Figure 13. The apparently constant P_2/P_1 and P_3/P_1 ratios for $[F] > 3 \times 10^{12}$ molecules cm^{-3} probably is a consequence of fast vibrational relaxation from the high $[H_2O]$. These low [F] experiments were especially difficult because k_{H_2O} is smaller than for most reagents (and HF(v) relaxation by H_2O is faster than for most reagents) and high $[H_2O]$ and $[D_2O]$ were required to obtain measurable IRCL signals at low [F]. In conclusion, these F/H_2O and F/D_2O experiments suggest that the contributions from secondary reaction are negligible for [F] below 5×10^{11} molecules cm^{-3}. However, the agreement between the calculated and experimental results is not quantitative for reasons stated.

In the course of these experiments, some data were collected for $F + D_2O$ at constant $[F] = 2.5 \times 10^{12}$ molecules cm^{-3} and varying $[D_2O]$. The emission from DF(v = 3 and 4) was below the S/N limit. The DF(v = 1 and 2) distributions showed a slight relaxation for $[D_2O] \geq 5 \times 10^{12}$ molecules cm^{-3} and the best P_1:P_2, 0.74:0.26, was entered in Table V as the nascent DF(v) distribution.

Registry No. HF, 7664-39-3; DF, 14333-26-7; HCl, 7647-01-0; DCl, 7698-05-7; HS, 13940-21-1; DS, 13780-23-9; CH_3O, 2143-68-2; F_2, 7782-41-4; Cl_2, 7782-50-5; H_2S, 7783-06-4; D_2S, 13536-94-2; H_2Se, 7783-07-5; D_2O, 7789-20-0; CH_3OH, 67-56-1; H_2O, 7732-18-5.

One- and Two-Electron Reduction of Metalloporphyrins. Radiation Chemical, Photochemical, and Electrochemical Studies. Kinetics of the Decay of π-Radical Anions

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One- and two-electron reduction products of several metalloporphyrins have been studied by steady-state and pulse radiolysis in aqueous and methanolic solutions and by photochemistry and electrochemistry in aqueous solutions. This study concentrates on the TMPyP (tetrakis(*N*-methyl-4-pyridyl)porphyrin) complexes of Ga^{III}, Ge^{IV}, and In^{III}, and the TPyP (tetra(3-pyridyl)porphyrin) complex of Sb^{V}, and compares them with the previously studied complexes of Zn^{II}, Al^{III}, and Sn^{IV}. All these porphyrins undergo one-electron reduction on the ligand to form π-radical anions. The rates of formation and decay of these species have been studied under various conditions. The lifetimes of these radicals were found to vary greatly; those of Sb^{V} and Sn^{IV} are completely stable while some others decay in the millisecond range. The stability decreases in the order Sb^{V}, Sn^{IV}, In^{III}, Ge^{IV}, Ga^{III}, Al^{III}, Zn^{II}, which was found to correspond to the order of the porphyrin ring reduction potentials determined under similar conditions. Increased lifetime of the radical upon increase in electronegativity of the metal was found to be due to inhibition of porphyrin ring protonation, which is a necessary step in the formation of final products. The final two-electron reduction products are mainly phlorin anions. The same products were observed upon photochemical reduction. The potentials for the first and second one-electron reduction of the porphyrins were determined by cyclic voltammetry. The separation between the first and second wave gives an indication of the stability of the π-radical anion.

Introduction

One-electron reduction of numerous metalloporphyrins produces π-radical anions, where the unpaired electron is delocalized over the π-system of the tetrapyrrole ligand.[1] These radical anions exhibit intense absorption bands at 700-750 nm with λ_{max} and ϵ only slightly dependent on the metal center.[2-7] Yet the lifetimes of these species vary widely. While Zn^{II} and Al^{III} porphyrins form short-lived radical anions, Sn^{IV} porphyrins yield very stable species.[5-7] To understand the parameters which affect the stability of the π-radical anions, we have studied a series of metalloporphyrins (Ga^{III}, Ge^{IV}, In^{III}, Bi^{III}, Sb^{V}) under different conditions. Correlation of the results for these porphyrins, and those reported previously, with the redox potentials led to the conclusion that a metal center with a higher electronegativity stabilizes the π-radical anion by retarding its protonation.

Metalloporphyrin π-radical anions are important intermediates in photochemical water splitting. They reduce water to hydrogen

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0022-3654/86/2090-2462\$01.50/0

on the surface of catalysts.[8,9] This process can predominate only if the radical–radical decay is slow. Therefore, it is important to understand the parameters which affect the radical decay. The present study is aimed at this problem.

Experimental Section[10]

Sb^VTPyP (TPyP = tetra(3-pyridyl)porphyrin), $Sn^{IV}TMPyP$ (TMPyP = tetrakis(*N*-methyl-4-pyridyl)porphyrin), H_2TMPyP, $Al^{III}TMPyP$, $Zn^{II}TMPyP$, Sb^VOEP (OEP = octaethylporphyrin), $Ga^{III}TPP$ (TPP = tetraphenylporphyrin), and $Ge^{IV}TPP$ were purchased from Midcentury Chemical Co. and used as received. $In^{III}TMPyP$[11] and $Pb^{II}TMPyP$[12] were prepared as before. $Ga^{III}TMPyP$ was prepared by a procedure identical with that used for $In^{III}TMPyP$ while $Bi^{III}TMPyP$ was prepared by the procedure used for $Pb^{II}TMPyP$. $Ge^{IV}TMPyP$ was obtained by heating $GeCl_4$ (2 g) and H_2TPyP (0.2 g) in anhydrous pyridine (25 mL) in a sealed tube at 180 °C for 24 h. The product was filtered, evaporated to dryness, and chromatographed on alumina with 2% pyridine in $CHCl_3$ as eluent. The $Ge^{IV}TPyP$ so isolated was methylated by stirring with excess iodomethane in benzene for 2 days and the iodide counterions were exchanged with chloride ions using an ion-exchange resin.

Water was purified by a Millipore Milli-Q system. The alcohols and inorganic compounds were analytical grade reagents. Methanol was made alkaline by dissolving sodium metal in it and diluting to the desired concentration. The concentration of sodium methoxide in MeOH was determined by diluting 1:10 with water and measuring the pH. The pH of the aqueous solutions of porphyrins was adjusted with KOH, $HClO_4$, sodium tetraborate, or sodium phosphates.

Solutions were prepared just prior to the experiment and were protected from unnecessary light. They were deoxygenated by bubbling with ultrahigh-purity nitrogen. Absorption spectra were recorded on a Cary 219 spectrophotometer. Radiolytic reduction was carried out in a Gammacell 220 ^{60}Co source with a dose rate of 10 krd/min. Kinetic spectrophotometric pulse radiolysis was done with 50-ns pulses of 2-MeV electrons from a Febetron 705 pulser. The optical detection system utilized a Varian 300-W xenon lamp, 2 cm optical path length irradiation cell, Bausch and Lomb monochromator, RCA 4840 photomultiplier, and the proper electronics and optical components. The signals were digitized with a Tektronix 7612 transient recorder and processed with a PDP 11/34 minicomputer. The dose per pulse was usually in the range of 500–1000 rd and was monitored by a toroidal detector. Chemical dosimetry was done with N_2O-saturated KSCN solutions.

Cyclic voltammetry studies were made with the apparatus described previously.[7] Solutions of metalloporphyrin (ca. 10^{-3} M) in water at pH 5 (except for $Pb^{II}TMPyP$ where the pH was maintained at 9 with 10^{-3} M borate) containing KCl (0.1 M) were purged thoroughly with N_2. The working electrode was a highly polished glassy carbon disk and it was polished before each scan.

Results and Discussion

The metalloporphyrins were reduced by radiolytic or chemical means in methanolic or aqueous solutions, as described previously.[5,6] Kinetics of one-electron reduction and short-term stability of the resulting radical anions were measured by pulse radiolysis. The long-term stability of radical anions and the nature of the two-electron-reduced products were examined in the γ-radiolysis and photochemical experiments.

TABLE I: Rates of One-Electron Reduction of Metalloporphyrins and Decay of Radical Anions

	0.01 M CH_3O^- in MeOH		1 M *i*-PrOH in water, pH 7	
metallo-porphyrin	$k(\dot{C}H_2O^-)$, $M^{-1}\ s^{-1}$	$2k$(decay), $M^{-1}\ s^{-1}$	$k((CH_3)_2\dot{C}OH)$, $M^{-1}\ s^{-1}$	$t_{1/2}$(decay)
$Ga^{III}TMPyP$	5.1×10^9	1×10^9.	1.7×10^9	0.5 ms
$Ge^{IV}TMPyP$	8.5×10^9	1×10^7	2.1×10^9	~3 s
$Bi^{III}TMPyP$	7.8×10^9	6×10^6	2.1×10^9	10 ms
$Pb^{II}TMPyP$			2.0×10^9	50 ms
$In^{III}TMPyP$		$<10^4$		~0.2 s
Sb^VTPyP	1.7×10^9	$<10^4$	1.8×10^9	>100 s
$Ga^{III}TPP$	8.3×10^8	1×10^8		
$Ge^{IV}TPP$		4×10^4		

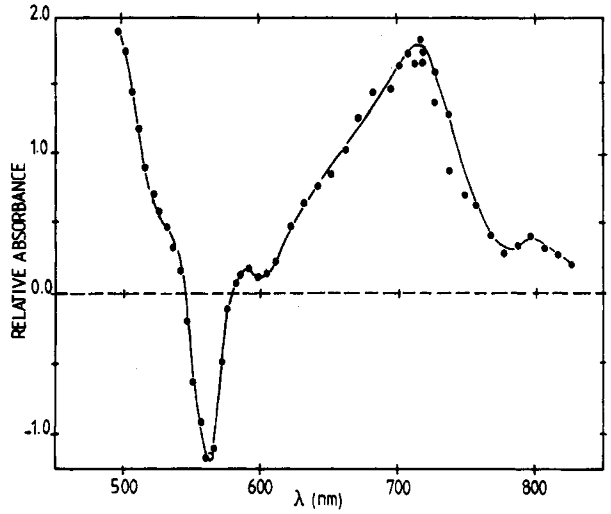

Figure 1. Differential absorption spectrum of the π-radical anion of $In^{III}TMPyP$. Recorded with 5×10^{-5} M $In^{III}TMPyP$ in aqueous solution containing 10% *i*-PrOH at pH 7, phosphate buffered, bubbled with N_2. A unit on the relative absorbance scale correspond to $\epsilon = 10^4\ M^{-1}\ cm^{-1}$ for species produced with a yield of $G = 6$.

Kinetics of One-Electron Reduction. All the porphyrins are reduced with solvated electrons in a diffusion-controlled reaction ($k \geq 1 \times 10^{10}\ M^{-1}\ s^{-1}$).[4,13]

$$M\text{-}P + e_s^- \rightarrow M\text{-}P^{\cdot -} \tag{1}$$

The other radicals produced from methanol or water radiolysis are converted into reducing α-hydroxyalkyl radicals, which react with the porphyrins rapidly.[4] The rate constants for these reactions were determined by following the buildup of the $M\text{-}P^{\cdot -}$ absorption at 700 nm over the microsecond time scale. The results (Table I) indicate that $\dot{C}H_2O^-$ in MeOH reacts with the positively charged porphyrins very rapidly ($k = (5\text{–}8) \times 10^9\ M^{-1}\ s^{-1}$) and with the neutral

$$\dot{C}H_2O^- + M\text{-}P \rightarrow CH_2O + M\text{-}P^{\cdot -} \tag{2}$$

porphyrins somewhat more slowly ($k \sim 1 \times 10^9\ M^{-1}\ s^{-1}$). Reduction by $(CH_3)_2\dot{C}OH$ in neutral aqueous solutions takes place with $k = (2 \pm 0.5) \times 10^9\ M^{-1}\ s^{-1}$ for all the porphyrins examined (Table I). These rate constants are within an order of magnitude of the diffusion-controlled limit. At the concentrations used ($(2\text{–}10) \times 10^{-5}$ M) the porphyrins are reduced within a fraction of a millisecond, before any significant radical–radical decay takes place. The absorption spectra of the radicals were not recorded in detail in all cases, but several wavelengths were monitored between 600 and 800 nm to confirm that the species observed is indeed the radical anion with $\lambda_{max} \sim 700$ nm. A full spectrum recorded with $In^{III}TMPyP$ is shown in Figure 1 and the spectrum of $(Ga^{III}TMPyP)^{\cdot -}$ will be discussed below.

Kinetics of Radical Anion Decay in Alkaline Methanol and Neutral Water. Second-order decay rates of the radical anions

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[10] Certain commerical equipment, instruments, or materials are identified in this paper in order to specify adequately the experimental procedures. Such identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified are necessarily the best available for the purpose.

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were monitored by pulse radiolysis at 700 nm. For alkaline methanolic solutions we derive $2k$ values (Table I) from the calculated $2k/\epsilon l$ and the ϵ estimated from the transient absorbance at 700 nm and the radical concentration determined by thiocyanate dosimetry. We find that the decay rate constants vary from $\sim 10^9$ M^{-1} s^{-1} for $(Ga^{III}TMPyP)^{\cdot -}$ to practically nil for $(Sb^{V}TPyP)^{\cdot -}$, which is very stable. This comparison parallels the situation with Zn^{II}TMPyP and Sn^{IV}TMPyP studied previously.[5,6] Table I indicates the existence of intermediate cases with Ge and In porphyrins.

For aqueous solutions we report in Table I only the approximate first half-lives of the decay at pH 7. Shorter half-lives were observed in acid solutions. However, before attempting full discussion of these results we present the spectra of the stable products and examine the transients from Ga^{III}TMPyP as a function of pH.

Stable Products of Radiolytic Reduction. The spectra of the porphyrins and the products formed upon γ-radiolytic reduction, and in certain cases chemical reduction, are presented in Figure 2. Radiolysis of Ga^{III}TMPyP, Ge^{IV}TMPyP, and Bi^{III}TMPyP in alkaline methanolic solutions yields in all cases the phlorin anions (i.e. the products of two electron reduction with a single protonation at a meso position) characterized by their absorption at ~800 nm (λ_{max} = 792, 820, 805 nm, respectively). These results are similar to those obtained with Zn^{II}TMPyP and Al^{III}TMPyP.[5,6] The reactions occurring in this system, as well as the nature of the products, have been discussed in detail before.[5,6] All these metalloporphyrins yield unstable radical anions, which disproportionate and protonate to form the phlorin anions.

$$2\text{M-P}^{\cdot -} \xrightarrow{H^+} \text{M-P} + \text{M-PH}^- \qquad (3)$$

Sb^{V}TPyP exhibited a very different behavior. The product has intense absorption at 697 nm and a weaker band at 804 nm. Both bands are formed and disappear simultaneously and must be assigned to a stable radical anion. The stability is comparable with that observed for Sn^{IV} porphyrins.[6,7] Although most porphyrin radical anions exhibit only one absorption band centered around 700 nm, with only a tail at 800 nm, several cases show clear bands at 800 nm as well (e.g., Sn^{IV}TPMPyP[6] and In^{III}TMPyP (Figure 1)) so that the present spectrum of $(Sb^{V}TPyP)^{\cdot -}$ is not surprising. This assignment was confirmed also by pulse radiolysis experiments showing both 700- and 800-nm peaks immediately after one-electron reduction of Sb^{V}TPyP. The radical anion of Sb^{V}TPyP is less stable in neutral methanol; γ-radiolysis yields initially some radical anion but after subequent irradiations only the phlorin anion remains, with λ_{max} = 815 nm. Sb^{V}OEP behaved differently in that only the phlorin anion (λ_{max} = 795 nm) was found as the final product even in alkaline MeOH.

In^{III}TMPyP exhibits an intermediate behavior. Its radical anion (715 and 800 nm) is sufficently stable to be observed in the initial stages of γ-radiolysis in alkaline MeOH, but further radiolysis forms a mixture of radical and phlorin and eventually only phlorin (800 nm).

Ga^{III}TPP and Ge^{IV}TPP also formed phlorin anions upon reduction in alkaline MeOH (λ_{max} = 800 and 830 nm, respectively). These porphyrins, however, produced partial yields of chlorins (two-electron-reduction products protonated on the pyrrole rings) (λ_{max} = 625 nm). While the radical anions and the phlorins are easily oxidized by oxygen back to the parent porphyrins, the chlorins remain unchanged.

Chemical reduction was attempted with $NaBH_4$. This was found to reduce Sb^{V}TPyP to the radical anion and the Sb^{V}OEP to the phlorin anion, with spectra identical with those found after γ-radiolysis, but no reduction took place with Ga^{III}-, Ge^{IV}-, or Bi^{III}TMPyP.

Several γ-radiolysis experiments were carried out also with aqueous solutions. Sb^{V}TPyP at pH 7 gave the radical anion with the same two bands at 697 and 804 nm. Chemical reduction with $NaBH_4$ gave the phlorin anion (815 nm). Radiolysis at pH 1 also produced initially some radical anion along with some chlorin (or isobacteriochlorin, see below) (617 nm), but further irradiation formed more chlorin while the radical anion slowly disappeared.

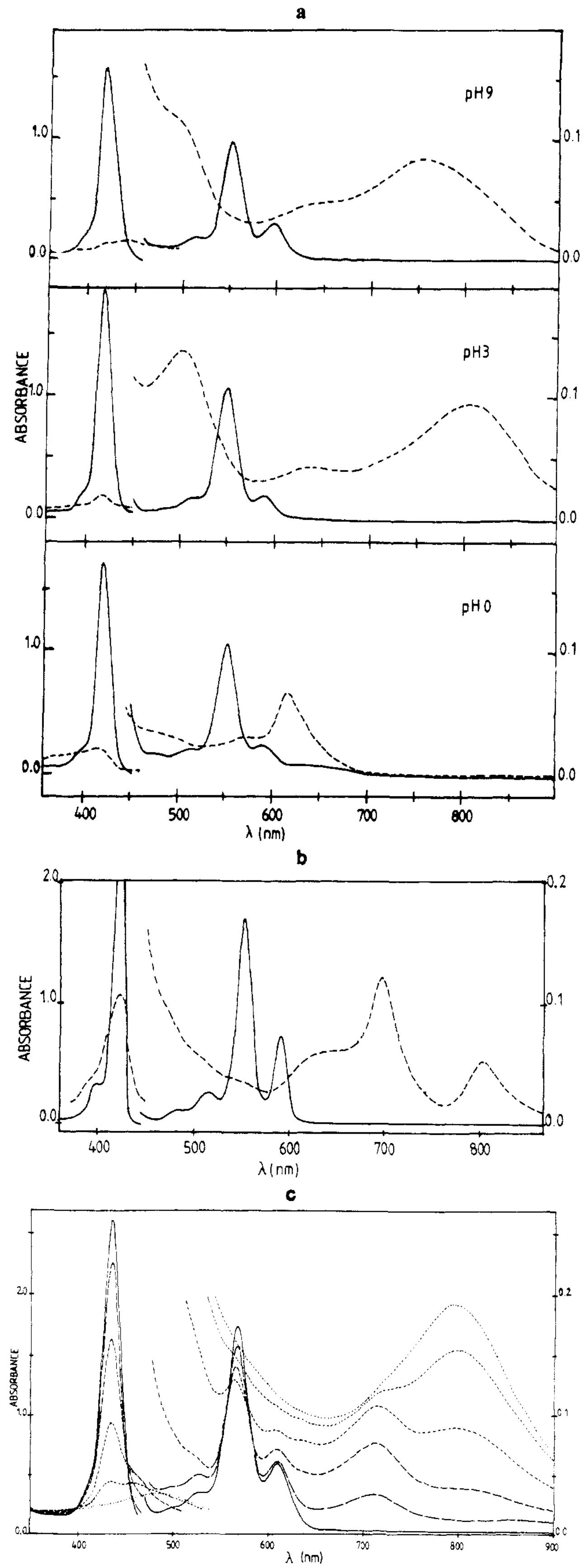

Figure 2. (a) Radiolytic reduction of Ga^{III}TMPyP in deoxygenated aqueous solutions containing 10% *i*-PrOH at various pH's. The spectra are recorded before (—) and after (---) irradiation. (b) Chemical reduction of Sb^{V}TPyP with $NaBH_4$ in alkaline methanolic solution. The spectra are for Sb^{V}TPyP (—) and its π-radical anion (---). Similar spectra were obtained by γ-radiolytic reduction. (c) Radiolytic reduction of In^{III}TMPyP in alkaline methanolic solution. The spectra were taken before irradiation (solid line) and after successive irradiations (dashed and dotted lines). Note that the absorbance scale on the right is explanded by a factor of 10 as compared with the scale on the left.

$In^{III}TMPyP$ in alkaline aqueous solution exhibited the same behavior as in the methanolic solution, with the radical anion (715, 800 nm) observed in the initial stages and finally only the phlorin anion (800 nm). At pH 7 the radical anion is not sufficiently stable to be observed in the steady-state experiments (minutes) and the phlorin anion (830 nm) was produced. The shift in the phlorin anion peak from 800 to 830 nm is probably due to protonation of axial OH.

Radiolysis of $Ge^{IV}TMPyP$ at pH 1 gave the phlorin (781 nm), but $Bi^{III}TMPyP$ formed no phlorin at all, only some chlorin.

Stable Products of Photochemical Reduction. Visible light ($\lambda > 500$ nm) irradiation of the metalloporphyrins in outgassed aqueous solutions containing sodium ascorbate (5×10^{-2} M) or NADH (2×10^{-3} M) as electron donor resulted in formation of the same products as noted in the radiolytic reductions. Thus, photoreduction of $Ga^{III}TMPyP$ and $Ge^{IV}TMPyP$ ($5 < pH < 14$) resulted in formation of the phlorin anion (λ_{max} 795 and 814 nm, respectively, at pH 13). With $In^{III}TMPyP$, the π-radical anion (λ_{max} 710 and 800 nm) was observed upon short irradiations at pH 13 but longer irradiations, or photolysis at pH < 11, resulted in formation of the phlorin anion (λ_{max} 800 at pH 13). Photoreduction of $Zn^{II}TMPyP$ and $Al^{III}TMPyP$ at pH 13 gave the phlorin anions (λ_{max} 780 and 800 nm, respectively) while photoreduction of $Sn^{IV}TMPyP$ gave the π-radical anion (λ_{max} 693 and 800 nm at pH 13) at pH > 11 and the phlorin anion (λ_{max} 830 at pH 7) at pH <10. In all the above cases, aeration of the photolyzed solutions restored the original metalloporphyrin. In alkaline solution, aerial oxidation of the π-radical anions and phlorin anions gave quantitative re-formation of the original metalloporphyrin but at pH <9 aeration resulted in partial formation of chlorins. In particular, Zn and Al porphyrins are prone to chlorin formation upon photoreduction at pH <9.

Visible light irradiation of $Sb^{V}OEP$ in neutral methanol containing benzoin (10^{-2} M) as electron donor resulted in formation of the phlorin anion (λ_{max} 760 nm). In alkaline methanol (10^{-2} M NaOMe), the π-radical anion (λ_{max} 612 and 750 nm) is formed upon short irradiations and the phlorin anion (λ_{max} 790 nm) upon prolonged photolysis.

With $Sb^{V}TPyP$, visible light irradiation in the presence of ascorbate or NADH resulted in formation of the π-radical anion (λ_{max} 692 and 788 nm at pH <11; λ_{max} 701 and 808 nm at pH 13). The absorption spectra of these species are identical with those obtained from the pulsed and steady-state radiolytic reductions, confirming the "two-banded spectrum". Aeration of the solutions gave quantitative re-formation of $Sb^{V}TPyP$. Long irradiations at pH >9 gave the phlorin anion (λ_{max} 812 nm at pH 13) while prolonged irradiation at pH <7 resulted in formation of the chlorin (λ_{max} 622 nm), bacteriochlorin (λ_{max} 765 nm), and isobacteriochlorin (λ_{max} 616 nm). These chlorins were unaffected by the presence of O_2.

Methylation of the pyridyl N atoms on $Sb^{V}TPyP$ had little effect upon the photochemistry, at least in qualitative terms. Thus, for $Sb^{V}TMPyP$ the π-radical anion (λ_{max} 690 and 790 nm at pH < 11; λ_{max} 700 and 808 nm at pH 13), and phlorin anion (λ_{max} 815 nm at pH 13), and chlorin (λ_{max} 624 nm) could all be easily identified.

Stable Products Summary. The above findings concerning the nature of stable products as a function of solvent, pH, and the electronegativity of the central metal ion are generally in line with those reported previously.[5,6] From all the results we can outline the following trends. The tendency to form phlorin rather than chlorin is higher in alcohol than in water; it decreases with lowering the pH, and depends on the porphyrin structure in the order TMPyP > TPyP > TPP. This tendency also parallels the stability of the radical anion, with the longer lived radical producing more phlorin. The stability for a particular ligand decreases with the metal ion in this order: Sb^{V}, Sn^{IV}, In^{III}, Ge^{IV}, Ga^{III}, Al^{III}, Zn^{II}. The radical anion of $Sb^{V}TPyP$ is sufficiently stable to be observed in the γ-radiolysis experiments even at pH 1, of $Sn^{IV}TMPyP$ (and other Sn^{IV} porphyrins) in neutral solutions, and of $In^{III}TMPyP$ only in alkaline solutions. The radical anions of the other porphyrins are observed only at short times in the pulse radiolysis experiments. It is obvious that the electronegativity of the metal ion plays a major role in determining the lifetime of the porphyrin radical anions. The electronegativity can be expressed by its effect on the redox potential of the metalloporphyrin. Therefore, reduction potentials were measured by cyclic voltammetry.

TABLE II: **Electrochemical Half-Wave Potentials[a] for One- and Two-Electron Reduction of the Porphyrins in Aqueous Solution**

compound	$E_{1/2}^1$	$E_{1/2}^2$	K_D
$Sb^{V}TPyP$	−0.20	−0.40	2400
$Sn^{IV}TMPyP$	−0.28	−0.45	750
$In^{III}TMPyP$	−0.51	−0.65	230
$Ge^{IV}TMPyP$	−0.56	−0.70	230
$Pb^{II}TMPyP$	−0.58	−0.72	230
$Ga^{III}TMPyP$	−0.59	−0.72	160
$Al^{III}TMPyP$	−0.65	−0.72	15
$Zn^{II}TMPyP$	−0.69	−0.73	5[b]
H_2TMPyP	−0.10	−0.13	3[b]

[a] Potentials in V vs. NHE. [b] Derived from the peak half-widths only.

One- and Two-Electron Reduction Potentials. The metalloporphyrins used in this work undergo successive electron additions of the type

$$M{-}P \xrightarrow[E_{1/2}^1]{e} M{-}P^{\cdot -} \xrightarrow[E_{1/2}^2]{e} M{-}P^{2-} \tag{4}$$

for which the disproportionation constant (K_D) can be expressed in the form:

$$K_D = \frac{[M{-}P^{\cdot -}]^2}{[M{-}P][M{-}P^{2-}]} = \exp\left[\frac{(E_{1/2}^1 - E_{1/2}^2)F}{RT}\right] \tag{5}$$

When the half-wave potentials for addition of the first ($E_{1/2}^1$) and second ($E_{1/2}^2$) electrons are expressed in millivolts, $K_D = \exp(\Delta E_{1/2}/25{\cdot}69)$ at 298 K. Evaluation of the half-wave potentials can be made by cyclic voltammetry, and where $\Delta E_{1/2} > 180$ mV the individual peaks are well resolved and unaffected by each other. When $\Delta E_{1/2} < 150$ mV the two peaks are not fully resolved, but the individual $E_{1/2}$ values can be determined from the peak half-widths and the separation of anodic and cathodic peaks.[14,15] This latter treatment was used to derive half-wave potentials for reduction of the various metalloporphyrins in N_2-saturated aqueous solution at pH 5 containing KCl (0.1 M) and the values are collected in Table II.

Cyclic voltammograms recorded for aqueous solutions of $Sb^{V}TPyP$ and $Sn^{IV}TMPyP$ showed quasi-reversible behavior with the two reduction peaks separated by 200 and 170 mV, respectively. For both compounds, the reduction waves are well resolved and calculation of the individual $E_{1/2}$ values is straightforward. Substitution of the derived values (Table II) into eq 5 gives disproportionation constants of 2400 and 750, respectively, for $Sb^{V}TPyP$ and $Sn^{IV}TMPyP$. Thus, both compounds should show fairly stable π-radical anions in aqueous solution.

$In^{III}TMPyP$ and $Ge^{IV}TMPyP$ also showed quasi-reversible electrochemical behavior but the two reduction peaks were not fully resolved. Here, $\Delta E_{1/2}$ was found to be 140 mV in both cases. This corresponds to a K_D value of 230 so that these π-radical anions should be less stable toward disproportionation than the above species.

With $Ga^{III}TMPyP$, $Al^{III}TMPyP$, and $Pb^{II}TMPyP$, the cyclic voltammograms showed evidence for a chemical reaction following the first reduction. In these cases, the two reduction peaks were not fully resolved and the peak currents for the reversed scans (anodic) were somewhat less than seen on the forward (cathodic) scan. This behavior is consistent with the π-radical anions undergoing disproportionation and the derived K_D values support this idea. Thus, K_D decreases in the order Pb > Ga > Al. (Note, the cyclic voltammograms recorded with $Pb^{II}TMPyP$ were at pH 9.)

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Both H_2TMPyP and Zn^{II}TMPyP underwent irreversible reductions. For both compounds, the first reduction step involved a two-electron reduction and it was not possible to resolve the individual peaks. There was little, if any, sign of a peak on the reverse scan and the $E_{1/2}$ values were determined from the peak half-widths only. The π-radical anions of these compounds are prone to disproportionation in aqueous solution.

Comparison of the electrochemical data given in Table II shows that the central metal ion exerts a pronounced effect upon both $E_{1/2}{}^1$ and K_D. The inductive effect of the metal ion upon the half-wave potential is well documented,[1,16] and it is known to depend upon the electronegativity of the metal ion.[17] The trend found here is in good agreement with the effect of the central metal ion upon $E_{1/2}$ found by previous workers[1] with water-insoluble metalloporphyrins. In particular, the order of $E_{1/2}{}^1$ values agrees quite well with the "induction parameter" introduced by Fuhrhop et al.[17] However, for water-insoluble metalloporphyrins the central metal ion affects the position of both $E_{1/2}{}^1$ and $E_{1/2}{}^2$ so that $\Delta E_{1/2}$ remains relatively insensitive to the nature of the central metal ion.[1] Clearly, this is not the case with the metal TMPyP complexes used in this study. This effect is demonstrated by comparing the behavior found for Sn^{IV}TMPyP and Zn^{II}TMPyP. The former compound shows two well-resolved and reversible reduction peaks while the latter undergoes an irreversible two-electron reduction step.

For H_2TMPyP, the first reduction peak involves a two-electron process which decreases by 60 mV per pH unit. This step is believed to correspond to direct reduction to the phlorin[8]

$$H_2\text{-P} \xrightarrow[2H^+]{2e} H_2\text{-PH}_2 \qquad (6)$$

and Zn^{II}TMPyP seems to undergo an identical process to form the corresponding porphodimethene (two-electron-reduction product doubly protonated at the meso positions). With Al^{III}TMPyP, the two peaks are just resolved but the reduction product seems to be a porphodimethene rather than a genuine phlorin anion. This is evidenced by absorption spectroscopy. At pH 13, the spectra obtained after reduction of H_2-, Zn^{II}-, and Al^{III}TMPyP show broad, relatively low-intensity bands around 800 nm whereas the plorin anions formed from the other metalloporphyrins show intense, fairly sharp bands in this region. At lower pH, absorption spectra of reduced H_2-, Zn^{II}-, and Al^{III}TMPyP show very little absorption above 700 nm whereas the other metalloporphyrins retain the characteristic phlorin anion and π-radical anion spectra. Thus, electrochemical reduction of H_2-, Zn^{II}-, and Al^{III}TMPyP at pH 5 seems to give direct formation of the diprotonated porphodimethene. The other compounds form the π-radical anion upon reduction and its tendency to disproportionate at pH 5 is set by the electronegativity of the central metal ion.

The two-electron reduction of H_2TMPyP is thought[19] to be due to partial localization of the electron on the substituent via resonance forms of the type:

Such species should be easily reduced[19] so that addition of the second electron occurs almost simultaneously. This is followed by protonation to form the porphodimethene in which the two electrons/two protons are located at opposite meso C atoms.

With the more electronegative metal ions, the electron density on the π-radical anion will be attracted toward the metal ion and away from the *N*-methylpyridinium group. This has the effect of making addition of the second electron more difficult as compared with addition of the first electron, and hence the increase in $\Delta E_{1/2}$. It is obvious, however, that both E^1 and E^2 are more positive when the metal center is more electronegative. Also, increasing the electronegativity of the metal ion makes it more difficult to protonate the reduction product so that phlorin anions are observed rather than porphodimethenes. For strongly electronegative ions, such as Sn^{IV}, the magnitude of $\Delta E_{1/2}$ is sufficient for the two-electron additions to be completely resolved. By affecting the electron density, the electronegativity of the metal ion also influences the absorption spectrum of the π-radical anion. With Sb^{V}, Sn^{IV}, and In^{III} porphyrins where the electron density is attracted toward the central metal ion, the π-radical anions exhibit the well-defined "two banded" spectra described earlier. For the other cases, the spectra are broader and lacking the lower energy band.

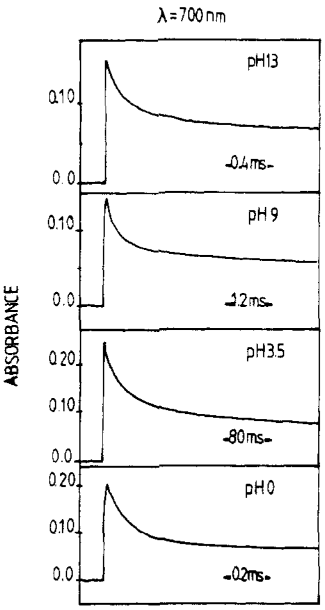

Figure 3. Effect of pH on the decay of the 700-nm absorption of the π-radical anion of Ga^{III}TMPyP ($\sim 8 \times 10^{-5}$ M porphyrin solution in water containing 10% *i*-PrOH, N_2 bubbled, 1.1 krd/pulse).

Because Sb^{V}TPyP has a strongly electronegative ion and the substituent, even when methylated, cannot counteract the negative charge on the π-system, the two-electron additions are well resolved. Thus, the π-radical anion is stable with respect to disproportionation and the phlorin anion does not protonate further.

Pulse Radiolysis of Ga^{III}TMPyP in Aqueous Solutions. It has been noted in the initial pulse radiolysis experiments that the decay rates of the radical anions are strongly dependent on the pH. Furthermore, while the decay of the radical anion ($\sim$700 nm) in alkaline methanol was accompanied by a concomitant buildup of the phlorin anion ($\sim$800 nm), the two processes did not occur simultaneously in aqueous solutions. To investigate these effects we carried out a more detailed pulse radiolysis study on Ga^{III}TMPyP.

Figure 3 shows kinetic traces of the decay at 700 nm at various pH values. It clearly shows that not only the time scale of the decay changes but so does the percentage of absorbance decaying in the first process. The differences are accentuated in the three representative spectra shown in Figure 4. Kinetic traces at 700 and 800 nm monitored at pH 9 are shown in Figure 5. These traces indicate a multitude of processes occurring after the initial formation of $(\text{Ga}^{III}\text{TMPyP})^{\cdot -}$. These processes probably involve dimerization of the radical anion followed by protonation and disproportionation, as suggested previously.[5,13] The spectral and kinetic overlaps make it difficult to investigate the details of these processes. The spectra in Figure 4 indicate, however, that in strongly acidic solutions the decay becomes simpler; i.e., one process leads to the disappearance of practically all the initial absorption. We find a discontinuity in behavior upon changing the pH; in basic solutions the initial decay process bleaches about half the absorption at 700 nm, at pH 5–3 the extent of this initial decay decreases and finally disappears, while a slower decay process leading to nearly full bleaching sets in, this process becomes

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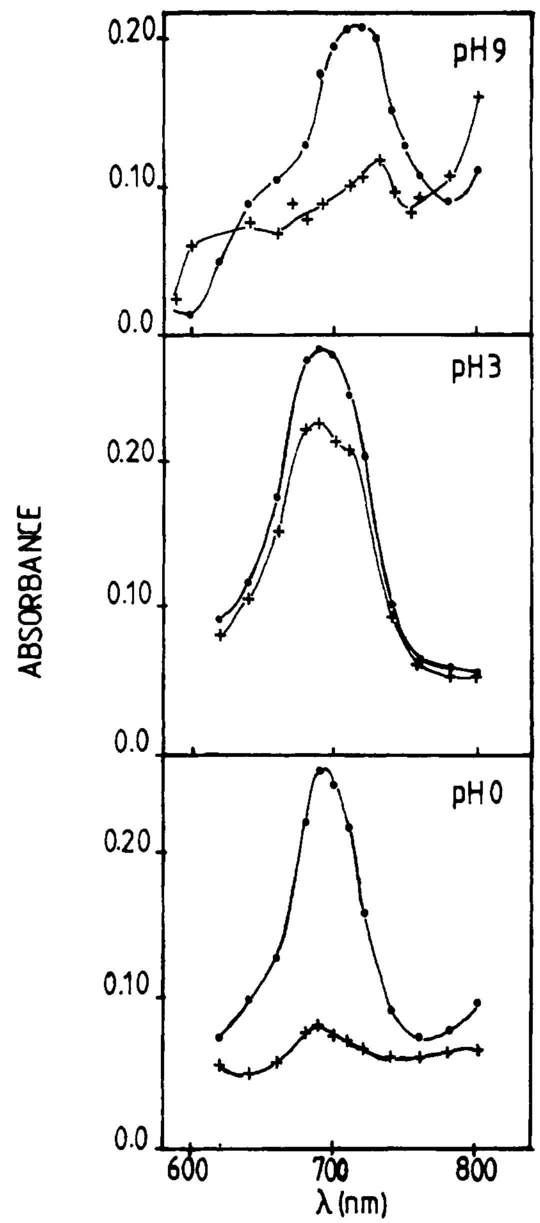

Figure 4. Spectra recorded upon pulse radiolysis of $Ga^{III}TMPyP$ at different pH values. Aqueous solutions containing ~8 × 10^{-5} M porphyrin and 10% *i*-PrOH were bubbled with N_2 and irradiated with 1.1 krd pulses. The spectra were recorded 10–20 μs after the pulse (●) and ~1.5 ms later (+).

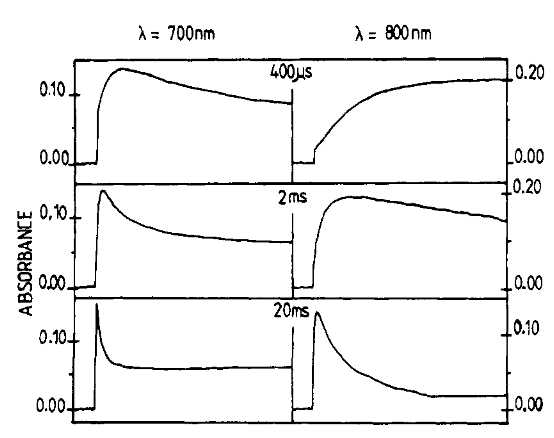

Figure 5. Kinetic traces recorded upon pulse radiolytic reduction of $Ga^{III}TMPyP$ at pH 9.2. (Aqueous solutions containing 10% *i*-PrOH, ~8 × 10^{-5} M porphyrins, and 1 mM borate buffer were bubbled with N_2 and irradiated with 1.1 krd pulses.) The time scale given is for the full trace.

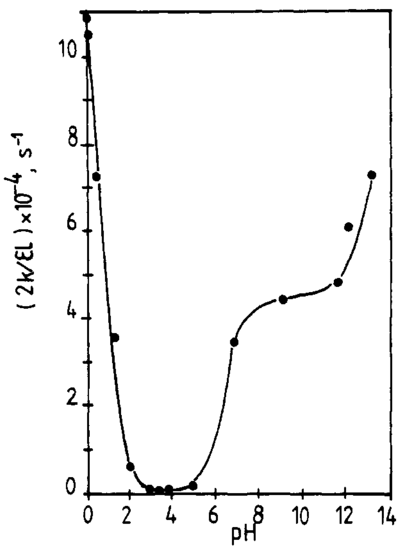

Figure 6. Effect of pH on the second-order decay of the π-radical anion of $Ga^{III}TMPyP$, monitored at 700 nm.

prevalent and more rapid at lower pH. This discontinuity indicates a change in mechanism. The full pH dependence is shown in Figure 6 but the part above pH 5 should be considered independently from that below pH 3.

$Ga^{III}TMPyP$ has two pK_a values for the axial water molecules

$$[(H_2O)_2Ga^{III}TMPyP]^+ \rightleftarrows [(H_2O)(HO)Ga^{III}TMPyP] + H^+ \qquad pK_a = 6.5 \quad (7)$$

$$[(H_2O)(HO)Ga^{III}TMPyP] \rightleftarrows [(HO)_2Ga^{III}TMPyP]^- + H^+ \qquad pK_a = 11.7 \quad (8)$$

(determined from pH effect on the spectrum). Similarly, the radical anion is expected to have two equilibria.

$$[(H_2O)_2Ga^{III}TMPyP]^{\cdot} \rightleftarrows [(H_2O)(HO)Ga^{III}TMPyP]^{\cdot -} + H^+ \rightleftarrows [(HO)_2Ga^{III}TMPyP]^{\cdot 2-} + 2H^+ \quad (9)$$

These correspond to the changes in decay rates shown in Figure 6. The first pK_a ~ 6.5 is similar to that of the parent molecule while the second pK_a ~ 12–13 is slightly higher. An increase in pK_a is expected for a less positively charged species.

The rate of decay is found to increase with pH from pH 5 to 14. This increase corresponds to the decrease in the overall positive charge of the decaying species (from +4 to +3 and +2). It should be noted that the process considered here is the initial interaction between two radicals to form probably a dimer. This process becomes slow at pH < 4.

In the strongly acidic solutions the increase in the decay rate is most probably due to protonation of the radical. Even a small fraction of protonated radicals can enhance the decay very strongly (as was found for $O_2^{\cdot -}$ decay, for example)[20] if reaction 11 is much faster than reaction 12.

$$M\text{-}P^{\cdot -} + H^+ \rightleftarrows M\text{-}\dot{P}H \quad (10)$$

$$M\text{-}\dot{P}H + M\text{-}P^{\cdot -} \rightarrow M\text{-}PH^- + M\text{-}P \quad (11)$$

$$M\text{-}P^{\cdot -} + M\text{-}P^{\cdot -} \rightleftarrows M\text{-}P + M\text{-}P^{2-} \left(\xrightarrow{H^+} M\text{-}P + M\text{-}PH^-\right) \quad (12)$$

The pK_a for protonation of the radical $[(H_2O)_2Ga^{III}TMPyP]^{\cdot}$, probably on the meso carbon position, is apparently very low since the initial spectrum at pH 0 is very similar to that at pH 3 (Figure 4).

Stability of Radical Anions. It is obvious from the above discussion and from previous work that protonation plays a major role in the decay process, whether protonation of the radical directly (in strong acid) or protonation of the dimer. Increasing the electronegativity of the central metal ion results in electron withdrawal from the ligand. This effect in turn lowers the reduction potential as well as the capacity to protonate. Therefore,

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[20] Bielski, B. H. J.; Allen, A. O. *J. Phys. Chem.* **1977**, *81*, 1048.

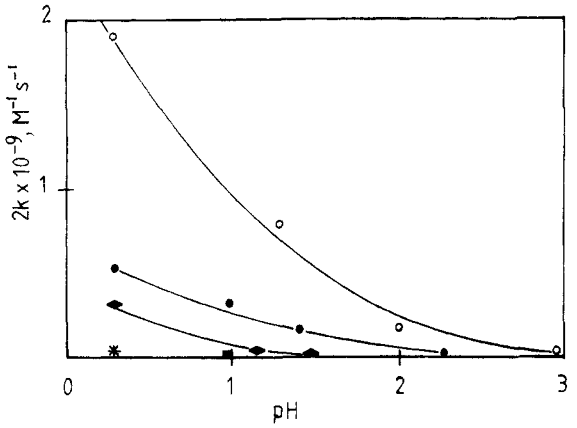

Figure 7. Effect of pH on the second-order decay of π-radical anion of different porphyrins: Ga^{III}TMPyP (○), Ge^{IV}TMPyP (●), In^{III}TMPyP (◆), Sn^{IV}TMPyP (■), and Sb^{V}TPyP (*).

it results in a decrease in the decay rate. Correlation between redox potential and pK_a has been noted previously[19,21] and is extended here to the stability of the radical anion.

Final confirmation for this dependence is obtained from the effect of pH on the rate of decay of the various metalloporphyrins in strongly acidic solutions (Figure 7). The decay rates for Al^{III}- and Ga^{III}TMPyP radicals increase sharply below pH 3, those for Ge^{IV} and In^{III} only below pH 2 and pH 1, respectively, and the decay of the Sb^{V}TPyP π-radical anion does not become measurable even at pH 0. However, for Sb^{V}TPyP it should be remembered that the pyridyl N atoms become protonated at pH <2 so that there will be increased electrostatic repulsion between the radicals in acidic solution.

In conclusion, this work has shown that the stability of metalloporphyrin π-radical anions in aqueous solutions depends markedly upon the electronegativity of the central metal ion and upon pH. The pH effects need to be divided into two classes. Firstly, axially bound water molecules undergo acid/base equilibria that affect both the overall electronic charge (and hence any bimolecular processes) and the electron density on the porphyrin ring. Secondly, the π-radical anion may partially protonate in acid solution and, as is often the case, the neutral radical disproportionates, with itself or with a radical anion, more rapidly than does the corresponding radical anion. The electronegativity of the central metal ion affects the electron density on the porphyrin ring. With TMPyP complexes, electrons are pulled from the ring toward the alkylated N atom. Resonance structures can be drawn from the π-radical anion that put the radical character onto the pyridyl group, favoring a two-electron reduction. This effect is counterbalanced by having a strongly electronegative central metal ion (e.g., Sb^{V} or Sn^{IV}) which pulls electron density toward the porphyrin core. This favors a one-electron reduction and also renders the phlorin anion difficult to protonate.

Similar considerations need to be invoked to explain the relative tendency of porphyrins to form chlorins or phlorins upon two-electron reduction. Chlorins have the two electrons/two protons added at pyrrole C atoms while the phlorin involves reduction at meso C atoms. With TMPyP complexes, electron density becomes localized at the meso positions and on the substituent, thus favoring phlorin formation. More electronegative metal ions will also favor phlorin formation. In contrast, TPP complexes will be more prone to chlorin formation.

Of the compounds studied here, Sb^{V}TPyP and Sn^{IV}TMPyP give the most stable π-radical anions but only $Sb^{V}TPyP^{\cdot -}$ can be regarded as being stable over a wide pH range.[22] Previously, it was shown[23] that photoreduction of Sn^{IV}TMPyP at pH 7.5 in the presence of colloidal Pt resulted in efficient formation of H_2. Similar experiments with Sb^{V}TPyP also gave H_2 although the rate was slow. From the measured $E_{1/2}$ values it seems likely that the active water reductant is the phlorin anion not $SbVTPyP^{\cdot -}$. Photoreduction in the presence of Pt at pH <7 led to increased amounts of chlorin so that, overall, the system is not really useful for H_2 photogeneration.

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