 2S-H \rightleftharpoons H_4P^{2+} + H_2P + 2S^\cdot$$
$$H_4P^{2+} \rightleftharpoons H_2P + 2H^+$$
$$2H_3P^+ \rightleftharpoons H_4P^{2+} + H_2P$$

The product of the overall reaction being the protonated form of the free base, the reversibility of the process is thus ascribed to the reduction of the protons leading back to the free base + H_2.

The nature of the substrate SH could not be determined. The present study was performed in a weakly nucleophilic, strictly anhydrous medium, (PhCN, Bu_4NPF_6). Change of the solvent (CH_2Cl_2) or electrolyte (Et_4NClO_4) did not modify the reaction product. The water content of the PhCN–Bu_4NPF_6 solution could be estimated as low as 3×10^{-5} mol l^{-1}, *i.e.*, 20 times less than the concentration of the free base in our experiments (7×10^{-4} mol l^{-1}). Moreover, in the presence of higher concentration of the free base in the same medium up to 10^{-2} mol l^{-1}, or in the presence of an excess of added H_2O (H_2O : porphyrin ≈ 300), oxidations lead to the same results. NMR shows also that the porphyrin ring is not the source of protons. These observations illustrate the efficiency of the electron/proton transfer process to the π-cation radical. Such a reaction has also been observed for the oxidation of some nitrogenous bases.[28]

The present results could aid understanding of the behaviour of some biological electron-transfer processes that are often coupled with a proton transfer as in PCET ('Proton coupled electron-transfer'). The present results can also explain why the oxidized form of free base is non-reactive towards metal porphyrin derivatives, contrary to thermodynamic considerations [E_{ox}(free base) > E_{ox}(metal porphyrin)] discussed by Scheidt and co-workers[25] Moreover the UV/VIS data could indicate that the oxidation product, *i.e.*, the protonated free base, would be the same one as that proposed during the (flash) photooxidation of H_2TPP in the presence of quinone.[23] We have currently been studying the electronic delocalization between oxidized forms of metallic and free base porphyrins. These results can now be understood and rationalized.[24,26]

Experimental

Chemicals

The porphyrins, TPP (tetraphenylporphyrin) and OEP (octaethylporphyrin), were purchased commercially from Aldrich and used without further purification. The porphyrin H_2C_2diE was synthesized at Stanford (Professor Collman's Group).[24] The solvent, [mainly benzonitrile (PhCN)] and the supporting electrolyte, tetrabutylammonium hexafluorophosphate (Bu_4NPF_6), were purified as previously described.[24] CH_2Cl_2 was refluxed on calcium hydride. Tetraethylammonium perchlorate (Et_4NClO_4) was recrystallized twice from ethanol. Solutions of the supporting electrolyte were prepared in the dry box, stored on molecular sieves (Linde 4Å) and twice percolated through an activated (400 °C under vacuum for 48 h) neutral alumina (Merck) column. The oxidized forms of the derivatives were generated electrochemically and each spectrum was recorded in the presence of the supporting electrolyte. For the physico-chemical studies, solutions were transferred from the electrochemical cell to EPR tubes, UV/VIS cuvettes or NMR tubes and sealed prior to removal from the dry box.

Apparatus

All experiments were performed on a small fraction (0.2–0.5 mg) dissolved in low volumes (*ca.* 300–500 μl) of solvent, and carried out in a dry nitrogen atmosphere box with carefully deoxygenated and dried solvents and chemicals. The dry box was manufactured by Jaram. The nitrogen flow was continuously purified by passage through molecular sieves at ambient temperature and divided copper BTS catalyst (BASF) at 100 °C. The electrochemical cell was specifically designed to fit the rotating disk electrode (EDI Tacussel) for a minimum volume of solution in the main compartment. The auxiliary and reference (ferrocenium/ferrocene = Fc^+/Fc) electrodes were in separate compartments connected to the main one through ground joints terminated by frits (Vycor tips from PAR). For voltammetric measurements, a platinum disk (diameter = 2 mm) was used, and the electrolyses were performed with the same type of electrode, but rotated and equipped with a 4 mm diameter disk. For the purpose of comparison, the formal potential of Fc^+/Fc *versus* SCE is 0.43 V measured in the same medium (PhCN, 0.2 mol dm^{-3} Bu_4NPF_6). A model PAR 173 potentiostat, equipped with a PAR 179 digital coulometric unit, was monitored by a PAR 175 programmer. The chart recorder was a T-2Y SEFRAM Enertec. UV/VIS spectra were recorded on a Varian CARY 219 spectrophotometer. The spectroelectrochemical cell was a 0.1 cm deep quartz cell equipped with a Pt grid as a working electrode, an Ag pseudo-reference and a Pt counter electrode. A Jeol FE3X apparatus was used for the EPR spectroscopy. Spectra were recorded from solutions ($V = 40$ μl) at a concentration of 7×10^{-4} mol dm^{-3} in quartz tubes with a power of 1 mW and frequency close to 9.2 GHz. Proton NMR spectra were recorded on Bruker AC300 and Bruker DRX400 spectrometers. NMR spectra of electrolysed solutions were obtained by using CD_2Cl_2/Et_4NClO_4 (0.1 mol dm^{-3}) electrolyte solutions directly transferred to the NMR tubes.

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